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FLUORESCENCE STUDIES OF THE EXCITED-STATE INTERMOLECULAR PROTON-TRANSFER REACTION OF 1-AZACARBAZOLE

A Thesis in

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by

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ABSTRACT

The excited-state intermolecular proton-transfer reaction of 1-azacarbazole (1AC) has been studied in isolated hydrogen-bonded complexes and bulk protic solvents using steady-state and time-resolved fluorescence spectroscopy. Linear free-energy relationships for 1AC and the related molecule 7-azaindole (7AI) suggest the reaction rate may be separated into contributions from an intrinsic proton-transfer rate and a solvent factor. Progress toward determining the magnitude of each of these contributions is documented.

The catalytic tautomerization of 1AC in binary complexes with acetic acid is very rapid, and using an irreversible proton-transfer kinetic scheme the rate constant is estimated to be $k_{PT} = (1.5 \pm 0.5) \times 10^{12} \text{ s}^{-1}$. Noncatalytic reactions of 1AC in complexes with lactams and amides are measurably slower, and the observed kinetics are compared to model calculations estimating the driving force of the reaction.

The solvent-catalyzed reaction rates of 1AC and 7AI appear extraordinarily slow in diols and water when compared to reactions in neat alcohols. However, the excitedstate reaction in ethylene glycol may be compared on an equal footing to that in methanol if the effects of hydrogen-bond dynamics as measured by the solvent dielectric relaxation time (τ_1) are considered. In addition to a discussion of the anomalous reactions observed in hydroxylic solvents, the noncatalytic excited-state reaction of 1AC in bulk amides is examined. The reaction mechanism is further elucidated in a study of the excited-state tautomerization of 1AC in methanol / methanol-OD mixtures. Although the experimental results do not allow the double-proton-transfer reaction to be classified either as stepwise or concerted, recent published studies suggest that a stepwise mechanism may be preferred. The significance of the observed kinetic isotope effects is discussed.

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Chapter 1

INTRODUCTION

1-Azacarbazole (1AC) and 7-azaindole (7AI) are two molecules which tautomerize through intermolecular excited-state proton transfer.¹ The reactions of 7AI and 1AC are very similar. As suggested by *Scheme 1.1* on page 2, the transfer of the hydrogen atom from the nitrogen atom in the five-membered (pyrrole) ring of 1AC (or 7AI) to the nitrogen atom in the six-membered (pyridine) ring of 1AC requires the assistance of another molecule that can both accept and donate a proton. This model of the reaction assumes the formation of a molecular complex having a cyclical, hydrogenbonded structure to facilitate the intermolecular transfer of the hydrogen atom. Because the tautomerization occurs only when 1AC (or 7AI) is in the excited-state, the reaction must be initiated by ultraviolet light. Once started, the progress of the reaction may be followed in the excited state by monitoring the fluorescence of reactant and product species. These spectroscopic features give an experimentalist excellent control for studying the reaction.



Scheme 1.1

Why is this tautomerization reaction interesting? 7AI has been studied intensively for biological applications, including its use as a probe of protein structure and dynamics² and as a model system in the study of double-well potentials and photomutagenesis in DNA base pairs.³⁻⁵ More fundamental work has considered 7AI as a probe of hydrogen-bonding structure and dynamics in solvents.⁶⁻¹³ Such study of solvent effects on the rate of chemical reaction is at the heart of chemistry. Although the excitedstate intermolecular proton-transfer reaction of 7AI has been studied for approximately 35 years, our understanding is yet incomplete. Since the photochemistry of 1AC is closely related to 7AI, study of the remarkable similarities and differences between these two molecules should advance understanding of the excited-state proton-transfer reaction. Toward this goal, studies reported in this dissertation continue the efforts initiated one decade ago by Moog and Maroncelli.⁶⁻¹³

Chapter 2 presents an overview of the solvent dependence of the excited-state reaction of 1AC. Chapter 3 summarizes the time dependence of 1AC fluorescence and reviews analysis of two-state kinetic theory applicable to this class of reaction. Earlier work by Moog, Maroncelli, Chapman and Boryschuk⁷⁻¹⁰ demonstrated a linear free-energy relationship for the reactions of 1AC and 7AI in alcohols (*cf. Figure 3.2*). This relationship suggests that the observed reaction rate may be decomposed into two terms:

 $k_{obs} = f(intrinsic transfer) * f(solvent).$

The observed rate depends on some function of the intrinsic proton transfer and on some function of the solvent. The decomposition of <u>one</u> rate into <u>two</u> terms is an underdetermined problem that generally has no unique solution. In order to evaluate the relative influences of each of these factors on the reaction rate, other physical constraints must be established.

Given this model of the reaction, one basic question guiding this dissertation research then follows: What is the character of the intrinsic proton-transfer step? In particular, how quickly does the intrinsic proton transfer occur? Do the two protons move in a concerted or stepwise mechanism? When the effects of the extended hydrogen-bond network in protic solvents are removed, then the characteristics of the intrinsic proton transfer step may be studied. Toward this end, the excited-state tautomerization of 1AC within isolated hydrogen-bonded complexes is examined in Chapter 4. The reaction of 1AC in isolated complexes formed in nonpolar solvents is ultrafast. For example, we estimate that the proton transfer occurs in 0.7 ± 0.2 picoseconds (ps) in isolated complexes with the catalytic partner acetic acid. A study of the kinetic isotope effects of 1AC in Chapter 7 seeks to understand the reaction mechanism for double-proton transfer in 1AC. Although the results support neither a concerted nor stepwise mechanism for 1AC conclusively, recent published studies of 7AI suggest that a stepwise reaction may be preferred.

In contrast to the ultrafast reaction in isolated complexes, the tautomerization of 1AC (or 7AI) is considerably slower in bulk alcohols, and yet even slower in bulk diols, water, and amides. Given the two-term model of the reaction, a second basic question guiding this dissertation research follows: What is the character of the solvent factor, especially in the apparently "anomalous" solvents like ethylene glycol and water? Chapters 5 and 6 summarize inquiries into the origin of these apparently anomalously slow reactions for 1AC. In Chapter 5, the temperature dependence of the excited-state proton-transfer reaction of 1AC in diols and water is studied. Efforts to understand more complicated kinetics observed at lower temperatures lead to a consideration of (random) molecular motions controlling the reaction. When the observed reaction times are normalized by solvent dielectric relaxation times (τ_1 ; a measure of the dynamics of hydrogen-bond formation in the solvent), then the normalized reaction rates of 1AC in diols and water are not so anomalous when plotted on the $E_T(30)$ polarity scale with the normalized rates of 1AC in other primary alcohols. The reaction thus appears to be

partially controlled by solvent dynamics related to the equilibration of broken or formed hydrogen bonds. In Chapter 6, we confirm that fluorescence is emitted from the neutral form of 1AC in water at neutral pH. Therefore the slower observed rate cannot be attributed to an acidic or basic form of 1AC in water. Also in Chapter 6, the tautomerization of 1AC in bulk amides is characterized for the first time. This study complements the study of the proton-transfer reaction of 1AC in isolated complexes with amides and lactams reported in Chapter 4.

The excited-state intermolecular proton-transfer reactions of 1AC and 7AI have been introduced in this chapter, and main results of this dissertation research have been summarized here. Chapters 2 through 7 describe the experiments and their interpretations in greater detail. The experimental procedures for all these studies are described in Chapter 8, and this work is concluded with a Select Bibliography.

ENDNOTES

¹ A bibliography of work related to 1-azacarbazole and 7-azaindole is collected in the Select Bibliography following Chapter 8.

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Chapter 2

SOLVENT DEPENDENCE OF THE PHOTOPHYSICS AND PHOTOCHEMISTRY OF 1-AZACARBAZOLE

2.1 Introduction

The study of solvent-catalyzed, excited-state proton-transfer reactions has utilized systematic variations in both the solute molecules and the solvents in order to gain insight into the reaction mechanism. 1-Azacarbazole (1AC) and 7-azaindole (7AI) are two representatives of the class of molecules that tautomerize through intermolecular excited-state proton transfer.^{1,2} The present study focuses primarily on the reaction of 1AC, and it extends the efforts of Moog and Maroncelli on the study of hydrogen-bonding and dynamics in protic solvents initiated one decade ago.³⁻¹⁰ Fluorescence from 1AC in various solvent environments provides indirect information about the excited-state proton-transfer reaction. The collection of rate dependencies on solvent parameters such as "polarity," isotopic substitution and temperature forms the basic information that will be used to develop models to explain the reaction. As a prelude to this rate data, in this chapter the absorption and emission behavior of 1AC in a variety of neat solvents is summarized and analyzed to provide general information about the photophysics and photochemistry of this proton-transfer molecule.

2.2 Steady-State Absorption and Emission Spectra

The series of spectra presented in *Figure 2.1*, *Figure 2.2*, and *Figure 2.3* give an overview of the observed spectroscopy. *Figure 2.1* surveys the behavior of 1AC in a wide range of solvents. *Figure 2.2* details the change in the vibronic structure of the bands as the solvent polarity increases in aprotic solvents from methylcyclohexane to tetrahydrofuran. *Figure 2.3* documents the spectra of 1AC in the solvents examined more closely in Chapters 5 and 6.

Electronic transitions in 1AC lead to three absorption bands in the ultraviolet region of the spectrum (250-400 nm) as illustrated in *Figure 2.4* and *Figure 2.5*. Of these absorption bands, our primary interest is in the first band (~28000-32000 cm⁻¹) because fluorescence and the excited-state reaction occur from this state, S_1 . Some overlap of the bands due to S_1 and S_2 transitions is apparent in all of these absorption spectra. However, in very dilute solutions of 1AC in neat aprotic solvents, only a single emission band is observed and is attributed to fluorescence from the normal form of 1AC. That this emission band is a mirror image of the first absorption band is a good indication that fluorescence occurs from the first excited state S_1 .

As the solvent polarity increases from the nonpolar solvent methylcyclohexane to the polar solvent water [*Figure 2.1*], the vibronic structure on the absorption and emission bands disappears and the Stokes shifts increase. In polar protic solvents such as the alcohols, the dual fluorescence observed from 1AC indicates the presence of an excited-state reaction. The ultraviolet emission (~27000 cm⁻¹) originates from the "normal" form of 1AC as in the aprotic solvents, but the visible emission band in the yellow region of the spectrum (~18000 cm⁻¹) is identified as 1AC tautomer fluorescence.¹¹ To understand the role of protic solvents in promoting this tautomerization reaction is the motivation for this study. In addition to the aliphatic alcohols,¹² dual fluorescence is observed in other protic solvents such as benzyl alcohol and ethylene glycol [*Figure 2.3*]. Although tautomer emission is much less obvious in the spectra of 1AC in the liquid amides formamide and N-methylformamide, timeresolved spectroscopy does reveal the presence of an excited-state reaction. In water only a single, broad emission band is observed [*Figure 2.1*], and experiments indicate that reaction in this solvent is very slow.

Quantitative features of the steady-state absorption and emission bands are summarized in *Table 2.1*. Since the S₁ and S₂ absorption bands for 1AC are not cleanly separated [*Figure 2.4* and *Figure 2.5*], the band widths and shifts were determined relative to 1AC in methylcyclohexane. Thus the absorption spectrum of 1AC in methylcyclohexane was convoluted with a Gaussian lineshape with width parameter Γ and shift Δv to reproduce the bands observed in the other solvents.¹³ The absorption band maxima of 1AC in methylcyclohexane are ~30700 cm⁻¹ (S₁) and ~33800 cm⁻¹ (S₂).^{14,15} Each emission spectrum of normal 1AC was characterized directly by the width of the band measured at half of the maximum intensity (FWHM) and by the first moment frequency (<v>).¹⁶ The energy difference between the absorption and emission bands, here called the Stokes shift Δv_{ss} , is reported relative to its value in methylcyclohexane:

$$\Delta v_{\rm SS} = \Delta v_{\rm em} - \Delta v_{\rm abs} (330 \text{ nm}) = (v_{\rm abs} - \langle v_{\rm em} \rangle)_{\rm solvent} - (v_{\rm abs} - \langle v_{\rm em} \rangle)_{\rm mchex} \quad (2.1)$$

Also included in *Table 2.1* are three popular measures of "solvent polarity" (discussed in Section 2.5) and calculated radiative rates and transition moments of 1AC in various solvents (described in Section 2.4).

2.3 Solvent Dependence of the Stokes Shift

One molecular property that may be estimated from steady-state absorption and emission spectra is the change in magnitude of a chromophore's dipole moment following excitation. This value is interesting because it provides a measure of the electronic redistribution in the excited state compared to the ground state. Thus it can be used to assess the accuracy of excited-state charge distributions calculated by quantum chemical methods. It may also be employed directly as an electrostatic parameter in models and simulations of molecular interactions. Furthermore, the calculation of the change in magnitude of the dipole moment is based on a model of general solvent interactions. Thus the model may be used to identify solvents for which specific interactions with the solute lead to spectral shifts more pronounced than expected.

Application of dielectric continuum models allows the magnitude of the dipole moment change ($\Delta\mu$) to be estimated from the slope of the correlation between the Stokes shift ($\Delta\nu$) and the reaction field factor (F(ϵ_0 , *n*)):¹⁷⁻¹⁹

$$\frac{\Delta(\Delta \boldsymbol{n})}{\Delta F} = \frac{2(\Delta \boldsymbol{m})^2}{\mathrm{hca}^3}, \text{ where } \qquad F(\boldsymbol{e}_o, \boldsymbol{n}) = \frac{\boldsymbol{e}_o - 1}{\boldsymbol{e}_o + 2} - \frac{n^2 - 1}{n^2 + 2} \tag{2.2}$$

The reaction field factor depends on the static dielectric constant ε_0 and the refractive index *n* of the solvent. The radius *a* of the cavity in the dielectric continuum is an important parameter in this determination;²⁰ here, the van der Waals volume (V) of the solute is employed to estimate this cavity size: V ~ 4/3 π a³.

The Stokes shifts of 7AI and 1AC show similar dependence on reaction field, as presented in *Figure 2.6*. The strongest deviations from the linear correlation are noted for 1AC in the protic solvents methanol, ethylene glycol, formamide, benzyl alcohol, and water. These solvents may be involved in specific intermolecular (hydrogen-bonding) interactions with 1AC that the reaction field was not intended to capture.^{21,22}

Using slopes from linear regressions to the data *Figure 2.6* and estimating the van der Waals volumes using published recipes,^{23,24} we find that $\Delta\mu_{7AI} = 3.2 \text{ D} (a = 2.9 \text{ Å})$ and $\Delta\mu_{1AC} = 2.4 \text{ D} (a = 3.3 \text{ Å})$. For reference, the ground state dipole moments of these molecules calculated using quantum chemical methods (HF/6-31G*//HF/6-31G*) are $\mu_{7AI} = 1.6 \text{ D}$ and $\mu_{1AC} = 1.1 \text{ D}$.

2.4 Calculation of the Radiative Rates and Transition Moments

Our spectroscopic investigations of the reaction of 1AC depend on the emission of photons from the excited-states of the reactant (normal form of 1AC) and product (tautomer form of 1AC). Radiative (k_{rad}) and nonradiative (k_{nr}) rates are directly related to the measured quantum yield and excited-state lifetime. The quantum yield expresses

the ratio of the number of photons emitted to the total number of photons absorbed. In the absence of a reaction, the quantum yield is:

$$\boldsymbol{j} = \frac{\boldsymbol{k}_{rad}}{\boldsymbol{k}_{rad} + \boldsymbol{k}_{nr}} \tag{2.3}$$

Similarly, the excited-state lifetime is defined as the time for which only 37% (1/e) of the initial excited-state population remains in the excited state. The other fraction of the excited-state population has decayed into other states by radiative or nonradiative processes:

$$\boldsymbol{t} = \frac{1}{k_{rad} + k_{nr}} \tag{2.4}$$

It is necessary to determine the radiative and nonradiative rates for 1AC in solvent environments where it is believed that a reaction does not occur. These values then establish a baseline that allows the quantum yield and excited-state lifetimes to be interpreted when the proton-transfer reaction is catalyzed by the solvent. If a distinction is made between the proton-transfer rate and all other nonradiative processes, then the expressions for the quantum yield and excited-state lifetime follow:

$$j = \frac{k_{rad}}{k_{rad} + k_{nr} + k_{PT}}$$
, and (2.5)

$$t = \frac{1}{k_{rad} + k_{nr} + k_{PT}}$$
 (2.6)

Should the proton-transfer be the dominant nonradiative process, other nonradiative rates may be neglected in the analysis of the quantum yield. Should the proton-transfer rate be much faster than the radiative and other nonradiative rates, the excited-state lifetimes may be interpreted directly as the average reaction times. The radiative and nonradiative rates for 1AC in nonprotic solvents are calculated from quantum yield and lifetime data and are summarized in *Table 2.3*. These quantities will be discussed later in the dissertation.

In addition to the quantum yield and lifetime data, the steady-state absorption and emission spectra contain valuable information that allows the radiative rate of emission to be calculated independently of direct measurement in special cases. In these latter calculations, the transition moments are extracted from analysis of the absorption and emission bands for each electronic state.²⁵ The transition moments are related to the radiative rates through the Einstein coefficients. In addition, the transition moments are themselves interesting since they are related to the states involved in the electronic transition ($p \rightarrow q$):

$$M_{pq} = \langle p | \mu | q \rangle$$
 (2.7)

where μ is the electric dipole moment operator. If the transition moments of 1AC are reasonably constant in a variety of solvent environments, then a model of the reaction involving only two electronic states is appropriate.²⁶ That is, only the ground state and one excited state need to be considered for the reaction.

Determination of the transition moments from absorption spectra requires the isolation of particular absorption bands. Two cases are considered in *Figure 2.4* and *Figure 2.5*: 1AC in the nonpolar, aprotic solvent methylcyclohexane and 1AC in the polar, protic solvent methanol.²⁷ Exploiting the mirror symmetry of the normal emission and first absorption bands allowed the extent of the first absorption band to be estimated for the necessary integrations.²⁸ The band decompositions used in this work are noted by dashed lines in *Figure 2.4* and *Figure 2.5*.

The calculation of the transition moments from absorption and emission spectra proceeds as follows.^{26,29-31} The transition moment between the ground and (Franck-Condon) excited state is determined from absorption spectra:

$$\left|\mathbf{M}_{01}\right|^{2} = \operatorname{constant} \cdot \frac{1}{\mathbf{F}(\mathbf{n})} \cdot \int_{\mathbf{A}} \frac{\boldsymbol{e}(\boldsymbol{n})}{\boldsymbol{n}} d\boldsymbol{n} \qquad (2.8)$$

where the integration is over the frequency-weighted molar absorptivity $\varepsilon(v)$ for an appropriate absorption band (A), and some correction for the index of refraction [F(n)] is applied. The transition moment between the (relaxed) excited and ground states is obtained from emission spectra:

$$\left|\mathbf{M}_{10}\right|^{2} = \text{constant'} \cdot \frac{\mathbf{k}_{\text{rad}}}{\mathbf{F}'(\mathbf{n})} \cdot \frac{\int \mathbf{E}(\mathbf{n}) d\mathbf{n}}{\int \mathbf{E}(\mathbf{n}) \mathbf{n}^{-3} d\mathbf{n}} \approx \text{constant'} \cdot \frac{\mathbf{k}_{\text{rad}}}{\mathbf{F}'(\mathbf{n})} \cdot \frac{1}{\langle \mathbf{n} \rangle^{3}}$$
(2.9)

where the integrations over the emission band [E(v)] are nearly equal to the cube of the first moment of the band ($\langle v \rangle^3$), and a different correction for the index of refraction

[F'(n)] is applied. The radiative rate may be determined experimentally using the quantum yield and measured fluorescence lifetime, $k_{rad} = \phi / \tau$, as noted above.

The photophysical behavior thus calculated for 1AC is quite revealing. In the nonpolar solvent methylcyclohexane, the transition moments calculated from absorption and emission spectra of 1AC are identical within uncertainty (~10-15%), here using the Birks convention for the index of refraction correction³⁰: $|\mathbf{M}_{01}| = 1.5 \pm 0.2$ D and $|\mathbf{M}_{10}| = 1.6 \pm 0.2$ D.

The transition moments for 1AC in methanol are more challenging to interpret: $|M_{01}| = 2.0 \pm 0.3 \text{ D}$ and $|M_{10}| = 1.3 \pm 0.2 \text{ D}$. The sum of the estimated uncertainties is less than the difference of the magnitudes of these transition moments. Examination of the steady-state spectra of 1AC in methylcyclohexane and methanol provides insight into the source of the difference. If one compares the S₁ bands of 1AC in methylcyclohexane and methanol directly, one may observe that the S₁ band in methanol is significantly broadened. Since the peak molar absorptivity constants for the S₁ bands are nearly identical in these two solvents, the broadening of the S₁ band in methanol accounts for the increased M₀₁ transition moment calculated via Equation 2.8.

The 1AC emission transition moments (M_{10}) have been examined in many solvents having a range of polarities. The data is provided in *Figure 2.7* and *Table 2.1*. Although the emission transition moments appear to decrease slightly with increasing solvent polarity or hydrogen-bond donating ability of the solvent as measured by the $E_T(30)$ polarity scale (see Section 2.5), the change is obscured by the uncertainty associated with the experiment. For example, two extreme values are equal within uncertainty: $M_{10} = 1.6 \pm 0.2$ D for 1AC in methylcyclohexane and $M_{10} = 1.2 \pm 0.2$ D for 1AC in water. Thus, M_{10} for 1AC is reasonably constant in all solvents. The two measured absorption transition moments (M_{01}) for 1AC are also equal within uncertainty: $M_{01} = 1.5 \pm 0.2$ D for 1AC in methylcyclohexane and $M_{01} = 2.0 \pm 0.3$ D for 1AC in methanol. From these two measurements we postulate that the absorption transition moments are equal in all solvents. A final interpretation of the observations of the absorption and emission transition moments leads to the conclusion that a two electronic-state model for 1AC is warranted.

We note in passing that for nonreactive and rigid molecules,^{31,32} the transition moments may be equated $|M_{01}| = |M_{10}|$ to provide a means for estimating the radiative rate directly from the steady-state spectra:

$$k_{rad} = constant'' \cdot F''(n) \cdot \langle \boldsymbol{n} \rangle^3 \cdot \int \frac{\boldsymbol{e}(\boldsymbol{n})}{\boldsymbol{n}} d\boldsymbol{n} \qquad (2.10)$$

1AC satisfies the assumptions of this equation in the nonpolar, nonprotic solvent methylcyclohexane. The calculated radiative rate, $k_{rad} = 4.6 \times 10^7 \text{ s}^{-1}$, is consistent with the observed rate $k_{rad} = 4.9 \times 10^7 \text{ s}^{-1}$.^[33]

The mirror symmetry of the normal emission and first absorption band provides good evidence that emission is occurring from the lowest excited state S₁. The magnitudes of higher transition moments and the corresponding radiative rates also support this interpretation. In methylcyclohexane and methanol, respectively, the transition moments to the second excited state are calculated to be $|M_{02}| = 2.8 \text{ D}$ $(k_{rad} = 1.5 \text{ x } 10^8 \text{ s}^{-1})$ and $|M_{02}| = 3.0 \text{ D}$. Experimentally, the observed normal radiative

rates are independent of the excitation wavelength and are in better agreement with the radiative rates calculated for the first excited state S_1 . If mixing of excited states (S_1 and S_2) occurred in the more polar solvents (as debated for indole and its derivatives), the net radiative rate might be expected to increase rather than to decrease as observed. Thus, 1AC excited into a higher electronic state undergoes rapid internal conversion prior to emission from the first excited state (S_1).

2.5 Solvent Polarity and Related Scales

Previous discussions have alluded to scales of solvent polarity which are attempts to rank or classify solvents. We conclude this chapter on the steady-state spectroscopy of 1AC in various solvents by introducing several scales that incorporate some quantitative metric for solvent characterization. The vital connection between the solvent properties and their effects on chemical reactions is yet being pursued, and it is indeed necessary for understanding the solvent-catalyzed proton-transfer reactions of 1AC or 7AI. While the chemical idea of polarity is intuitive,³⁴ its quantitative description is nontrivial. The crux of the problem lies in the difficulty in isolating specific intermolecular interactions for clean identification as sources of solvent polarity. If molecular aspects of the solvent are ignored,¹⁸ then the solvent may be modeled as a dielectric continuum whose net effect on the electrical properties of an encapsulated solute is described by the "reaction field."³⁵ To gain access to specific intermolecular interactions such as hydrogen bonding, molecular probes are frequently used to create empirical solvent polarity scales that correlate spectral shifts with chemical properties of probes and solvents. Two popular

examples are the $E_T(30)$ polarity scale³⁶⁻³⁸ and the π^* polarity scale.³⁹⁻⁴¹ Since the π^* scale is more of a measure of nonspecific intermolecular interactions, it has been less useful for understanding trends in hydrogen-bonding problems including excited-state proton transfer.⁴ Alternatively, the $E_T(30)$ scale is based on the solvent dependence of the absorption transition energy of a betaine dye. Since the $E_T(30)$ scale is constructed from a molecule containing sites sensitive to hydrogen-bonding and polarity, this scale may be a better measure of the polarity sensed by the proton-transfer molecules such as 7AI and 1AC.³ Recent experimental work has demonstrated an excellent correlation between the $E_T(30)$ scale and the hydrogen-bond donating ability of alcohols.⁴² The $E_T(30)$ polarity scale thus provides a useful surrogate measure for the strengths of specific hydrogen-bonding interactions that are undoubtedly important for understanding the proton-transfer reaction.

Although the $E_T(30)$ scale is by no means a unique measure of the hydrogen-bond donating ability of a solvent, its general use is promoted by the plethora of solvents included in its coverage. For a double proton-transfer reaction in which a measure of the hydrogen-bond accepting ability of a solvent is important as well, Petrich and coworkers have noted the autoprotolysis constant is another suitable measure for characterizing the solvents.^{43,44} The α scale of hydrogen bond donating ability provides a third empirical scale that can be used to characterize the effect of hydrogen bonds on spectral shifts,^{45,46} and even other measures of acidity have been employed in studies of 7AI.⁴⁷ Perhaps not surprisingly, all these measures of hydrogen-bonding strength are well correlated with each other (see *Figure 2.8* and *Table 2.2*),⁴⁸ extending reassurance that the interpretation of the underlying physical causes of the linear trends is reasonable. Note the amides differ from the alcohols in acidity-related measures due to resonance stabilization in the O=C-N group following abstraction of a proton. Since more solvents in this study are included in tabulation for the $E_T(30)$ scale than are available in the α scale or for the autoprotolysis constant, the use of the $E_T(30)$ scale will be continued here.

| | So | lvent So | ale | Absorption | | | | Emission | | | | Transition Moment | | |
|--------------------------------|------|----------------------|--------|-----------------------|------------------------|------------------------|-----------------------|------------------------|-----------------------|-----------------------|-----------------------|-------------------|-----------------------|----------|
| Solvent | π* | $\mathbf{E_{T}}^{N}$ | F(e,n) | Δν | Г | Δν | Γ | <v></v> | Δν | FWHM | Stokes | n | k _{rad} (N) | M_{10} |
| | | | | 300nm | 300nm | 330nm | 330nm | Normal | Normal | Normal | Shift | | | |
| | | | | $10^3 {\rm cm}^{-1}$ | 10^3 cm^{-1} | 10^3cm^{-1} | $10^3 {\rm cm}^{-1}$ | 10^3 cm^{-1} | $10^3 {\rm cm}^{-1}$ | $10^3 {\rm cm}^{-1}$ | $10^3 {\rm cm}^{-1}$ | | 10^7 s^{-1} | D |
| Methylcyclohexane | 0.00 | 0.006 | 0.00 | 0.00 | 0.00 | 0.00 | 0.00 | 27.95 | 0.00 | 2.86 | 0.00 | 1.423 | 4.9 | 1.6 |
| 1,1,2-Trichlorotrifluoroethane | 0.01 | 0.077 | 0.10 | -0.04 | 0.22 | -0.02 | 0.35 | 27.82 | 0.13 | 3.03 | 0.15 | 1.356 | 3.5 | 1.4 |
| Diisopropylether | 0.19 | 0.105 | 0.27 | 0.15 | 0.18 | 0.47 | 0.48 | 27.17 | 0.78 | 3.15 | 0.31 | 1.366 | 3.4 | 1.5 |
| Diethyl Ether | 0.24 | 0.117 | 0.30 | 0.12 | 0.24 | 0.44 | 0.51 | 26.98 | 0.97 | 3.30 | 0.53 | 1.350 | 3 * | 1.4 * |
| Tetrahydrofuran | 0.55 | 0.207 | 0.44 | 0.23 | 0.34 | 0.56 | 0.65 | 26.75 | 1.20 | 3.36 | 0.64 | 1.405 | 3 * | 1.3 * |
| N,N-Dimethylformamide | 0.88 | 0.386 | 0.67 | 0.29 | 0.55 | 0.68 | 0.71 | 26.22 | 1.73 | 3.61 | 1.05 | 1.431 | 3.4 | 1.4 |
| Acetonitrile | 0.66 | 0.460 | 0.71 | -0.03 | 0.45 | 0.31 | 0.69 | 26.45 | 1.50 | 3.69 | 1.19 | 1.342 | 2.5 | 1.3 |
| t-Butanol | | 0.389 | 0.56 | 0.29 | 0.51 | 0.90 | 0.84 | 26.12 | 1.83 | 3.58 | 0.93 | 1.385 | 1.5 * | 1.0 * |
| 2-Propanol | 0.48 | 0.546 | 0.63 | 0.27 | 0.53 | 0.80 | 0.76 | 26.05 | 1.90 | 3.65 | 1.10 | 1.375 | 2.8 * | 1.4 * |
| 1-Pentanol | | 0.586 | 0.57 | 0.44 | 0.88 | 0.87 | 0.75 | 26.09 | 1.86 | 3.58 | 1.00 | 1.407 | 2.0 | 1.1 |
| Benzyl Alcohol | 0.98 | 0.608 | 0.47 | | | 0.80 | 0.96 | 25.54 | 2.41 | 3.91 | 1.61 | 1.538 | 0.8 | 0.7 |
| 1-Propanol | 0.52 | 0.617 | 0.63 | 0.29 | 0.55 | 0.86 | 0.67 | 25.96 | 1.99 | 3.67 | 1.13 | 1.384 | 2.1 | 1.2 |
| N-Methylformamide | | 0.722 | 0.72 | 0.33 | 0.58 | 0.72 | 0.89 | 25.79 | 2.16 | 3.89 | 1.44 | 1.432 | 2.2 | 1.2 |
| Methanol | 0.60 | 0.762 | 0.71 | 0.15 | 0.58 | 0.73 | 0.73 | 25.71 | 2.24 | 3.92 | 1.51 | 1.327 | 2.0 | 1.3 |
| Methanol-OD | | 0.760 | 0.71 | 0.21 | 0.91 | 0.78 | 0.91 | 25.76 | 2.19 | 3.91 | 1.41 | 1.327 | 2.1 | 1.3 |
| Formamide | 0.97 | 0.775 | 0.71 | 0.34 | 0.75 | 0.68 | 0.86 | 25.38 | 2.57 | 4.24 | 1.88 | 1.447 | 1.1 | 0.86 |
| Ethylene Glycol | 0.92 | 0.790 | 0.67 | 0.31 | 0.67 | 0.83 | 0.85 | 25.30 | 2.65 | 4.12 | 1.82 | 1.431 | 1.7 | 1.1 |
| Water | 1.09 | 1.000 | 0.76 | -0.01 | 0.83 | 0.59 | 0.86 | 23.90 | 4.05 | 5.00 | 3.46 | 1.333 | 1.4 | 1.2 |
| Deuterium Oxide | | 0.991 | 0.76 | 0.03 | 0.75 | 0.62 | 0.91 | 23.96 | 3.99 | 5.01 | 3.37 | 1.333 | 1.2 | 1.1 |

Table 2.1: 1AC Steady-State Spectral Characterizations and Emission Transition Moments

See Table 2.2 for References for the three solvent scales. For the solvent scale $F(\varepsilon,n)$, ε is the static dielectric constant and n is the index of refraction of the solvent. Shifts (Δv) and width parameters (Γ) of the absorption spectra are reported with respect to the spectrum in methylcyclohexane. The uncertainty in the absorption band fit parameters is estimated to be $\pm 50 \text{ cm}^{-1}$. Shifts and widths of normal emission bands were measured directly. Values denoted by an asterisk contain greater uncertainties (~20%) than the other values (~10%). See text for discussion on the determination of the emission transition moments.

| Solvent | $F(\varepsilon_0,n)^{(a)}$ | π* ^(b) | α (c) | $E_T^{N(d)}$ | pK _{auto} (e) | pKa ^(f) |
|--------------------------------|----------------------------|--------------------------|-------|--------------|------------------------|--------------------|
| Methylcyclohexane | 0.00 ⁽³⁾ | 0.00 ⁽³⁾ | | 0.006 (*) | | |
| 1,1,2-Trichlorotrifluoroethane | 0.10 ⁽²⁾ | 0.01 (3) | | 0.077 | | |
| Diisopropylether | 0.27 (2) | 0.19 (1) | | 0.105 | | |
| Diethyl Ether | 0.30 ⁽²⁾ | 0.24 (1) | | 0.117 | | |
| Tetrahydrofuran | 0.44 (2) | 0.55 (1) | | 0.207 | | |
| N,N-Dimethylformamide | 0.67 (2) | 0.88 (1) | | 0.386 | | |
| t-Butanol | 0.56 (4) | 0.41 (2) | 0.42 | 0.389 | 27.65 | 19.10 |
| Acetonitrile | 0.71 (2) | 0.66 (1) | 0.19 | 0.460 | | |
| 2-Propanol | 0.63 (2) | $0.48^{(2)}$ | 0.76 | 0.546 | 20.16 | 17.6 |
| 1-Butanol | 0.61 (2) | 0.47 (2) | 0.84 | 0.586 | 21.23 | 16.10 |
| 1-Pentanol | 0.57 (2) | | 0.84 | 0.586 | 20.73 | |
| Benzyl Alcohol | 0.47 (1) | $0.98^{(2)}$ | 0.60 | 0.608 | | |
| 1-Propanol | 0.63 (2) | 0.52 (2) | 0.84 | 0.617 | 19.32 | 15.97 |
| Ethanol | 0.67 (2) | 0.54 (2) | 0.86 | 0.654 | 19.02 | 15.90 |
| Propylene Glycol | 0.65 (1) | | | 0.722 | 17.21 | 14.85 |
| N-Methylformamide | 0.72 (1) | | 0.62 | 0.722 | 10.74 | -0.04 |
| Methanol-OD | 0.71 (3) | | | 0.760 | | |
| Methanol | 0.71 ⁽²⁾ | $0.60^{(2)}$ | 0.98 | 0.762 | 16.74 | 15.43 |
| Formamide | 0.71 ⁽²⁾ | $0.97^{(2)}$ | 0.71 | 0.775 | 16.90 | -0.48 |
| Ethylene Glycol | 0.67 (2) | $0.92^{(2)}$ | 0.91 | 0.790 | 15.84 | 14.7 |
| 2,2,2-Trifluoroethanol | | 0.73 (2) | 1.49 | 0.898 | | |
| Deuterium Oxide | 0.76 (3) | | | 0.991 | | |
| Water | 0.76 (4) | 1.09 (2) | 1.17 | 1.000 | 14.00 | 15.7 |

Table 2.2: Solvent Scales of Polarity and Hydrogen-Bonding Strength

(a) Reaction field factor $F(\varepsilon_{0,n}) = (\varepsilon_{0}-1)/(\varepsilon_{0}+1) - (n^{2}-1)/(n^{2}+1)$. (1) M. L. Horng, J. A. Gardecki, A. Papazyan, and M. Maroncelli, *J. Phys. Chem.*, **99**, 17311 (1995). (2) L. Reynolds, J. A. Gardecki, S. J. V. Frankland, M. L. Horng, and M. Maroncelli, *J. Phys. Chem.*, **100**, 10337 (1996). (3) Estimated from the protiated solvent. (4) Calculated for this work.

(b) The π^* solvent scale. (1) C. Laurence, P. Nicolet, M. T. Dalati, J.-L. M. Abboud, and R. Notario, *J. Phys. Chem.*, **98**, 5807 (1994). (2) M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham, and R. W. Taft, *J. Org. Chem.*, **48**, 2877 (1983). (3) Estimated from closely related solvent.

(c) Taft and Kamlet's scale of hydrogen-bond donation ability. Values from M. J. Kamlet, J.-L. M. Abboud, M. H. Abraham, and R. W. Taft, *J. Org. Chem.*, **48**, 2877 (1983), as compiled by Y. Marcus, *J. Solution Chem.*, **20**, 929 (1991).

(d) Normalized $E_T(30)$ scale. C. Reichardt, *Chem. Rev.*, **94**, 2319 (1994). (*) Estimated from closely related solvent.

(e) Mean values of autoprotolysis constants calculated from data tabulated in: (1) S. Rondinini, P. Longhi, P. R. Mussini, and T. Mussini, *Pure & Appl. Chem.*, **59**, 1693 (1987). (2) J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Organic Solvents*. (New York, Wiley, 1986).

(f) Mean values of acid dissociation constants calculated from data tabulated in: (1) J. A. Riddick, W. B. Bunger, and T. K. Sakano, *Organic Solvents*. (New York, Wiley, 1986). (2) P. H. Howard and W. M. Meylan, Eds., *Handbook of Physical Properties of Organic Chemicals*. (Boca Raton, FL, Lewis Publishers [CRC Press, Inc.], 1997.). (3) L. G. Wade, Jr., *Organic Chemistry*. (Englewood Cliffs, N.J., Prentice-Hall, Inc., 1987). p. 414.
| Bulk Aprotic Solvents | | Total | | Normal | | | k _{nr} (N) | k _{rad} (N) | | |
|--------------------------------|------|-------------|-----------------|----------------------|-----------------------|------------------------|-------------------------|-----------------------|-----------------------|-------------------------|
| [295±2 K] | | ϕ_{em} | | $\tau_{\rm fl}$ (ns) | | | 10^{6} s^{-1} | 10^6 s^{-1} | | |
| Methylcyclohexane | | 0.54 | | 11 | | | 42 | 49 | | |
| 1,1,2-Trichlorotrifluoroethane | | 0.29 | | 8.2 | | | 86 | 35 | | |
| Diisopropyl ether | | 0.33 | | 8.8 | | | 80 | 34 | | |
| Diethyl ether | | 0.2 | | 7.3 | | | 1_{00} | 30 | | |
| Tetrahydrofuran | | 0.2 | | 8.4 | | | 1_{00} | 30 | | |
| N,N-Dimethylformamide | | 0.40 | | 12 | | | 51 | 34 | | |
| Acetonitrile | | 0.21 | | 8.5 | | | 93 | 25 | | |
| | | | | | | | | | | |
| Bulk Protic Solvent | | Total | Tautomer | Normal | Tautomer | Tautomer | k _{PT} | k _{rad} (N) | $k_{rad}(T)$ | $\alpha = k_{rad}(N) /$ |
| [295±2 K] | | ϕ_{em} | $\phi_{\rm em}$ | $\tau_{\rm fl}$ (ns) | rise τ_{fl} (ns) | decay τ_{fl} (ns) | 10^9 s^{-1} | 10^6 s^{-1} | 10^6 s^{-1} | $k_{rad}(T)$ |
| t-Butanol | | (0.029) | (0.00072) | 1.85 | 0.50 | 1.86 | 0.54 | (15) | (1.4) | 11 |
| 2-Propanol | (**) | (0.033) | (0.0012) | 1.12 | 0.42 | 1.13 | 0.89 | (28) | (2.9) | 9.9 |
| 1-Pentanol | (**) | 0.021 | 0.0012 | 0.97 | 0.45 | 1.03 | 1.0 | 20 | 2.7 | 7.4 |
| Benzyl Alcohol | (**) | ~0.0027 | 0.00038 | 0.30 | 0.25 | 0.45 | 3.6 | 8 | 0.8 | 10 |
| 1-Propanol | (**) | 0.019 | 0.0011 | 0.82 | 0.41 | 0.86 | 1.2 | 21 | 2.7 | 7.9 |
| N-Methylformamide | | 0.11 | 0.0012 | 4.78 | 0.34 | 5.1 | 0.20 | 22 | 3.5 | 6.2 |
| Methanol | (**) | 0.011 | 0.00068 | 0.51 | 0.29 | 0.52 | 1.94 | 20 | 2.3 | 8.6 |
| Methanol-OD | | 0.054 | 0.0012 | 2.51 | 0.41 | 2.46 | 0.40 | 21 | 2.9 | 7.3 |
| Formamide | | 0.022 | 0.00042 | 1.85 | 0.23 | 1.94 | 0.53 | 11 | 1.8 | 6.2 |
| Ethylene glycol | | 0.019 | 0.00091 | 1.05 | 0.31 | 1.08 | 0.94 | 17 | 2.9 | 5.8 |
| 2,2,2-Trifluoroethanol | (**) | 0.0007 | 0.0003 | ~0.022 | 0.027 | ~0.21 | 41 | 16 | 1.5 | 10 |
| Deuterium oxide | | 0.10 | * | 8.46 | * | 8.37 | 0.12 | 12 | * | * |
| Water | | 0.035 | * | 2.54 | * | 2.58 | 0.39 | 14 | * | * |
| | | | | | | | | | | |
| Mean, 11 solvents [Std. | | | | | | | | 2.3 [0.8] | 8.2 [1.8] | |
| Mean, Selected Solvents | | | | | | | | 2.2 [0.8] | 9.0 [1.1] | |

Table 2.3: Summary of Time-Resolved Emission for 1AC in Various Solvents

(continued on next page)

Table 2.3 (cont.)

 φ_{em} , τ_{fl} , k_{rad} , and k_{nr} denote the emission quantum yield, fluorescence lifetime, radiative and nonradiative rates for the normal (N) and tautomer (T) species, respectively. Quantum yields were determined relative to quinine sulfate in 1N H₂SO₄ [φ =0.546]^{1,2} or in 0.1 N HClO₄ [φ =0.59]¹, and many values are the average of two or three independent measurements. Uncertainties in quantum yields and radiative rates are estimated to be ±10%, although in many of the aprotic solvents the quantum yield, lifetimes, and nonradiative rates are expected to be less accurate [on the order ±20%] due to quenching impurities. The tautomer bands were fit using a scaled lineshape of the tautomer emission of 1AC in benzyl alcohol. When multiexponential emission lifetimes represent, the best estimates for the normal emission lifetime were extracted for a single time constant. Many lifetimes represent the average of at least two independent measurements. The tautomer radiative rate and quantum yield assume a complete reaction with k_{PT} >> k_N . Values in parentheses are more uncertain, and asterisks indicate the value was not resolved. The main nonradiative rate of the normal species in protic solvents has been identified with the proton-transfer rate k_{PT} . The choice of the six selected solvents (**) was based on the observed rapid k_{PT} which should be free from possible contamination from the normal deactivation rate k_N .

¹ R.A. Velapoldi and K.D. Mielenz, *NBS Special Publication 260-64*, pp. 50-52, (1980). ² J.N. Demas and G. A. Crosby, *J. Phys. Chem.*, **75**, 991 (1971).



Figure 2.1: Absorbance and Fluorescence Spectra of 1AC: An Overview



Figure 2.2: Absorbance and Fluorescence of 1AC in Ethers and Methylcyclohexane



Figure 2.3: Absorbance and Fluorescence of 1AC in Other Protic Solvents



Figure 2.4: Resolution of S_1 and S_2 Bands in the Absorption Spectrum of 1AC in Methylcyclohexane



Figure 2.5: Resolution of S_1 and S_2 Bands in the Absorption Spectrum of 1AC in Methanol



Figure 2.6: Comparison of 1AC and 7AI Stokes Shifts

Most 7AI data are from C. F. Chapman and M. Maroncelli, *J. Phys. Chem.*, **96**, 8430 (1992). Numbered solvents are discussed in Chapters 5 and 6: (1) Water. (2) Deuterium oxide. (3) Formamide. (4) Ethylene Glycol. (5) Benzyl Alcohol.



Figure 2.7: 1AC Absorption and Emission Transition Moments

Solid triangles are absorption moments from ground to excited state, M_{01} , in the solvents methylcyclohexane ($E_T^{\ N} = 0$) and methanol ($E_T^{\ N} = 0.76$). The emission moments M_{10} are for the following classes of solvents: solid squares, aprotic solvents; open squares, alcohols; open triangles, protic amides; open circles, diols and water. The linear regression is to all emission data except formamide (1), benzyl alcohol (2), and t-butanol (3).



Figure 2.8: Various Correlations of Hydrogen-Bond Donating Ability

Various measures of hydrogen-bond donating ability are correlated to the normalized $E_T(30)$ scale (E_T^N) . See Table 2.2 for References to the values used in these plots. Correlation coefficients: pKauto vs. E_T^N , $R^2 = 0.68$; pKa vs. E_T^N , $R^2 = 0.57$ (excluding NMF and FA); and, Alpha vs. E_T^N , $R^2 = 0.63$.

ENDNOTES

¹ The photophysics and photochemistry of 7-azaindole with applications are included in a recent review by A. V. Smirnov, D. S. English, R. L. Rich, J. Lane, L. Teyton, A. W. Schwabacher, S. Luo, R. W. Thornburg, and J. W. Petrich, *J. Phys. Chem. B.*, **101**, 2758-2769 (1997).

² A selected bibliography of work related to 1-azacarbazole and 7-azaindole follows Chapter 8.

³ R. S. Moog, S. C. Bovino, and J. D. Simon, J. Phys. Chem., 92, 6545-6547 (1988).

⁴ R. S. Moog and M. Maroncelli, J. Phys. Chem., 95, 10359-10369 (1991).

⁵ C. F. Chapman and M. Maroncelli, J. Phys. Chem., 96, 8430-8441 (1992).

⁶ C. F. Chapman, Ph.D. Thesis, The Pennsylvania State University, 1993.

⁷ S. J. Boryschuk, M.S. Thesis, The Pennsylvania State University, 1993.

⁸ See pp. 2761-2762 of A. V. Smirnov, D. S. English, R. L. Rich, J. Lane, L. Teyton, A. W. Schwabacher, S. Luo, R. W. Thornburg, and J. W. Petrich, *J. Phys. Chem. B.*, **101**, 2758-2769 (1997).

⁹ S. Mente and M. Maroncelli, J. Phys. Chem. A, **102**, 3860-3876 (1998).

¹⁰ S. Mente, S. J. V. Frankland, L. Reynolds, and M. Maroncelli, *Chem. Phys. Lett.*, **293**, 515-522 (1998).

¹¹ C. Chang, N. Shebestary, and M. A. El-Bayoumi, Chem. Phys. Lett., 75, 107 (1980).

¹² J. Waluk, S. J. Komorowski, and J. Herbich, J. Phys. Chem., **90**, 3868 (1986).

¹³ The calculated absorption spectra did not always converge well for the fragments of the bands chosen for fits by the computer program "absfit" [M. Maroncelli]. The uncertainty in the absorption band fit parameters is estimated to be $\pm 50 \text{ cm}^{-1}$.

 14 El-Bayoumi and coworkers in Endnote 11 identified S_1 and S_2 as the 1L_a and 1L_b states, respectively, by comparison to polarization measurements on the related molecule carbazole.

¹⁵ K. Fuke, T. Yabe, N. Chiba, T. Kohida, and K. Kaya, J. Phys. Chem., 90, 2309, (1986).

¹⁶ The first moment of the emission spectra $\langle v \rangle$ were determined over the range 21-31 kK except for water whose entire emission band was measured. Including tautomer emission in the determination of $\langle v \rangle$ changed values by $\sim 2\%$. Including consideration of the absolute uncertainty in the widths ($\sim 10\%$) and average frequencies ($\langle 0.5\% \rangle$) due to differences in instrument correction factors, the experimental uncertainties in the widths and $\langle v \rangle$ are estimated to be ±300 cm⁻¹.

¹⁷ M. L. Horng, J. A. Gardecki, A. Papazyan, and M. Maroncelli, *J. Phys. Chem.*, **99**, 17311 (1995).

¹⁸ M. Maroncelli and G. R. Fleming, J. Chem. Phys., 86, 6221 (1987).

¹⁹ G. van der Zwan and J. T. Hynes, J. Phys. Chem., 89, 4181 (1985).

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²¹ The photophysics of coumarin 153 in a similar selection of solvents reveals that the correlation between the Stokes shift and reaction field is linear even for hydrogen-bond donating solvents. See, for example, Endnote 17.

²² Earlier studies have noted that simple hydrogen-bonding to the N-H group of related heterocyclic molecules is unable to account alone for the notable spectral shifts in highly polar solvents. See, for example, discussions on alkylated indole [S. R. Meech, D. Phillips, and A. G. Lee, *Chem. Phys.*, **80**, 317 (1983).] and carbazole derivatives [R. W. Bigelow and G. P. Ceasar, *J. Phys. Chem.*, **83**, 1790, (1979)].

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²⁴ J. T. Edward, J. Chem. Ed., 47, 261 (1970).

²⁵ During this work, L. Reynolds realized that the computer program "spcany" [M. Maroncelli] was incorrectly converting absorption or excitation spectra between wavelength and frequency representations. The error arose in the unnecessary application of the factor $1/\lambda^2$ (or $1/\nu^2$) to the data prior to conversion. This conversion factor is required for proper treatment of the emission data. The error apparently affected all absorption data in the Maroncelli Group's earlier work (prior to February 1997), but happily the distortion reportedly caused negligible damage to conclusions reached from normalized data.

²⁶ J. E. Lewis and M. Maroncelli, *Chem. Phys. Lett.*, **282**, 197 (1998).

²⁷ Magnitudes of the molar absorptivity constants were taken from reported values.
 L. Reynolds confirmed magnitudes of 1AC molar absorptivity constants in more concentrated methylcyclohexane solutions.

(a) V. M. Clark, A. Cox, and E. J. Herbert, J. Chem. Soc. C., 1968, 831.

(b) L. Stephenson and W. K. Warburton, J. Chem. Soc. C., 1970, 1355.

(c) R. S. Moog (Franklin and Marshall College, Lancaster, PA.), communication March 31, 1995.

²⁸ This method was mentioned by C. A. Parker, *Photoluminescence of Solution*. (Amsterdam, Elsevier Pub. Co., 1968). pp. 22-28.

²⁹ S. Hirayama and D. Phillips, J. Photochemistry, **12**, 139 (1980).

³⁰ J. B. Birks, *Photophysics of Aromatic Molecules*. (London, Wiley-Interscience, 1970). Chapters 3 and 4.

³¹ S. J. Strickler and R. A. Berg, J. Chem. Phys., 37, 814 (1962).

³² J. B. Birks [*Photophysics of Aromatic Molecules*. (London, Wiley-Interscience, 1970). p. 87.] notes that the equivalence of transition moments implies little difference in the nuclear configurations in the ground and excited states.

³³ The agreement between calculated and observed radiative rates is also consistent with observations reported by K. Fuke, K. Tsukamoto, F. Misaizu, and K. Kaya, *J. Chem. Phys.*, **95**, 4074 (1991) for 1AC monomer in a molecular beam.

³⁴ Consider, for example, the general rule "like dissolves like."

³⁵ The reaction field is some function of the static dielectric constant and the index of refraction for a solvent, $F(\varepsilon_0,n)$, and describes an effective electric field at the solute due to the surrounding solvent molecules. Various definitions of the reaction field fragment the literature. One popular expression is $F(\varepsilon_0,n) = (\varepsilon_0-1)/(2\varepsilon_0+1) - (n^2-1)/(2n^2+1)$. Another form which is exploited regularly by M. Maroncelli *et al.* is $F(\varepsilon_0,n) = (\varepsilon_0-1)/(\varepsilon_0+1) - (n^2-1)/(n^2+1)$. For further discussion and application, see for example, A. T. Amos and B. L. Burrows, *Adv. Quantum Chem.*, **7**, 289 (1973).

³⁶ See, for example, C. Reichardt, *Solvents and Solvent Effects in Organic Chemistry, 2nd Rev. and Enl. Ed.,* (New York, VCH, 1988).

³⁷ C. Reichardt, *Chem. Rev.*, **94**, 2319 (1994).

³⁸ C. Reichardt in *Molecular Interactions, Volume 3*. [H. Ratajczak and W. J. Orville-Thomas, Eds.] (New York, John Wiley and Sons, Ltd., 1982). pp. 241-282.

³⁹ C. Laurence, P. Nicolet, M. T. Dalati, J.-L. M. Abboud, and R. Notario, *J. Phys. Chem.*, 98, 5807 (1994).

⁴⁰ M. J. Kamlet, J.-L. Abboud, and R. W. Taft, Prog. Phys. Org. Chem., 13, 485 (1981).

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⁴² See, for example, J. Catalán, P. Pérez, J. Elguero, and W. Meutermans, *Chem. Ber.*, 126, 2445 (1993).

⁴³ Y. Chen, F. Gai, and J. W. Petrich, *Chem. Phys. Lett.*, **222**, 329 (1994).

⁴⁴ Recent tabulations of the autoprotolysis constants include:

(a) S. Rondinini, P. Longhi, P. R. Mussini, and T. Mussini, *Pure & Appl. Chem.*, **59**, 1693 (1987).

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⁴⁵ M. J. Kamlet, J.-L. Abboud, M. H. Abraham, and R. W. Taft, *J. Org. Chem.*, **48**, 2877 (1983).

⁴⁶ Y. Marcus, J. Solution Chem., **20**, 929 (1991).

⁴⁷ J. Konijnenberg, A. H. Huizer, and C. A. G. O. Varma, *J. Chem. Soc., Faraday Trans.* 2, **84**, 163 (1988).

⁴⁸ For example, relationships between the different solvent scales are discussed by Kamlet *et al.* (Endnote 45); Marcus (Endnote 46); and Matyushov *et al.* (Endnote 41); and Reichardt (Endnotes 36, 37, and 38).

Chapter 3

TIME-RESOLVED FLUORESCENCE AND TWO-STATE KINETIC MODELS FOR 1-AZACARBAZOLE

3.1 Introduction

The characteristics of the steady-state fluorescence of 1AC in various neat solvents were described and analyzed in Chapter 2. In this chapter we summarize the observed time-dependence of 1AC emission. In order to facilitate interpretation of the measured excited-state lifetimes to be discussed in later chapters, a number of two-state kinetic schemes are presented. Sections 3.3 and 3.4 contain details of analysis that will be used in Chapters 6 and 7, and the reader may wish to defer reading these sections until later.

In a time-resolved fluorescence experiment, the following fluorescence decay behavior is typically observed. The fluorescence of the normal species of 1AC in neat solvents may be typically characterized by one or two decay components or lifetimes. One short lifetime component may be attributed to the dynamic Stokes shift that results from solvent molecules reorganizing about a different charge distribution of the solute in an excited-state. The second lifetime component is attributed to the time-dependence of the normal species' population. In aprotic solvents that do not catalyze the tautomerization reaction, the normal lifetime is about 10 ns. In protic solvents that promote the reaction, the emission is quenched and the lifetimes are approximately 10 times shorter. Fluorescence appearing from the tautomer species is typically characterized by three lifetime components: one rising component (attributed to the deactivation of the tautomer) and one or two decaying components attributed to the reaction time and, in some cases, to trace impurities.

3.2 Irreversible Proton-Transfer Scheme

A great simplification of a proton-transfer reaction is illustrated in *Figure 3.1*. This irreversible proton-transfer kinetic scheme has proven successful in interpreting photochemistry of 7AI and 1AC in bulk alcohols¹⁻⁸ and isolated complexes. The surrounding solvent molecules are neglected temporarily as we focus on the hydrogenbonded complex presumed to catalyze the reaction. Although acetic acid is paired with 1AC in this example, any of the protic solvents considered in this thesis could be drawn in its place.

Below the molecular cartoon in *Figure 3.1* is a two-state kinetic scheme. The relative energetics of the normal and tautomer species deduced from experiment have also been verified by quantum chemical calculations for 7AI.⁹ The normal form of 1AC is lowest in energy and thus the ground-state population of 1AC predominantly consists of this form. If 1AC is promoted to the first excited-state S_1 following absorption of an ultraviolet photon (as discussed in Chapter 2), then one of three processes will depopulate this excited state. (1) The excited normal form may return to the ground state by emitting a photon (the radiative rate, k_{rad}^{N}). (2) The excited normal form may return to the ground

state by transferring energy to surrounding molecules (the nonradiative rate, k_{nr}^{N}). (3) The excited normal form will react to form an excited tautomer species (the reaction rate, k_{PT}). It is assumed in the irreversible proton-transfer scheme that once the excited tautomer species is formed, only radiative (k_{rad}^{T}) or nonradiative (k_{nr}^{T}) processes will depopulate this product state. Because the ground-state tautomer species is higher in energy than the ground-state normal species, additional proton-transfer reactions occur over a longer time to produce the normal species again (the ground-state reaction rate, $k_{T_{ar}N}$).

In this model the populations of the excited-state normal $(N^*(t))$ and tautomer $(T^*(t))$ species can be described by the following expressions

$$N^{*}(t) = N^{*}(0)\exp(-kt)$$
 (3.1)

$$T^{*}(t) = N^{*}(0)(\frac{k_{PT}}{k - k^{T}})[\exp(-k^{T}t) - \exp(-kt)]$$
 (3.2)

where
$$k = k_{PT} + k_{rad}^N + k_{nr}^N$$
, and (3.3)

$$k^T = k_{rad}^T + k_{nr}^T \tag{3.4}$$

If the proton-transfer reaction is the dominant pathway for depopulating the excited normal species, then the normal species' fluorescence lifetime (1/k) will be a measure of the proton-transfer time. The tautomer emission is predicted to be biexponential with one of its two lifetimes corresponding to the proton-transfer time $(1/k_{PT})$, and the other to the deactivation of the tautomer species thus formed time $(1/k^T)$. Note that the rising component of the tautomer species does not necessarily correspond to the growth of the product during the reaction. Instead, it is the relative rates of the reaction and of the

tautomer deactivation that determine the correct interpretation of the tautomer rise time. If the tautomer deactivation rate is less than the reaction rate, then the prefactor $k_{\text{PT}}/(k-k^{\text{T}})$ in Equation 3.2 is greater than zero and the tautomer rise time corresponds to the reaction. On the other hand, if the tautomer deactivation rate is greater than the reaction rate, then this prefactor is negative and the tautomer rise time corresponds to the tautomer deactivation. The importance of the relative magnitudes of the reaction rate and tautomer deactivation rate has also been illustrated in the observation of the excited-state double-proton-transfer in 3-cyano-7-azaindole in water.¹⁰

The time-resolved emission spectra of 1AC and 7AI in bulk alcohols at room temperature are indeed largely characterized this way (see, for example, *Table 2.3*).¹⁻⁵ As already mentioned, it may be necessary to include a rapid decay time in the normal emission to account for a dynamic Stokes shift attributed to solvation dynamics unrelated to the reaction,¹ and a long lifetime with small amplitude (< 5%) to account for impurities.^{1-4,11,12} But the underlying kinetics does conform to this scheme in most cases. Additional verification of the model is provided by the consistency of the radiative rates in many bulk protic solvents (*Table 2.3*) determined on the basis of Equations 3.1-3.4.

In cases when the proton-transfer rate is too fast to be resolved, this scheme provides an alternative means for estimating the rate using other quantities which may be more easily measured in experiment. Assuming that an irreversible reaction completely depopulates the normal excited state, the proton-transfer rate is simply:^{1-4,6-8}

$$k_{\rm PT} = \frac{k_{\rm rad}^{\rm N}}{k_{\rm rad}^{\rm T}} \frac{\phi^{\rm T}}{\phi^{\rm N}} k^{\rm T} \qquad (3.5)$$

 ϕ^{N} and ϕ^{T} are the quantum yields of the normal and tautomer species, respectively. Equation 3.5 will be used both to estimate k_{PT} when the rate is too fast to measure and to separate $k_{rad}^{N} + k_{nr}^{N}$ from k_{PT} in the observed rate k when k_{PT} becomes slow. To use Equation 3.5, we need $k_{rad}^{N} / k_{rad}^{T}$ which can be obtained in different ways. One way is to assume that the ratio is independent of solvent. The observed rate has been measured in 11 bulk protic solvents at room temperature, and the ratio of radiative rates in this expression falls within the range (Table 2.3):¹³

$$\alpha(1AC) = k_{rad}^{N} / k_{rad}^{T} = 8.1 \pm 20\%.$$
 (3.6)

3.3 Prompt Emission and the Irreversible Proton-Transfer Model

As will be discussed in Section 6.5, it is possible that some fraction of the reactants are poised to undergo reaction at a rate greater than can be resolved by our instrumentation (*i.e.*, $k > (25 \text{ ps})^{-1}$). In such cases the emission kinetics we detect will reflect only the slower, remaining portion of the population. Proper interpretation of the kinetics of these reactions depends on being able to assess whether or not an unresolvably rapid reaction has occurred. In this section we discuss how the fraction of a proposed unresolved reaction component can be estimated.

The excited-state tautomerization reaction of 1AC is again examined within the framework of the two-state kinetic model in *Figure 3.1*. The populations of the excited-state normal $N^*(t)$ and tautomer $T^*(t)$ species are rewritten below:

$$N^{*}(t) = N^{*}(0) \exp(-k t)$$
 (3.7)

$$T^{*}(t) = N^{*}(0) \beta \exp(-kt) - [N^{*}(0) \beta - T^{*}(0)] \exp(-k^{T}t)$$
(3.8)

where
$$k = k^{N} + k^{PT}$$
 (3.9)

and
$$\beta = k^{PT} / (k^T - k).$$
 (3.10)

If the entire reaction is observed, then $T^*(0) = T_0 = 0$, and Equation 3.8 assumes the form of Equation 3.2. If a subset of the normal population reacts more quickly than may be observed with the experiment's time-resolution, then "prompt fluorescence" of the tautomer species will be measured in addition to the emission recorded during the observed reaction. This fraction undergoing prompt reaction $[f = T_0 / N_0]$ may be determined by the following analysis.

The (ideal) tautomer decay is described by a biexponential fit:

$$F_{\rm T}(\lambda, t) = a_{\rm PT} \exp(-k t) + a_{\rm T} \exp(-k^{\rm T} t), \qquad (3.11)$$

where one of the normalized amplitudes is negative. The amplitudes of Equation 3.11 are identified with the appropriate coefficients of $T^*(t)$ in Equation 3.8:

$$1 + a_{\rm T}/a_{\rm PT} = T_0 / (N_0 \beta). \tag{3.12}$$

If the proton-transfer rate is much greater than the rate of the normal deactivation $(k^{PT} \gg k^N)$, the observed tautomer population $T^*(t)$ is equal to the observed normal population N_0 and the population T_0 formed by the prompt reaction. With this assumption Equation 3.12 simplifies to the following expression for the fraction of species involved in a prompt reaction:

$$1 + \frac{a_{\rm T}}{a_{\rm PT}} = \frac{f}{1 - f} \left(\frac{\tau^{\rm PT}}{\tau^{\rm T}} - 1\right), \text{ or } f = \frac{r}{1 - r} \text{ with } r = \left(1 + \frac{a_{\rm T}}{a_{\rm PT}}\right) \left(\frac{\tau^{\rm PT}}{\tau^{\rm T}} - 1\right). \quad (3.13)$$

In earlier work, it was noted that the emission band of the normal species extended into the region of tautomer fluorescence.¹ To account for this possible spectral contamination

in the tautomer emission, the analysis may be extended. The measured fluorescence is directly related to the species emitting:

$$F(\lambda,t) = f_{N}(\lambda) \cdot k_{rad}^{N} \cdot N^{*}(t) + f_{T}(\lambda) \cdot k_{rad}^{T} \cdot T^{*}(t), \qquad (3.14)$$

where $f_X(\lambda)$ is the fraction of species X emitting at a given wavelength and normalized such that $\int f_X(\lambda) d\lambda = 1$. Using the constant $c(\lambda)$ defined in Equation 3.15, Equation 3.16 describes a tautomer pseudopopulation (correcting the population of Equation 3.8) which produces the fluorescence described by Equation 3.17.

$$c(\lambda) = \frac{f_N(\lambda) \cdot k_{rad}^N}{f_T(\lambda) \cdot k_{rad}^T}$$
(3.15)

$$F_{T'}(\lambda, t) = a_{PT} \exp(-k t) + a_T \exp(-k^T t).$$
 (3.17)

If $c(\lambda) \ll \beta$, the correction is not important. Should the correction be significant, the correct amplitude a_{PT} may be obtained from the measured a_{PT} , by scaling with the fraction $\beta/(c(\lambda) + \beta)$. The fraction of species producing prompt fluorescence is determined by application of Equation 3.13.

3.4 Two-State Kinetic Model in Mixed Solvents

Two different mixed solvents will be considered later in this dissertation. In Chapter 6, the reaction of 1AC will be measured in mixtures of methanol and water. In Chapter 8, kinetic isotope effects of 1AC will be studied in mixtures of methanol and methanol-OD. The following model is useful in understanding the time-dependence of the emission of 1AC in such mixed solvents.

In each of the aforementioned experiments, the total population of 1AC is measured (Scheme 3.1). Using notation appropriate to the case of water and methanol, we have:



Scheme 3.1

Assuming that proton-transfer is the dominant pathway for deactivation of the normal species with rates characteristic for methanol $k(M) = k_M$ and for water $k(W) = k_W$, the total population of 1AC is given by:

$$\frac{N(t)}{N(0)} = \frac{\mathbf{r} - \mathbf{r}_{+}}{\mathbf{r}_{-} - \mathbf{r}_{+}} e^{-\mathbf{r}_{+}} t + \frac{\mathbf{r}_{-} - \mathbf{r}_{+}}{\mathbf{r}_{-} - \mathbf{r}_{+}} e^{-\mathbf{r}_{-}} t \qquad (3.18)$$
where $\mathbf{r}_{\pm} = 1/2\{(\mathbf{a} + \mathbf{a}') \pm \sqrt{(\mathbf{a} - \mathbf{a}')^{2} + 4\mathbf{b}\mathbf{b}'}\}$

$$\rho = (1 - X_{M}) k_{M} + X_{M} k_{W} + k_{ex}$$

$$\alpha = k_{M} + X_{M} k_{ex} \qquad (3.19)$$

$$\alpha' = k_{W} + (1 - X_{M}) k_{ex}$$

$$\beta = X_{M} k_{ex}$$

$$\beta' = (1 - X_{M}) k_{ex}$$

In the limit of rapid exchange of solvent molecules, $k_{ex} \gg (k_M, k_W)$, Equation 3.18 becomes a single exponential function whose argument involves the average rate of proton-transfer:

$$N(t)/N(0) \sim \exp\{-(X_M k_M + (1-X_M) k_W) t\}$$
(3.20)

In the limit of very slow exchange, $k_{ex} \ll (k_M, k_W)$, Equation 3.18 separates into a biexponential function whose rates correspond to the individual proton-transfer rates:

$$N(t)/N(0) \sim X_{M} \exp\{-k_{M} t\} + (1-X_{M}) \exp\{-k_{W} t\}$$
(3.21)

3.5 Solvent Dependence of the Observed Reaction Rates

The time-resolved emission and quantum yields of 1AC in a variety of solvents are summarized in *Table 2.3* in the previous chapter. The fluorescent lifetimes observed for the normal and tautomer species of 1AC are consistent with the irreversible protontransfer scheme (with essentially no prompt tautomer emission) described in this chapter. In this section an overview of the solvent dependence of the observed reaction rates is presented in order to motivate the studies discussed in the following chapters.

An initial study of the proton-transfer reaction of 7AI noted a remarkable correlation between the rate of excited-state tautomerization of 7AI in bulk alcohols and the $E_T(30)$ solvent polarity scale.¹ A similar correlation was later identified for the reaction involving 1AC.⁴ (See *Figure 3.2* for a representative summary of these correlations.) This pair of correlations establishes a linear free-energy relationship¹⁴ between these two structurally similar proton-transfer molecules. The rate of excitedstate tautomerization depends on the hydrogen-bond strength between the proton-transfer molecule and the solvent (hence the correlation with the $E_T(30)$ solvent scale), and it depends upon some intrinsic feature of the proton-transfer molecules themselves (hence the difference in rates for a given solvent). Nearly temperature-independent kinetic isotope effects⁵ for 7AI (IE ~ 3) and 1AC (IE ~ 5) in bulk alcohols further suggested that an intrinsic proton-transfer rate might be conceptually separated from the solvent's role in the reaction.⁵ The proposed decomposition of the observed proton-transfer rate,^{5,15}

$$k_{obs} = k_{PT} \exp(-\Delta G/RT) \qquad (3.22)$$

essentially divides the rate into a product of factors consistent with the linear free-energy relationship.

The decomposition of the one observed rate for the excited-state reaction of 7AI or 1AC in any particular bulk protic solvent into two (or more) contributions from different physical effects allows flexibility in interpretation. A two-step model is naturally supported by free-energy relationships that reveal that the observed rates depend on both solute (*e.g.*, intrinsic proton transfer step) and solvent (*e.g.*, polarity) effects. Is one step rate-determining? In Chapter 4 we discuss the ultrafast proton-transfer rate in isolated complexes that adds support to the possibility of a rapid intrinsic rate for a catalytic reaction. Solvent effects are considered in Chapters 5 and 6. In this arena, computer simulations have assisted the interpretation of some experimental observations. For example, the absence of significant prompt tautomer fluorescence (<5%) in all the bulk solvents studied is consistent with recent computer simulations that demonstrate the rarity of cyclically hydrogen-bonded complexes in alcohol solvents.¹⁵ And while the remarkable correlation of the rate with the hydrogen-bond donating ability

of the solvent is consistent with either extreme of a two-step model, recent computer simulations lend support toward the strong influence of the solvent factor through a correlation between the observed rates and "relative reactive fractions."¹⁵ On the other hand, the reaction of 1AC in solvents such as diols and water appear to be anomalously slow when compared to the rate correlations with other alcohols on the $E_T(30)$ solvent scale. These "anomalously slow" reactions are considered in detail in Chapters 5 and 6.



Figure 3.1: Irreversible Proton-Transfer Scheme



Figure 3.2: 1AC and 7AI Reaction Rate Correlations with E_T(30) Solvent Scale

Earlier studies noted a remarkable correlation between the excited-state proton-transfer reaction time and the $E_T(30)$ polarity scale for alcohol solvents. 7AI data are from: (a) R. S. Moog and M. Maroncelli, *J. Phys. Chem.*, **95**, 10359 (1991). (b) C. F. Chapman and M. Maroncelli, *J. Phys. Chem.*, **96**, 8430 (1992). 1AC data are from: S. J. Boryschuk, M.S. Thesis, The Pennsylvania State University, 1993. The solvents that appear to be anomalous on this correlation are considered in Chapters 5 and 6. The numbered points correspond to the solvents: (1) Water. (2) Ethylene Glycol. (3) Glycerol.

ENDNOTES

¹ R. S. Moog and M. Maroncelli, J. Phys. Chem., 95, 10359-10369 (1991).

² C. F. Chapman and M. Maroncelli, J. Phys. Chem., 96, 8430-8441 (1992).

³ C. F. Chapman, Ph.D. Thesis, The Pennsylvania State University, 1993.

⁴ S. J. Boryschuk, M.S. Thesis, The Pennsylvania State University, 1993.

⁵ See pp. 2761-2762 of A. V. Smirnov, D. S. English, R. L. Rich, J. Lane, L. Teyton, A. W. Schwabacher, S. Luo, R. W. Thornburg, and J. W. Petrich, *J. Phys. Chem. B.*, **101**, 2758-2769 (1997).

⁶ J. Herbich, J. Sepiol, and J. Waluk, J. Mol. Struct., **114**, 329-332 (1984).

⁷ M. A. El-Bayoumi, P. Avouris, and W. R. Ware, J. Chem. Phys., **62**, 2499 (1975).

⁸ Quantitative discussions are also available in standard texts. See, for example, J. I. Steinfeld, J. S. Francisco, and W. L. Hase, *Chemical Kinetics and Dynamics*, (Englewood Cliffs, N.J., Prentice Hall, 1989).

⁹ See, for example, G. M. Chaban and M. S. Gordon, *J. Phys. Chem. A.*, **103**, 185-189 (1999).

¹⁰ P.-T. Chou, W.-S. Yu, C.-Y. Wei, Y.-M. Cheng, and C.-Y. Yang, *J. Am. Chem. Soc.*, **123**, 3599-3600 (2001).

¹¹ In the case of 7AI, at least two groups have noted the presence of additional fluorescent impurities that are difficult to remove by recrystallization or vacuum sublimation. See: (1) S. K. Kim and E. R. Bernstein, *J. Phys. Chem.*, **94**, 3531 (1990). (2) Y. Chen, F. Gai, and J. W. Petrich, *Chem. Phys. Lett.*, **222**, 329 (1994).

¹² An alternative state of solvation ["blocked species"] has been advocated to account for this long lifetime by Y. Chen, F. Gai, and J. W. Petrich, *Chem. Phys. Lett.*, **222**, 329 (1994). Their model is addressed in Chapter 6.

¹³ Although the relative tautomer radiative rate is slightly longer (smaller α values) in the very polar solvents like formamide, N-methylformamide, and ethylene glycol, the average of α values for the wide variety of protic solvents will be the best determination of the relative radiative rates for 1AC isolated complexes. (If one chooses to be more

selective about the choice of solvents used in the determination of the ratio of radiative rates, a different value will be obtained; for example, $\alpha(1AC) = 9.0 \pm 10\%$ (*Table 2.3*).)

¹⁴ T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, *Third Edition*. (New York, HarperCollinsPublishers, 1987). p. 143.

¹⁵ S. Mente and M. Maroncelli, J. Phys. Chem. A, **102**, 3860-3876 (1998).

Chapter 4

EXCITED-STATE INTERMOLECULAR PROTON-TRANSFER IN COMPLEXES INVOLVING 1-AZACARBAZOLE

4.1 Introduction

The excited-state tautomerization reactions of 7AI and 1AC are assumed to occur through hydrogen-bonded complexes that complete a geometry for efficient shuttling of two protons,¹⁻¹¹ as shown schematically in Figure 3.1 in Chapter 3. (In bulk alcohols, such cyclical hydrogen-bonded complexes are rare.⁸) For 7AI in bulk alcohols, Petrich and coworkers have presented evidence that the tautomerization involves the concerted motion of two protons,^{1,12} although some recent studies indicate that in 7AI dimers formed in a molecular beam or in nonpolar solvents the double- proton-transfer reaction occurs in sequential steps through an intermediate.^{13-19,45} The specific reaction mechanism for 1AC is examined later in Chapter 7. In both 7AI and 1AC the rate of this excited-state tautomerization is strongly dependent on the extent of hydrogen bonding within the solvent. In isolated complexes in dilute solution, the excited-state doubleproton-transfer rate for 7AI or 1AC is very rapid, whereas in bulk protic solvents the reaction rate is slower by one to three orders of magnitude. A discussion of this remarkable change in rate is postponed until the reaction in isolated complexes has been examined in more detail.

In nonpolar solvents, both 7AI and 1AC may form hydrogen-bonded complexes that catalyze or promote tautomerization in the excited-state. Taylor, El-Bayoumi, and Kasha reported the excited-state double-proton-transfer reaction in 7AI dimers,¹¹ which has been intensively studied since their classic work.¹³⁻⁶⁵ Tautomer emission from 1AC dimers was later identified,⁶⁶ and soon thereafter the excited-state reaction involving the 1AC-7AI heterodimer was discussed, along with mention of additional reactions occurring in 1AC complexes with acetic acid or the lactam methylveronal.⁶⁷ More recently, isolated complexes of 7AI with carboxylic acids and phosphoric acids,^{51,68} alcohols⁵¹, and lactams⁶⁹ have been studied using absorption and fluorescence spectroscopy. In much of this work, the presence of excited-state proton transfer has been established, but many of the rates have eluded determination. Reported rates are summarized in Table 4.1. These include the ultrafast proton-transfer rate in 7AI dimer complexes in solution and in molecular beams,^{13-19,23,31,36,45-48} as well as lower bounds for rates involving heterogeneous 7AI complexes.^{10,37,68,69} The rate of the ground-state proton-transfer reaction that replenishes the normal form of 7AI dimers $(TT \rightarrow NN)$ is much slower, but the cyclical nature of the reaction scheme $(NN \rightarrow NN^* \rightarrow TT^* \rightarrow TT \rightarrow NN)$ has been confirmed.^{33-35,53} Even fewer measurements on the proton-transfer complexes involving 1AC have been reported, and these are rates for reactions in molecular beams.^{36,37,70}

A further distinction may be made between catalytic and noncatalytic protontransfer reactions.⁶⁹ In catalytic reactions (*e.g.* alcohols, carboxylic acids), the chemical identity of the complexing agent does not change as a result of proton-transfer in the excited-state of 1AC or 7AI. In noncatalytic reactions (*e.g.* dimers, amides, lactams), however, the ground-state complexing agent tautomerizes along with the excited-state 1AC or 7AI molecule. This chemical change in the latter case decreases the driving force for reaction and presumably also increases the barrier to reaction. Chou *et al.* have observed that the excited-state reaction of 7AI is prevented when the lactam-to-lactim tautomerism of the complexing agent requires more energy than is available from the exothermic tautomerism of 7AI.⁶⁹ Noncatalytic partners therefore provide a means of tuning the rate of reaction and thereby enable reaction rates to be measured with modest picosecond time-resolution.

The present work examines the excited-state proton-transfer rate of 1AC in isolated complexes with the partners sketched in *Figure 4.1*. A better understanding of the intrinsic reaction rate in isolated complexes [k_{PT} of one current model^{7,8} described in Chapter 3] is sought, with special emphasis on the role of energetics in controlling this rate at room temperature. The complexing agents selected for study have structures favoring the formation of (stable) bimolecular complexes with 1AC. The catalytic complexing agents were acetic acid and deuterated acetic acid, since (unlike alcohols⁷¹) they were expected to complex strongly with 1AC. The noncatalytic complexing agents included: (1) 1AC present in dimers; (2) two lactams; and, (3) five amides anticipated to complex like the lactams but with different functional groups to allow tuning of the free energy of the reaction.⁷² The small size of these complexing agents also allowed some higher-level quantum chemical calculations to be performed.

The results obtained for catalytic complexing agents are discussed first, followed by the noncatalytic agents 1AC, the lactams, and the amides. The experimental data are interpreted within the framework of an irreversible proton-transfer kinetic scheme, which provides a useful description of the reaction for both 7AI and 1AC in bulk alcohols⁷³ and in many isolated complexes at room temperature. Finally, the observed reaction rates are considered in relation to estimates of reaction energetics.

4.2 Results

4.2.1 1-Azacarbazole Complexes with Acetic Acid

Strong complex formation was expected between 1AC and dilute acetic acid in methylcyclohexane,⁷⁴ based upon previous studies of 1:1 complexes of 7AI with acetic acid in cyclohexane for which the association constant was determined to be K_a =[1.8±0.5] x 10⁴ M^{-1.51,68,75} As 1AC is spectrophotometrically titrated with acetic acid, the red-edge of the first absorption band (S₁, identified as ¹L_a^{66,76}) increases in intensity, similar to the titration presented later for 1AC:HHQ complexes. This red-shifted absorption band is attributed to the 1AC:AA complex, and excitation at 348 nm (28740 cm⁻¹) produces dual emission that was identified using excitation spectroscopy as fluorescence from normal uncomplexed 1AC and from tautomers formed in the reacting complexes. Since our interest here is in the determination of the excited-state proton-transfer rate, a large excess of acetic acid was added to the 1AC in methylcyclohexane in

an effort to completely complex the 1AC.⁷⁷ Although the tautomer fluorescence remained nearly constant after the first addition of neat acetic acid (~1 µL AA/mL 1AC) since most of the 1AC was complexed,⁷⁸ the normal emission intensity continued to decrease with excess acid as the 1AC monomer concentration decreased. (Too much acid eventually protonates the 1AC, which produces a new fluorescence emission band located between the normal and tautomer bands.) The resulting steady-state emission spectra for the 1AC-acetic acid complexes are shown in *Figure 4.2*, where the dual fluorescence of 1AC in bulk methanol has been plotted for contrast. Note the dramatic difference in the relative amount of normal (N*) and tautomer (T*) emission in these two cases. Whereas tautomer emission is primarily observed from the 1AC:AA complexes primed for rapid excited-state reaction, fluorescence from the normal species of 1AC in methanol is dominant since the occurrence of complexes properly formed for reaction is greatly reduced.

Time-resolved emission measurements at 440 nm (22730 cm⁻¹) revealed no obvious fluorescence from the normal form of 1AC:AA when compared to identical measurements on a solvent blank. Since N* is initially prepared, this absence of N* signal implies a reaction too fast to measure (τ_{rxn} < 25 ps). The tautomer fluorescence of 1AC at 560 nm (17860 cm⁻¹) decayed with lifetimes of 1.23 ns and 1.92 ns in the AA and AA-D complexes, respectively. No rise time was observed in the tautomer, consistent with reaction too rapid (τ_{rxn} < 25 ps) to measure directly with this photon-counting experiment in either the normal or tautomer regions. The proton-transfer rate will be estimated more carefully in Section 4.3. The isotope effect on the tautomer decay rate

(based on lifetimes observed at 560 nm) $k_H/k_D = 1.6$ is in good agreement with the ratio of the corresponding tautomer quantum yields ($I_D/I_H = 1.4$). This isotope effect of ~1.4 for tautomer deactivation has also been observed in studies of 7AI and 1AC in bulk alcohols.³⁻⁶ (Chapter 7 continues a discussion about the observed isotope effects.)

4.2.2 1-Azacarbazole Dimers

Analogous to 7AI, in dry alkane solvents containing >20 μ M 1AC, dimerization of 1AC occurs^{24-27,66} with a reported association constant K_a=(6.8±0.7) x 10² M⁻¹ at 21 °C.^{66,9} Although oligomer and cluster formation has been reported for 7AI,^{25,30,40,45,49,50} to our knowledge analogous 1AC oligomers have not been observed and thus we assume that 1:1 dimer complexes are formed in nonpolar solution. (Oligomer formation may be sterically disfavored in 1AC compared to 7AI.) A foot appearing on the red-edge of the first absorption band is attributed to the dimer complexes, and excitation at 348 nm (28740 cm⁻¹) produces dual fluorescence emission ascribed to normal 1AC monomers and tautomer emission from the reacting dimers. The tautomer emission at 560 nm (17860 cm⁻¹) decays with a lifetime of 910 ps. No rise time was observed in the tautomer emission, again implying a reaction too rapid to measure ($\tau_{rxn} < 25$ ps).⁷⁹

4.2.3 1-Azacarbazole Complexes with Lactams

Chou et al. recently discussed the formation and subsequent excited-state tautomerization in three complexes involving 7AI and lactams.⁶⁹ They observed an excited-state proton-transfer reaction in 7AI with δ -valerolactam but not with 3,4,5,6,7,8hexahydro-2(1H)-quinoline. Our choice of lactams was motivated by their study,⁶⁹ although our interest is in the rate of excited-state reaction. These lactams are soluble in methylcyclohexane, which allowed good control of complex formation with 1AC using spectrophotometric titration. Absorption and emission spectra of dilute mixtures of 1AC and the lactams HHQ and δ -VL are presented in *Figure 4.3* and *Figure 4.4*, respectively. In each case, the red-shift and the foot at 28,500 cm⁻¹ in the first absorption band of 1AC with increasing lactam concentration is attributed to 1:1 complex formation. Estimation of the association constants for 1AC: δ-VL and 1AC:HHQ complexes is described in Endnote 80. Dual fluorescence is observed from the complexes excited at 348 nm, and the red fluorescence is 1AC tautomer emission formed via excited-state proton transfer. The blue fluorescence consists of both 1AC monomer emission (also observed in the 7AI:lactam study⁶⁹) and a small component due to normal complex emission.

Time-resolved fluorescence was measured in both the normal and tautomer regions, and the lifetime results are shown in the bottom panels of *Figure 4.3* and *Figure 4.4* and are summarized in *Table 4.2*. In the normal region, longer lifetimes attributed to uncomplexed 1AC emission were measured as well. For both lactam complexes, the decay time of normal 1AC is equal to the rise time of the tautomer species, showing that tautomer is directly produced from the normal species, consistent with the irreversible
proton-transfer scheme of Chapter 3 and Section 4.3. The ratio of amplitudes $[A_{decay}/A_{rise}]$ in the tautomer emission is nearly unity, verifying that all of the reaction producing excited-state tautomer is observed during the experiment.

4.2.4 1-Azacarbazole Complexes with Amides

A variety of amides were explored as complexing agents for 1AC. The insolubility of solid and liquid amides in methylcyclohexane prevented the use of spectrophotometric titrations to form the complexes, so the sonication method described in Section 8.4 was employed. For the solid amides, 1AC complex formation with acetamide and 2,2,2-trifluoroacetamide was successful; with benzamide and succinimide the results were poorer; and, little or no complex formation was observed using 2-cyanoacetamide or 2,3,4,5,6-pentafluorobenzamide. Although the composition of the NMF emulsion is not well characterized, interesting qualitative information was obtained from this one experiment.⁸¹ For these insoluble amides we assume the predominant species in solution are 1:1 complexes.

Examples of steady-state spectra of the 1AC:amide complexes are recorded in *Figure 4.5.* Like the complexes previously discussed, the red-shift and foot in the first absorption band of 1AC is attributed to complex formation, and excited-state tautomerization was identified in many of the 1AC:amide complexes. One difference occurs for the normal emission band of the 1AC:Benzamide (and 1AC:NMF) complexes: this band noticeably red-shifts, broadens and increases in intensity, suggesting additional electronic perturbations due to the complexing agents. (Additional interactions

envisioned between 1AC and benzamide, for example, are π - π electronic overlap of the aromatic rings or the formation of only one hydrogen bond in the complex.)

Decays observed for the amide complexes are summarized in *Table 4.2* and examples are illustrated in *Figure 4.6*. Since the fluorescence intensity from the 1AC complexes with benzamide or succinimide was weak, these time-resolved lifetimes are subject to more uncertainty. The rate of excited-state tautomerism in 1AC:Benzamide (and 1AC:NMF) complexes is measurably fast like the 1AC:lactam complexes. In contrast, however, a rise time in the tautomer emission corresponding to the decay time of the normal species was not observed for all 1AC:amide complexes. For these latter complexes, the irreversible proton-transfer scheme does not satisfactorily describe the observed kinetics, and efforts toward understanding this difference are discussed in Section 4.3. In addition to the lifetimes of the reacting species in the normal region, *Table 4.2* records additional (longer) decay times that are attributed to a population of nonreacting 1AC.

4.3 Irreversible Proton-Transfer Kinetic Scheme

Although the proton-transfer reaction in the 1AC:acetic acid complexes was too rapid to measure directly, the steady-state fluorescence spectra contain additional information which allows the excited-state proton-transfer rate to be estimated using the kinetic scheme illustrated in Figure 3.1 of Chapter 3. This irreversible proton-transfer kinetic scheme discussed in Chapter 3 also describes the measured kinetics of the 1AC reaction involving the lactams and at least some of the amides.

The fluorescence lifetimes of the 1AC complexes and estimates of the tautomer quantum yield are summarized in *Table 4.2*. Note that the 1AC normal excited lifetime is kinetically related to the tautomer lifetime in several cases. In order to aid the interpretation of the measured lifetimes, the quantum yields of the tautomer emission in all of the complexes were estimated. Since corresponding values for the tautomer radiative rates are consistent for the different 1AC complexes, and since they are nearly equal to the tautomer radiative rates determined for 1AC in bulk alcohols $(k_{rad}^{T} = 2.3 \times 10^{6} \text{ s}^{-1} \text{ from } Table 2.3 \text{ in Chapter 2})$, we interpret the decaying lifetime in the tautomer emission as the deactivation of the tautomer excited-state.

In cases when the proton-transfer rate is too fast to be resolved temporally, the irreversible proton-transfer scheme provides an alternative means for estimating the rate using quantities more easily measured in experiment. Assuming an irreversible reaction completely depopulates the normal excited state, the proton-transfer rate is simply (from Chapter 3):

$$k_{\text{PT}} = \frac{k_{\text{rad}}^{\text{N}}}{k_{\text{rad}}^{\text{T}}} \frac{\phi^{\text{T}}}{\phi^{\text{N}}} k^{\text{T}}$$
(4.1)

where k^N and k^T are the specified rates and ϕ^N and ϕ^T are the quantum yields of the normal and tautomer species, respectively. As noted in Chapter 3, the ratio of radiative rates falls within the range⁸²

$$\alpha(1AC) = k_{rad}^{N} / k_{rad}^{T} = 8.1 \pm 20\%$$
 (4.2)

To explore this scheme further, the proton-transfer rate in 1AC:lactam and 1AC:benzamide complexes can be computed and compared directly to the measured

rate.⁸³ Since determination of the rate via Equation 4.1 requires independent measurement of the quantum yields of the normal and tautomer species in the complex, we must use estimates for the normal quantum yield ϕ^N , since uncomplexed 1AC emission in the region of the complexed normal 1AC obscures this value. Assuming the emission band profiles are similar for all the complexes, a ratio of the integrated band intensity to the intensity at a single wavelength was formed using the 1AC-acetic acid spectra (see below). This allowed relative quantum yields to be estimated from emission intensity in the normal (430 nm) and tautomer (520 nm) regions in the other 1AC-lactam complexes:

$$\varphi^{\rm T}/\varphi^{\rm N} = c \left[I^{\rm T}(520)/I^{\rm N}(430) \right]$$
(4.3)

where the proportionality factor was approximately c = 0.85. The normal quantum yield was further corrected by estimating the fraction of actual complex emission contributing to the steady-state intensity using the time-resolved spectra⁸⁴: $f_{PT}=a_{PT}\tau_{PT} / \Sigma a_i\tau_i$. The estimate for the ratio of quantum yields for Equation 4.1 follows:

$$\phi^{T}/\phi^{N} = [c / f_{PT}] [I^{T}(520)/I^{N}(430)]$$
 (4.4)

The estimated proton-transfer rates using this scheme are presented in *Table 4.2* along with the rates measured directly, establishing agreement within half an order of magnitude with the values that could be time-resolved. The greatest source of uncertainty in these calculations lies in the quantum yields of the normal complex species.

Having established the accuracy of the irreversible proton-transfer scheme to estimate the reaction rate, we now apply Equations 4.1, 4.2 and 4.4 to deduce the rates for

the unresolvably fast reactions. For the 1AC-acetic acid complexes, the relative quantum yields were obtained by integrating the normal and tautomer spectral regions shown in *Figure 4.2*. The quantum yield values were corrected for contamination by a longer-lifetime fluorescence impurity in the normal region detected by time-resolved emission spectroscopy. Within experimental error, the relative quantum yields for both the regular and the deuterated acetic acid complexes are equal: $\phi^T/\phi^N = 230$. The tautomer lifetimes are noted in *Figure 4.2*, and the final rate estimates for the excited-state tautomerism are recorded in *Table 4.2*. The predicted proton-transfer time of 0.7 ± 0.2 ps in the 1AC:AA complex is similar to the ultrafast proton-transfer times predicted for 7AI complexes,⁸⁵ and is nearly 1000 times faster than the excited-state tautomerism for 1AC in bulk methanol. The estimated reaction rate involving deuterated acetic acid reveals a smaller isotope effect [1.7±0.8] compared to that measured in bulk alcohols [4.9± 0.3]⁶ (See Chapter 7).

If the irreversible proton-transfer scheme is applied to the 1AC:amide complexes, rapid tautomerization rates for 1AC complexes with acetamide, 2,2,2-trifluoroacetamide, or succinimide are predicted which are consistent with our inability to measure the reaction rise time in the tautomer emission. (See *Table 4.2.*) However, the origin of the ~100 ps lifetime of these normal complexed species remains unknown.⁸⁶

4.4 Discussion and Model Calculations

The rate of excited-state proton-transfer is ultrafast in 1AC complexes with acetic acid. For the 1AC complexes with lactams and benzamide, the rates are slower,

presumably because the complexing agents tautomerize along with the 1AC. The observed rates in the 1AC complexes with amides are more complicated as discussed in Section 4.3. In order to understand these results, a simple model involving the driving force of the reaction is proposed.

Knowledge of the excited-state energy barrier between the normal and tautomer species should enable the reaction to be modeled and thus allow the reaction rates to be calculated. If the excited-state proton-transfer is an activated barrier crossing, then the rate could be modeled using transition state theory in which the absolute rate coefficient is strongly related to this barrier ($k \sim \exp(-E_{barrier}/k_BT)$). If the excited-state proton transfer involves tunneling, then knowledge of the potential energy surface is still needed in order to model the rates. However, the size of these chemical systems make high-level quantum chemical calculations difficult or unfeasible, especially for characterization of the excited-state potential energy surface. Therefore, we begin by estimating the groundstate interaction energies of 1AC with various complexing agents using a combination of quantum chemical and classical models.⁸⁷ An attempt will then be made to deduce excited-state energetics, in particular the driving force of the reaction. Additional descriptions of the excited-state reaction in 1AC dimers,⁸⁸ 7AI dimers,⁸⁹ and 7AI:water complexes⁹⁰⁻⁹⁴ have been proposed based on earlier experimental, theoretical or computational studies.

Since we anticipate the reaction rate to be correlated with the driving force for the reaction, the driving force will be estimated using the following approximate scheme:





Because the sizes of the 1:1 complexes are currently too large to permit energetics to be calculated directly using high-quality quantum chemical methods, we estimate the energetics using the following approximations. The ground state energies of all normal and tautomer species are calculated using Hartree-Fock methodology. The pair energies of the normal and tautomer species in cyclic complexes are then estimated within a classical force field. Reorganization energies within the complex are ignored. The driving force for the reaction is obtained by assuming that energy is conserved in Scheme 4.1 illustrated above:

$$\Delta E(T^*-N^*) = \Delta E(T-N) + (h\nu_T - h\nu_N) \cong \Delta E(T-N) + \text{constant} \qquad (4.5)$$

The constant is estimated from the absorption and emission spectra. Note that the energies quoted here are electronic interaction energies rather than free energies. Before the results are presented for this scheme, we discuss the approximations employed here in a little more detail.

4.4.1 Hartree-Fock Calculations of the Monomer Energies

Optimized geometries, electronic energies, and atom-centered point charges fit to the molecular electrostatic potential^{95,96} were determined for the ground states of all of the molecules considered here. These calculations were realized at the HF/6-31G* level of theory using the Gaussian 94 program.⁹⁷ For comparison, several single-point calculations were repeated using the density functional theory B3LYP/6-31G*. The molecular geometries for these single-point calculations were optimized at HF/6-31G*.

The monomer molecular energies of the normal and tautomer species calculated at these two levels of theory are presented in *Table 4.3*. The energy changes due to tautomerization have an absolute uncertainty on the order of 4 kJ/mol, as estimated from comparison of these two model chemistries.

4.4.2 Classical Estimates of the Pair Energies in the Complexes

Interaction energies of 1AC with the various complexing agents were estimated using a molecular mechanics approach for the pair of molecules.^{98,9} These energies were modeled using standard, all-site Lennard-Jones parameters and the ESP-fit atomic charges noted above for the Coulombic interactions.^{9,98} A Monte Carlo algorithm was employed to locate complex geometries having minimum energies. These classical force field calculations are approximations to the full quantum chemical calculations of pair energies.

For comparison, interaction energies of the smallest complexes were also calculated at the HF/6-31G* level of theory. The complex geometries generated by the Monte Carlo minimizations were used as input for the quantum chemical calculations. The geometry of the supermolecule was then completely optimized to a stationary point using Gaussian 94. Complexation energies were calculated via

$$\Delta E_{(N \text{ or } T)} = E_{\text{complex}} - E_{1AC (N \text{ or } T)} - E_{\text{agent} (N \text{ or } T)}. \qquad (4.6)$$

As computational resources are improved in the future, this algorithm for estimating the complexation energies may be refined to include corrections omitted here.⁹⁹

The calculated energy differences between the ground state normal and tautomer complex species are summarized in *Table 4.3.* The normal interaction energy refers to the change in the total energy when the normal form of 1AC complexes with the normal form of the complexing agent, and a similar definition applies to the tautomer interaction energy. These values were calculated efficiently using the Monte Carlo molecular mechanics program discussed above. For cases involving catalytic partners, the classical energies are within ~5 kJ/mol of the corresponding interaction energies calculated using HF/6-31G* model chemistry. Similar good agreement has been observed for catalytic complexes involving 7AI,^{9,98} and the 1AC interaction energies [HF/6-31G*] are similar to those reported for 7AI complexes with catalytic agents.⁵¹ The classical calculations, however, predict the normal interaction energies in the 1AC:amide complexes to be ~12 kJ/mol lower than the quantum chemical model. This increased stabilization is due to the choice of nitrogen atom Lennard-Jones parameters used with the ESP-fit charges.¹⁰⁰

4.4.3 Extraction of Absorption and Emission Energies from Spectra

If the vertical transition energies $\Delta E(N \rightarrow N^*) \cong hv_N$ and $\Delta E(T^* \rightarrow T) \cong hv_T$ change little in the various isolated complexes in methylcyclohexane, then the change in the ground state energy between the normal and tautomer species is a surrogate measure for the change in free energy in the excited states and is directly related to the barrier height of the reaction.¹⁰¹ Thus we must establish the constancy of these transition energies in order to validate our approximation leading to the driving force of the reaction.

Analysis of the tautomer emission spectra reveals that $\Delta E(T^* \rightarrow T)$ does not depend significantly on the complexing agent: the tautomer emissions fall in the range $v_{max} = (18.67 \pm 0.16) \times 10^3 \text{ cm}^{-1} \text{ or } \langle v \rangle = (19.20 \pm 0.20) \times 10^3 \text{ cm}^{-1}$, except for succinimide which is $0.55 \times 10^3 \text{ cm}^{-1}$ higher in energy for either measure of frequency. The constancy of the term hv_N cannot be established for the complexes, for either the spectra of complexes overlap with uncomplexed molecules or we observe no N* emission. Nevertheless, the near constancy of the location of the first absorption band of 1AC in various neat aprotic and protic solvents lends considerable support to our assertion that hv_N is constant in complexes. (For the 17 solvents summarized in Table 2.1, the shift of the first absorption band with respect to the spectrum of 1AC in methylcyclohexane is $\Delta v = (0.20 \pm 0.14) \times 10^3 \text{ cm}^{-1}$.) The constancy of the term ($hv_T - hv_N$) in Equation 4.5 is thus established.

We may further estimate the value of this constant term $(hv_T - hv_N)$ using experimental values. The excitation of the 1AC complexes at 348 nm sets an upper bound $\Delta E(N \rightarrow N^*) = 28.7 \times 10^3 \text{ cm}^{-1}$. If the mean frequency $\langle v \rangle = 19.2 \times 10^3 \text{ cm}^{-1}$ of the tautomer emission is an acceptable measure of $\Delta E(T^* \rightarrow T)$, then

 $(hv_T - hv_N) \cong 9.5 \times 10^3 \text{ cm}^{-1} = 110 \text{ kJ/mol.}$ An alternative choice for the tautomer 0-0 transition would be at the blue edge of the emission band, say 21 kK. Then the constant term $(hv_T - hv_N) \cong 7.7 \times 10^3 \text{ cm}^{-1} = 92 \text{ kJ/mol.}$ Thus we estimate the constant from the spectra to be $(hv_T - hv_N) \cong 90-110 \text{ kJ/mol}$, or simply $100\pm10 \text{ kJ/mol.}$

4.4.4 Model Energetics for Understanding Reaction Rates

As the combination of uncertainty for the interaction and tautomerization energies is on the order of 8-12 kJ/mol, these energies may be useful in rationalizing trends but not in predicting variations among complexing agents of the same chemical class, where the calculated differences are smaller. The total change in energy reported in *Table 4.3* for the systems is the sum of changes due to tautomerization in 1AC and the complex agent and to changes in the interaction energies within the complex. The total change in energy ranges from $\Delta E(T-N) \cong 50$ kJ/mol in the catalytic complexes to $\Delta E(T-N) \cong 115$ kJ/mol in the complexes involving lactams or amides.

The calculated interaction energies may be used to estimate the driving force of the reaction through Equation 4.5, employing the constant value $(hv_T - hv_N) \cong 100\pm10 \text{ kJ/mol}$. For the catalytic excited-state reactions, $\Delta E(T \rightarrow N) \cong 50\pm8 \text{ kJ/mol}$ which implies the driving force for the excited-state tautomerism of 1AC is approximately $50\pm13 \text{ kJ/mol}$. This is similar to the driving force estimated by Chou and coworkers for 7AI.⁵¹ The lactam and amide results predict $\Delta E(T \rightarrow N) \cong 115 \pm 12 \text{ kJ/mol so that the calculated driving force is near zero,}$

 -5 ± 16 kJ/mol. The magnitude of the driving force for the lactam and amides lends some support to the possibility that an excited-state equilibrium might explain the interesting kinetics observed in some of the amide complexes. The details, however, are obscured by the uncertainty in the calculations.

Figure 4.7 summarizes the dependence of the excited-state proton-transfer rates on the estimated driving forces calculated above. The rates measured directly for the lactam and benzamide complexes are presented as lower bounds for the rates for the amide complexes in general. A rough correlation between the rate of excited-state tautomerism and some measure of the driving force is apparent, with general trends correctly predicted: the carboxylic acid reacts faster than the dimer which is faster than the lactam and amide complexes.

As noted earlier, the uncertainties of the model calculations obscure comparisons among complexing agents of a given class of molecules. The lack of sensitivity in the interaction energies for the amides and lactams is perhaps not surprising. In the classical model employed, the Lennard-Jones potentials for the C,O,N,H atoms in the functional group were equivalent, and the Coulombic charges obtained from the ESP fits to the *ab initio* calculations did not show significant deviations in the lactam, lactim, amide and aci-amide structures. (The standard deviations were less than 15% of the mean value of charge on the proton and proton-acceptor involved in the reaction.) Although the potentials used for the interaction energies seem to be reasonable for the catalytic complex agents acetic acid and methanol, these results suggest that the classical model for the amides may be inadequate for describing the interaction energy in molecular simulations with fine resolution needed here.^{100,102}

In addition to improving the potentials, the static model developed here does not account for dynamic parameters. For example, our work confirms other calculations^{14,51,87} that show that the distance between the molecules in the complex decreases in the transition from the normal form to the tautomer form. Since the rate of proton transfer depends strongly on the distance (an exponential dependence if tunneling), this modulation of the distance which has been neglected in this analysis is expected to be an important parameter in describing the reaction.^{103,104}

4.5 Conclusion

The measurements or estimates of the rates of excited-state tautomerization in ten complexes involving 1AC confirm that the reaction is rapid within isolated complexes having suitable geometry. For the strong complexes involving the catalytic complexing agent acetic acid, the rate has been estimated using the irreversible proton-transfer scheme to be $k_{PT} = (0.7\pm0.2 \text{ ps})^{-1}$ for 1AC. For 1AC complexes with lactams and amides, the reaction is as much as one to two orders of magnitude slower; although the observed kinetics in several cases is more complex and possibly suggestive of excited-state equilibrium. The excited-state tautomerization in 1AC dimers in nonpolar solution is greater than the resolution of this experiment [(25 ps)⁻¹] and within an order of magnitude of the rate in 7AI dimers. The reaction rates are consistent with the estimated driving forces of the reactions. Although current model calculations lack sufficient accuracy to

clarify the rate dependencies for molecules within a given class, they do afford insight into the relative rates among the three classes studied in this work, with carboxylic acids > dimers > lactams and amides.^{105,106}

A survey of recent observations of 7AI complexes with protic partners (except dimers) in molecular beam^{38,39,45,52,107-109} and in supercritical fluids^{110,111} reveals that a reaction has not yet been observed or reported in these environments. Dimer studies have also noted the presence of different conformers with only one having geometry appropriate for excited-state tautomerization.^{25,36,38,40,45,52,55} These results are consistent with the importance of obtaining a correct geometry for proton-transfer. Complexing agents like carboxylic acids or amides whose geometry is better suited for 7AI or 1AC may be good candidates for further study in molecular beam experiments.

| 7-Azaindole | Experiment | Rate, s ⁻¹ | Resolution | Reference |
|--------------------|--|--|------------|-----------|
| Dimers | molecular beam | $\sim 10^{12}$ | ns | 1 |
| Dimers | molecular beam | $> 1 \times 10^{12}$ | ps,fs | 10 |
| | molecular beam, stepwise mechanism: | | | |
| Dimers | excitation at origin | $1.5 \ge 10^{12}$ and $3.0 \ge 10^{11}$ | fs | 2 |
| Dimers | excitation at origin + \sim 350 cm ⁻¹ | $5.0 \ge 10^{12}$ and $6.3 \ge 10^{11}$ | fs | 2 |
| Dimers, deuterated | excitation at origin + \sim 350 cm ⁻¹ | 3.3×10^{11} and 4.0×10^{10} | fs | 2 |
| Dimers | molecular beam (excitation at 312 nm), stepwise | $1.5 \ge 10^{12}$ and $2 \ge 10^{11}$ | fs | 13 |
| | mechanism | | | |
| | | | | |
| Dimers | 3-methylpentane, 77 K | $(\sim 5 \times 10^8)$ | ns | 3 |
| Dimers | 3-methylpentane, RT and 77 K | $> 2 \times 10^{11}$ | ps | 4 |
| Dimers | hexadecane, RT | 7.1×10^{11} | fs | 5 |
| Dimers, deuterated | hexadecane, RT | 2.5×10^{11} | fs | 5 |
| Dimers | hexane | 9.1 x 10 ¹¹ | fs | 11 |
| Dimers | nonpolar solvents, normal decay | $1 \ge 10^{12}$ | fs | 12 |
| Dimers, deuterated | nonpolar solvents, normal decay | 2.2×10^{11} | fs | 12 |
| Dimers | hexane, RT | 9.1×10^{11} | fs | 14 |
| Dimers, deuterated | hexane, RT | 6.3×10^{11} | fs | 14 |
| Dimers | hexane, RT, excitation 280-307 nm: ultrafast | $5 \ge 10^{12}$ | fs | 15 |
| | emission component attributed to internal | | | |
| | conversion | | | |
| Dimers | 3-methylpentane or n-hexadecane, RT, excitation | $\sim 4 \times 10^{12}$ and 1 x 10 ¹² | fs | 16 |
| | at 320 nm for transient absorption and 266 nm or | | | |
| | 310 nm for fluorescence upconversion | | | |
| | measurements, stepwise mechanism | | | |
| Dimers, deuterated | (Fiebig et al. 1999): transient absorption | $3.6 \ge 10^{12}$ and $2 \ge 10^{11}$ | fs | 16 |
| Dimers, deuterated | (Fiebig et al. 1999): fluorescence upconversion | N decay, $IE = 5$; T rise, $IE = 1.4$ | fs | 16 |
| | | | | |

Table 4.1: Reported Rates for Excited-State Proton-Transfer in 7-Azaindole and 1-Azacarbazole Complexes

(continued on next page)

Table 4.1 (continued)

| 7-Azaindole | Experiment | Rate, s ⁻¹ | Resolution | Reference |
|--|--|--|----------------------------------|----------------------------|
| Heterodimer with 1-Azacarbazole | molecular beam | ~ 10 ⁹ | ns | 1 |
| Complex with carboxylic acids or phosphoric acids | cyclohexane (RT) | >> 5 x 10 ⁹ | ps | 6 |
| Complex with 2-azacyclohexanone (&-valerolactam) | cyclohexane (RT) | $> 5 x 10^9$ | ps | 7 |
| Complex with 4-azatricyclo- [4.3.1.1 ^{3.8}] undecan-5-one | cyclohexane (RT) | > 5 x 10 ⁹ | ps | 7 |
| Complex with 3,4,5,6,7,8-hexahydro- 2(1H)-quinolinone | cyclohexane (RT) | no reaction | ps | 7 |
| 1: 1 Complexes with alcohols | alkane solvent (RT) | $> 3 \times 10^{10}$ | | 8 |
| 3-Formyl-7-Azaindole | | | | |
| Dimer Dimer, deuterated Complex with acetic acid Complex with deuterated acetic acid Complex with 2-azacyclohexanone | cyclohexane (RT~298 K) cyclohexane (RT~298 K) cyclohexane (RT~298 K) cyclohexane (RT~298 K) cyclohexane (RT~298 K) | (estimated) 2.9×10^{12} (estimated) 1.5×10^{12} (estimated) 5.3×10^{12} (estimated) 2.8×10^{12} (estimated) 2.4×10^{11} | ps ps ps ps ps ps | 17 17 17 17 17 |
| 3-Iodo-7-Azaindole | single crystal at 10 K | $> 5 \ge 10^9$ | ps | 18 |

| 1-Azacarbazole | Experiment | Rate, s ⁻¹ | Resolution | Reference |
|----------------|---|-----------------------|------------|-----------|
| Dimers | molecular beam | $\sim 10^{9}$ | ns | 1 |
| Dimers | molecular beam, excite at origin | $3.0 \ge 10^9$ | ps | 9 |
| Dimers | molecular beam, | 7.7 x 10 ⁹ | ps | 9 |
| | excitation at origin + 109 cm ⁻¹ | | | |

(continued on next page)

Table 4.1 (continued)

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| Amide and Lactam Complexes | Normal (430-440 nm) | | | | | Tautomer (550-560 nm) | | | | | | | |
|----------------------------|---------------------|-------|----------------|---------------|---------------|-----------------------|--------|----------------|----------------|---------------|---------------|---------------------|------------------|
| | a1 | a_2 | a ₃ | τ_1 (ns) | τ_2 (ns) | τ ₃ (ns) | a1 | a ₂ | a ₃ | τ_1 (ns) | τ_2 (ns) | τ ₃ (ns) | $<\tau_{decay}>$ |
| Acetamide | 0.79 | 0.09 | 0.12 | 0.086 | 0.91 | 6.0 | | 1.00 | | | 1.31 | | |
| Benzamide | 0.75 | 0.10 | 0.16 | 0.056 | 0.82 | 8.7 | -11.44 | 11.23 | 1.22 | 0.049 | 1.26 | 2.7 | 1.4 |
| Succinimide | 0.53 | 0.23 | 0.24 | 0.120 | 1.70 | 8.3 | | 0.25 | 0.75 | | 0.87 | 3.1 | 2.5 |
| 222-Trifluoroacetamide | 0.70 | 0.11 | 0.20 | 0.018 | 0.71 | 9.3 | | 0.96 | 0.04 | | 1.42 | 6.1 | 1.6 |
| δ-Valerolactam | 0.94 | 0.04 | 0.02 | 0.032 | 0.70 | 5.7 | -24.49 | 25.49 | | 0.031 | 1.32 | | |
| HHQ ^(a) | 0.89 | 0.08 | 0.04 | 0.070 | 0.60 | 7.3 | -41.60 | 41.60 | 1.00 | 0.066 | 0.53 | 2.0 | 0.56 |
| (N-Methylformamide) | 0.70 | 0.04 | 0.25 | 0.053 | 0.72 | 13.0 | -54.72 | 54.40 | 1.31 | 0.057 | 1.29 | 7.0 | |

Table 4.2: Measured and Estimated Rates for 1-Azacarbazole Complexes

| Complex Partner with 1AC | Tautomer | k ^T rad | Experimental | Model | Best Estimate |
|--------------------------|--|--|--|--|--|
| | φ _{em} estimate ^(b) | 10° s ⁻¹ estimate ^(b) | $k_{PT}^{(u)}$ 10 ¹⁰ s ⁻¹ | k_{PT} (0) 10^{10} s^{-1} | $\frac{k_{PT}}{10^{10}}$ s ⁻¹ |
| Acetic Acid | 0.0035 | 2.9 | * | 150±50 | 150±50 |
| Acetic Acid-D | 0.0049 | 2.6 | * | 90±30 | 90±30 |
| | | | | | |
| 1-Azacarbazole | 0.0024 | 2.6 | * | | (f) |
| δ-Valerolactam | 0.0033 | 2.5 | 3.1 | 11 | 3.1 ± 0.3 |
| HHQ ^(a,c) | (0.0015) | (2.8) | 1.4 | 6.9 | 1.4 ± 0.2 |
| Acetamide | 0.0038 | 2.9 | >1.2 | 31 | (f) |
| Benzamide | 0.0036 | 2.5 | 1.8 | 8.0 | 1.8 ± 0.2 |
| 2,2,2-Trifluoroacetamide | 0.0047 | 3.3 | >5.6 | 64 | (f) |
| Succinimide | 0.0070 | 2.8 | >0.8 | 31 | (f) |

(continued on next page)

Table 4.2 (continued)

Top Table: Summary of lifetimes measured in normal and tautomer emission from 1AC complexes. The reported amplitudes and lifetimes represent the average of two independent measurements. (The data presented for 1AC complexes with N-methylformamide were measured once, and these lifetimes are more uncertain due to the difficulty in controlling the composition of the solution.)

Bottom Table: Summary of estimated rates at 298 K.

(a) HHQ is 3,4,5,6,7,8-Hexahydro-2(1H)-quinoline. (b) The tautomer quantum yields were calculated assuming $\varphi_{em} = 0.54$ for 1AC and $\varphi_{em} = 0.0038$ for the tautomer of the 1AC:acetamide complex [λ_{ex} =328 nm and 348 nm], and the remaining quantum yields have been determined relative to one another. The tautomer radiative rate $k_{rad}^{T} [\lambda_{ex}$ =348 nm] assumes a complete reaction and follows from $k_{rad}^{T} = \varphi_{em}^{T} / \tau_{dec}^{T}$. Uncertainty in the tautomer quantum yields and tautomer radiative rates is estimated to be < 20%. (c) Values in parentheses indicate more uncertain values (measured once, or involve larger estimates). Asterisks in the table indicate the lifetime was too fast to be resolved by the TCSPC experiment. (d) The proton-transfer rate in 1AC dimers is more rapid than (25 ps)⁻¹. When the reaction could not be measured in both the normal and tautomer emission, the fastest lifetime in the normal region is used as a lower bound for the reaction rate. (e) The proton transfer rate for the complexes is estimated within an irreversible proton-transfer scheme using a combination of steady-state and time-resolved emission data. Uncertainty in the model estimates is at least 30%. [See text.] (f) The best estimates of the observed rates are those measured directly or estimated more confidently using the irreversible proton-transfer kinetic scheme. For the other complexes in which a rise time was not observed in the tautomer region, the observed reaction rate is simply stated as more rapid than 4 x 10¹⁰ s⁻¹.

| | Monomer | Energetics ^(a) | Complex Interaction Energies ^(b) | | | | | | |
|------------------------|-----------|---------------------------|---|---------------------------------|----------|--------|----------|----------------------|----------|
| | ΔE (N>T) | ∆E (N>T) | N | Monte Carlo Model Quantum Chemi | | | al Model | Total ^(c) | |
| Complex Agent | HF/6-31G* | B3LYP/6-31G* | Normal | Tautomer | ΔE (N>T) | Normal | Tautomer | ∆E (N>T) | ∆E (N>T) |
| | kJ/mol | kJ/mol | kJ/mol | kJ/mol | kJ/mol | kJ/mol | kJ/mol | kJ/mol | kJ/mol |
| | | | | | | | | | |
| 1-Azacarbazole | 64.10 | 56.40 | -65.94 | -94.35 | -28.41 | | | | 99.79 |
| Acetic Acid | 0.00 | | -63.68 | -78.70 | -15.02 | -58.37 | -76.11 | -17.74 | 49.08 |
| Methanol | 0.00 | | -39.66 | -49.83 | -10.17 | -36.57 | (-50.67) | (-14.10) | 53.93 |
| | | | | | | | | | |
| δ-Valerolactam | 58.24 | 54.31 | -64.14 | -68.83 | -4.69 | | | | 117.7 |
| "HHQ" | 63.22 | 60.58 | -66.53 | -74.60 | -8.08 | | | | 119.2 |
| Formamide | 59.58 | | -66.36 | -73.09 | -6.69 | -51.30 | -75.56 | -24.27 | 117.0 |
| N-Methylformamide | 57.53 | | -62.72 | -65.69 | -3.01 | -51.30 | -70.79 | -19.50 | 118.6 |
| Acetamide | 64.64 | | -62.84 | -76.11 | -13.26 | | | | 115.5 |
| 222-Trifluoroacetamide | 69.12 | | -63.18 | -78.03 | -14.85 | | | | 118.4 |
| Benzamide | 62.55 | 59.20 | -63.39 | -76.40 | -13.01 | | | | 113.6 |
| Succinimide | 82.72 | | -63.81 | -95.52 | -31.71 | | | | 115.1 |

Table 4.3: Calculated Energetics of 1-Azacarbazole Complexes

^(a) The difference in electronic energy between the normal and tautomer species $\Delta E (N \rightarrow T) = E(T) - E(N)$ is presented for two model chemistries as indicated. The molecular geometry for both cases was optimized at HF/6-31G*. ^(b) Interaction energies in the Monte Carlo method were calculated directly using a combination of Lennard-Jones and Coulombic potentials as described in the text. The electronic interaction energies calculated in the quantum chemical method represent a supermolecule calculation: $E(\text{interaction}) = E(\text{complex}) - (\Sigma E(\text{agents}))$. The parenthetical quantum chemical values did not formally converge to a stationary point. The *ab initio* interaction energies are presented in S. Mente, S. J. V. Frankland, L. Reynolds, and M. Maroncelli, *Chem. Phys. Lett.*, **293**, 515-522 (1998). ^(c) The total change in the *ground state* energy represents the difference in energy between the normal and tautomer forms of 1AC and the complexing agent including the difference in the interaction energy.



Figure 4.1: Chemical Structures of Complexing Agents



Figure 4.2: Spectroscopy of 1AC:AA Complexes

Top panels: Steady-state fluorescence of 1AC:AA complexes reveals mostly tautomer emission, while mostly normal emission is observed for 1AC in bulk methanol. Bottom panel: Time-resolved emission decays recorded for the 1AC:AA tautomer complex. The instrument response function is plotted for reference.



Figure 4.3: Spectroscopy of 1AC:HHQ Complexes

(a) The spectrophotometric titration monitors the increased absorption intensity on the red-edge of the first absorption band as complexing agent is added. (b) Spectrophotometric titration using emission excited at 348 nm. The large spike rising from the normal emission is due to Raman scattering. (c) and (d) illustrate the time-resolved emission of the normal (430-440 nm) and tautomer (550-560 nm) species, respectively.



Figure 4.4: Spectroscopy of 1AC: δ-VL Complexes

(a) Absorption and emission bands prior to (dashed line) and following (solid lines) spectrophotometric titration. The large spike rising from the normal emission is due to Raman scattering. (b) and (c) are time-resolved emission spectra of the normal (430-440 nm) and tautomer (550-560 nm) species, respectively.



Figure 4.5: Steady-State Spectroscopy of 1AC:Acetamide and 1AC:Benzamide Complexes

Left panels are absorption spectra of 1AC prior to (dashed lines) and following (solid lines) sonication with the solid amides. Right panels are emission spectra demonstrating complex formation leading to excited-state tautomer fluorescence.



Figure 4.6: Time-Resolved Emission of 1AC:Acetamide and 1AC:Benzamide Complexes

- (a) and (b) 1AC: Acetamide emission at 430 nm and 525 nm, respectively.
- (c) and (d) 1AC:Benzamide emission at 440 nm and 550 nm, respectively.



Figure 4.7: 1AC:Complex Rate Dependence on Model Energetics

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⁷³ See Chapter 3.

⁷⁴Moog and coworkers (Franklin and Marshall College, Lancaster, PA) have not yet published their study that includes the determination of the K_a of 1AC:AA. Therefore, an alternative perspective is based on model calculations at HF/6-31G* which indicate the complexation energy $\Delta E \sim \Delta H$ for 1AC:AA [-14.0 kcal/mol] is nearly equal to that for 7AI:AA [-14.2 kcal/mol] (See Endnote 51).

⁷⁵ The association constant for the formation of 1:1 complexes of 1AC and acetic acid in methylcyclohexane is K_a =[1.0±0.2] x 10⁴ M⁻¹. This value is extracted from the free energy of formation based on data reported by Rick Moog and coworkers in S. Mente, S. J. V. Frankland, L. Reynolds, and M. Maroncelli, *Chem. Phys. Lett.*, **293**, 515-522 (1998).

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(2) The equilibrium constant K_a is important because it is related to the magnitude of the interaction energy of the molecules involved in the complex: $K_a \sim \exp(-\Delta E/kT)$, where ΔE is the interaction energy. Strictly speaking, the equilibrium constant is related to the free energy of formation: $K_a = \exp(-\Delta_f G/kT)$.

(3) We take the single isobestic point in the first absorption band (328 nm) as further evidence that 1:1 complexes are forming between 1AC and acetic acid.

⁷⁸ Model equilibrium calculations neglecting the self-association of acetic acid predict that at least 99% of the 1AC is complexed after the first addition of neat acetic acid.

⁷⁹ Due to poor choice of a cut-off filter, good data was not recorded in the normal region (430 nm) for 1AC dimers. Ideally this work would be pursued further for a better estimate of the reaction rate.

⁸⁰ Equilibrium constants K_a and molar absorptivity constants $\varepsilon(\lambda)$ were obtained from a least-squares fit to the series of absorption spectra in the spectrophotometric titrations for 1AC:lactams, assuming 1:1 complex formation and neglecting selfassociation of the lactams. The results showed a good fit of the calculated spectra with the observed data within experimental uncertainty. The observation of an isobestic point at ~328 nm in the first absorption band also suggests the formation of 1:1 complexes. 1AC- δ -VL: $K_a = (7\pm8) \times 10^3 \text{ M}^{-1}$, $\varepsilon(348 \text{ nm}) = 1000 \pm 400$; 1AC-HHQ: $K_a = (4\pm7) \times 10^3 \text{ M}^{-1}$, $\varepsilon(348 \text{ nm}) = 1300 \pm 700$. The significant uncertainties arise from the measurements on very dilute solutions in 1 cm cuvettes.

Although HHQ has substantial absorbance (λ_{max} *ca*. 250 nm) at the concentrations used in the dilute solutions, its contribution to the complex absorption band (λ > 345 nm) is negligible. The HHQ also accounts for some impurity emission in the region of the normal fluorescence of the 1AC:HHQ complex.

The total tautomer emission intensity as a function of lactam concentration was also fit to a 1:1 complexation model to obtain best values for the equilibrium constants.

In this model, the fluorescence intensity is directly related to the complex concentration: $I^T \sim I_0 \varepsilon l \phi^T$ [complex]. Since the absorptivity constants ε , the path lengths l, and the initial excitation intensity I_0 are approximately the same for the two lactams, the constant obtained in addition to K_a will be directly related to the relative quantum yields. 1AC- δ -VL: $K_a=(3.0 \pm 0.5) \times 10^3 \text{ M}^{-1}$, constant = $(7.7 \pm 0.6) \times 10^{10}$; 1AC-HHQ: $K_a=(3 \pm 1) \times 10^3 \text{ M}^{-1}$, constant = $(4.0 \pm 0.7) \times 10^{10}$. Note that the fits predict the relative quantum yields 1AC-HHQ ~ 1/2 1AC- δ -VL, which is consistent with the direct measurements presented in Table 4.2. These results indicate the improved sensitivity of the fluorescence emission measurements, and the values of K_a determined by this method and from absorption spectroscopy agree within experimental error. These association constants, however, still lack sufficient resolution to predict which 1AC:lactam complexes involve higher interaction energies.

The least-squares analysis involved an extension of the method described in D. C. Harris, *Quantitative Chemical Analysis, 2nd. Ed.* (New York, W. H. Freeman and Company, 1987.) pp. 381-383 and 535-537.

⁸¹ A second experiment was attempted but failed due to difficulty in controlling the composition of the emulsion. We present the results of the first experiment as interesting observations, and note this as an example of the difficulty in controlling the composition of hydrogen-bonded liquids in nonpolar alkane solvents.

⁸² Although the relative tautomer radiative rate is slightly longer (smaller α values) in the very polar solvents like formamide, N-methylformamide, and ethylene glycol, the average of α values for the wide variety of protic solvents will be the best determination of the relative radiative rates for 1AC isolated complexes. (If one chooses to be more selective about the choice of solvents used in the determination of the ratio of radiative rates, a different value will be obtained: for example, $\alpha(1AC) = 9.0 \pm 10\%$ from *Table 2.3.*)

⁸³A similar comparison may be made using literature values for 7AI dimers. The ratio of radiative rates for 7AI may be estimated using values for methanol summarized in the extensive tabulation by Chapman and Maroncelli [Endnote 4]: α (7AI) ≈ 22 . Suzuki, Okuyama, and Ichimura [Endnote 32] report the quantum yield of the dimer complex to be $\varphi^{N}=0.00_{6}$ and $\varphi^{T}=0.16$, and Tokumura, Watanabe, and Itoh [Endnote 35] report the decay rate of the tautomer in nonpolar solvent to be $3.3 \times 10^{8} \text{ s}^{-1}$ (3.0 ns) [consistent with Endnote 46] These measurements then predict $k_{PT}=2 \times 10^{11} \text{ s}^{-1}$ (5 ps), in agreement within half an order of magnitude with the measured rate of 7.1 x 10^{11} s^{-1} (1.4 ps). [See Table 4.1]. In the same way, the ultrafast-rate of the excited-state tautomerism of 7AI complexed by acetic acid may be estimated. The quantum yields are again quoted from Suzuki, Okuyama, and Ichimura [Endnote 32], $\varphi^{N}=0.00_{2}$ and $\varphi^{T}=0.11$, and the tautomer

decay rate was measured by Chang *et al.*[Endnote 68] to be $3.8 \times 10^8 \text{ s}^{-1}$ (2.62 ± 0.08 ns). The predicted proton-transfer rate in 7AI:AA is therefore 5 x 10¹¹ s⁻¹ (2 ps).

⁸⁴H. Szmacinski and J. R. Lakowicz, in *Topics in Fluorescence Spectroscopy, Volume 4: Probe Design and Chemical Sensing.* J. R. Lakowicz, Ed. (New York, Plenum Press, 1994). p. 304.

⁸⁵ One may be troubled that the estimated rates for the 7AI complexes are smaller than the corresponding rates for the 1AC complexes, especially since in bulk alcohols the excited-state tautomerization rate is greater for 7AI than 1AC. This scheme for estimating rates is approximate, and able to predict rates within 0.5-1 order of magnitude based on the 7AI dimer comparison. On the other hand, it is interesting that the driving force is sufficient to allow the 1AC:HHQ reaction to occur, while the corresponding 7AI:HHQ reaction has not been observed [Endnote 69]. This suggests that protontransfer reactions in isolated complexes with 1AC could actually be faster.

⁸⁶ Chapman and Maroncelli [Endnote 4] mention the possibility that the normal emission could contain an additional short lifetime due to the dynamic Stokes shift. Since this feature was not obvious in the emission from all complexes considered here, this explanation was not pursued further.

⁸⁷Similar quantum chemical calculations are reported for 7AI. See, for example, Endnotes 51, 68, 69 and M. S. Gordon, *J. Phys. Chem.*, **100**, 3974 (1996).

⁸⁸ (1) Waluk and coworkers have proposed that the activation energy required for the proton transfer in 1AC arises from two contributions: a significant viscositydependent energy barrier as the molecules in the dimer complex adjust for a proper arrangement for proton-transfer, and a small or negligible energy barrier for the intrinsic proton transfer. For experimental arguments, see (a) Endnote 24. (b) J. Waluk, J. Herbich, D. Oelkrug, and S. Uhl, *J. Phys. Chem.*, **90**, 3866 (1986). For INDO/S calculations, see: (a) Endnote 24. (b) J. Waluk, H. Bulska, A. Grabowska, and A. Mordzinski, *Nouv. J. Chim.*, **10**, 413 (1986).

(2) Fuke, Kaya, and coworkers have identified the vibrational modes responsible for promoting the excited-state reaction of 1AC dimers in molecular beams. See Endnotes 36, 37, 38, 70, and K. Fuke, T. Yabe, N. Chiba, T. Kohida, and K. Kaya, *J. Phys. Chem.*, **90**, 2309 (1986).

(3) El-Bayoumi and coworkers estimated the reaction barrier for 1AC dimers in 3-methylpentane to be 2.95 kcal/mol [Endnote 66]. For comparison, the Arrhenius activation energy for the viscosity of 3-methylpentane is 1.7 kcal/mol. [Viscosity data

(200-330 K) from C. L. Yaws, *Handbook of Viscosity, Vol. 2.* (Houston, Gulf Publishing Co., 1995).]

⁸⁹ (1) Early work debated the role of tunneling in the 7AI dimer tautomerizations. Work by Kasha, El-Bayoumi, and coworkers argued for a tunneling reaction, with a barrier of 1.4 kcal/mol [500 cm⁻¹]. See Endnotes 20, 21, 22. Later work challenged these interpretations, suggesting that the excited-state reaction did not involve tunneling but instead was an activated process with little or no barrier to the intrinsic proton-transfer. An estimated small barrier [~100-200 cm⁻¹] was attributed to subtle intermolecular movement necessary for the proton-transfer to occur, and calculations suggested that the driving force for 7AI was greater than 1AC. See Endnotes 24, 25, 26, 27, and J. Waluk, H. Bulska, A. Grabowska, and A. Mordzinski, *Nouv. J. Chim.*, **10**, 413 (1986).

(2) Fuke, Kaya and coworkers also identified the vibrational modes responsible for promoting the excited-state reaction of 7AI dimers in molecular beams. See Endnotes 36, 37 and 38.

(3) Time-resolved studies of the 7AI dimer tautomerization have revealed more than one pathway for the reaction, and recent experimental evidence indicates support for a stepwise proton-transfer. Eisenthal and coworkers estimated the barrier to be 700 cm⁻¹ [Endnote 31]. Further experimental studies examining facets of the reaction are listed in Endnotes 13, 15, 16, 18, 19, 31, 45, 46, 47, 48, and 56; and, examples of computational efforts are noted in Endnotes 41, 42, 14, 56, 59, and 63.

⁹⁰ M. K. Shukla and P. C. Mishra, *Chem. Phys.*, **230**, 187-200 (1998).

⁹¹ G. M. Chaban and M. S. Gordon, J. Phys. Chem. A., 103, 185-189 (1999).

⁹² A. Fernandez-Ramos, Z. Smedarchina, W. Siebrand, M. Z. Zgierski, and M. A. Rios, *J. Am. Chem. Soc.*, **121**, 6280-6289 (1999).

⁹³ Z. Smedarchina, W. Siebrand, A. Fernandez-Ramos, L. Gorb, and J. Leszczynski, J. *Chem. Phys.*, **112**, 566-573 (2000).

⁹⁴ A. Fernandez-Ramos, Z. Smedarchina, W. Siebrand, and M. Z. Zgierski, *J. Chem. Phys.*, **114**, 7518-7526 (2001).

⁹⁵ U. C. Singh and P. A. Kollman, J. Comput. Chem., 5, 129 (1984).

⁹⁶ B. H. Besler, K. M. Merz, Jr., and P. A. Kollman, J. Comput. Chem., **11**, 431 (1990).
⁹⁷ Gaussian 94, Revision B.1: M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, J. A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, (Gaussian, Inc., Pittsburgh PA, 1995).

⁹⁸ S. J. V. Frankland, Ph.D. Thesis, The Pennsylvania State University, 1997.

⁹⁹ See the discussion in S. Schneiner, *Hydrogen Bonding: A Theoretical Perspective*. (New York, Oxford University Press, 1997). Chapter 1. The complexation energies reported here are the electronic interaction energies ΔE_{elec} . The thermodynamic interaction energy ΔE contains additional corrections for translational, rotational, zeropoint and thermal vibrational energies. No corrections were applied for possible basis set superposition errors, although the magnitude of such corrections are anticipated to be on the order of +8 kJ/mol based on a counterpoise correction for the normal complex of 7AI:Methanol. No corrections were applied for electron correlation. In order to make a fair comparison to experimental results, the thermodynamic interaction energy should be converted to an enthalpy or free energy, and for comparison to solution data, the effects of solvation must be considered as well.

¹⁰⁰ See the discussion in Endnote 9 and J. Pranata, S. G. Wierschke, and W. L. Jorgensen, *J. Am. Chem. Soc.*, **113**, 2810 (1991).

¹⁰¹ These concepts are components of the well-known Marcus theory. See, for example:

(a) R. A. Marcus, Angew. Chem. Int. Ed. Engl., 32, 1111 (1993).

(b) T. H. Lowry and K. S. Richardson, *Mechanism and Theory in Organic Chemistry*, *3rd. Edition*. (New York, HarperCollinsPublishers, 1987). pp. 222-227.

¹⁰² One has also noted a remarkable compensation in which changes in the tautomerization energies are offset by changes in complexation energies.

¹⁰³ See, for example, Endnotes 42, 14, 100, and L. Meschede and H.-H. Limbach, *J. Phys. Chem.*, **95**, 10267, 1991.

¹⁰⁴ A similar geometric parameter which may effect the reaction rate is the flexibility of the complex.

¹⁰⁵ A recent experiment estimated the excited-state proton-transfer rates of 3-formyl-7azaindole in isolated complexes with acetic acid, 3-formyl-7-azaindole, or 2-azacyclohexanone. The ranking of rates (acetic acid > dimer > lactam) was identical to the results of the experiment reported in this chapter. For additional details, see: P.-T. Chou, G.-R. Wu, C.-Y. Wei, M.-Y. Shiao, and Y.-I Liu, *J. Phys. Chem. A*, **104**, 8863-8871 (2000).

¹⁰⁶ Chou and coworkers have also recently demonstrated that the reaction rate may be tuned by changing the functional groups and the substitution positions on 7AI. For a comparison of 7AI, 4-azabenzimidazole, and 6-isobutylpurine, see: P.-T. Chou, C.-Y. Wei, G.-R. Wu, and W.-S. Chen, *J. Am. Chem. Soc.*, **121**, 12186-12187 (1999).

¹⁰⁷ Y. Huang, S. Arnold, and M. Sulkes, J. Phys. Chem., **100**, 4734 (1996).

¹⁰⁸ S. K. Kim and E. R. Bernstein, J. Phys. Chem., **94**, 3531 (1990).

¹⁰⁹ D. E. Folmer, E. S. Wisniewski, J. R. Stairs, and A. W. Castleman Jr., *J. Phys. Chem. A*, **104**, 10545-10549 (2000).

¹¹⁰ D. L. Tomasko, B. L. Knutson, J. M. Coppom, W. Windsor, B. West, and C. A. Eckert, Chapter 17 in *Supercritical Fluid Engineering Science: Fundamentals and Applications*. [J. F. Brennecke and E. Kiran, Eds.] (Washington, DC: American Chemical Society, 1993) {ACS Symposium Series 514} pp. 220-227.

¹¹¹ D. L. Tomasko, B. L. Knutson, F. Pouillot, C. L. Liotta, and C. A. Eckert, *J. Phys. Chem*, **97**, 11823 (1993).

Chapter 5

STUDIES OF 1-AZACARBAZOLE IN BULK PROTIC SOLVENTS – I. DIOLS

5.1 Introduction

The study of excited-state tautomerism of 1-azacarbazole (1AC) in isolated hydrogen-bonded complexes has demonstrated that the proton-transfer is rapid [Chapter 4]. Although it is generally assumed that some hydrogen-bonded complex is necessary for promoting the excited-state tautomerization in bulk protic solvents, a molecular-level description of the reaction mechanism and identification of a rate-determining step continue to be discussed for the bulk protic solvents.¹⁻³⁷ Early work established that protic solvents catalyze the tautomerization reactions,¹⁻⁸ and noted the remarkable connection between the activation energy of the reaction and that of the bulk viscosity of alcohols, a connection that was interpreted to mean that large-amplitude molecular motion controls the reaction.^{5,6} At that time, neither the geometric structure^{5,7} nor the hydrogen-bonding strength^{2,5,7} of the alcohol solvents were deemed important for controlling the reaction.

Kinetic models of this reaction advanced with the advent of time-resolved measurements of sufficient resolution to monitor the entire reaction.³⁸ Many of the early experiments on 7-azaindole (7AI) in bulk alcohols indicated that solvent dynamics was

one important factor in controlling the rate of the reaction.^{16,29,34} Some workers also noted that the proton-transfer rate was strongly correlated to the hydrogen-bonding strength or acidity of the alcohol solvents.^{33,16} A dominant theme in the description of the reaction was that the mechanism could be understood as a two-step process.^{34,33,16,29}

The following examples illustrate the two-step models proposed for the mechanism. Differences among the interpretations arise mainly from whether static or dynamic aspects of the first step control the reaction. In the first direct measurement of the excited-state proton-transfer rate of 7AI in alcohols, McMorrow and Aartsma³⁴ proposed a model invoking two types of solvent configurations to explain two lifetimes growing into the decay of 7AI tautomer fluorescence at 510 nm. A pre-formed, cyclically hydrogen-bonded complex was proposed to enable instantaneous proton transfer (20 ps in methanol), while other configurations exhibited a slower response (165 ps in methanol) as solvent-solute reorganization dynamics determined the rate of attaining the cyclically hydrogen-bonded complex needed for the proton-transfer event. Later measurements were unable to reproduce the amplitude of the rise time in the tautomer fluorescence in alcohols attributed to this intrinsic proton-transfer step.^{16,29,33,39} Even with subpicosecond resolution, the ultrafast component proposed by McMorrow and Aartsma has not been observed.^{25,26} Two years later, Varma and coworkers explained the reaction as a two-step process in which a tunneling proton transfer (for the two protons) followed the formation of a cyclically hydrogen-bonded 7AI-alcohol complex.³³ This kinetic model satisfactorily accounted for their observations of a temperature-independent kinetic isotope effect and of rate dependence on the acidity of

the alcohols rather than on viscosity or solvent aggregation.³³ Moog and Maroncelli¹⁶ retained and modified the two-step model of McMorrow and Aartsma³⁴ in order to explain an interesting¹¹ temperature dependence of the kinetic isotope effect on the reaction rate.

Study of the excited-state tautomerization of 7AI and 1AC has continued at a fervent pace. The interpretation of the reaction mechanism has evolved and no longer maintains that "solvation dynamics" is relevant in the discussion.^{10,11,20} The issue of the temperature dependence of the reactions of 7AI and 1AC in alcohols was revisited by Maroncelli *et al.*,^{10,11,13,14} and the observed reaction rate is currently modeled by

$$k_{obs} = k_{PT} \exp(-\Delta G/kT) \qquad (5.1)$$

where k_{PT} is the intrinsic proton-transfer rate in a proper configuration and ΔG is the equilibrium solvation free energy needed to achieve that cyclic complex.^{10,11} The essence of this model is very similar to that originally proposed by Varma and coworkers one decade earlier.³³ Advocating a different physical picture, Petrich and coworkers recently argued that the rate-determining step involves the actual proton-transfer rather than the solvent reorganization required to form the necessary cyclic hydrogen-bonded complex.²⁰ The challenge faced by all models is the decomposition of the <u>one</u> observed rate into <u>two</u> or more contributions from likely physical processes occurring in solution.

Linear correlations of the proton-transfer rates of 7AI and 1AC with some measure of the hydrogen-bond donating ability of the neat protic solvents were introduced in Chapter 3. These linear free-energy relationships are consistent with the general decomposition of the observed rate into some solvent independent intrinsic rate and a rate factor depending on the solvent. Interesting deviations from the linear relationships observed in bulk alcohols have been noted for highly polar and viscous solvents such as diols, water, and amides.⁴⁰ Do these deviations suggest that the excited-state of 7AI or 1AC is depopulated via alternative pathways? This question has been explored at length for 7AI in water without convergence to a clear under-standing.^{1,2,15,18-32,36} Since the photophysics and photochemistry of 1AC is similar to that of 7AI, experimental studies on the excited-state tautomerism of 1AC in these bulk protic solvents were undertaken in an attempt to understand the origin of these differences.

5.2 1AC in Diols

Noted in earlier studies of the excited-state tautomerism of 7AI and 1AC,^{16,13} the measured reaction rates in diols and water appear to be anomalously slow when compared to the rates of alcohols plotted on the $E_T(30)$ polarity scale (*cf. Figure 3.2*). If the reaction rate is determined by some form of solvent dynamics, it might be expected to be much slower in the very viscous diols. However, the reported rates do not correlate in any simple way with bulk viscosities or alternative measures of solvation dynamics.^{33,16,13} To develop a better understanding of these slow reaction rates, the temperature dependence of excited-state tautomerization of 1AC was examined in ethylene glycol, ethylene glycol-D₂, and propylene glycol over the range 1 °C - 70 °C. Experiments on 7AI in ethylene glycol were also repeated to provide a base of comparison with earlier results.¹⁶

5.2.1 Temperature Dependence of 1AC Lifetimes

At temperatures above 40-50 °C, the time-resolved emission of 1AC in diols indicates kinetics consistent with an irreversible proton-transfer model as described in Chapter 3. A minor component to describe possible impurity fluorescence (<5%, τ ~5 ns) and a component to account for a dynamic Stokes shift (<100 ps) in the normal region are added to this model. For example at 70 °C in ethylene glycol (EG), the 1AC normal emission decays in 430 ps as the tautomer emission exhibits a decay (reaction) time of 420 ps and a rise (tautomer deactivation) time of 250 ps. (Recall from Chapter 3 that the rise time of the tautomer species does not necessarily correspond to the growth of the product during the reaction. Instead, it is the relative rates of the reaction and of the tautomer deactivation that determine the correct interpretation of the tautomer rise time.)

At or below room temperature, however, the kinetics become more complicated. For reference, at 20 °C in ethylene glycol (EG) the 1AC normal emission decays in 1.01 ns as the tautomer emission exhibits a decay (reaction) time of 1.05 ns and a rise (tautomer deactivation) time of 320 ps. The complications become more apparent when the lifetimes are plotted as a function of temperature. A plot of the tautomer rise (deactivation) times does not increase steadily with decreasing temperature as might be anticipated (*Figure 5.1*), a feature also present in the temperature dependence for ethylene glycol-D₂ (*Figure 5.2*) and propylene glycol (*Figure 5.3*). Two alternative fits of the tautomer emission are explored in order to assess the significance of these observations. In the first alternative fit, the term to model possible impurity emission is constrained to a long nanosecond lifetime. This affects little change in the behavior of the tautomer rise (deactivation) time for 1AC. In the second alternative fit, the tautomer rise (deactivation) times at high temperatures are extrapolated to lower temperatures (as indicated in *Figure 5.1, Figure 5.2* and *Figure 5.3*) and constrained with the impurity term while fitting the emission decay. At lower temperatures, an additional component is then needed to fit the tautomer rise, and the overall effect does lengthen the tautomer rise (deactivation) times. Physical interpretation of the biexponential rise times may lack warrant, however, since a weighted average value of the tautomer rise times differs little from that fit without constraints. (See *Table 5.1, Table 5.2, Table 5.3, Table 5.6, Table 5.7*, and *Table 5.8* for summaries of the temperature studies of 1AC in ethylene glycol.)

In retrospect, it is not clear that these alternative fits for 1AC in ethylene glycol provide useful perspective on the reaction and especially the tautomer rise (deactivation) times at low temperatures. The various lifetimes of multiexponential fits to the emission data may not necessarily have a unique physical interpretation. Nevertheless, good estimates of the reaction and tautomer deactivation rates are needed for modeling the reaction in general. The extraction of these parameters is complicated by the apparent slowness of the reaction rate especially when compared to the normal deactivation rate k^N observed in aprotic solvents. This general consideration is discussed in the next section before we present the best estimates for the reaction rates in diols.

5.2.2 Reaction Rate Determination with Possible k^N Contamination

The irreversible proton-transfer kinetic scheme requires $k_{rxn} \gg k^N$ in order to interpret the observed rate k_{obs} as the reaction rate k_{rxn} . Because the 1AC observed rates k_{obs} are close to the 1AC normal deactivation rates k^N , a correction may need to be applied to the observed rates in order to account for this alternative pathway of deactivation (k^N) and to extract the true reaction rate. Although this correction is simply $k_{rxn} = k_{obs} - k^N$, the actual determination of k^N may be troublesome. Three possibilities are explored to estimate the magnitude of k^N and to assess the change between the observed rate and the reaction rate.

(Method 1) One could assume that the deactivation rate k^N of the normal species in protic solvents is equal to that in aprotic solvents, and the observed rates could be corrected using the aprotic values of k^N . For example at room temperature, $k^N = (1.1\pm0.2) \ge 10^8 \text{ s}^{-1}$ for the aprotic solvents (*Table 2.3*). When this correction is applied to the protic solvents at room temperature (*Table 2.3*), many corrected reaction rates are slower by ~10-20% of the observed rates, with notable exceptions including methanol-OD (~ 30%) and N-methylformamide (~ 50%).

(**Method 2**) The reaction rate may be estimated directly from the expression derived in Chapter 3,

$$k_{rxn} = (k_{rad}^{N} / k_{rad}^{T}) (\phi^{T} / \phi^{N}) k^{T}, \qquad (5.2)$$

and compared the observed rate to determine k^N . For this comparison at room temperature, the average value of $k_{rad}^N / k_{rad}^T = 9 \pm 1$ for six protic solvents is used in the calculation of the reaction rates for all protic solvents since this ratio is assumed to be

representative of all of them (*Table 2.3*: MeOH, 1-PrOH, 1-PeOH, 2-PrOH, BzOH, and TFE). Although this approach predicts negative values of k^N , within experimental uncertainty the rates of many protic solvents are in agreement with k^N determined from the aprotic solvents. Exceptions include methanol-OD, 1-pentanol, ethylene glycol, formamide and N-methylformamide. Many estimated reaction rates k_{rxn} are slightly faster than the observed rates, but with the exception of t-butanol and ethylene glycol, agree within experimental uncertainty.

The comparisons in Methods (1) and (2) are made using data recorded at room temperature. The normal deactivation rate k^N does depend on the temperature of the experiment, so k^N must be estimated at each temperature at which the correction to the observed rate is made. The tautomer deactivation rate k^T also depends on temperature and must be measured directly in each protic solvent. The concern over k^N is especially important in interpreting the isotope and low temperature studies. The correction of rates at low temperatures is summarized elsewhere,^{13,14} but the data of 1AC in ethylene glycol is reexamined here with additional detail. The following third method of analysis provides one means for estimating the temperature dependence of k^N .

(Method 3) The following analysis is summarized in *Table 5.6*, *Table 5.7*, and *Table 5.8*. Method (3) is like Method (2) except that the temperature dependence of the quantum yield ratios $\varphi^{T} / \varphi^{N}$ are determined directly from normalized emission spectra.⁴¹ The total quantum yields for 1AC in ethylene glycol at the temperatures in this experiment are estimated by scaling the relative quantum yields to the absolute quantum yield φ =0.019 at 295±2 K from *Table 2.3*. The quantum yields for 1AC in ethylene

glycol- D_2 are estimated in a similar fashion. Although a quantum yield for 1AC in ethylene glycol- D_2 is not available in *Table 2.3*, it is estimated from the quantum yield of 1AC in ethylene glycol by assuming that 1AC has the same normal radiative rate in the deuterated solvent. Thus, for 1AC in ethylene glycol- D_2 the quantum yield is estimated ϕ =0.051 at 295±2 K (based on an isotope effect of 2.7 in the normal lifetime). The radiative rates are determined from the quantum yield estimates and the fluorescent lifetimes of the normal and tautomer species. In both these solvents, the normal radiative rate is constant over the range 1-70 °C with $k_{rad}^{N} = 1.7 \times 10^{7} \text{ s}^{-1} \pm 2\%$. The tautomer radiative rates are dependent on the method of fitting the time-resolved emission as noted above, and they are constant or slowly increasing with decreasing temperature (assuming a complete and irreversible reaction). The ratio $k_{rad}^{N} / k_{rad}^{T}$ is reasonably constant over the entire temperature range, although it is almost a factor of two smaller than the average value for the six protic solvents chosen in Method (2). The estimates for k^{N} using the "second alternate fit" are in best agreement with the aprotic rate $k^{N} = 1.1 \times 10^{8} \text{ s}^{-1}$. With $k_{rad}^{N} / k_{rad}^{T} \sim 5$, approximately one-half of the predicted values of k^N are negative (not realistic), but the predicted reaction rates are within 20% of the observed rates. With $k_{rad}^{N} / k_{rad}^{T} \sim 9$, the predicted values of k^N are all significantly negative (not realistic), and the predicted reaction rates are all significantly larger than the observed rates.

The results of Methods (2) and (3) suggest that the either the ratio $k_{rad}^{N} / k_{rad}^{T}$ displays a modest solvent (*e.g.*, polarity) dependence, or that extracting lifetimes with accurate physical interpretation is difficult as the reaction slows. Without a means of independently determining k^{N} in protic solvents at the temperatures studied, and

considering the observations noted above, the rates k_{rxn} and k^{T} will be uncertain by at least 10-20%. The best estimates for rates and isotope effects for the temperature studies will include the quantum yield correction described in Method (3) using the ratio k_{rad}^{N}/k_{rad}^{T} determined at high temperatures.

5.2.3 Temperature Dependence of 1AC Reaction Rates in Diols

The best estimates of the reaction rates (based on the second alternative fit) are summarized in *Figure 5.5*. Unlike the temperature dependence of 7AI in bulk alcohols, the estimated activation energy for the reaction is only ~60% of that for viscosity (*Table 5.11*). The isotope effect appears to be largely independent of temperature. This temperature-independent isotope effect is similar to that for the related tautomerization in bulk alcohols except that its magnitude is slightly smaller (see Chapter 7).^{11,13}

5.2.4 Temperature Dependence of 7AI in Diols

The temperature dependence of the 7AI reaction in ethylene glycol and propylene glycol is similar to that observed for 1AC. At high temperatures the kinetics are consistent with the irreversible proton-transfer scheme: the normal fluorescence of 7AI decays with lifetime of ~170 ps as the tautomer emission appears with a 140 ps rise (reaction) time before decaying (deactivation) with a lifetime of 450 ps. In diols, the excited-state reaction for 7AI is three times faster than for 1AC. Note that this example for 7AI is consistent with the usual interpretation of the decay and rise components in the

time-resolved fluorescence of a two-state reaction. The normal form of the molecule disappears (emission decay) at the rate of the reaction while the tautomer form of the molecule appears (emission rise) at the rate of the reaction before disappearing (emission decay) at a different rate. This interpretation stands in contrast to that for 1AC.

Below room temperature, the kinetics are again more complicated. The alternative fitting models described for 1AC reactions in diols did provide insight into the interpretation of the excited-state lifetimes observed for 7AI in the viscous diols. The most striking illustration involves the reaction in propylene glycol (*Figure 5.4*). The tautomer rise (reaction) times do not increase monotonically with decreasing temperature as might be expected. If the high temperature tautomer decay (deactivation) times are extrapolated to lower temperatures and constrained (the second alternative fit model), then the refit rise (reaction) times do increase monotonically. At low temperatures, the rise (reaction) and decay (deactivation) times are then nearly equal. Since this model fits the data as well as the original fit, it suggests that quantitative measurements of the interesting interplay between the reaction rate and tautomer deactivation rate are obscured in the data. This near crossover in interpretation of the tautomer rise (reaction to deactivation) and decay (deactivation to reaction) times is consistent with the model for the reaction of 7AI in water, where the tautomer decay time was interpreted as the measure of the reaction time.¹⁵

Possible corrections to the time-resolved fluorescence of 7AI in ethylene glycol were not as severe as those described for the reaction in propylene glycol. (See *Table 5.1, Table 5.4*, and *Table 5.5* for summaries of fits.) Biexponential rise (reaction) times

for 7AI in ethylene glycol were observed at low temperatures. An effort to fit these data using a nonexponential model was unsuccessful.⁴² The best estimates for the reaction times using the second alternative fit with corrections based on relative quantum yields are compared to the 1AC results (*Figure 5.5*). Like 1AC, the Arrhenius activation energy of the 7AI reaction is ~60% of that for viscosity (*Table 5.11*), and the isotope effect is largely independent of temperature, consistent with earlier reports.¹¹

5.2.5 Comparison of 7AI Reaction Rates in Diols to Literature Values

Petrich and coworkers have reported lifetime measurements for the normal form of 7AI in ethylene glycol and propylene glycol.²⁰ In this work emission was collected over the entire normal band (320 - 460 nm) and was fit to a sum of two exponentials $F(t) = a_1 \exp(-t/\tau_1) + a_2 \exp(-t/\tau_2)$. Their results are summarized, $N(t) = a_1 (\tau_1) + a_2 (\tau_2)$:²⁰

EG (20 °C)
$$N(t) = 0.31 (0.141 \text{ ns}) + 0.69 (0.461 \text{ ns})$$

PG (20 °C) $N(t) = 0.31 (0.197 \text{ ns}) + 0.69 (0.816 \text{ ns})$

The shorter lifetime was interpreted as the reaction time, and the longer lifetime was interpreted as emission from 7AI in a "blocked" form of solvation. The time dependencies of the normal bands measured by Petrich and coworkers are similar to those recovered in the experiments reported in this dissertation. In order to compare the results directly, a biexponential fit is constructed from weighted averages of corresponding terms in the multiexponential fit to the normal emission at 370 nm:

EG (20 °C) N(t) = 0.32 < 0.084 ns > + 0.68 < 0.43 ns >PG (20 °C) N(t) = 0.55 < 0.098 ns > + 0.45 < 0.89 ns > We interpret these lifetimes differently than Petrich and coworkers:²⁰ the short time is attributed to a dynamic Stokes shift,⁴³ and the long (mean) time is attributed to the reaction time.

Our measurements of the tautomer emission at 560 nm reveal average rise times that are faster than the (long) decay times of the normal emission:

| EG (20 °C) | T(t) = - 8.41 < 0.32 ns > + | 9.41 <0.77 ns> |
|------------|---|----------------|
| PG (20 °C) | T(t) = -10.1 < 0.62 ns + -10.1 = | 11.1 <0.95 ns> |

In the simple irreversible proton-transfer scheme for 7AI, the normal emission decay (reaction) time should be equal to the measured tautomer rise (reaction) time. As noted above, the reaction of 7AI in propylene glycol may be difficult to measure directly because of ambiguity in the lifetimes obtained from the fits to the emission. The reaction of 7AI in ethylene glycol may more closely approach an irreversible proton-transfer scheme. If weighted average normal lifetimes are calculated from the data of Petrich and coworkers,²⁰ their agreement with the mean reaction (rise) times measured in the tautomer is good. It may be possible that our measurements are unable to separate completely a time constant for the dynamic Stokes shift so that the averaged short lifetime $<\tau_1>$ includes some contribution from reacting 7AI. It is unlikely that two or more distinct populations involving these proton-transfer molecules should exist in solution based on recent experiments and simulations which indicate the short-lived nature of hydrogen-bonded complexes in protic solvents.^{44,10}

5.3 Temperature Study of 1AC in Benzyl Alcohol

Since the observed rates of 1AC are anomalously fast in benzyl alcohol on the basis of the $E_{T}(30)$ correlation, a brief study of the temperature dependence of the reaction was undertaken to estimate the Arrhenius activation energy. The data are summarized in Figure 5.6 and Table 5.9. The observed lifetimes of the normal and tautomer species are difficult to interpret uniquely at room temperature. At temperatures above 45 °C, the lifetime of the normal species matches the rise time of the tautomer species suggesting that the rise time is the reaction time. This is like the "usual" interpretation for a two-state reaction as observed for 7AI in most protic solvents. At temperatures below 15 °C, non-exponential behavior is observed, and the lifetime of the normal species approaches the decay time of the tautomer species. This is like the interpretation for a two-state reaction as observed for 1AC in most of the protic solvents. This crossover in interpretation is similar to the observed kinetics for 7AI in propylene glycol and water, in which the decay time rather than the rise time of the tautomer's emission is taken as a measure of the reaction rate. The Arrhenius activation energy of the reaction is only 50-60% of that for viscous flow⁵⁰ determined over the temperature range 25 °C - 65 °C. The best estimate for the reaction time of 1AC in benzyl alcohol at room temperature is 0.29 ± 0.02 ns.

5.4 Interpretation of the Anomalous Low Temperature Behavior

The more complicated kinetics (*i.e.*, kinetics not conforming to a simple two-state model) observed at low temperatures in the diols has also been noted in other solvent systems. For 7AI in 1-propanol and 1-butanol, like 7AI in propylene glycol, the tautomer rise (reaction) times do not increase monotonically with decreasing temperature but instead exhibit a turnover in the region 200-230 K.¹⁴ For 1AC in methanol, the tautomer rise (deactivation) times approach a constant value in the region below 200 K, and for 1AC in 1-propanol the tautomer rise (deactivation) times are nearly constant over the range 200-300 K (with much more scatter in the 1AC/PrOD results).¹³ For 1AC in benzyl alcohol and in N-methylformamide (Chapter 6), similar behavior is observed near 0 °C.

In an effort to identify possible underlying molecular phenomena leading to these observations, we examined several simple expressions related to models for translational and rotational molecular motion. Random molecular motion may transport matter from one part of a system to another by the process named diffusion. The Stokes-Einstein law is a hydrodynamic theory that models the diffusion constant D of a spherical molecule with radius *r* in a (continuous) solvent medium with viscosity η :⁴⁵

$$D = \frac{k_B T}{6 phr} \tag{5.3}$$

The ratio η / T was examined for each of the solvents noted above over the range of experimental temperatures to look for a common value that might be suggestive of the influence of (random) molecular motions controlling the reaction. The time scale of

molecular rotations may also be estimated from hydrodynamic theory. The rotational times of 1AC and 7AI in these solvents are calculated using

$$\tau_{rot}^{(2)} = C_{obs} f V_p \eta / k_B T,$$
 (5.4)

where the constants C_{obs} and f are estimated from a recent study⁴⁶, and the volume of the solute V_p and the viscosity η are determined using published algorithms.⁴⁷⁻⁵⁰

Table 5.10 summarizes temperature-normalized solvent viscosities and the estimated rotation times and their dependence on temperature and solvent for 1AC and 7AI. The shaded regions of *Table 5.10* indicate regions in which the observed kinetics begin to show deviations from the simple irreversible proton-transfer scheme. In the viscosity data, the deviations for 1AC begin to appear at an effective (room temperature) viscosity of approximately 2.5 cP in methanol, 1-propanol and N-methylformamide. The deviations for 7AI begin to appear at an effective (room temperature) viscosity of approximately 14 cP in ethylene glycol and 1-propanol. It is interesting to note that the effective diffusion constant based on the effective viscosity for 1AC is nearly five times greater than that for 7AI, perhaps corresponding to the reaction times for which 1AC is about five times greater than 7AI. (The estimates of the effective diffusion constants require the approximate radii of 1AC and 7AI which are estimated in Chapter 2 to be 3.3 Å and 2.9 Å, respectively.)

In the molecular rotation time data, the estimated rotation times of 7AI and 1AC in the different protic solvents are 100-200 ps and ~50-200 ps at the onset of deviations, respectively. Even though these times are inexact and may require rescaling, these times are suggestive of a regime in which molecular motion does influence the reaction or the

deactivation of the tautomer species. This molecular motion may involve interactions between the proton-transfer molecule and the protic solvent molecules or just among the protic solvent molecules.⁵¹ Since the ratios of reaction times to rotation times are not obviously constant at the onset of deviations [*e.g.*, $\tau_{rxn} / \tau_{rot} \sim 40$ (1AC in 1-PrOH), 10 (7AI in 1-PrOH), 5 (1AC in EG), and 3 (7AI in EG)], the limiting molecular interactions may be occurring among the solvent molecules.

The correlation of rotation times with the onset of the low temperature anomalous behavior prompted a more careful examination of the time-scales of possible molecular dynamics. The temperature dependence of the dielectric relaxation of the primary alcohols and ethylene glycol provides insight in this matter.⁵² The primary alcohols such as 1-propanol exhibit three dielectric relaxation times, and the dielectric dispersion data of ethylene glycol may be decomposed into two times.⁵² The relaxation times are ordered τ_1 (~50+ ps) > τ_2 (~20-40 ps) > τ_3 (~2 ps), with τ_1 making the dominant contribution to the total dispersion.⁵² Following the interpretation of Garg and Smyth, the first relaxation time is attributed to rotation of alcohol molecules in clusters, the second time is attributed to rotation of free alcohol monomers, and the shortest time is attributed to rotation of the -OH group.⁵² Berg and coworkers have demonstrated that the dielectric relaxation (τ_1 or τ_D) is proportional to the dynamics of hydrogen-bond formation,⁴⁴ an important step prior to the breaking of covalent bonds in the protontransfer reaction. Berg and coworkers note that the lifetime of a hydrogen bond is not simply the time required to break a hydrogen bond, but the time involved in the equilibration of the solvent about the newly broken or formed hydrogen bond.⁴⁴

In earlier studies on 7AI, no good correlations were reported between the longitudinal relaxation times (τ_L , or other measures of solvation dynamics) and the reaction times (τ_{rxn}) .¹⁶ However, an interesting correlation exists for many solvents between the dielectric relaxation times τ_1 and the reaction times τ_{rxn} . (The dielectric relaxation times τ_1 used here are summarized in *Table 5.12.*) The correlations for 1AC in methanol, ethylene glycol, a portion of 1-propanol, and formamide and the correlations for 7AI in methanol and ethylene glycol are illustrated in *Figure 5.7*. Similar correlations have been observed for 1AC in 1-propanol, water, and N-methylformamide and for 7AI in 1-propanol and 1-butanol. For each of these solvents, the reaction time and relaxation time show a direct relationship over the range of temperatures studied. The correlation plots of the observed reaction rates and the dielectric relaxation times for 1AC and 7AI in methanol/methanol-OD and ethylene glycol/ethylene glycol- D_2 (*Figure 5.8*) remind us that other factors are important in modeling the reaction. In this example (Figure 5.8), the isotope effects attributed to the intrinsic proton-transfer step cause the offsets of the correlation curves.

The plots in *Figure 5.7* and *Figure 5.8* are interpreted to indicate that the reactions of 7AI or 1AC in methanol and ethylene glycol are quite similar based on the overlap of the correlations. This agreement may not be surprising since the structure of ethylene glycol is like two bonded methanol units. On the other hand, the lack of correlation among the very different solvents emphasizes the involvement of additional factors in determining the reaction rates. The observed reaction time τ_{rxn} is currently modeled as the product of an intrinsic proton-transfer time τ_{PT} and a solvent factor here denoted by the variable *S*:

$$\tau_{rxn} = \tau_{PT} S. \tag{5.5}$$

The solvent factor *S* will be interpreted liberally to include contributions from effects such as the solvent polarity S_{polarity} and the dynamics of hydrogen-bond formation $S_{\text{H-bond}}$:

$$\tau_{rxn} = \tau_{PT} S_{\text{H-bond}} S_{\text{polarity}}.$$
 (5.6)

Above we noted that the dielectric relaxation τ_1 is proportional to the dynamics of hydrogen-bond formation,⁴⁴ $S_{\text{H-bond}} = \tau_1 S_{\text{H-bond}}$ ', whose substitution into equation (5.6) yields the expression:

$$\tau_{rxn} = \tau_1 \tau_{PT} S_{\text{H-bond}} S_{\text{polarity}}.$$
 (5.7)

If the intrinsic proton transfer time and solvent factors $S_{\text{H-bond}}$ ' S_{polarity} are the same or very similar for a group of solvents, then the reaction times for all such solvents should be directly related to the dynamics of hydrogen-bond formation. This may be the case for the reaction of 7AI in methanol and ethylene glycol and for the reaction of 1AC in methanol and ethylene glycol. On the other hand, if a factor such as the intrinsic proton transfer time differs, then the plots of the reaction times will be offset when plotted as a function of the dielectric relaxation times. This explains why the correlations for 7AI and 1AC in methanol and ethylene glycol do not overlap (different τ_{PT} arising from different molecules), why the correlations for 7AI and 1AC in protiated and deuterated solvent pairs do not overlap (different τ_{PT} arising from isotope effects), and why the correlations for 1AC in the various solvents may not overlap (different *S*).

To view the correlation between the reaction time and the dielectric relaxation time in a slightly different format, *Figure 5.9* illustrates the ratio τ_I / τ_{rxn} plotted on the $E_T(30)$ solvent polarity scale. This plot represents the reaction rate normalized by a measure of the cooperative hydrogen-bond dynamics as a function of solvent polarity. These normalized reaction times for the alcohols, ethylene glycol and water show an exponential dependence on this measure of polarity, consistent with the mathematical form of Equation (5.1). Furthermore, the points for ethylene glycol and water now lie along the same linear correlation for the primary alcohols with the $E_T(30)$ scale. (The reaction in water is also discussed in more detail in Chapter 6.)

Because the $E_T(30)$ polarity scale is a measure of hydrogen-bond strength based on the absorption of betaine dyes,⁵³ this scale is insensitive to the dynamics of hydrogen bonds. Of course, the dynamics of hydrogen bonds ultimately depend on potential barriers (a static property). It appears that the $E_T(30)$ scale does not probe such energetics well. When the effects of the hydrogen bond dynamics are removed from the reaction rates, then we observe the corrected rates' direct dependence on solvent polarity and hydrogen-bond strengths.

5.5 Conclusion

The original question driving this study of the reaction of 1AC in the diols was based on the interesting deviations of these reaction rates from the linear relationships observed for bulk alcohols plotted on the $E_T(30)$ scale. Do these deviations suggest that

the excited-state of 7AI or 1AC is depopulated via alternative pathways? Based on the correlation of the reaction times with the dielectric relaxation times, we conclude that the proton-transfer reaction in ethylene glycol is *not* intrinsically different than that observed in methanol. Rather, it is simply in a different regime determined by the dynamics of cooperative hydrogen-bond formation. Future study of the excited-state reaction of 7AI or 1AC in the alcohol / diol solvent pairs such as ethanol / 1,3-butanediol or ethanol / 1,4-butanediol may further support this hypothesis.

In the preceding analyses, good correlations were observed between the anomalous kinetics at lower temperatures and estimated rotation times, and between the reaction and (Debye) dielectric relaxation times, both of which are related to viscosity. And noted in *Table 5.11*, the Arrhenius activation energies for the reactions, the dielectric relaxation (τ_1), and viscosity are often similar in magnitude. As viscosity is also one measure of the solvent "friction" along the reaction coordinate,⁴⁴ future understanding of this concept may be able to untangle the physical mechanisms leading to these interesting correlations for the proton-transfer reactions. Until then, the data indicate that (dynamic) solvent effects related to the equilibration of broken or formed hydrogen bonds partially control the rate of the excited-state tautomerizations of 7AI and 1AC.

The present results do indicate that "solvation dynamics" or more specifically cooperative hydrogen-bonding dynamics is a significant part of the problem in the case of the proton-transfer reaction of 7AI or 1AC in ethylene glycol. When the observed rates are normalized by a measure of hydrogen-bond lifetimes,⁴⁴ the reactions of 7AI or 1AC in methanol and ethylene glycol may be compared on nearly equal footing. In

demonstrating that the 1AC reactions in the diols and water are not necessarily anomalous when plotted on the $E_T(30)$ solvent scale, however, a few new "anomalous" solvents were uncovered: 2-propanol, t-butanol, and glycerol. Interestingly, these secondary and tertiary alcohols also did not quite fit the model in the computer simulations by Mente and Maroncelli.¹⁰ Future work should address the reaction of 1AC and 7AI in these solvents.

The enthalpy changes measured experimentally refer to the differences in energy between a hydrogen-bonded state and a nonbonded state involving an incompletely solvated solvent molecule.⁴⁴ These enthalpy changes are consistent with the interpretation that the reaction activation energy for 7AI (and 1AC) is the enthalpy change in forming the cyclically hydrogen-bonded complex necessary for reaction.¹⁰ Such an interpretation provides an alternate picture for the large-amplitude solvent motion advocated earlier for controlling the excited-state proton-transfer rate, an interpretation based on the similarities between the Arrhenius activation energies for reaction and the temperature dependence of viscosity.^{5,6,16,29}

Table 5.1: Temperature Dependence of the Normal Emission of 7AI and 1AC in Ethylene Glycol

| | 7AI / EG | Normal | | | | |
|---|--|---|---|--|--|--|
| | Temperature (K) | <a1></a1> | <a2></a2> | <τ1> NS | <t2> ns</t2> | |
| | 275 | 0.21 | 0.79 | 0.072 | 0.68 | |
| | 283 | 0.28 | 0.72 | 0.065 | 0.59 | |
| | 294 | 0.32 | 0.68 | 0.084 | 0.43 | |
| | 303 | 0.30 | 0.70 | 0.055 | 0.32 | |
| | 314 | 0.27 | 0.73 | 0.044 | 0.26 | |
| | 323 | 0.25 | 0.76 | 0.042 | 0.21 | |
| | 333 | 0.24 | 0.77 | 0.037 | 0.18 | |
| | 343 | 0.20 | 0.80 | 0.048 | 0.17 | |
| 1 | 7AL/EG-Da | Normal | | | | |
| | Temperature (K) | Horman | | | <τ ₂ > ns | IE |
| | 275 | | | | 1.35 | 2.0 |
| | 283 | | | | 1.08 | 1.8 |
| | 294 | | | | 0.79 | 1.8 |
| | 303 | | | | 0.69 | 2.2 |
| | 314 | | | | 0.57 | 2.2 |
| | 324 | | | | 0.51 | 2.4 |
| | 334 | | | | 0.43 | 2.4 |
| | 344 | | | | 0.39 | 2.3 |
| 1 | | Nerrecel | | | | |
| | TAC / EG | Normai | 10.5 | | | |
| | | <a1></a1> | <a2></a2> | $<\tau_1 > ns$ | $<\tau_2 > ns$ | |
| | 2/4 | 0.27 | 0.73 | 0.09 | 1.75 | |
| | 283 | 0.53 | 0.47 | 0.05 | 1.37 | |
| I | • • • • | 0.04 | 0.70 | 0.00 | 1 01 | |
| | 293 | 0.24 | 0.76 | 0.06 | 1.01 | |
| | 293 303 314 | 0.24 0.45 0.25 | 0.76 0.55 | 0.06 | 1.01 0.82 | |
| | 293 303 314 323 | 0.24 0.45 0.35 0.34 | 0.76 0.55 0.65 | 0.06 0.06 0.03 | 1.01 0.82 0.66 0.55 | |
| | 293 303 314 323 333 | 0.24 0.45 0.35 0.34 0.43 | 0.76 0.55 0.65 0.66 0.58 | 0.06 0.06 0.03 0.02 0.02 | 1.01 0.82 0.66 0.55 0.49 | |
| | 293 303 314 323 333 344 | 0.24 0.45 0.35 0.34 0.43 0.40 | 0.76 0.55 0.65 0.66 0.58 0.60 | 0.06 0.06 0.03 0.02 0.02 0.02 | 1.01 0.82 0.66 0.55 0.49 0.43 | |
| | 293 303 314 323 333 344 | 0.24 0.45 0.35 0.34 0.43 0.40 | 0.76 0.55 0.65 0.66 0.58 0.60 | 0.06 0.06 0.03 0.02 0.02 0.02 | 1.01 0.82 0.66 0.55 0.49 0.43 | |
| | 293 303 314 323 333 344 1AC / EG-D ₂ | 0.24 0.45 0.35 0.34 0.43 0.40 Normal | 0.76 0.55 0.65 0.66 0.58 0.60 | 0.06 0.03 0.02 0.02 0.02 0.02 | 1.01 0.82 0.66 0.55 0.49 0.43 | |
| | 293 303 314 323 333 344 1AC / EG-D ₂ Temperature (K) | 0.24 0.45 0.35 0.34 0.43 0.40 Normal <a_1></a_1> | 0.76 0.55 0.65 0.66 0.58 0.60 | 0.06 0.03 0.02 0.02 0.02 0.02 | 1.01 0.82 0.66 0.55 0.49 0.43 | IE |
| | 293 303 314 323 333 344 IAC / EG-D ₂ Temperature (K) 275 | 0.24 0.45 0.35 0.34 0.43 0.40 Normal <a_1> 0.37</a_1> | 0.76 0.55 0.65 0.66 0.58 0.60 <a_2> 0.64</a_2> | 0.06 0.06 0.03 0.02 0.02 0.02 <₹t₁> ns 0.1 | 1.01 0.82 0.66 0.55 0.49 0.43 <t_2> ns 4.6</t_2> | |
| | 293 303 314 323 333 344 IAC / EG-D ₂ Temperature (K) 275 283 | 0.24 0.45 0.35 0.34 0.43 0.40 Normal <a_1> 0.37 0.33</a_1> | 0.76 0.55 0.65 0.66 0.58 0.60 <a_2> 0.64 0.68</a_2> | 0.06 0.03 0.02 0.02 0.02 <₹t₁> ns 0.1 0.09 | 1.01 0.82 0.66 0.55 0.49 0.43 <₹ ₂ > ns 4.6 3.6 | IE 2.6 2.6 |
| | 293 303 314 323 333 344 1AC / EG-D ₂ Temperature (K) 275 283 293 | $\begin{array}{c} 0.24 \\ 0.45 \\ 0.35 \\ 0.34 \\ 0.43 \\ 0.40 \\ \hline \\ \hline \\ \hline \\ Normal \\ \hline \\ \hline \\ ca_1 > \\ 0.37 \\ 0.33 \\ 0.29 \\ \hline \end{array}$ | 0.76 0.55 0.65 0.66 0.58 0.60 <a_2> 0.64 0.68 0.72</a_2> | 0.06 0.03 0.02 0.02 0.02 0.02 < ₹t₁> ns 0.1 0.09 0.06 | $ \begin{array}{c} 1.01\\ 0.82\\ 0.66\\ 0.55\\ 0.49\\ 0.43\\ \hline <\tau_2> ns <\tau_2> ns 4.6 3.6 2.8 $ | IE 2.6 2.6 2.7 |
| | 293 303 314 323 333 344 1AC / EG-D ₂ Temperature (K) 275 283 293 303 | $\begin{array}{c} 0.24 \\ 0.45 \\ 0.35 \\ 0.34 \\ 0.43 \\ 0.40 \\ \hline \\ $ | 0.76 0.55 0.65 0.66 0.58 0.60 <a_2>0.640.680.720.68</a_2> | 0.06 0.03 0.02 0.02 0.02 < ₹t ₁ > ns 0.1 0.09 0.06 0.03 | $ \begin{array}{c} 1.01\\ 0.82\\ 0.66\\ 0.55\\ 0.49\\ 0.43\\ \hline <\tau_2> ns <\tau_2> ns 4.6 3.6 2.8 2.37 $ | IE 2.6 2.7 2.9 |
| | 293 303 314 323 333 344 <u>1AC / EG-D₂ Temperature (K) 275 283 293 303 314</u> | $\begin{array}{c} 0.24 \\ 0.45 \\ 0.35 \\ 0.34 \\ 0.43 \\ 0.40 \\ \hline \\ $ | 0.76 0.55 0.65 0.66 0.58 0.60 <a_2>0.640.680.720.680.62</a_2> | 0.06 0.03 0.02 0.02 0.02 0.02 < ₹t ₁ > ns 0.1 0.09 0.06 0.03 0.02 | 1.01 0.82 0.66 0.55 0.49 0.43 <tz> ns<tz> ns4.63.62.82.371.99</tz></tz> | IE 2.6 2.7 2.9 3.0 |
| | 293 303 314 323 333 344 <u>1AC / EG-D2</u> Temperature (K) 275 283 293 303 314 323 | $\begin{array}{c} 0.24 \\ 0.45 \\ 0.35 \\ 0.34 \\ 0.43 \\ 0.40 \\ \hline \\ $ | 0.76 0.55 0.65 0.66 0.58 0.60 <a_2>0.640.680.720.680.620.54</a_2> | 0.06 0.03 0.02 0.02 0.02 0.02 < ₹t ₁ > ns 0.1 0.09 0.06 0.03 0.02 0.01 | 1.01 0.82 0.66 0.55 0.49 0.43 <tz> ns<tz> ns4.63.62.82.371.991.75</tz></tz> | IE 2.6 2.7 2.9 3.0 3.2 |
| | 293 303 314 323 333 344 <u>1AC / EG-D2</u> Temperature (K) 275 283 293 303 314 323 314 323 334 | $\begin{array}{c} 0.24 \\ 0.45 \\ 0.35 \\ 0.34 \\ 0.43 \\ 0.40 \\ \hline \\ $ | 0.76 0.55 0.65 0.66 0.58 0.60 <a_2>0.640.680.720.680.620.540.55</a_2> | 0.06 0.03 0.02 0.02 0.02 0.02 <\tau_1> ns 0.1 0.09 0.06 0.03 0.02 0.01 0.02 0.01 0.02 | 1.01 0.82 0.66 0.55 0.49 0.43 $<\tau_2>$ ns 4.6 3.6 2.8 2.37 1.99 1.75 1.59 | IE 2.6 2.7 2.9 3.0 3.2 3.3 |

Average lifetimes from multiexponential fits are presented as the best measurements of the observed rate. The slow times $\langle \tau_2 \rangle$ were separated from the more rapid times $\langle \tau_1 \rangle$ attributed to the dynamic Stokes shift. The kinetic isotope effect is defined as IE = $\langle \tau_2(D) \rangle / \langle \tau_2(H) \rangle$.

| 1AC / EG | (| Original Fit | Tautomer | | | | |
|----------|----------------|----------------|----------------|-------------|-------------|-------------------|-------------|
| T (K) | a ₁ | a ₂ | a ₃ | τ_1 ns | τ_2 ns | τ ₃ ns | τ_4 ns |
| 274 | -1.94 | 2.58 | 0.36 | 0.31 | | 1.66 | 3.60 |
| 283 | -2.71 | 3.71 | | 0.30 | | 1.42 | |
| 293 | -3.10 | 4.10 | | 0.31 | | 1.07 | |
| 303 | -5.99 | 6.99 | | 0.31 | | 0.83 | |
| 314 | -7.01 | 8.01 | | 0.29 | | 0.66 | |
| 323 | -9.64 | 10.64 | | 0.28 | | 0.56 | |
| 333 | -9.55 | 10.55 | | 0.26 | | 0.49 | |
| 344 | -11.29 | 12.29 | | 0.24 | | 0.42 | |

Table 5.2: Temperature Dependence of Tautomer Emission of 1AC in Ethylene Glycol

| 1AC / EG | A | Alt. Fit #1 | Tautomer | | | | | | | | |
|----------|----------------|----------------|----------------|----------------|-------------|-------------|-------------|-------------|-------------------|----------|-----------------|
| T (K) | a ₁ | a ₂ | a ₃ | a ₄ | τ_1 ns | τ_2 ns | τ_3 ns | τ_4 ns | <l(570)></l(570)> | <α(570)> | τ_{rxn} ns |
| 274 | -1.88 | | 2.77 | 0.12 | 0.31 | | 1.76 | <u>6</u> | 0.032 | 5.48 | 1.43 |
| 283 | -2.68 | | 3.66 | 0.03 | 0.30 | | 1.40 | 6 | 0.041 | 5.28 | 1.10 |
| 293 | -3.16 | | 4.12 | 0.04 | 0.32 | | 1.05 | 5 | 0.049 | 6.34 | 0.98 |
| 303 | -6.03 | | 7.02 | 0.01 | 0.31 | | 0.83 | <u>5</u> | 0.056 | 6.71 | 0.82 |
| 314 | -7.27 | | 8.26 | 0.01 | 0.30 | | 0.65 | 5 | 0.065 | 7.12 | 0.69 |
| 323 | -9.57 | | 10.56 | 0.01 | 0.28 | | 0.55 | <u>5</u> | 0.069 | 7.47 | 0.61 |
| 333 | -9.83 | | 10.82 | 0.01 | 0.26 | | 0.48 | 5 | 0.071 | 7.66 | 0.55 |
| 344 | -11.64 | | 12.62 | 0.01 | 0.25 | | 0.42 | <u>5</u> | 0.076 | 7.76 | 0.48 |
| | | | | | | | | | | -6 73 | 1 |

| 1AC / EG | A | Alt. Fit #2 | Tautomer | | | | | | | | | | |
|----------|--------|----------------|----------------|------|-------------|-------------|-------------|-------------|-------------------|-------------------|-----------------|-------------------------|----------------|
| T (K) | a₁ | a ₂ | a ₃ | a4 | τ_1 ns | τ_2 ns | τ_3 ns | τ_4 ns | <l(570)></l(570)> | <a(570)></a(570)> | τ_{rxn} ns | <tanl< td="">ns</tanl<> | <tan> ns</tan> |
| 274 | -0.83 | -1.19 | 2.89 | 0.13 | <u>0.44</u> | 0.26 | 1.72 | <u>6</u> | 0.032 | 7.92 | 1.83 | 0.33 | 1.39 |
| 283 | -1.73 | -1.24 | 3.94 | 0.04 | <u>0.40</u> | 0.22 | 1.37 | <u>6</u> | 0.041 | 7.12 | 1.32 | 0.32 | 1.05 |
| 293 | -6.87 | 3.84 | 3.99 | 0.04 | <u>0.36</u> | 0.40 | 1.05 | <u>5</u> | 0.049 | 7.05 | 1.00 | | |
| 303 | -5.94 | | 6.93 | 0.01 | <u>0.33</u> | | 0.83 | <u>5</u> | 0.056 | 7.19 | 0.80 | | |
| 314 | -7.27 | | 8.26 | 0.01 | <u>0.30</u> | | 0.65 | <u>5</u> | 0.065 | 7.12 | 0.62 | | |
| 323 | -9.57 | | 10.56 | 0.01 | <u>0.28</u> | | 0.55 | <u>5</u> | 0.069 | 7.47 | 0.55 | | |
| 333 | -9.83 | | 10.82 | 0.01 | <u>0.26</u> | | 0.48 | <u>5</u> | 0.071 | 7.66 | 0.50 | | |
| 344 | -11.64 | | 12.62 | 0.01 | <u>0.25</u> | | 0.42 | <u>5</u> | 0.076 | 7.76 | 0.43 | | |
| | | | | | | | | | | <7.41> | | | |

| 1AC / EG-I | D_2 | Original Fi | t Tauto | mer | | |
|------------|----------------|-------------|---------|-----|-------------|-------------------|
| T (K) | a ₁ | | a₃ | | τ_1 ns | τ ₃ ns |
| 274 | -1.57 | | 2.57 | | 0.46 | 4.97 |
| 283 | -2.87 | | 3.87 | | 0.47 | 3.78 |
| 293 | -0.21 | | 1.21 | | 0.42 | 3.51 |
| 303 | -3.69 | | 4.69 | | 0.42 | 2.51 |
| 314 | -4.11 | | 5.11 | | 0.40 | 2.06 |
| 324 | -4.41 | | 5.41 | | 0.37 | 1.80 |
| 334 | -4.73 | | 5.73 | | 0.34 | 1.62 |
| 345 | -4.47 | | 5.47 | | 0.31 | 1.48 |

Table 5.3: Temperature Dependence of Tautomer Emission of 1AC in Ethylene Glycol-D₂

| 1AC / EG-E | D_2 | Alt. Fit #1 | Tautome | er | | | | | | | |
|------------|----------------|----------------|---------|-------|-------------|-------------|-------------|-------------|-------------------|----------|-----------------|
| T (K) | a ₁ | a ₂ | a_3 | a_4 | τ_1 ns | τ_2 ns | τ_3 ns | τ_4 ns | <l(570)></l(570)> | <α(570)> | τ_{rxn} ns |
| 274 | -1.68 | | 1.86 | 0.82 | 0.55 | | 3.21 | <u>10</u> | 0.021 | 8.16 | 4.32 |
| 283 | -2.93 | | 3.38 | 0.55 | 0.49 | | 3.30 | <u>8</u> | 0.025 | 5.97 | 3.26 |
| 293 | -1.66 | | 2.27 | 0.39 | 1.08 | | 1.58 | 8 | 0.029 | 23.40 | 6.10 |
| 303 | -3.75 | | 4.55 | 0.19 | 0.45 | | 2.30 | <u>8</u> | 0.033 | 5.87 | 2.23 |
| 314 | -4.15 | | 5.02 | 0.13 | 0.41 | | 1.96 | 8 | 0.036 | 5.85 | 1.90 |
| 324 | -4.45 | | 5.37 | 0.08 | 0.38 | | 1.75 | <u>7</u> | 0.036 | 5.96 | 1.72 |
| 334 | -4.59 | | 5.54 | 0.06 | 0.34 | | 1.59 | 7 | 0.035 | 6.25 | 1.64 |
| 345 | -4.40 | | 5.35 | 0.04 | 0.32 | | 1.46 | <u>7</u> | 0.034 | 6.30 | 1.52 |
| | | | | | | | | | | <6.05> | |

| 1AC / EG-E | D ₂ | Alt. Fit #2 | Tautome | er | | | | | | | | | |
|------------|-----------------------|----------------|----------------|----------------|-------------|-------------|-------------|-------------|-------------------|----------|---------------------|-----------------------|----------------|
| T (K) | a ₁ | a ₂ | a ₃ | a ₄ | τ_1 ns | τ_2 ns | τ_3 ns | τ_4 ns | <l(570)></l(570)> | <α(570)> | τ _{rxn} ns | <tan< td="">ns</tan<> | <tan> ns</tan> |
| 274 | -1.72 | -0.23 | 1.98 | 0.97 | <u>0.64</u> | 0.20 | 2.83 | <u>10</u> | 0.021 | 10.86 | 4.31 | 0.59 | 3.94 |
| 283 | -3.93 | -0.61 | 4.41 | 1.13 | <u>0.57</u> | 0.09 | 2.87 | <u>8</u> | 0.025 | 8.02 | 3.22 | 0.51 | 2.86 |
| 293 | -0.40 | 0.25 | 0.88 | 0.26 | 0.51 | 0.06 | 2.29 | 8 | 0.029 | 7.61 | 2.45 | | |
| 303 | -3.74 | | 4.51 | 0.23 | <u>0.46</u> | | 2.25 | <u>8</u> | 0.033 | 6.17 | 1.95 | | |
| 314 | -4.15 | | 5.02 | 0.13 | <u>0.41</u> | | 1.96 | <u>8</u> | 0.036 | 5.85 | 1.61 | | |
| 324 | -4.45 | | 5.37 | 0.08 | <u>0.38</u> | | 1.75 | <u>7</u> | 0.036 | 5.96 | 1.46 | | |
| 334 | -4.59 | | 5.54 | 0.06 | <u>0.34</u> | | 1.59 | <u>7</u> | 0.035 | 6.25 | 1.39 | | |
| 345 | -4.40 | | 5.35 | 0.04 | 0.32 | | 1.46 | <u>7</u> | 0.034 | 6.30 | 1.29 | | |
| | | | | | | | | | | <7.13> | | | |

| 7AI / EG | (| Driginal Fit | Tautomer | | | | | | |] | |
|----------|----------------|----------------|----------------|-------|-------------|-------------|-------------|-------------|-------------------------|-------------------|-----------------|
| T (K) | a ₁ | a_2 | a₃ | a4 | τ_1 ns | τ_2 ns | τ_3 ns | τ_4 ns | <τ _{rise} > ns | | |
| 275 | -5.29 | -0.74 | 7.03 | | 0.58 | 0.11 | 1.06 | | 0.52 | | |
| 283 | -8.01 | -0.89 | 9.90 | | 0.48 | 0.08 | 0.87 | | 0.44 | | |
| 294 | -7.71 | -0.60 | 9.32 | | 0.35 | 0.04 | 0.76 | | 0.32 | | |
| 303 | -5.28 | | 6.28 | | 0.26 | | 0.69 | | | | |
| 314 | -6.18 | | 7.18 | | 0.21 | | 0.61 | | | | |
| 323 | -6.16 | | 7.16 | | 0.18 | | 0.56 | | | | |
| 333 | -7.13 | | 7.97 | 0.16 | 0.18 | | 0.46 | 1.65 | | | |
| 343 | -6.18 | | 7.07 | 0.11 | 0.16 | | 0.43 | 2.04 | | | |
| | | | | | | | | | | | |
| 7AI / EG | A | Alt. Fit #1 | Tautomer | | | | | | | | |
| T (K) | a 1 | a ₂ | a ₃ | a_4 | τ_1 ns | τ_2 ns | τ_3 ns | τ_4 ns | <l(570)></l(570)> | <a(570)></a(570)> | τ_{rxn} ns |
| 275 | | -3.38 | 4.33 | 0.04 | | 0.45 | 1.12 | <u>6</u> | 0.098 | 25.59 | 0.86 |
| 283 | | -4.99 | 5.95 | 0.04 | | 0.41 | 0.89 | <u>6</u> | 0.131 | 16.66 | 0.52 |
| 294 | | -5.99 | 6.93 | 0.06 | | 0.35 | 0.73 | <u>5</u> | 0.156 | 13.59 | 0.36 |
| 303 | | -5.86 | 6.80 | 0.06 | | 0.27 | 0.66 | <u>5</u> | 0.192 | 12.51 | 0.26 |
| 314 | | -6.81 | 7.75 | 0.06 | | 0.22 | 0.59 | <u>5</u> | 0.210 | 12.92 | 0.21 |
| 323 | | -7.30 | 8.23 | 0.06 | | 0.19 | 0.54 | <u>5</u> | 0.227 | 12.73 | 0.18 |
| 333 | | -7.37 | 8.30 | 0.07 | | 0.16 | 0.50 | <u>5</u> | 0.253 | 12.11 | 0.15 |
| 343 | | -6.38 | 7.31 | 0.06 | | 0.14 | 0.45 | <u>5</u> | 0.262 | 12.03 | 0.13 |
| | | | | | | | | | | <13.2> | |
| | | | | | | | | | | | |
| 7AI / EG | A | Alt. Fit #2 | Tautomer | | | | | | | | |
| T (K) | a1 | a ₂ | a ₃ | a4 | τ_1 ns | τ_2 ns | τ_3 ns | τ_4 ns | <l(570)></l(570)> | <a(570)></a(570)> | τ_{rxn} ns |
| 275 | -0.98 | -10.84 | 12.73 | 0.09 | 0.10 | 0.67 | 0.94 | <u>6</u> | 0.098 | 14.20 | 0.74 |

Table 5.4: Temperature Dependence of Tautomer Emission of 7AI in Ethylene Glycol

| 7AI / EG | A | Alt. Fit #2 | Tautomer | | | | | | | | | |
|----------|-------|----------------|----------------|------|-------------|-------------|-------------------|-------------------|-------------------|----------|---------------------|-------------------------|
| T (K) | a₁ | a ₂ | a ₃ | a4 | τ_1 ns | τ_2 ns | τ ₃ ns | τ ₄ ns | <l(570)></l(570)> | <α(570)> | τ _{rxn} ns | <τ _{rise} > ns |
| 275 | -0.98 | -10.84 | 12.73 | 0.09 | 0.10 | 0.67 | <u>0.94</u> | <u>6</u> | 0.098 | 14.20 | 0.74 | 0.62 |
| 283 | -1.09 | -10.45 | 12.46 | 0.08 | 0.07 | 0.49 | <u>0.84</u> | <u>6</u> | 0.131 | 13.07 | 0.50 | 0.45 |
| 294 | -1.82 | -15.68 | 18.37 | 0.13 | 0.03 | 0.35 | <u>0.74</u> | <u>5</u> | 0.156 | 13.38 | 0.37 | 0.32 |
| 303 | | -5.78 | 6.72 | 0.06 | | 0.27 | <u>0.67</u> | <u>5</u> | 0.192 | 12.93 | 0.27 | |
| 314 | | -6.81 | 7.75 | 0.06 | | 0.22 | 0.59 | <u>5</u> | 0.210 | 12.92 | 0.22 | |
| 323 | | -7.30 | 8.23 | 0.06 | | 0.19 | <u>0.54</u> | <u>5</u> | 0.227 | 12.73 | 0.18 | |
| 333 | | -7.37 | 8.30 | 0.07 | | 0.16 | 0.50 | <u>5</u> | 0.253 | 12.11 | 0.15 | |
| 343 | | -6.38 | 7.31 | 0.06 | | 0.14 | 0.45 | 5 | 0.262 | 12.03 | 0.13 | |
| | | | | | | | | _ | | <12.9> | | |

| 7AI / EG-D | 0_2 (| Original Fit | Tautomer | | |
|------------|---------|----------------|----------------|-------------|-------------|
| T (K) | | a ₂ | a ₃ | τ_2 ns | τ_3 ns |
| 275 | | -3.69 | 4.69 | 0.65 | 2.09 |
| 283 | | -5.95 | 6.95 | 0.65 | 1.53 |
| 294 | | -7.97 | 8.97 | 0.62 | 1.17 |
| 303 | | -11.09 | 12.09 | 0.55 | 0.96 |
| 314 | | -12.31 | 13.31 | 0.46 | 0.83 |
| 324 | | -11.50 | 12.50 | 0.38 | 0.77 |
| 334 | | -11.30 | 12.30 | 0.34 | 0.70 |
| 344 | | -11.65 | 12.65 | 0.30 | 0.64 |
| | | | | | |

Table 5.5: Temperature Dependence of Tautomer Emission of 7AI in Ethylene Glycol-D₂

| 7AI / EG-D ₂ | | Alt. Fit #1 | Tautomer | | | | | | | | |
|-------------------------|----------------|----------------|----------|------|-------------|-------------|-------------|-------------|-------------------|----------|-----------------|
| T (K) | a ₁ | a ₂ | a₃ | a4 | τ_1 ns | τ_2 ns | τ_3 ns | τ_4 ns | <l(570)></l(570)> | <α(570)> | τ_{rxn} ns |
| 275 | | -3.74 | 4.72 | 0.02 | | 0.66 | 2.06 | <u>7</u> | 0.070 | 45.0 | 2.16 |
| 283 | | -7.78 | 8.62 | 0.16 | | 0.72 | 1.35 | 7 | 0.083 | 22.6 | 1.19 |
| 294 | | -14.13 | 14.94 | 0.20 | | 0.71 | 1.00 | 7 | 0.097 | 14.4 | 0.75 |
| 303 | | -18.69 | 19.53 | 0.16 | | 0.62 | 0.85 | <u>7</u> | 0.109 | 12.5 | 0.57 |
| 314 | | -18.96 | 19.82 | 0.14 | | 0.52 | 0.74 | 7 | 0.115 | 12.5 | 0.47 |
| 324 | | -13.52 | 14.41 | 0.12 | | 0.43 | 0.70 | 7 | 0.122 | 13.5 | 0.42 |
| 334 | | -14.63 | 15.52 | 0.11 | | 0.38 | 0.64 | 7 | 0.118 | 14.4 | 0.40 |
| 344 | | -14.38 | 15.28 | 0.10 | | 0.33 | 0.59 | 7 | 0.121 | 14.8 | 0.35 |
| | | | | | | | | _ | | <13.7> | |

| 7AI / EG-D2 | 2 A | Alt. Fit #2 | Tautomer | | | | | | | | |
|-------------|-------|-------------|----------------|------------|-------------|-------------|-------------------|-------------|-------------------|----------|-----------------|
| T (K) | a1 | a_2 | a ₃ | a 4 | τ_1 ns | τ_2 ns | τ ₃ ns | τ_4 ns | <l(570)></l(570)> | <α(570)> | τ_{rxn} ns |
| 275 | -0.84 | 24.73 | -23.14 | 0.25 | 0.26 | 1.40 | <u>1.18</u> | 7 | 0.070 | 17.0 | 1.42 |
| 283 | | -33.59 | 34.37 | 0.22 | | 0.93 | <u>1.07</u> | <u>7</u> | 0.083 | 13.9 | 0.92 |
| 294 | | -20.93 | 21.73 | 0.20 | | 0.75 | <u>0.95</u> | <u>7</u> | 0.097 | 12.9 | 0.69 |
| 303 | | -17.55 | 18.39 | 0.16 | | 0.62 | <u>0.86</u> | <u>7</u> | 0.109 | 12.8 | 0.56 |
| 314 | | -16.05 | 16.91 | 0.14 | | 0.49 | <u>0.77</u> | <u>7</u> | 0.115 | 13.5 | 0.47 |
| 324 | | -13.52 | 14.41 | 0.12 | | 0.43 | <u>0.70</u> | <u>7</u> | 0.122 | 13.5 | 0.41 |
| 334 | | -14.63 | 15.52 | 0.11 | | 0.38 | <u>0.64</u> | <u>7</u> | 0.118 | 14.4 | 0.38 |
| 344 | | -14.38 | 15.28 | 0.10 | | 0.33 | <u>0.59</u> | <u>7</u> | 0.121 | 14.8 | 0.34 |
| | | | | | | | | | | <14.1> | |

| 1AC / EG | φ (total) | φ(T) | φ (N) | τ (N) ns | k _{rad} (N) |
|--|---|---|---|---|---|
| Temperature (°C) | | | | | 10 ⁷ s ⁻¹ |
| | | | | | |
| 1 | 0.033 | 0.0014 | 0.031 | 1.75 | 1.79 |
| 10 | 0.025 | 0.0013 | 0.023 | 1.37 | 1.71 |
| 20 | 0.019 | 0.0013 | 0.018 | 1.05 | 1.69 |
| 30 | 0.015 | 0.0012 | 0.014 | 0.82 | 1.68 |
| 40 | 0.012 | 0.0010 | 0.011 | 0.66 | 1.70 |
| 50 | 0.010 | 0.0009 | 0.009 | 0.55 | 1.73 |
| 60 | 0.009 | 0.0008 | 0.008 | 0.49 | 1.70 |
| 71 | 0.008 | 0.0008 | 0.007 | 0.43 | 1.70 |
| | | | | mean: | 1.71 ± 2% |
| | | | | | |
| | | | | | |
| 1AC / EG-D ₂ | φ (total) | φ(T) | φ (N) | τ (N) ns | k _{rad} (N) |
| 1AC / EG-D ₂ Temperature (°C) | φ (total) | φ (T) | φ (N) | τ (N) ns | k _{rad} (N) 10 ⁷ s⁻¹ |
| 1AC / EG-D ₂ Temperature (°C) | φ (total) | φ (T) | φ (N) | τ (N) ns | k _{rad} (N) 10 ⁷ s⁻¹ |
| 1AC / EG-D ₂ Temperature (°C) 1 | φ (total) 0.078 | φ(T) 0.0026 | φ (N) 0.076 | τ (N) ns 4.6 | k _{rad} (N) 10 ⁷ s ⁻¹ 1.65 |
| 1AC / EG-D ₂ Temperature (°C) 1 10 | φ (total) 0.078 0.064 | φ(T) 0.0026 0.0022 | φ (N) 0.076 0.062 | τ (N) ns 4.6 3.6 | k _{rad} (N) 10 ⁷ s ⁻¹ 1.65 1.71 |
| 1AC / EG-D ₂ Temperature (°C) 1 10 20 | φ (total) 0.078 0.064 0.051 | φ (T) 0.0026 0.0022 0.0020 | φ (N) 0.076 0.062 0.049 | τ (N) ns 4.6 3.6 2.8 | k _{rad} (N) 10 ⁷ s ⁻¹ 1.65 1.71 1.76 |
| 1AC / EG-D ₂ Temperature (°C) 1 10 20 30 | φ (total) 0.078 0.064 0.051 0.043 | φ (T) 0.0026 0.0022 0.0020 0.0019 | φ (N) 0.076 0.062 0.049 0.041 | τ (N) ns 4.6 3.6 2.8 2.37 | k _{rad} (N) 10 ⁷ s ⁻¹ 1.65 1.71 1.76 1.75 |
| 1AC / EG-D ₂ Temperature (°C) 1 10 20 30 40 | φ (total) 0.078 0.064 0.051 0.043 0.036 | φ (T) 0.0026 0.0022 0.0020 0.0019 0.0016 | φ (N) 0.076 0.062 0.049 0.041 0.035 | τ (N) ns 4.6 3.6 2.8 2.37 1.99 | k _{rad} (N) 10 ⁷ s ⁻¹ 1.65 1.71 1.76 1.75 1.75 |
| 1AC / EG-D ₂ Temperature (°C) 1 10 20 30 40 50 | φ (total) 0.078 0.064 0.051 0.043 0.036 0.032 | φ (T) 0.0026 0.0022 0.0020 0.0019 0.0016 0.0014 | φ (N) 0.076 0.062 0.049 0.041 0.035 0.031 | τ (N) ns 4.6 3.6 2.8 2.37 1.99 1.75 | k _{rad} (N) 10 ⁷ s ⁻¹ 1.65 1.71 1.76 1.75 1.75 1.77 |
| 1AC / EG-D ₂ Temperature (°C) 1 10 20 30 40 50 60 | φ (total) 0.078 0.064 0.051 0.043 0.036 0.032 0.030 | φ (T) 0.0026 0.0022 0.0020 0.0019 0.0016 0.0014 0.0015 | φ (N) 0.076 0.062 0.049 0.041 0.035 0.031 0.028 | τ (N) ns 4.6 3.6 2.8 2.37 1.99 1.75 1.59 | k _{rad} (N) 10 ⁷ s ⁻¹ 1.65 1.71 1.76 1.75 1.75 1.77 1.77 |
| 1AC / EG-D ₂ Temperature (°C) 1 10 20 30 40 50 60 71 | φ (total) 0.078 0.064 0.051 0.043 0.036 0.032 0.030 0.027 | φ (T) 0.0026 0.0022 0.0020 0.0019 0.0016 0.0014 0.0015 0.0013 | φ (N) 0.076 0.062 0.049 0.041 0.035 0.031 0.028 0.026 | τ (N) ns 4.6 3.6 2.8 2.37 1.99 1.75 1.59 1.51 | k _{rad} (N) 10 ⁷ s ⁻¹ 1.65 1.71 1.76 1.75 1.75 1.75 1.77 1.69 |

Table 5.6: Estimated Temperature Dependence of Quantum Yields and Radiative Rates for Normal 1AC in Ethylene Glycol and Ethylene Glycol- D₂

The total quantum yields were estimated by scaling relative quantum yields to $\varphi = 0.019$ at 20 °C for 1AC / EG and $\varphi = 0.051$ at 20 °C for 1AC / EG-D₂ (*Table 2.3*). The extent of the tautomer emission band was estimated using a tautomer lineshape obtained from 1AC in benzyl alcohol.

| Temperature (°C) | Tautomer | k _{rad} (T) | $k_{rad}N$ / $k_{rad}T$ | k _{obs} | k _{rxn} calculated | k ^N | k _{rxn} | k ^N |
|------------------|--------------|-------------------------------|-------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|---------------------------------|
| | rise, ns | 10 ⁶ s⁻¹ | α | 10 ⁹ s ⁻¹ |
| | | | | | | | | |
| | Alt. fit #2 | | | | α = 5.2 | | α = 9.0 | |
| 1 | 0.44 | 3.2 | 5.6 | 0.57 | 0.53 | 0.043 | 0.91 | -0.34 |
| 10 | 0.40 | 3.2 | 5.4 | 0.73 | 0.70 | 0.030 | 1.21 | -0.48 |
| 20 | 0.36 | 3.6 | 4.7 | 0.95 | 1.04 | -0.091 | 1.81 | -0.85 |
| 30 | 0.33 | 3.6 | 4.6 | 1.22 | 1.37 | -0.15 | 2.37 | -1.1 |
| 40 | 0.30 | 3.4 | 5.1 | 1.52 | 1.56 | -0.043 | 2.70 | -1.2 |
| 50 | 0.28 | 3.1 | 5.6 | 1.82 | 1.70 | 0.12 | 2.94 | -1.1 |
| 60 | 0.26 | 3.2 | 5.4 | 2.04 | 1.98 | 0.065 | 3.42 | -1.4 |
| 71 | 0.25 | 3.1 | 5.5 | 2.33 | 2.20 | 0.13 | 3.80 | -1.5 |
| mean: | | 3.3 ± 0.2 | 5.2 ± 0.4 | | | | | |
| | | | | | | | | |
| | Alt. fit #1 | | | | α = 4.8 | | α = 9.0 | |
| 1 | 0.31 | 4.5 | 4.0 | 0.57 | 0.69 | -0.12 | 1.30 | -0.73 |
| 10 | 0.30 | 4.2 | 4.1 | 0.73 | 0.86 | -0.13 | 1.62 | -0.89 |
| 20 | 0.32 | 4.0 | 4.2 | 0.95 | 1.08 | -0.13 | 2.03 | -1.1 |
| 30 | 0.31 | 3.8 | 4.4 | 1.22 | 1.34 | -0.12 | 2.52 | -1.3 |
| 40 | 0.30 | 3.4 | 5.1 | 1.52 | 1.44 | 0.077 | 2.70 | -1.2 |
| 50 | 0.28 | 3.1 | 5.6 | 1.82 | 1.57 | 0.25 | 2.94 | -1.1 |
| 60 | 0.26 | 3.2 | 5.4 | 2.04 | 1.82 | 0.22 | 3.42 | -1.4 |
| 71 | 0.25 | 3.1 | 5.5 | 2.33 | 2.03 | 0.30 | 3.80 | -1.5 |
| mean: | | 3.7 ± 0.5 | 4.8 ± 0.6 | | | | | |
| | | | | | | | 1 | |
| | original fit | | | | α = 4.7 | | α = 9.0 | |
| 1 | 0.31 | 4.5 | 4.0 | 0.57 | 0.68 | -0.11 | 1.30 | -0.73 |
| 10 | 0.30 | 4.2 | 4.1 | 0.73 | 0.84 | -0.11 | 1.62 | -0.89 |
| 20 | 0.31 | 4.1 | 4.1 | 0.95 | 1.10 | -0.14 | 2.10 | -1.1 |
| 30 | 0.31 | 3.8 | 4.4 | 1.22 | 1.32 | -0.096 | 2.52 | -1.3 |
| 40 | 0.29 | 3.5 | 4.9 | 1.52 | 1.46 | 0.059 | 2.79 | -1.3 |
| 50 | 0.28 | 3.1 | 5.6 | 1.82 | 1.54 | 0.28 | 2.94 | -1.1 |
| 60 | 0.26 | 3.2 | 5.4 | 2.04 | 1.79 | 0.25 | 3.42 | -1.4 |
| 71 | 0.24 | 3.2 | 5.3 | 2.33 | 2.07 | 0.26 | 3.96 | -1.6 |
| mean: | | $\textbf{3.7}\pm\textbf{0.5}$ | 4.7 ± 0.6 | | | | | |

Table 5.7: Estimated Reaction Rates for 1AC in Ethylene Glycol Based on the Irreversible Proton-Transfer Scheme

The observed rate k_{obs} is compared to calculated reaction rates. Two values of the ratio of normal to tautomer radiative rates (α) are tested: $\alpha \sim 5$ determined from EG data and $\alpha = 9$ from Table 2.3. The values of k^N provide an indication of the quality of the estimated rates, with negative values of k^N being nonphysical solutions.

| Temperature (°C) | Tautomer | k _{rad} (T) | $k_{rad}N / k_{rad}T$ | k _{obs} | k _{rxn} calculated | k ^N | k _{rxn} | k ^N |
|------------------|--------------|----------------------|-----------------------|------------------|-----------------------------|----------------|------------------|----------------|
| | rise, ns | 4 06 -1 | | 409 -1 | 409 -1 | 409 -1 | calculated | 409 -1 |
| | | 10° S | α | 10° S | 10° S | 10° S | 10° S | 10° S |
| | A 12 412 110 | | | 1 | | | | |
| | Alt. fit #2 | | | | $\alpha = 4.4$ | | $\alpha = 9.0$ | |
| 1 | 0.64 | 4.0 | 4.1 | 2.17 | 2.32 | -0.15 | 4.75 | -2.6 |
| 10 | 0.57 | 3.9 | 4.4 | 2.78 | 2.77 | 0.0031 | 5.68 | -2.9 |
| 20 | 0.51 | 3.9 | 4.6 | 3.57 | 3.45 | 0.13 | 7.05 | -3.5 |
| 30 | 0.46 | 4.1 | 4.3 | 4.22 | 4.32 | -0.10 | 8.84 | -4.6 |
| 40 | 0.41 | 3.8 | 4.6 | 5.03 | 4.85 | 0.18 | 9.92 | -4.9 |
| 50 | 0.38 | 3.8 | 4.7 | 5.71 | 5.38 | 0.33 | 11.0 | -5.3 |
| 60 | 0.34 | 4.3 | 4.1 | 6.29 | 6.78 | -0.49 | 13.9 | -7.6 |
| 71 | 0.32 | 4.0 | 4.3 | 6.62 | 6.82 | -0.20 | 14.0 | -7.3 |
| mean: | | 4.0 ± 0.2 | 4.4 ± 0.2 | | | | | |
| | | | | | | | | |
| | Alt. fit #1 | | | | α = 4.8 | | $\alpha = 9.0$ | |
| 1 | 0.55 | 4.6 | 3.5 | 2.17 | 2.95 | -0.77 | 5.53 | -3.4 |
| 10 | 0.49 | 4.5 | 3.8 | 2.78 | 3.52 | -0.74 | 6.60 | -3.8 |
| 20 | 1.1 | 1.8 | 9.7 | 3.57 | 1.78 | 1.8 | 3.33 | 0.24 |
| 30 | 0.45 | 4.2 | 4.2 | 4.22 | 4.82 | -0.60 | 9.04 | -4.8 |
| 40 | 0.41 | 3.8 | 4.6 | 5.03 | 5.29 | -0.26 | 9.92 | -4.9 |
| 50 | 0.38 | 3.8 | 4.7 | 5.71 | 5.87 | -0.16 | 11.0 | -5.3 |
| 60 | 0.34 | 4.3 | 4.1 | 6.29 | 7.39 | -1.1 | 13.9 | -7.6 |
| 71 | 0.32 | 4.0 | 4.3 | 6.62 | 7.44 | -0.82 | 14.0 | -7.3 |
| mean: | | 3.9 ± 0.8 | 4.8 ± 0.2 | | • | | • | |
| | | | | | | | | |
| | original fit | | | | α = 3.9 | | $\alpha = 9.0$ | |
| 1 | 0.46 | 5.6 | 3.0 | 2.17 | 2.86 | -0.69 | 6.61 | -4.4 |
| 10 | 0.47 | 4.7 | 3.6 | 2.78 | 2.98 | -0.20 | 6.88 | -4.1 |
| 20 | 0.42 | 4.7 | 3.8 | 3.57 | 3.71 | -0.14 | 8.56 | -5.0 |
| 30 | 0.42 | 4.5 | 3.9 | 4.22 | 4.20 | 0.023 | 9.68 | -5.5 |
| 40 | 0.40 | 3.9 | 4.4 | 5.03 | 4.41 | 0.62 | 10.2 | -5.1 |
| 50 | 0.37 | 3.9 | 4.5 | 5.71 | 4.90 | 0.82 | 11.3 | -5.6 |
| 60 | 0.34 | 4.3 | 4.1 | 6.29 | 6.01 | 0.28 | 13.9 | -7.6 |
| 71 | 0.31 | 4.1 | 4.1 | 6.62 | 6.24 | 0.38 | 14.4 | -7.8 |
| mean: | I. | 4.5 ± 0.5 | 3.9 ± 0.5 | | 1 | | 1 | |

Table 5.8: Estimated Reaction Rates for 1AC in Ethylene Glycol- D_2 Based on the Irreversible Proton-Transfer Scheme

The observed rate k_{obs} is compared to calculated reaction rates. Two values of the ratio of normal to tautomer radiative rates (α) are tested: $\alpha \sim 5$ determined from EG data and $\alpha = 9$ from Table 2.3. The values of k^N provide an indication of the quality of the estimated rates, with negative values of k^N being nonphysical solutions.

| r | | | | | r | | |
|---------------------------|-------|----------------|--------|-------|---------------------|---------------------|---------------------|
| | T (K) | a ₁ | a_2 | a_3 | τ ₁ (ns) | τ ₂ (ns) | τ ₃ (ns) |
| | | | | | | | |
| Normal | 278.2 | 0.37 | 0.63 | | 0.26 | 0.61 | |
| (λ _{em} =400 nm) | 288.2 | 0.31 | 0.69 | 0.00 | 0.21 | 0.43 | 5.0 |
| | 298.2 | 1.00 | | 0.01 | 0.30 | | 1.6 |
| | 308.7 | 1.00 | | 0.00 | 0.24 | | 2.2 |
| | 318.2 | 0.99 | | 0.01 | 0.20 | | 3.2 |
| | 328.2 | 1.00 | | 0.00 | 0.18 | | 2.8 |
| | 338.2 | 0.99 | | 0.01 | 0.16 | | 3.0 |
| | | | | | | | |
| Tautomer | 278.2 | -7.05 | 8.05 | | 0.30 | 0.68 | |
| (λ _{em} =560 nm) | 288.2 | -11.67 | 12.67 | | 0.28 | 0.53 | |
| | 298.2 | -15.57 | 16.56 | 0.00 | 0.25 | 0.45 | 10 |
| | 308.7 | -23.30 | 24.29 | 0.01 | 0.21 | 0.40 | 10 |
| | 318.2 | -38.85 | 39.82 | 0.03 | 0.18 | 0.37 | 10 |
| | 328.2 | -112.97 | 113.91 | 0.07 | 0.17 | 0.33 | 10 |
| | 338.2 | -228.87 | 229.72 | 0.15 | 0.15 | 0.31 | 10 |

Table 5.9: Temperature Dependence of 1AC Lifetimes in Benzyl Alcohol

| | MeOH | 1-PrOH | 1-BuOH | BzOH | EG | PG | Water | FA | NMF |
|----------------------|------|--------|--------|---------------------------|-----------|-------|-------|------|------|
| Viscosity (cP, 298K) | 0.54 | 1.95 | 2.61 | 5.50 | 17.75 | 48.40 | 0.90 | 3.34 | 1.66 |
| | | | | | | | | | |
| | K) | | | | | | | | |
| Temperature (K) | | | | | | | | | |
| 223 | 6.1 | 14.2 | | | | | | | |
| 233 | 4.3 | 9.1 | | | | | | | |
| 243 | 3.2 | 6.0 | 8.3 | | | | | | |
| 253 | 2.5 | 4.1 | 5.2 | | | | | | |
| 263 | 2.0 | 2.9 | 3.4 | | 6.6 | 15.6 | | | |
| 273 | 1.6 | 2.1 | 2.3 | 2.7 | 3.6 | 6.3 | 2.2 | 2.3 | 1.9 |
| 283 | 1.3 | 1.5 | 1.6 | 1.8 | 2.1 | 2.8 | 1.5 | 1.6 | 1.4 |
| 293 | 1.1 | 1.1 | 1.2 | 1.2 | 1.3 | 1.4 | 1.1 | 1.2 | 1.1 |
| 298 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 | 1.0 |
| 303 | 0.9 | 0.9 | 0.9 | 0.8 | 0.8 | 0.7 | 0.9 | 0.9 | 0.9 |
| 313 | 0.8 | 0.7 | 0.6 | 0.6 | 0.5 | 0.4 | 0.7 | 0.7 | 0.7 |
| 323 | 0.7 | 0.5 | 0.5 | 0.5 | 0.4 | 0.3 | 0.6 | 0.5 | 0.6 |
| 333 | 0.6 | 0.4 | 0.4 | 0.4 | 0.3 | 0.2 | 0.5 | 0.4 | 0.5 |
| | | | - | τ> estim | nate 1AC | ns | | | |
| 223 | 45 | 308 | | | | P0 | | | |
| 233 | 32 | 197 | | | | | | | |
| 243 | 24 | 131 | | | | | | | |
| 253 | 18 | 89 | | | | | | | |
| 263 | 15 | 63 | | | | | | | |
| 273 | 12 | 45 | | 225 | 655 | 3276 | 21 | 93 | 38 |
| 283 | 10 | 33 | | 145 | 378 | 1469 | 15 | 65 | 29 |
| 293 | 8 | 25 | | 99 | 230 | 720 | 11 | 47 | 22 |
| 298 | 7 | 22 | | 83 | 183 | 519 | 10 | 40 | 20 |
| 303 | 7 | 19 | | 70 | 147 | 381 | 8 | 35 | 18 |
| 313 | 6 | 15 | | 51 | 98 | 216 | 7 | 26 | 14 |
| 323 | 5 | 12 | | 38 | 68 | 130 | 5 | 21 | 12 |
| 333 | 4 | 9 | | 30 | 49 | 83 | 4 | 17 | 10 |
| | | | | | | | | 1 | |
| | | _ | < | <τ _{rot} > estin | nate 7AI, | ps | 1 | 1 | |
| 223 | 31 | 210 | | | | | | | |
| 233 | 22 | 134 | 15- | | | | | | |
| 243 | 16 | 89 | 173 | | | | | | |
| 253 | 13 | 61 | 109 | | | | | | |
| 263 | 10 | 43 | 72 | | | | | | |
| 273 | 8 | 31 | 49 | | 444 | 2229 | 14 | | |
| 283 | 7 | 23 | 34 | | 256 | 999 | 10 | | |
| 293 | 5 | 17 | 24 | | 156 | 490 | 7 | | |
| 298 | 5 | 15 | 21 | | 124 | 353 | 7 | | |
| 303 | 5 | 13 | 18 | | 100 | 259 | 6 | | |
| 313 | 4 | 10 | 13 | | 67 | 147 | 5 | | |
| 323 | 3 | 8 | 10 | | 46 | 89 | 4 | | |
| 333 | 3 | 6 | 8 | | 33 | 56 | 3 | | |

Table 5.10: Estimated Temperature Dependence of Solute Rotation Times in Various Protic Solvents

Table Notes

The temperature dependence of viscosities were calculated according to the algorithms of (a) C. L. Yaws, *Handbook of Viscosity*. (Houston, Gulf Pub. Co., 1995). (b) D. S. Viswanath and G. Natarajan, *Data Book on the Viscosity of Liquids*. (New York, Hemisphere Pub. Corp., 1989).

Rotational times were estimated for 1AC and 7AI assuming the following values for C_{obs} [M. L. Horng, J. A. Gardecki, and M. Maroncelli, *J. Phys. Chem. A.*, **101**, 1030 (1997)]: 0.64 (Methanol, MeOH), 0.52 (1-Propanol, 1-PrOH), 0.55 (1-Butanol, 1-BuOH), 0.7 (Benzyl Alcohol, BzOH), 0.48 (Ethylene Glycol, EG), 0.5 (Propylene Glycol, PG), 0.5 (Water), 0.56 (Formamide, FA), and 0.56 (N-Methylformamide, NMF). The calculations further assumed f = 0.6, $V_p(1AC) = 147 \text{ Å}^3$, and $V_p(7AI) = 104 \text{ Å}^3$.

The shaded regions indicate the onset of "anomalous" kinetic behavior of 1AC or 7AI. The regions not shaded in this table mean that experimental data are not available or that the observed kinetics are consistent with the simple irreversible proton-transfer scheme.

| | | | 1AC | 7AI |
|-------------------|--|---|-------------------|--|
| Solvent (1) | E(η) kJ/mol | $E(\tau_D) kJ/mol$ | Eact kJ/mol | E _{act} kJ/mol |
| | | | | |
| Methanol | 10.9 ^a , 10.5 ^b | 17 ± 2^{k} , 15.8 ^{<i>l</i>} | 9.5 ^p | 13 ^q , 9.9 ^b , 9.7 ^a |
| Ethanol | 9.7 °, 11 ^d , 14.8 ^a | | | 9.1 ^{c,r} , 20 ^d , 16 ^q , 12.7 ^a |
| 1-Propanol | 18. ^d | 20.5 ^{<i>l</i>} | 12.6 ^p | 26 ^d |
| 1-Butanol | 18. °, 29 ^d , 19.3 ^b | | | 16 °, 31 ^d , 17.5 ^b |
| Benzyl Alcohol | 21.4 ^e | | ~10 | |
| Ethylene Glycol | 27.9 ^a , 31 ^{e,f} | 22 ^m , 29 \pm 2 ^k | 18 | 17 ^a , 20 |
| Propylene Glycol | 42 ^g | 26 ^m | ~21 | ~27 |
| Water | 15.5 ^h , 15 ⁱ | $16 \pm 1 \text{ or } 12 \pm 1^{\text{ n}}$ | 9.6 | 8.8 ^I , 10.3 ^{b,s} |
| | | | | |
| Formamide | 19.5 ° | 13.8 ± 0.8 °, 17 ± 2 $^{\rm k}$ | 13 | |
| N-Methylformamide | 14.2 ^j | 9.1 ± 0.1 ° | 15 | |

Table 5.11: Arrhenius Activation Energies (20 $^{\circ}$ C) for Solvent Properties and Reaction Rates of 1AC and 7AI

¹ Because the observed isotope effects are largely independent of temperature, the E_{act} do not differ greatly from the normal alcohols, diols, or water. Data for viscous solvents was fit for a small range about room temperature (~10 - 40 °C).

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| Solvent | <τ _{D1} > (ps) | Reference | τ _{rxn} (1AC) (ps) |
|---------------------|----------------------------|-----------|--------------------------------|
| | | | |
| Primary Alcohols | | | |
| methanol | 54 | 1,2 | 540 |
| ethanol | 191 | 1,2,3 | 790 |
| 1-propanol | 430 | 1 | 770 |
| 1-butanol | 581 | 1,4,5 | 860 |
| 1-pentanol | 879 | 1,3 | 900 |
| 1-heptanol | 1378 | 1,3 | 1210 |
| 1-octanol | 1755 | 1,3 | 1160 |
| 1-nonanol | 2030 | 1,3 | 1280 |
| 1-decanol | 2115 | 1,3 | 1290 |
| 1-undecanol | 1538 | 1 | 1060 |
| benzyl alcohol | 250 | 6 | 290 |
| 2-methyl-1-propanol | | | 850 |
| | | | |
| Secondary Alcohols | | | |
| 2-propanol | 411 | 2,7 | 1130 |
| 2-butanol | 490 | 5 | |
| 3-pentanol | | | 1590 |
| cyclohexanol | 2290 | 8 | 1340 |

Table 5.12: Solvent Dielectric Relaxation Times

| 1-octanol | 1755 | 1,3 | 1160 |
|---------------------|------|---------|------|
| 1-nonanol | 2030 | 1,3 | 1280 |
| 1-decanol | 2115 | 1,3 | 1290 |
| 1-undecanol | 1538 | 1 | 1060 |
| benzyl alcohol | 250 | 6 | 290 |
| 2-methyl-1-propanol | | | 850 |
| Secondary Alcohols | | | |
| 2-propanol | 411 | 2,7 | 1130 |
| 2-butanol | 490 | 5 | |
| 3-pentanol | | | 1590 |
| cyclohexanol | 2290 | 8 | 1340 |
| | | | |
| Tertiary Alcohols | | | |
| 2-methyl-2-propanol | 331 | 4,9,10 | 1920 |
| 2-methyl-2-butanol | 210 | 11 | 2210 |
| 3-ethyl-3-pentanol | | | 3810 |
| | - | | 1 |
| Diols | | | |
| ethylene glycol | 143 | 3,12 | 940 |
| propylene glycol | 430 | 3,13 | 1860 |
| <u> </u> | 1 | | 1 |
| Triols | | | |
| glycerol | 1719 | 13 | 2640 |
| | | | |
| Water | 8.5 | 9,10,14 | 2320 |

Solvent (Debye) dielectric relaxation times measured at 20 or 25 °C are from the sources listed below:

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- The observed reaction rates for 1AC in these solvents are listed for comparison. Most of the data is from
- S. J. Boryschuk, M. S. Thesis, The Pennsylvania State University, 1993.



Figure 5.1: Temperature Dependence of 1AC Lifetimes in Ethylene Glycol



Figure 5.2: Temperature Dependence of 1AC Lifetimes in Ethylene Glycol-D₂



Figure 5.3: Temperature Dependence of 1AC Lifetimes in Propylene Glycol



Figure 5.4: Temperature Dependence of 7AI Lifetimes in Propylene Glycol





The reaction rates were determined using "alternative fit #2" discussed in Section 5.2. The temperature dependence of the viscosity of ethylene glycol is shown for comparison. [Viscosity data from (a) D. S. Viswanath and G. Natarajan, *Data Book on the Viscosity of Liquids*. (New York, Hemisphere Pub. Co., 1989). (b) D. Bohne, S. Fischer, and E. Obermeier, *Ber. Bunsenges. Phys. Chem.*, **88**, 739, (1984).]



Figure 5.6: Temperature Dependence of 1AC in Benzyl Alcohol



Figure 5.7: Comparison of Observed Rates and Solvent Dielectric Times (τ_1)

The reaction rate data in methanol and 1-propanol is from S. J. Boryschuk, M.S. Thesis, The Pennsylvania State University, 1993. Sources of the dielectric data used here are noted in Section 5.4 (Endnote 52).



Figure 5.8: Isotope Effects in the Correlation between Reaction Rates and Solvent Dielectric Relaxation Times for 1AC and 7AI



Figure 5.9: Solvent Dependence of 1AC Reaction Rates Normalized by a Measure of Hydrogen-Bond Lifetimes

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³⁸ In an early study of the excited-state tautomerization reaction of 1AC in bulk alcohols, Waluk and coworkers suggested that at least two types of ground-state solvation structures could account for the kinetics observed with limited time-resolution. (Endnote 9)

³⁹ In an abstract, D. McMorrow may indicate that the intrinsic proton transfer rate is even shorter (D. McMorrow, *Bull. Am. Phys. Soc.*, **33**, 1635 (1988).)

⁴⁰ Preliminary measurements of 1AC in bulk primary, secondary, and tertiary amines reveal photophysical and photochemical behavior again different than that observed for 1AC in bulk alcohols. The amines [butylamine, diethylamine, and triethylamine] were distilled immediately prior to use to remove significant fluorescence impurities and natural oxidation products. In these weakly associating, hydrogen-bonded solvents, the normal form of 1AC is quenched rapidly (~10-20 ps) and little steady-state emission is observed. Emission in the region where the tautomer is expected to fluoresce is observed (rise time too rapid to measure, decay times ~0.43 - 0.49 ns). At slightly lower temperatures (1 °C), the reaction remains too rapid to measure well. The triethylamine was intended to be a control solvent in which no reaction is expected, but it is possible that trace impurities catalyzed the reaction anyway.

⁴¹ A scaled lineshape of a fit of the tautomer emission in benzyl alcohol was used to estimate the extent of the tautomer band in these determinations, as practiced for the

quantum yield values listed in Chapter 2, but unlike the use of discrete intensities applied in the earlier temperature work reported in *Table 5.2*, *Table 5.3*, *Table 5.4*, and *Table 5.5*. The quantum yield ratios determined for this work in *Table 5.6* differ from those in Chapter 2 because two different emission instrument correction files were used over the time in which the measurements where made.

⁴² An empirical expression involving a stretched exponential $N(t) = N(0)exp[-(kt)^{\beta}]$ has been found useful for representing dispersive kinetics in glassy solvents. See the discussion in W. Siebrand and T. A. Wildman, *Acc. Chem. Res.*, **19**, 238, (1986) for an introduction.

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Chapter 6

STUDIES OF 1-AZACARBAZOLE IN BULK PROTIC SOLVENTS – II. WATER AND AMIDES

6.1 Introduction

Like the reactions in the diols, the observed rates attributed to reaction of 7AI and 1AC in water appear anomalously slow when plotted on the $E_T(30)$ polarity scale.^{1,2} This behavior for 7AI has been examined extensively without convergence to a clear understanding.³⁻²¹ Disagreement remains, for example, on the actual rate of tautomerization of 7AI in water. Petrich and coworkers suggest that only a small fraction of 7AI reacts quickly (~20% at ~70 ps, measured in emission and transient absorption experiments).⁶⁻¹⁸ On the other hand, Chapman and Maroncelli have argued that the tautomerization is slower (~830 ps in water) and that the nonradiative decay rate of the tautomer formed is much faster (5 x 10⁹ s⁻¹) than in alcohols.⁵ For this reason, only one fluorescence band is observed for 7AI in water, as the tautomer emission is weak and is partially hidden under the normal band.^{5,3,19} Examination of the reaction of 1AC in water is therefore warranted to help to clarify the interpretation of the observed rates in both solutes.

The steady-state and time-resolved fluorescence spectroscopy of 1AC in water is reviewed first and is discussed within the context of the results of Chapter 5. Two

additional studies then explore the nature of the 1AC emission in water. An examination of the pH dependence of the 1AC reaction in water confirms that it is the neutral species present in the excited-state reaction. In the subsequent section, the dependence of the rates observed in mixed water-methanol systems indicates that a rapid solvent exchange model describes the observed kinetics and that the reaction of 1AC in water is indeed slow.

The chapter concludes with a discussion of the excited-state reaction of 1AC catalyzed by yet another family of bulk protic solvents: the amides. This work complements the study of the reaction of 1AC in isolated complexes involving amides and lactams presented in Chapter 4. The reaction rate of 1AC in bulk protic solvents is again observed to be significantly slower than in the isolated complexes.

6.2 Photochemistry of 1AC in Water

6.2.1 Steady-State and Time-Resolved Spectroscopy

At room temperature, the steady-state fluorescence spectrum of 1AC in water or deuterium oxide appears as a single broad band, unlike the dual fluorescence observed in the alcohols. As shown in *Figure 6.1*, deuteration of the solvent methanol slows the proton-transfer rate and leads to decreased intensity in the region of tautomer emission.

In water the reaction rate is believed to be even slower than that in methanol, and the tautomer emission in water correspondingly lacks distinction from the normal emission.

The time-resolved emission of 1AC in water is unlike that measured in the bulk alcohols: emission [excited at 290 or 306 nm] from ~20 nm spectral windows across the band may be fit with one lifetime, and no tautomer rise (deactivation) time is cleanly resolved by the time-correlated single-photon-counting spectrometer. (In the deuterium oxide temperature dependence study, a ~0.9 ns lifetime with small amplitude was observed in the tautomer region, but this emission is attributed to protonated 1AC.) At 25 °C, the observed (reaction) rates of 1AC in water and deuterium oxide are 2.32 ns and 7.35 ns, respectively, indicating an isotope effect (3.2) slightly smaller than for reactions in alcohols (~5) (see Chapter 7). The isotope effect of 1AC in water (3.2) is considerably greater than the isotope effects anticipated for the normal decay times (~1 since no proton or deuteron is transferred) or observed for the tautomer decay times (1.6 ± 0.2; see Chapter 7). This large isotope effect also supports the interpretation that the observed decay time of 1AC in water is most likely the reaction time.

The temperature dependence of the observed (reaction) rates are summarized in *Figure 6.2* and *Table 6.1*, and show that the isotope effect is independent of temperature and that the Arrhenius activation energy is ~60% of that for viscosity (*Table 5.11*).

6.2.2 Solvation Dynamics in Water

This apparently slow reaction in water is quite interesting. Various measurements indicate that "solvation dynamics" is very rapid in this solvent,^{22,23} although such

"solvation dynamics" may actually be introducing concepts that are inappropriate for understanding the problem at hand. In Chapter 5, the observed (reaction) rates for the diols and alcohols were compared with the solvent dielectric relaxation rates as a measure of cooperative hydrogen-bond dynamics. Like the alcohol and diol data presented there, the observed rates in water are also directly and linearly related to the rapid water relaxation times. As illustrated in *Figure 5.9*, the observed (reaction) rate for water normalized by the Debye relaxation rate lies along the linear correlation with primary alcohols and diols on the $E_T(30)$ solvent polarity scale. This suggests that the slow observed rate normalized by a measure of the hydrogen-bonding dynamics in water is consistent with the high polarity or hydrogen-bond strength of water measured on the $E_T(30)$ scale.

6.2.3 pH Dependence of 1AC in Water

The photochemical behavior of 1AC in water was surveyed for a wide pH range in order to determine the species fluorescing at neutral pH. In order to make stable measurements near pH=7, it was necessary to use a buffer (MES, 4-morpholineethanesulfonic acid, $pK_a = 6.1$). 1AC fluorescence lifetimes and steady-state emission band shapes showed little difference at neutral pH with or without added buffer.

Absorption and emission spectra from an acidic spectrophotometric titration are presented in *Figure 6.3* and *Figure 6.4*. The absorption spectra indicate a ground-state equilibrium ($pK_a = 4.0\pm0.1$) established between 1AC and 1AC-H⁺. The absorption of the protonated form 1AC-H⁺ is red-shifted with respect to the neutral form 1AC. The

emission spectra excited at the isobestic point (330 nm) also reveal the presence of at least two species with one isoemissive point at ~540 nm. At extremes in the pH range, emission from only one species is apparent: at high pH = 2, 1AC-H⁺ emits with $\lambda_{max} \sim 480$ nm; and, at neutral pH = 6-8, 1AC emits with $\lambda_{max} \sim 400$ nm. Plots of the total fluorescence intensities or normalized intensities at given wavelengths as a function of pH (*Figure 6.5*) all suggest that the excited-state emission reflects the underlying ground-state equilibrium (pK_a ~ 4).

Time-resolved emission decays recorded at different wavelengths and pHs support the identifications made in the steady-state spectra. For excitation at the isobestic point at 331 nm, the emission at 480 nm is characterized by one lifetime at high pH ($\tau = 0.98$ ns, 20 °C, pH <2.5), by one lifetime at neutral pH ($\tau = 2.5$ ns, 20 °C, pH 5-8), and by some combination of these two lifetimes at intermediate pH. (See *Table 6.2* for representative lifetimes.) Since the decays were fit well with constrained lifetimes, the following model of non-interconverting species is used to explore the connection between the normalized amplitudes and the populations of two species.

The time dependence of the fluorescence is given by

$$F(\lambda,t) = f_A(\lambda) k_{rad}(A) A^*(t) + f_{AH}(\lambda) k_{rad}(AH) AH^*(t)$$
(6.1)

where $A^*(t)$ and $AH^*(t)$ describe the time-dependence of the total normal 1AC and protonated 1AC-H⁺ populations, $f_X(\lambda)$ describes the fraction of species X emitting at the noted wavelength normalized such that $\int f_X(\lambda) d\lambda = 1$, and $k_{rad}(X)$ are the radiative rates determined at the appropriate acidic and neutral ends of the titration. The populations $A^*(t)$ and $AH^*(t)$ are described by single exponential decays $X^*(t) = X_o^* \exp(-t/\tau_X)$ as noted earlier. Necessary data for the model are obtained from the steady-state spectra at appropriate pH levels: the quantum yield of protonated 1AC is ~1/10 that of the neutral species in water; f_A (400 nm) = 1.15 x 10⁻², f_{AH} (400 nm) = 3.62 x 10⁻⁴, f_A (480 nm) = 2.46 x 10⁻³, and f_{AH} (480 nm) = 7.53 x 10⁻³.

The normalized amplitudes of the time-resolved emission

$$F(\lambda,t) = a_A \exp(-t/\tau_A) + a_{AH} \exp(-t/\tau_{AH})$$
 (6.2)

are identified with terms in Equation 6.1 and renormalized to yield the relative populations of 1AC and 1AC-H⁺. These values are summarized in *Table 6.2*.

The spectrophotometric titrations thus reveal ground-state equilibrium $(pK_a = 4.0\pm0.1)$ and an equilibrium value in the excited-state that really reflects the ground-state equilibrium $(pK_a \sim 4)$. Little change occurs in the populations in the excited-state because equilibrium is apparently not established during lifetime of the excited-state of 1AC in water. The Förster cycle may be used to estimate the pK_a^* corresponding to an excited-state equilibrium proton exchange.²⁴

The Förster cycle method is based on the thermodynamic equivalence of all routes leading from the ground-state acid (or base) to the thermally-equilibrated conjugate base (or acid) in the lowest excited singlet state. A Förster cycle is illustrated in *Figure 6.6*. In the ground and excited states, equilibria may be written between the species 1AC and 1AC-H+ and between 1AC* and 1AC-H+*, respectively. The electronic transition energies (E_{1AC} and E_{1AC-H+}) between the ground and lowest excited states may be estimated from steady-state absorption or emission spectra. The entropies of protonation in the ground and excited states are assumed to be identical so that the enthalpies may be expressed as free energies ΔG and ΔG^* . The change in energy between 1AC-H+ and 1AC* may then be expressed using two thermodynamically equivalent routes:

$$E_{1AC} + \Delta G^* = E_{1AC-H+} + \Delta G, \text{ or} \qquad (6.3)$$

$$\Delta pK_{a} = pK_{a} - pK_{a}^{*} = (E_{1AC} - E_{1AC-H+}) / (2.303 \text{ R T})$$

$$pK_{a} - pK_{a}^{*} = [(N_{A} h) / (2.303 \text{ R T})] (v_{1AC} - v_{1AC-H+}).$$
(6.4)

In the last expression, N_A is Avogadro's number, *h* is Planck's constant, R is the universal gas constant, T is the absolute temperature of the reaction, and v is the frequency of radiation involved in the transition from the ground to lowest excited state.

Using the mean of the long-wavelength absorption and the short-wavelength emission to estimate the frequencies $v_{1AC} = 27780$ cm⁻¹ and $v_{1AC-H+} = 25000$ cm⁻¹, we estimate the difference in equilibrium constants to be pK_a – pK_a^{*} = 5.9. The excited-state equilibrium constant is thus estimated to be pK_a^{*} ~ -2. This means that 1AC-H+ is a stronger acid (and 1AC a correspondingly weaker base) in the excited state, so that the concentration of 1AC in the excited state at neutral pH increases significantly compared to 1AC-H+. *Table 6.2* indicates an additional rapid quenching process occurs in strongly acidic solutions, but this effect vanishes by neutral pH levels where we wish to measure the rate of excited-state tautomerization in water.²⁵ Thus, 1AC is the only species observed by these time-resolved fluorescence measurements at neutral pH.

The pH dependence of 1AC has been reported in earlier studies. An early paper simply noted that "the acidity of the pyrrole proton and the basicity of the aza-nitrogen increase by 1.3 and 1.8 pK units respectively."²⁶ A later analysis applied the Förster cycle to steady-state absorption and emission spectra to calculate significant changes in

the equilibrium constants between the ground- and excited-states: for 1AC-H⁺/1AC, $pK_a = 4.2 \pm 0.2$ and $\Delta pK_a = +7.5 \pm 0.5$; for 1AC/1AC-, $pK_a = 14.3 \pm 1.0$ and $\Delta pK_a = -10.8 \pm 1.0$.^[27] The latter equilibrium constants indicate that 1AC- is a stronger base (and 1AC a correspondingly weaker acid) in the excited state, so that the concentration of 1AC in the excited state at neutral pH again increases significantly compared to 1AC-.

The ground-state equilibrium constant for 1AC-H⁺/1AC determined in this work is in good agreement with the previously reported value.²⁷ The observed $\Delta p K_a$ compared to the $\Delta p K_a$ predicted by the Förster cycle suggests that the proton-exchange equilibria between 1AC and 1AC-H+ and between 1AC and 1AC- are not established in the excited state. Since the primary focus of this pH study was to determine the species emitting at neutral pH, careful investigations of the photochemical behavior of 1AC in regions of extreme pH (which often involve additional quenching mechanisms) were not pursued. We conclude that 1AC (as it reacts to form the tautomer) is the primary species observed at neutral pH.

The pH dependence of 7AI is very similar to that of 1AC. The ground state equilibrium constants are 7AI-H⁺/7AI, $pK_a = 4.5 \pm 0.1$ and 7AI/7AI-, $pK_a = 12.1$.^[28,12,17] Like 1AC, two sets of excited-state equilibrium constants have been proposed based on two different analysis methods. Förster cycle analysis predicts $\Delta pK_a = +8.3$ for the N₁-H proton in the excited-state.²⁹ Direct steady-state and time-resolved emission titrations, on the other hand, have indicated that the excited-state equilibrium constants change little from the ground-state values.^{4,11,12,17} It appears that excited-state equilibrium may not be achieved for 7AI.

The charge redistribution in the excited-state that leads to shifts in acid and base strengths is implicated as the driving force for the proton-transfer reactions.³⁰ INDO/S calculations suggest that the driving force is smaller for 1AC than for 7AI,²⁷ which is certainly consistent with the observed rates attributed to the excited-state tautomerizations in water. The discrepancy between the Förster cycle analysis and the direct fluorescence measurements does suggest that equilibrium is not achieved during the fluorescence lifetime. The slow tautomerization rates deduced from the emission lifetimes are also consistent with a small driving force for these reactions in water.

6.3 Proton-Transfer Reactions in Methanol / Water Mixtures

6.3.1 1AC in Methanol/Water Mixtures

The absence of a rise (deactivation) time in the tautomer emission of 1AC in water is one distinguishing feature that could indicate that the reaction in water is different than in the alcohols and diols. Since few pure solvents are available with which to bridge the gap in polarity between water and methanol, a series of mixtures of methanol and water were used to explore the spectroscopy of 1AC in solvents of intermediate polarity. The steady-state normal emission band red-shifts monotonically and the band width broadens almost linearly with increasing water concentration (*Table 6.3*).³¹ The time-resolved spectroscopy reveals that the normal emission may be fit with a single lifetime³² and that the tautomer emission may be fit with dominant rise and decay lifetimes, as summarized in *Table 6.3*. As the water concentration increases, the rate attributed to proton-transfer decreases monotonically, and the rate attributed to tautomer deactivation (1/rise time) increases monotonically. Indeed, the experiment is unable to cleanly resolve a rise time in the tautomer emission of 1AC in water.

Chapter 3 reviewed a two-state kinetic model with rapid solvent exchange. The measured rates for 1AC in the methanol-water mixture clearly fall in the limit of rapid solvent exchange for this model, as shown by the linear relationship in *Figure 6.7* and the single-exponential decays. The continuous change in the observed decay time from pure methanol to pure water is also an indication that reaction is occurring in water and that the observed decay time is the reaction time.

6.3.2 Other Proton-Transfer Reactions in Methanol/Water Mixtures

Earlier studies of mixtures of water and methanol have employed proton dissociation reactions of photoacids as probes of the structure of water.³³⁻³⁵ Naphtholtype photoacids (R-OH) exhibit dissociation rates that increase with increasing concentration of water, and cationic photoacids (RNH_3^+) display dissociation rates that increase in the water-rich region with addition of organic solvent prior to sharply decreasing in the organic-rich region.³³⁻³⁵ The observed rate dependence for 1AC is unlike these photoacids, suggesting that the observed reaction is not one controlled by a proton-transfer to solvent like the naphthol-type photoacids.

6.4 Photochemistry of 1AC in Bulk Amides

The excited-state proton-transfer reaction of 1AC has been studied extensively in the alcohols, diols, and water. These molecules serve as catalysts in promoting the reaction. In this section, the proton-transfer reaction of 1AC in bulk amides is characterized for the first time (to our knowledge). This family of solvents serves as noncatalytic agents in the reaction, themselves undergoing change as the normal form of 1AC is transformed into the tautomer form. The experiments described here complement the study of the reaction in isolated complexes of 1AC with amides or lactams reported in Chapter 4.

6.4.1 Steady-State and Time-Resolved Emission Spectroscopy

An excited-state reaction is observed for 1AC in the neat solvents formamide (FA) and N-methylformamide (NMF), but no reaction is observed in the aprotic solvent N,N-dimethylformamide (DMF). This study in the bulk amides permits the effects of extended solvent hydrogen-bonding on the proton-transfer reaction to be explored in a different family of protic solvents. Although the steady-state emission spectra of 1AC in FA and NMF do not display prominent tautomer emission like those in bulk alcohols (*Figure 2.3*), the emission quantum yields do reveal other nonradiative pathways for depopulating the excited normal form of 1AC as recorded in Table 2.3. Timeresolved emission spectra at 560 nm (the tautomer region) confirm the presence of an excited-state reaction: the fluorescence decays consist of both a rise-time and a decaytime. Lifetime measurements of 1AC at room temperature are summarized in *Table 2.3*, and representative time-resolved emission decays of 1AC in formamide are presented in *Figure 6.8.* The behavior of 1AC in these bulk solvents appears similar to that in diols and water noted above. The decay-time (equal for both the normal and tautomer) is attributed to the proton-transfer reaction and the rise-time is identified with the deactivation of the tautomer. The radiative rates of the normal and tautomer species help to substantiate this interpretation (see *Table 2.3*). (Measurement of an isotope effect in $FA-d_2$ to confirm the proton-transfer character of the reaction has not yet been successful.) It is remarkable that the proton-transfer rate has significantly decreased in these neat hydrogen-bonded liquids compared to the ultrafast rate observed in complexes with lactams and several amides discussed in Chapter 4. Although an ultrafast rate has not been measured directly in 1AC complexes with alcohols because of weak association, a similar rate decrease occurs in bulk alcohols as well.

The temperature dependence of the reaction has been measured over the range 0-60 °C and is presented in *Figure 6.9* and *Table 6.4* with comparison to the temperature dependence of the viscosity. The decay lifetimes attributed to the reaction show the strongest dependence on temperature, and the following Arrhenius activation energies are determined: 12.8 kJ/mol for the observed rate of 1AC in FA compared to 19.5 kJ/mol for FA viscous flow; and 14.6 kJ/mol for 1AC in NMF compared to 14.2 kJ/mol for NMF

viscous flow.^{36,37} The Arrhenius activation energies of the tautomer rise-lifetimes are similar for both formamide (7.6 kJ/mol) and N-methylformamide (7.0 kJ/mol), suggesting related physical mechanisms leading to the tautomer deactivation. The similarity between E_{act} and E_{η} for these solvents is analogous to the behavior of 7AI and 1AC in primary alcohols, diols, and water as summarized in *Table 5.11*.

6.5 Prompt Emission and the Irreversible Proton-Transfer Model

Since the excited-state tautomerization of 1AC is measurably fast in isolated complexes with several lactams and amides, the bulk amides provide a system in which to explore the possibility of prompt reaction. The amides' structure H-N-C=O has an excellent geometry for forming 1:1 complexes with 1AC, and it is possible that such 1AC:amide molecular complexes are formed in the bulk amide solvents. These "isolated" complexes would react more quickly than 1AC in a solvent environment having an extended hydrogen-bonding network. In this section, a discussion of the extent of reaction is discussed for amide solvents as well as for a number of the slower alcohol and diol reactions.

In Section 3.3 a two-state kinetic model was described with which one may estimate the fraction of the 1AC population that undergoes prompt fluorescence. Using Equation 3.13, we estimate that the fraction of the population of 1AC undergoing prompt fluorescence while reacting in methanol, methanol-OD, ethylene glycol, formamide and N-methylformamide is on the order of 5-10% for all these protic solvents. No correction for N* contamination was applied in this first estimate.

A more careful estimate of the prompt emission fraction using Equations 3.14, 3.15, 3.16 and 3.17 follows. For the determination of the constant $c(\lambda)$, $f_N(\lambda)$ is estimated from the steady-state emission spectra of 1AC in acetonitrile broadened by convolution with a Gaussian function and shifted to match the FWHM of the normal emission band of each protic solvent. The function $f_T(\lambda)$ is estimated by a log-normal fit to the tautomer emission in methanol obtained by subtracting $f_N(\lambda)$ from the measured line showing dual fluorescence. For this work, the ratio of radiative rates is assumed to be independent of solvent and has a mean value equal to 9 ± 1 (*Table 2.3*). These corrections for the contamination of tautomer emission by normal species further reduce the calculated fractions undergoing prompt fluorescence: NMF (2%), FA (2%), MeOH (4%), MeOD (8%), and EG (7%). Based on these values, we conclude that only a very small amount of 1AC is incorporated into a cyclically hydrogen-bonded complex that allows the reaction to occur promptly following the excitation of 1AC. Thus nearly the entire reaction of 1AC in these bulk protic solvents is observed in the time-resolved emission. This experimental result is consistent with recent computer simulations that also reveal the rarity of cyclical hydrogen-bonded complexes prepared for prompt reaction.³⁸

6.6 Conclusion

Earlier studies indicated that the excited-state proton-transfer reaction of 1AC occurs in diols and water but at a much slower rate than might be expected based on a reaction rate correlation on the $E_T(30)$ solvent scale. Here and in the previous chapter, it has been argued that the reaction of 1AC in these solvents is not functionally different

than the reaction in bulk alcohols. In this chapter the following experimental evidence has been cited to support the argument. (1) An examination of the pH dependence of the 1AC reaction in water confirms that it is the neutral species present in the excited-state reaction near pH = 7. (2) The dependence of rates observed in mixed water-methanol systems indicates that a rapid solvent exchange model describes the observed kinetics and that the reaction of 1AC in water is indeed slow. (3) The dependence of rates observed in mixed water-methanol systems also suggests that it is unlikely that an ion pair like the naphthol-type photoacids is produced by the reaction.

A number of interesting papers have been published since this experimental work on 1AC in water was concluded. Chou and coworkers have fully resolved the excitedstate proton-transfer reaction of 3-cyano-7AI in water: the normal species decays in 900 ps and the tautomer species shows a 900 ps rise time and a 3.3 ns decay time.⁴⁷ The deactivation rate of the tautomer is significantly decreased compared to the reaction rate in this 7AI analogue, and this allows the full reaction to be observed by time-resolved fluorescence spectroscopy. Thus Chapman and Maroncelli's interpretation⁵ that the reaction rate is much slower than the tautomer deactivation rate for 7AI in water is affirmed. Castleman and coworkers have observed proton-transfer in hydrated gas-phase 7AI (with 2-4 water molecules), but complete tautomerization remains to be resolved.⁴⁶ This molecular-beam experiment and others ^{44,45} provide additional insight into the molecular geometry required for excited-state double proton transfer. Finally, theoretical models are beginning to provide molecular-scale insight into the reaction of 7AI in water.^{39,43} For example, Fernandez-Ramos *et al.* argue that in solution two water molecules participate in the reaction.⁴¹ Based on their level of theory, it cannot be established with certainty whether this tautomerization is concerted or stepwise and should be described by tunneling or classical transfer. The authors do suggest, however, that their best estimate is a stepwise reaction with one-proton tunneling as the ratedetermining first step.⁴¹

The excited-state proton-transfer reaction of 1AC in the bulk amides formamide and N-methylformamide has been characterized in this chapter as well. In the future it is recommended that the isotope effect be measured in these solvents cleaned of impurities. The experimental data may also be compared to computer simulations of the reaction.

The study of the reaction of 1AC in bulk protic solvents is concluded with an examination of kinetic isotope effects. Does the reaction involve the concerted or stepwise motion of protons? Progress toward understanding the reaction mechanism is documented in the next chapter.

| | T (K) | a ₁ | a ₂ | τ_1 (ns) | τ ₂ (ns) |
|---------------------------------------|-------|----------------|-----------------------|---------------|---------------------|
| 1AC / H2O | | | | | |
| Normal | 283 | 1.00 | | 2.86 | |
| $(\lambda_{em} = 410 \text{ nm})$ | 293 | 1.00 | | 2.48 | |
| | 298 * | 1.00 | | 2.30 | |
| | 303 * | 1.00 | | 2.18 | |
| | 313 | 1.00 | | 1.90 | |
| | 323 | 1.00 | | 1.73 | |
| Tautomer | 283 | 1.00 | | 2.87 | |
| $(\lambda_{em} = 555 \text{ nm})$ | 293 | 1.00 | | 2.49 | |
| (0 , | 298 | 1.00 | | 2.35 | |
| | 303 * | 1.00 | | 2.20 | |
| | 313 | 0.97 | 0.03 | 1.89 | 4.16 |
| | 323 | 1.00 | 0.00 | 1.74 | 12.00 |
| | 298 | 0.83 | 0.17 | 2.42 | 0.63 |
| 1AC / D2O | | | | | |
| | | | | | |
| Normal | 283 * | 1.00 | | 9.05 | |
| $(\lambda_{em} = 410 \text{ nm})$ | 293 | 1.00 | | 7.91 | |
| | 298 | 1.00 | | 7.48 | |
| | 303 | 1.00 | | 7.00 | |
| | 313 | 1.00 | | 6.23 | |
| | 323 | 1.00 | | 5.58 | |
| | 298 | 0.97 | 0.03 | 7.42 | 0.66 |
| | 313 | 0.97 | 0.03 | 6.22 | 0.30 |
| Tautomer | 283 | 0.69 | 0.31 | 8.77 | 0.73 |
| $(\lambda_{em} = 555 \text{ nm})$ | 293 | 0.92 | 0.08 | 7.89 | 0.82 |
| , , , , , , , , , , , , , , , , , , , | 298 * | 0.76 | 0.24 | 7.28 | 0.67 |
| | 303 * | 0.95 | 0.05 | 6.98 | 0.68 |
| | 313 | 0.93 | 0.07 | 6.25 | 0.81 |
| | 323 | 1.00 | | 5.56 | |

Table 6.1: Temperature Dependence of 1AC Lifetimes in Water and Deuterium Oxide

An asterisk indicates the reported values are an average of at least two measurements. Measurements for which biexponential lifetimes were observed may contain a small amount of protonated 1AC.

| | Free Fits | | | Constrained Fits: | | | Relative | | | | |
|--------|------------|----------------|-----------------------|---------------------|---------------------|---------------------|--------------------|----------------|------------------------|----------|-------|
| | | | | | | | τ ₁ fix | ed at 0.9 | 977 ns | Popula | tions |
| рН | a 1 | a ₂ | a ₃ | τ ₁ , ns | τ ₂ , ns | τ ₃ , ns | a 1 | a ₂ | τ ₂ fit, ns | [1AC-H+] | [1AC] |
| 400 nm | | | | | | | | | | | |
| 1.79 | 0.44 | 0.55 | 0.10 | 0.018 | 0.94 | 3.56 | 0.65 | | | 1.00 | 0.00 |
| 2.02 | 0.48 | 0.27 | 0.25 | 0.009 | 0.91 | 1.89 | 0.37 | 0.26 | 1.97 | 0.99 | 0.01 |
| 2.50 | 0.07 | 0.28 | 0.66 | 0.112 | 1.10 | 2.49 | 0.24 | 0.70 | 2.44 | 0.98 | 0.02 |
| 2.82 | | 0.11 | 0.89 | | 0.69 | 2.38 | 0.14 | 0.86 | 2.43 | 0.95 | 0.05 |
| 3.09 | | 0.07 | 0.93 | | 0.63 | 2.45 | 0.10 | 0.90 | 2.49 | 0.93 | 0.07 |
| 3.36 | | 0.06 | 0.94 | | 0.25 | 2.46 | 0.07 | 0.94 | 2.50 | 0.90 | 0.10 |
| 3.62 | | | 1.00 | | | 2.47 | 0.05 | 0.95 | 2.52 | 0.86 | 0.14 |
| 3.91 | | | 1.00 | | | 2.50 | | | | | |
| 4.31 | | | 1.00 | | | 2.51 | | | | | |
| 4.67 | | | 1.00 | | | 2.52 | | | | | |
| 5.02 | | | 1.00 | | | 2.53 | | | | | |
| 5.48 | | | 1.00 | | | 2.53 | | | | | |
| 6.00 | | | 1.00 | | | 2.53 | | | | | |
| 480 nm | | | | | | | | | | | |
| 1.79 | 1.00 | | | 0.98 | | | 1.00 | | | 1.00 | 0.00 |
| 2.02 | 1.00 | | | 0.99 | | | 1.00 | | | 1.00 | 0.00 |
| 2.50 | 0.94 | 0.06 | | 0.96 | 2.03 | | 0.96 | 0.04 | 2.33 | 0.97 | 0.03 |
| 2.82 | 0.91 | 0.09 | | 0.96 | 2.25 | | 0.93 | 0.07 | 2.51 | 0.95 | 0.05 |
| 3.09 | 0.84 | 0.16 | | 0.94 | 2.25 | | 0.88 | 0.12 | 2.53 | 0.91 | 0.09 |
| 3.36 | 0.77 | 0.23 | | 0.95 | 2.38 | | 0.80 | 0.20 | 2.51 | 0.84 | 0.16 |
| 3.62 | 0.67 | 0.33 | | 0.94 | 2.43 | | 0.70 | 0.30 | 2.53 | 0.76 | 0.24 |
| 3.91 | 0.51 | 0.49 | | 0.89 | 2.43 | | 0.56 | 0.44 | 2.56 | 0.63 | 0.37 |
| 4.31 | 0.28 | 0.72 | | 0.80 | 2.45 | | 0.34 | 0.66 | 2.55 | 0.40 | 0.60 |
| 4.67 | 0.12 | 0.88 | | 0.70 | 2.47 | | 0.16 | 0.85 | 2.53 | 0.20 | 0.80 |
| 5.02 | 0.06 | 0.94 | | 0.66 | 2.49 | | 0.09 | 0.92 | 2.53 | 0.11 | 0.89 |
| 5.48 | | 1.00 | | | 2.51 | | 0.04 | 0.96 | 2.55 | 0.06 | 0.94 |
| 6.00 | | 1.00 | | | 2.52 | | | 1.00 | | 0.00 | 1.00 |

Table 6.2: pH Study of 1AC: Time-Resolved Emission

MES buffer was added to the water in order to help stabilize the pH measurements.

| % MeOH (by volume) | X (MeOH) | ν (low_½Max) 1000 cm ⁻¹ | <v> 1000 cm⁻¹</v> | Width = FWHM 1000 cm ⁻¹ |
|-----------------------|----------|---------------------------------------|----------------------------------|---------------------------------------|
| 100 | 1.00 | 23.82 ± 0.01 | 25.880 ± 0.001 | 4.12 ± 0.02 |
| 90 | 0.80 | 23.50 ± 0.03 | 25.674 ± 0.002 | 4.34 ± 0.05 |
| 70 | 0.51 | 22.99 ± 0.04 | 25.32 ± 0.04 | 4.67 ± 0.01 |
| 50 | 0.31 | 22.66 ± 0.06 | 25.04 ± 0.03 | 4.76 ± 0.05 |
| 30 | 0.16 | 22.00 ± 0.03 | 24.58 ± 0.04 | 5.15 ± 0.01 |
| 10 | 0.05 | 21.674 ± 0.001 | 24.23 ± 0.01 | 5.11 ± 0.02 |
| 0 | 0.00 | 21.459 | 24.035 | 5.15 |

Table 6.3: Steady-State Emission Band Characterization and Observed Rates for 1AC in Methanol-Water Mixtures

| % MeOH | Normal | Tautomer | Tautomer | 1+а _т /а _{РТ} | Prompt | k _{obs} | k' |
|--------|---------------|--------------------|---------------------|-----------------------------------|----------|---------------------------------|---------------------------------|
| | τ_1 , ns | rise τ_1 , ns | τ ₂ , ns | | emission | 10 ⁹ s ⁻¹ | 10 ⁹ s ⁻¹ |
| 100 | 0.52 | 0.29 | 0.54 | 0.06 | 0.06 | 1.92 | 3.50 |
| 90 | 0.59 | 0.27 | 0.64 | 0.13 | 0.08 | 1.69 | 3.70 |
| 70 | 0.87 | 0.24 | 0.87 | 0.23 | 0.08 | 1.15 | 4.21 |
| 50 | 1.16 | 0.19 | 1.16 | 0.42 | 0.07 | 0.86 | 5.41 |
| 30 | 1.61 | 0.11 | 1.59 | 0.67 | 0.05 | 0.62 | 9.35 |
| 10 | 2.09 | 0.02 | 2.01 | 0.49 | 0.01 | 0.48 | 46.5 |
| 0 | 2.34 | | 2.48 | 1.00 | 0.00 | 0.43 | |

Top Table: Steady-State Normal Emission Band Characterizations. The frequency at the low-frequency edge at the half-maximum, the average band frequency, and the band width are summarized as a function of solvent composition. The uncertainties indicate the size of the difference between the two independent measurements averaged for the reported value.

Bottom Table: Observed Rates. Values are an average of two independent measurements made on different days. A third long lifetime with small amplitude required for fits to the tautomer emission has been omitted from the table. The value of $1+a_T/a_{PT}$ reflects the relative sizes of the amplitudes for the tautomer rise (a_T) and decay (a_{PT}) times, and the fraction of "prompt fluorescence" is calculated as described in the text without correction for normal band contamination.

| 1AC / Formamide | T (K) | a ₁ | a_2 | a_3 | τ ₁ (ns) | τ ₂ (ns) | τ ₃ (ns) |
|---------------------------|-------|----------------|-------|-------|---------------------|---------------------|---------------------|
| | | | | | | | |
| Normal | 278.2 | 1.00 | | | 2.63 | | |
| (λ _{em} =400nm) | 288.2 | 1.00 | | | 2.18 | | |
| | 298.2 | 1.00 | | | 1.82 | | |
| | 308.2 | 1.00 | | | 1.52 | | |
| | 323.2 | 1.00 | | | 1.24 | | |
| | 338.2 | 1.00 | | | 0.98 | | |
| Tautomer | 278.2 | -0.90 | 1.78 | 0.12 | 0.31 | 2.56 | 4.70 |
| (λ _{em} =560 nm) | 288.2 | -1.17 | 2.06 | 0.11 | 0.26 | 2.14 | 4.50 |
| | 298.2 | -1.29 | 2.20 | 0.10 | 0.24 | 1.79 | 4.31 |
| | 308.2 | -1.49 | 2.41 | 0.08 | 0.22 | 1.51 | 4.25 |
| | 323.2 | -1.85 | 2.76 | 0.08 | 0.19 | 1.23 | 4.10 |
| | 338.2 | -2.11 | 3.03 | 0.08 | 0.17 | 1.00 | 3.90 |
| | r | 1 | | | | | |
| 1AC / NMF | T (K) | a ₁ | a_2 | a_3 | τ ₁ (ns) | τ ₂ (ns) | τ ₃ (ns) |
| | | | | | | | |
| Normal | 274.2 | 1.00 | | | 7.10 | | |
| (λ _{em} =400nm) | 283.2 | 1.00 | | | 5.70 | | |
| | 293.2 | 1.00 | | | 4.81 | | |
| | 298.2 | 1.00 | | | 4.42 | | |
| | 303.2 | 1.00 | | | 3.99 | | |
| | 313.7 | 1.00 | | | 3.22 | | |
| | 323.2 | 1.00 | | | 2.74 | | |
| | 333.2 | 1.00 | | | 2.25 | | |
| Tautomer | 274.2 | 1.61 | -0.61 | | 7.25 | 0.35 | |
| (λ _{em} =560 nm) | 283.2 | 1.29 | -0.75 | 0.46 | 5.40 | 0.38 | 7.95 |
| | 293.2 | 1.80 | -1.03 | 0.22 | 4.59 | 0.35 | 9.38 |
| | 303.2 | 2.00 | -1.10 | 0.10 | 4.03 | 0.30 | 10.30 |
| | 313.7 | 2.19 | -1.37 | 0.18 | 3.19 | 0.28 | 7.91 |
| | 323.2 | 2.51 | -1.69 | 0.19 | 2.68 | 0.26 | 7.54 |
| | 333.2 | 2.58 | -1.77 | 0.19 | 2.22 | 0.25 | 7.17 |

Table 6.4: Temperature Dependence of 1AC Lifetimes in Bulk Amide Solvents

Emission was collected over a 14 ns time range for 1AC in Formamide and over a 27 ns time range for 1AC in N-Methylformamide.



Figure 6.1: Comparison of Steady-State Emission Spectra of 1AC in Methanol or Methanol-OD and 1AC in Water or Deuterium Oxide

The (net) rate of tautomerization in water is much slower as revealed by the isotope effects on the emission spectra.


Figure 6.2: Temperature Dependence of 1AC Lifetimes in Water and Deuterium Oxide

Open triangles and squares represent normal (410 nm) and tautomer (555 nm) emission data, respectively.



Figure 6.3: Spectrophotometric pH Titration of 1AC in Water with the Buffer MES

The absorption spectra red-shift with increasing acid concentration. The data cover the range pH = 2 - 6.



Figure 6.4: Spectrophotometric pH Titration of 1AC in Water with the Buffer MES The emission spectra blue-shift with decreasing acid concentration. The data cover the range pH = 2 - 6.



Figure 6.5: pH Study of 1AC

Plotted are three fluorescence measures for the spectrophotometric titration: relative emission intensity at 400 nm (open boxes), total relative quantum yield (solid boxes), and amplitude of the lifetime attributed to protonated 1AC (0.98 ns) (open triangles). The solid triangles represent the relative population of protonated 1AC. All emission characteristics point to $pK_a \sim 4$, the same as the ground-state.



Figure 6.6: Schema of the Förster Cycle



Figure 6.7: 1AC in Methanol-Water Mixtures: Time-Resolved Emission

The linear dependence of the observed on the composition of the solution indicates a rapid solvent exchange kinetic model is appropriate.



Figure 6.8: Fluorescence Spectroscopy of 1AC in Formamide at 293 K.

Top panel: Steady-state emission reveals predominantly the normal species emission. Bottom panels: Time-resolved emission decays were recorded in the normal (400 nm) and tautomer (560 nm) spectral regions:

$$N^{*}(t) / N(0) = (1.00)^{*} \exp(-t/1.92 \text{ ns}).$$

T*(t) / T(0) = (-1.46)^{*} \exp(-t/265 \text{ ps}) + (2.28)^{*} \exp(-t/1.88 \text{ ns}) + (0.19)^{*} \exp(-t/3.4 \text{ ns})



Figure 6.9: Temperature Dependence of 1AC Lifetimes in Formamide (FA) and N-Methylformamide (NMF).

Solid symbols are the normal lifetimes, and the open symbols are the tautomer riselifetimes. The temperature dependence of the viscosity (scaled) is plotted for comparison. [Viscosity data is from: (a) D. S. Viswanath and G. Natarajan, *Data Book on the Viscosity of Liquids*. (New York, Hemisphere Pub. Co., 1989). (b) C. L. Yaws, *Handbook of Viscosity*. (Houston, Gulf. Pub. Co., 1995).]

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Chapter 7

EXCITED-STATE PROTON TRANSFER OF 1-AZACARBAZOLE IN MIXED METHANOL AND METHANOL-OD SOLVENTS

7.1 Introduction

Isotope effects provide a valuable means for testing kinetic mechanisms and pictures of the transition state in chemical reactions involving proton transfer.¹⁻⁴ Within the Born-Oppenheimer approximation, the substitution of one isotope for another does not change the potential energy surface. Although the binding forces remain the same, the masses of the isotopic atoms do change. Kinetic isotope effects are especially significant for hydrogen because deuterium is twice as massive as hydrogen. Thus the reaction rate corresponding to atomic motion involving hydrogen may show a substantial decrease when deuterium replaces the hydrogen atom. The elucidation of the mechanism of excited-state proton-transfer in 1AC should therefore be aided by consideration of the observed isotope effects. After briefly summarizing and interpreting the magnitudes and temperature dependence of the kinetic isotope effects for 7AI and 1AC in a number of protic solvents, we consider the reaction of 1AC in the mixed solvent methanol/methanol-OD.

7.2 Magnitude of the Kinetic Isotope Effects for 7AI and 1AC

The magnitude of the isotope effects observed for the reactions involving 7AI and 1AC reveals information about the excited-state reactions. *Table 7.1* summarizes the kinetic isotope effects; in general, the kinetic isotope effects for 7AI and 1AC in alcohols are 3 and 5, respectively. We conclude that the magnitude of the kinetic isotope effects is due to reacting protons in 7AI and 1AC, for isotope effects on simple solvation dynamics account for a much smaller effect. For example, solvation dynamics of methanol-OD is only 10% slower than that of methanol as probed by coumarin 102 in time-resolved fluorescence experiments.⁵

7.3 Temperature Dependence of Kinetic Isotope Effects for 7AI and 1AC

Chapman, Boryschuk and Maroncelli revisited the temperature dependence of the kinetic isotope effect for 7AI and 1AC in several bulk alcohols and concluded that the isotope effect has little or no temperature dependence.^{6,7,8} The results of the temperature studies of 1AC in ethylene glycol and water are consistent with these earlier conclusions (as described in Chapters 5 and 6). The temperature independence of the kinetic isotopic effect is rather remarkable since the reaction rate depends strongly on temperature as summarized in *Table 5.11*. Sühnel and Schowen note in their review of the theoretical basis for isotope effects that neither transition-state theory nor the Marcus theory can explain such large, temperature-independent primary isotope effects.⁹ Instead, a quantum-statistical mechanical theory is required: temperature-dependent but isotope-

independent solvent fluctuations lead to a "critical state" that is followed by a temperature-independent but isotope-dependent tunneling reaction.⁹ This theory is conceptually very similar to the model being examined in this dissertation.

7.4 Kinetic Isotope Effect of 1AC in Mixed Methanol/Methanol-OD

Experiments utilizing solvents of mixed protiated and deuterated composition to probe reaction mechanisms are now common.¹⁰⁻²⁷ In one strategy called the "proton inventory experiment," equilibrium or kinetic measurements are made as a function of solvent composition in an attempt to determine the number of active protons giving rise to the observed kinetic isotope effect.¹⁰⁻²⁷ Since the interpretation of the "proton inventory experiment" requires the exchange rates of the active hydrogen ligands with the solvent to be faster than their reaction rates,¹⁰⁻²⁷ it is not directly applicable to the excited-state reaction involving 1AC. (Recall from Chapter 6 that the kinetics of 1AC in watermethanol mixtures is consistent with rapid solvent exchange rather than rapid hydrogen ligand exchange.) Instead, a general strategy will be pursued in which the reaction rates are measured as a function of solvent composition (H/D), and then the predictions of kinetic models are compared to data to exclude unlikely mechanisms.

A recent study of the isotope effects for 7AI in mixed protiated and deuterated solvents provided evidence that this excited-state reaction involves the concerted motion of protons in a cyclic complex in alcohols such as methanol and ethanol.²⁷ Since the double proton-transfer reaction of 1AC is postulated to be like that of 7AI, 1AC was subjected to a similar solvent isotope-effect experiment to verify the reaction scheme. As

the isotope effect of 1AC is slightly larger than 7AI in alcohols [5 *vs.* 3], better experimental resolution for testing models is anticipated for this related proton-transfer molecule.¹⁸

The reactions of 1AC in methanol and methanol-OD mixtures were deemed the best systems for study. In these neat solvents, the normal time-resolved emission may be fit by clean, single lifetimes that allow accurate rate determinations. Experimental concerns limit the application of the solvent isotope-effect experiments in other solvents. For example, difficulties associated with the poor solubility and the possible contamination of observed rates by the normal deactivation rate k^N prevented the experiment in water and deuterium oxide. Likewise, multiple lifetimes required to fit the normal emission of 1AC in many alcohols and diols like 1-propanol and ethylene glycol complicate the extraction of rates. Thus this study of the 1AC reaction in methanol will be compared to the reported results of 7AI in methanol, ethanol, and water to examine the consistency of models proposed for both probes. Surprisingly, the results observed with 1AC appear to differ from those found with 7AI.

7.4.1 Determination of Reaction Rates

The first issue to address is the identification of the protons involved in the reaction.^{27,28} Two types of protons are involved, and each has a characteristic exchange rate. In the ground-state, the hydrogen or deuterium atoms bonded to the solute exchange (without reacting) negligibly slowly with the solvent compared to the time-scale of the reaction.²⁹ The hydrogen or deuterium atoms bonded to the solvent molecules in position

for reaction exchange rapidly as the solvent molecules exchange positions.³⁰ Thus a model of the ground-state systems prior to reaction may be divided into two independent populations (*Scheme 7.1*):



Scheme 7.1

Following excitation, the proton-transfer reactions proceed and depopulate these excitedstate ensembles. Since the observed rates for 1AC in mixed methanol-water solvents are consistent with a rapid solvent exchange limit, the time-dependence of the populations in these kinetic schemes follow Equation 3.20 of Section 3.4:

$$1AC-H (t) = 1AC-H (0) [exp\{-((1-X_D) k_{HH} + X_D k_{HD}) t]$$
(7.1)

$$1AC-D (t) = 1AC-D (0) [exp\{-((1-X_D) k_{DH} + X_D k_{DD}) t]$$
(7.2)

The experiment measures the total population of 1AC in the excited state:

$$1AC (t) = 1AC-H (t) + 1AC-D (t)$$

$$1AC (t) = 1AC(0) \{(1-X_D) \exp [-k^H t] + X_D \exp [-k^D t]\}$$
(7.3)

where the initial populations of 1AC-H and 1AC-D are directly related to the composition of the mixed solvent.³¹ These expressions are identical to those derived by

Petrich and coworkers in their study of 7AI.²⁷ Reviewing the model leading to Equations 7.1, 7.2, and 7.3, we have only needed to specify the possible reacting species in the limit of rapid solvent exchange.

The time-resolved emission data required fitting by a biexponential function, as summarized *Table 7.2* and illustrated in *Figure 7.1*. Since this biexponential behavior is predicted by the model, and since the amplitudes in unconstrained fits are similar to the mole fractions describing the composition of the mixtures, the amplitudes were constrained to the experimental mole fractions to obtain best estimates for the rates $k^{H} = 1/\tau^{H}$ and $k^{D} = 1/\tau^{D}$ of Equation 7.3. These constrained fits are also recorded in *Table* 7.2. The individual rate constants k_{HH} , k_{HD} , k_{DH} , and k_{DD} are obtained from plots of the measured rates k^{H} and k^{D} as functions of the mixture composition X_{D} . Each plot displayed in *Figure 7.2* reveals a linear relationship whose intercepts and slopes are identified with the following rates:

$$k^{H}$$
 vs. X_{D} : $k_{HH} + X_{D} (k_{HD} - k_{HH})$ (7.4)

$$k^{D}$$
 vs. X_{D} : $k_{DH} + X_{D} (k_{DD} - k_{DH})$ (7.5)

From linear regressions to the data³² the following rates are calculated:

$$k_{HH} = 1.97(3) \times 10^{9} \text{ s}^{-1}$$

$$k_{HD} = 0.55(5) \times 10^{9} \text{ s}^{-1}$$

$$k_{DH} = 1.18(1) \times 10^{9} \text{ s}^{-1}$$

$$k_{DD} = 0.38(2) \times 10^{9} \text{ s}^{-1}.$$
(7.6)

To confirm that the observed rates may be interpreted as reaction rates (*i.e.*, to confirm that the observed rates were not contaminated by the normal deactivation rate

 k^{N}), the mean proton-transfer rates were calculated using the irreversible protontransfer scheme (Chapter 3) which predicts

$$\mathbf{k}_{\mathrm{PT}} = \frac{\mathbf{k}_{\mathrm{rad}}^{\mathrm{N}} \mathbf{j}^{\mathrm{T}}}{\mathbf{k}_{\mathrm{rad}}^{\mathrm{T}} \mathbf{j}^{\mathrm{N}}} \mathbf{k}^{\mathrm{T}}.$$
 (7.7)

The ratio of radiative rates is nearly independent of solvent (7.4 for 1AC in methanol in particular), the ratios of quantum yields may be extracted from normalized steady-state emission spectra, and the tautomer deactivation rates are obtained from the rise times of the 1AC tautomer emission. The results demonstrate that the mean rates extracted from the normal and tautomer regions are within 10% agreement, which is less than the uncertainty inherent in the tautomer rise times.

7.4.2 Interpreting the Rates: Rule of the Geometric Mean

The rates for the four possible combinations of reacting species may provide insight into the pathway of the reaction. A kinetic model that tests the concerted nature of the two-proton switch leading to the formation of the excited-state tautomer has been studied.²⁰⁻²⁷ For each combination of hydrogen or deuterium atoms at the two sites L and L', the scheme appears as follows with emphasis on the postulated cyclic form (*Scheme 7.2*):



Scheme 7.2

Based on this scheme (Scheme 7.2), Petrich and coworkers²⁷ like Limbach and coworkers²⁰⁻²⁶ have derived the relationships necessary for the double-proton transfer to be a concerted process. Two conditions must be satisfied for a concerted reaction:²⁷ (1) If the reaction involves the stepwise transfer of the two protons, then an intermediate (Γ or I⁺) will be formed during tautomerization. When the populations of the postulated short-lived intermediates (Γ and I⁺) form the N and T species at equal rates ($k(I \rightarrow N) = k_{I-N} = k_{I-T}$ and $k_{I+N} = k_{I+T}$), then the reaction occurs in one kinetic step (a concerted reaction). (2) All isotope effects associated with the solute and solvent must be equal. Only when these conditions are met will the measured rates k_{HH} , k_{HD} , k_{DH} , and k_{DD} satisfy the "rule of the geometric mean":^{27,33} $k_{HD} = k_{DH} = (k_{HH} k_{DD})^{1/2}$.

Further explanation of the "rule of the geometric mean" is warranted here. In a concerted reaction, we expect that the isotope effects should be independent at each of the reactive sites. That is, if both protons are "in flight" in the transition state, one expects the isotope effects of the multiple sites in the single transition state to be independent.²⁷ When kinetic isotope effects fail to meet this expectation, the observation

is mechanistically significant.^{9,34} For the solvent-catalyzed, double-proton-transfer reaction of 1AC we must examine the independence of the isotope effects corresponding to the two protons exchanged in the reaction. Ratios of the four extracted rates may be formed to pursue this goal, where the rates are designated $k_{(L \text{ on } 1AC)(L' \text{ on } methanol)}$. The isotope effect for L' is indeed independent of the hydrogen or deuterium atom L originally bonded to 1AC:

$$\frac{k_{HD}}{k_{HH}} = 0.28(3) \approx \frac{k_{DD}}{k_{DH}} = 0.32(2) \tag{7.8}$$

It is much less clear, however, that the isotope effect for L on 1AC is independent of methanol's L':

$$\frac{k_{DH}}{k_{HH}} = 0.60(1) \longleftrightarrow \frac{k_{DD}}{k_{HD}} = 0.69(7)$$
(7.9)

In these comparisons, the relative uncertainties of the ratios were estimated from the relative errors of the rates added in quadrature. In a generous interpretation we may conclude that the isotope effects are indeed independent at each reactive site.

The second condition that the rate constants should satisfy for a confident interpretation of a concerted reaction is that the solute and solvent isotope effects must be equal.²⁷ For site-independent isotope effects, this constraint leads to the equalities $k_{HD} = k_{DH} = (k_{HH} k_{DD})^{\frac{1}{2}}$ which indeed have the form of a geometric mean. The idea is that if the isotope effects are not identical, then the rate of transfer of one proton may differ from that of the other proton and thus the reaction may be more consistent with a stepwise transfer. In practice, the breakdown of this geometric mean is interpreted as evidence for either tunneling (in either a concerted or stepwise reaction) or a stepwise reaction.^{22,27,34} The measured rates for 1AC in the methanol/methanol-OD mixtures clearly suggest that the primary isotope effects are different. The solute isotope effect is approximately

$$\frac{k_{HL'}}{k_{DL'}} \sim 1.6$$
 (7.10)

and the solvent isotope effect is approximately

$$\frac{k_{LH}}{k_{LD}} \sim 3.3.$$
 (7.11)

These observations indicate that a concerted double proton transfer is not obviously the reaction mechanism.

One final comment about this analysis should be highlighted. If the observed reaction rates indeed may be decomposed into two terms – one for solvent effects and one for the actual proton transfer – then the ratios of observed rates are expected to be largely independent of the solvent effects terms. That is, the isotope effects reported in this section may be attributed directly to the intrinsic proton-transfer step.

7.4.3 Interpreting the Rates: Tunneling and Stepwise Double Proton Transfer

While the "rule of the geometric mean" is one criterion expected be satisfied for a concerted reaction, its failure does not indicate that the reaction is not concerted. Subsequently, two alternatives must be considered: tunneling may be involved in the transfer, or the reaction may involve a stepwise transfer of the two protons.

7.4.3.1 Tunneling

While tunneling may be a feature of proton or hydrogen transfer reactions even at room temperature,^{9,35-37} direct experimental detection of this quantum mechanical phenomenon in solution is often difficult. Indicators for tunneling include the breakdown of the rule of the geometric mean or other exponential relationships involving isotope effects, or the observation of nonlinear temperature dependence of isotope effects in Arrhenius plots.^{34,38-40} For example, a recent study of the ground-state intermolecular proton transfer (prototropic equilibria) of 7-hydroxyquinoline provides an illustration of affirmative experimental indicators for tunneling.⁴¹

In the case of 1AC, we have noted the breakdown of the rule of the geometric mean. And as noted earlier, the unusual temperature independence of the kinetic isotope effect does suggest proton tunneling. (The postulated reaction mechanism involves two steps: solvent fluctuations lead to a state from which tunneling occurs. Examining the temperature dependence of the (cumulative) observed rate constants on Arrhenius plots is not helpful since the rate constants corresponding to the elementary reaction involving the proton transfer have not been isolated.) Other observations of temperature-independent kinetic isotope effects have also been interpreted as reactions involving proton tunneling.⁴²⁻⁴⁵

The issue of proton tunneling has been considered by Limbach and coworkers in their careful examinations of double proton-transfer reactions in a number of well-defined, cyclically hydrogen-bonded systems.^{20-26,46} *Table 7.3* summarizes some of their work emphasizing the relationship between the experimental indicators for tunneling

noted above and the mechanism of proton transfer deduced from each NMR study. Their case studies of intermolecular proton transfer are good examples for comparison to the excited-state proton-transfer in systems involving 7AI and 1AC, and they highlight the difficulty in distinguishing a tunneling reaction from a stepwise transfer.

7.4.3.2 Stepwise Proton Transfer

To attribute the double-proton-transfer reaction of 1AC conclusively as a stepwise transfer, kinetic models must be examined for which the predictions are valid whether or not tunneling is present. For example, in a double-proton-transfer reaction in a *symmetric* complex, specific relationships among the observed rates have been derived that will indicate a stepwise reaction.^{21,22,27,47} These are valid for reactions over a barrier or for reactions proceeding through tunneling.²² Because of the symmetry of the reaction, the rate constants k_{HD} and k_{DH} are equal, and this is a necessary assumption of the derivations. The reaction of 1AC in alcohols is not symmetric, so the results of this particular example are not applicable to the 1AC reaction catalyzed by methanol. Further work with such kinetic models for consecutive stepwise proton transfers have not been fruitful.

Strong experimental evidence for stepwise double-proton transfer for 1AC in methanol is currently wanting. A consecutive, stepwise proton-transfer mechanism illustrated in *Scheme 7.3* suggests the presence of an intermediate before the tautomer species is finally formed.



Scheme 7.3

Biexponential decays have been reported for the excited-state proton transfer in 7AI dimers.^{55,57,58,66,67} These observations with subpicosecond time resolution have been interpreted to indicate the presence of an intermediate.⁵⁵⁻⁶⁴ (As discussed in Section 7.6, others have also offered different interpretations of the biexponential decays.) The time resolution of the time-correlated single-photon counting experiment used in the study of 1AC in mixed methanol solvents, however, is inadequate for revealing the possible presence of such an intermediate.

7.5 Discussion: Isotope Effects

The magnitude and temperature dependence of the kinetic isotope effects for 7AI and 1AC summarized in *Table 7.1* have already been discussed. Two final observations follow from this data. (1) The connection between the magnitude of primary isotope effects and the structure of the transition state has already entertained much discussion.^{39,48,49} Earlier work on proton dissociation reactions noted that the kinetic isotope effect is often *not* constant but depends on the relative activation energy in the transition state as determined by surrogate measures such as rate or equilibrium

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constants.^{39,50-52} The estimated isotope effect for the ultrafast proton-transfer in 1AC:acetic acid complexes in methylcyclohexane is smaller (~2) than the observed KIE for the slower reaction in bulk alcohols (~5). If these differences are indeed real, then they provide evidence for the structure of the transition state, with the 1AC:acetic acid system having a more reactant-like transition state.

(2) Since the functional groups of 7AI and 1AC involved in the excited-state proton-transfer are the same, equal isotope effects for the two molecules in the same solvent might be expected. Interestingly, the isotope effects for 7AI and 1AC differ significantly in the alcohols. Although the source of this difference is currently unknown, future modeling of these isotope effects should provide additional insight into the nature of the excited-state reactions involving 7AI and 1AC.

The "proton inventory" experiments for 7AI in alcohols by Petrich and coworkers are consistent with a concerted reaction mechanism.²⁷ They concluded, however, that this reaction in water is qualitatively different than in bulk alcohols.²⁷ Note that the magnitude of the kinetic isotope effects reveals nothing obviously distinctive about the reaction of 7AI in water compared to 7AI in alcohols. In a similar comparison, the observed KIE for 1AC reactions in water and ethylene glycol are different than those for the bulk alcohols. Yet this thesis and other researchers⁵³ have argued that the 1AC reactions in water and ethylene glycol are not qualitatively different than those in bulk (primary) alcohols. This juxtaposition is a reminder that some caution is required in the interpretation of isotope effects.

7.6 Discussion: Stepwise or Concerted Reaction?

The observed rates of 1AC in the mixed solvent system methanol/methanol-OD, do not clearly support either a concerted or stepwise reaction mechanism. Since this experiment was completed, a number of papers have been published in support of either a stepwise or concerted reaction. The discussion has been intense.

Evidence for interpretation of a stepwise transfer has been reported by Hochstrasser and coworkers,⁵⁴ Zewail, Douhal and coworkers,⁵⁵⁻⁶¹ and Castleman and coworkers⁶²⁻⁶³⁶⁴ for the excited-state proton-transfer reaction in 7AI dimers in nonpolar solvents and in molecular beams. The photoelectron spectroscopy experiments of Lopez-Martens *et al.* are also taken as evidence for stepwise transfer.⁶⁵ On the other hand, Catalán, del Valle, and Kasha⁶⁹⁻⁷² and Takeuchi and Tahara^{66,67} argue that the double proton transfer reaction in 7AI dimers is a concerted reaction. Although these groups of researchers have already discussed the experimental evidence and its interpretations, a few observations are worthwhile to summarize here.

(1) Catalán, del Valle, and Kasha base their argument for a concerted reaction in gas-phase 7AI dimers on symmetry:⁶⁹

The lower state $(S_{1a}, 2A_g)$ in the C_{2h} geometry of the centro-symmetric planar H-bonded dimer is strictly electric-dipole forbidden for photon absorption from the ground state $(S_0, 1A_g)$. The upper exciton split level is S_{1b} , B_u and is allowed as an electric-dipole photon absorption. The key observations on the reality of molecular exciton states were the definitive observation by Fuke *et al.* ...that, indeed, there is a two-photon allowed $1A_g \rightarrow 2A_g$ ($S_0 \rightarrow S_{1a}$) electronic excitation in 7-AI H-bonded dimer (supercooled molecular beam), followed at slightly higher energy by a one-photon-allowed $1A_g \rightarrow 1B_u$ ($S_0 \rightarrow S_{1b}$) electronic excitation.

...As a consequence, all wave functions must be centro-symmetric for the dimer, and the driving force for concerted PT likewise should be centro-

symmetric. This observation of a biphotonic absorption is the spectroscopic basis for a concerted biphotonic mechanism in the photo-excited 7-AI H-bonded dimer.

Douhal *et al.* have discussed the limitations of this argument and "emphatically contradict" their conclusions.⁵⁹ The lack of symmetry in the tautomerization reaction of 1AC in alcohols, diols, or water prevents the application of such an argument to the solvent-catalyzed reactions.

(2) An ultrafast biexponential decay in the fluorescence of reacting 7AI dimers in solution could indicate a stepwise reaction. Takeuchi and Tahara have observed such emission with subpicosecond resolution, but they have attributed the first quick lifetime (~200 fs) to internal conversion (${}^{1}L_{b} \rightarrow {}^{1}L_{a}$ transition) and the second 1.1 ps lifetime to the concerted proton transfer reaction.^{66,67} In a red-edge excitation experiment, the biexponential decays with blue excitation become single-exponential decays following excitation near the 0-0 transition. Takeuchi and Tahara explain that red-edge excitation selectively populates ${}^{1}L_{a}$ state so that the ~200 fs lifetime in the biexponential decay vanishes.⁶⁷ In the fluorescence upconversion experiments of Fiebig *et al.*, red-edge excitation at 310 nm (cf. the 313 nm excitation in Takeuchi and Tahara's experiment) also produces decays with one lifetime (~1 ps) that could be attributed to the reaction (the effective rate of formation of the tautomer).⁵⁸ However, Fiebig *et al.* declare the reaction to be stepwise based on transient absorption measurements following red-edge pump excitation (320 nm) which reveal biexponential character.⁵⁸ Fiebig *et al.* provide a summary of the interpretations of the observed rates. Near the 0-0 transition, the stepwise reaction $N \rightarrow I \rightarrow T^{\text{excited}}$ is observed with $k_1 \sim 200 \text{ fs}^{-1}$ and $k_2 \sim 1 \text{ ps}^{-1}$. The

relaxation of T^{excited} takes place within tens of picoseconds. The nanosecond background in the femtosecond-resolution experiments is due to the vibrationally-cold tautomer population decaying with lifetime 3.2 ns.⁵⁸

Excitation away from the red-edge of the absorption band may provide excess energy above the reaction barrier so that the normal forms the vibrationally-excited tautomer species directly ($N \rightarrow T^{\text{excited}}$).⁵⁸ Only when the internal energy is low, however, can one examine the processes of tunneling and concertedness.⁵⁸ And in the solution phase, the coupling of solvation dynamics to the symmetric and antisymmetric vibrational motion (N—H^{...}N) of the dimer must also be considered for the excited-state double-proton transfer reaction.⁵⁸ Thus the red-edge excitation is only selecting a special and appropriate subset of the dimers in solution for study, and the interpretation of the stepwise reaction depends on the experimental conditions.

(3) Two recent computer simulations of the excited-state reactions of 7AI dimers and 7AI:water complexes have indicated that a stepwise mechanism is most likely. Guallar *et al.* have used a semiclassical molecular dynamics simulation to show that in the isolated 7AI dimer the stepwise transfer is lower in energy than the route for the concerted transfer.⁶⁸ In this simulation, the intermediate is mostly covalent in character.⁶⁸ That is, the intermediate is not zwitterionic because an electron transfer accompanies the first proton-transfer. This work also indicates that the initial excitation is localized on one of the monomer sites.⁶⁸ In a different dynamics calculation, Fernandez-Ramos *et al.* learned that the tautomerization reaction of 7AI in aqueous solution likely requires the participation of two water molecules.⁷³ Their best estimate is that the reaction is stepwise with one-proton tunneling occurring in the rate-determining first step.⁷³

7.7 Conclusion

Study of the excited-state proton-transfer reaction of 1AC in series of mixed methanol/methanol-OD solutions has afforded some insight into the mechanism of the reaction. The isotope effects at each of the reactive sites in 1AC appear to be independent of each other, although the magnitude of the isotope effects at each site are different. The KIE associated with the solute (1AC) is about 1.6, and the KIE associated with the solvent (MeOL, L = H or D) is about 3.3. Because the rates extracted from the experiment do not satisfy the "rule of the geometric mean," the reaction does not obviously involve the concerted motion of both protons. This failure may indicate the presence of tunneling (in a concerted or a stepwise reaction) or of a stepwise reaction. The temperature dependence of the KIE does suggest that proton tunneling is present in the reaction. The data are unable to affirm, however, either a (tunneling) concerted or stepwise reaction mechanism. Several published studies do suggest that a stepwise reaction mechanism may be preferred to describe the excited-state tautomerization reaction of 7AI (and thus 1AC presumably as well).

Table 7.1: Summary of Isotope Effects for 7AI and 1AC

| System | Solvent | KIE: Reaction Rate | KIE: Tautomer | Reference |
|------------------------------|-------------------|--------------------|---------------|-----------|
| | | (Normal) | Deactivation | |
| 7AI | Alcohols | 2.9 ± 0.6 | 1.3 ± 0.1 | 1, 3 |
| 7AI | Ethylene Glycol | 2 ± 0.1 | 1.4 ± 0.1 | 3,7 |
| 7AI | Water | 3.7, 3.4 | 2 ± 1 | 1, 2 |
| 7AI Dimers | Hexadecane | 2.9 | | 6 |
| 7AI Dimers | Nonpolar solvents | 4.5 N, "direct" | | 5 |
| | _ | 1.4 T, "rise" | | 5 |
| | | | | |
| 1AC | Alcohols | 4.9 ± 0.3 | 1.6 ± 0.2 | 4 |
| 1AC | Methanol | IE(solvent) = 3.4 | | 7 |
| | | IE(solute) = 1.6 | | 7 |
| 1AC | Ethylene Glycol | 3.0 | 1.4 | 7 |
| 1AC | Water | 3.2 | * | 7 |
| 1AC:Acetic Acid Complexes | Methylcyclohexane | ~2 * | 1.6 | 7 |

* This is the best estimate for the isotope effect. The rates were not measured directly due to limited time resolution of the experiment.

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| τ ₂ =k ^D) ⁹ s ⁻¹ |
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| .995 |
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| 622 |
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| .573 |
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| .478 |
| 000 |
| .399 |
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| |

Table 7.2: Determination of Rate Constants for 1AC in Methanol / Methanol-OD Mixtures

| System | Type of | Rule of the | Arrhenius Plots | Concluded | Reference |
|---------------------------------|----------|-------------|----------------------------|-------------------|-----------|
| | transfer | Geometric | | Mechanism | |
| | | Mean? | | | |
| Bis (p-fluorophenyl)formaminide | inter | Yes | observed linear; | concerted, or | 1 |
| dimers | | | IE temperature dependent | stepwise with | |
| | | | | compressed H- | |
| | | | | bonds | |
| Acetic Acid + Methanol in THF, | inter | No | observed linear; | intermolecular | 2 |
| 1:1 | | | IE temperature dependent | tunneling | |
| Acetic Acid + Methanol in THF, | inter | Yes | observed linear; | intermolecular | 2 |
| 2:1 | | | IE temperature independent | tunneling | |
| Azophenine | intra | No | observed linear; | stepwise transfer | 3 |
| | | | IE temperature independent | _ | |
| Oxalamidines | intra | No | observed linear; | stepwise transfer | 4 |
| | | | IE temperature independent | | |
| Porphyrin | intra | No | observed linear, | stepwise transfer | 5 |
| | | | except at very low | | |
| | | | temperature; | | |
| | | | IE temperature dependent | | |
| Acetylporphyrin | intra | No | observed linear; | stepwise transfer | 6 |
| | | | IE temperature dependent | | |
| meso-Tetraphenylprophyrin | intra | No | observed nonlinear; | stepwise transfer | 7 |
| | | | IE temperature dependent | - | |

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Figure 7.1: Time-Resolved Emission Spectra of PPO in Methanol and 1AC in Methanol/Methanol-OD Mixtures

Top Spectrum: PPO in dilute methanol solution decays with a single-exponential lifetime of 1.52 ns ($\chi^2 = 1.06$). This fluorescence standard provides a convenient means for confirming the time calibration and linearity of the photon-counting spectrometer.

linearity of the photon-counting spectrometer. **Bottom Spectrum:** 1AC in 75:25 MeOH:MeOD Mixture. One lifetime is inadequate for fitting the emission decay (upper panel of residuals: $\chi^2 = 1.48$), but the residuals in the lower panel indicate a good fit with two lifetimes ($\chi^2 = 1.08$).



Figure 7.2: Reaction Rates of 1AC in Methanol/Methanol-OD Mixtures

These plots exhibit the linear dependence of the extracted rates with the solvent composition as predicted by the model discussed in Chapter 7. The different symbols represent independent measurements made for each solvent mixture, and the lines are least-squares fits to mean rates.

ENDNOTES

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Chapter 8

EXPERIMENTAL PROCEDURES

8.1 Introduction

The excited-state proton-transfer reaction of 1AC was studied here using steadystate absorption and emission spectroscopy and time-correlated single-photon counting techniques. Experimental details are gathered in this chapter.

8.2 Reagents

1AC was synthesized following the recipe of Stephenson and Warburton.¹ The complexing agents used in the isolated complexes experiment were purchased from the Aldrich Chemical Company and were used as received: acetamide [99+%], acetic acid (AA) [99.7+%, ACS reagent grade], deuterated acetic acid (AA-D) [98 atom % D], benzamide [99.5+%, sublimed], 2-cyanoacetamide [99%], 3,4,5,6,7,8-hexahydro-2(1H)-quinoline (HHQ) [97%], methylcyclohexane [99%, spectrophotometric grade], N-methylformamide [99%], 2,3,4,5,6-pentafluorobenzamide [99%], succinimide [98%], 2,2,2-trifluoroacetamide [97%], and δ-valerolactam (δ-VL) [99%]. N-methylformamide was either used as received or distilled under nitrogen. Dry methylcyclohexane for the

complexation studies was prepared by refluxing for 30 minutes over calcium hydride followed by distillation under nitrogen.

Most reagents for the bulk protic solvent work were also used as obtained from Aldrich Chemical Company: (anhydrous) benzyl alcohol [99+%], deuterium oxide [99.9 atom % D], ethylene glycol [99+%, spectrophotometric grade], ethylene glycol-D2 [98 atom % D], formamide [99+%, spectrophotometric grade], methanol [99.9%, HPLC grade], methanol-OD [99.5+ atom % D], 1-pentanol [99+%; stored over molecular sieves], 1-propanol [99.5%, HPLC grade], 2-propanol [99.5%, HPLC grade], 1,2-propanediol [99.5+%, ACS reagent grade] and 2,2,2-trifluoroethanol [99+%]. The t-butanol was from Mallinckrodt. Ultrapure water [18 M Ω .cm] or distilled water $[\sim 0.5 \text{ M}\Omega.\text{cm}]$ was found to yield similar results. N-methylformamide and benzyl alcohol were either used as received or distilled under nitrogen. 2,2,2-Trifluoroethanol was distilled under nitrogen immediately prior to use. The aprotic solvents N,N-dimethylformamide (DMF) [99.9%, HPLC grade] and methylcyclohexane [99%, spectrophotometric grade] were from Aldrich Chemical Company. The DMF was distilled once under nitrogen. The aprotic solvents used in experiments were typically high quality solvents from Aldrich Chemical Company, and unless noted, were used as received without special drying procedures.

8.3 Instruments: Steady-State and Time-Resolved Spectrometers

Absorption spectra were recorded on a Hitachi U-3000 spectrophotometer with 1 nm resolution, and steady-state fluorescence measurements were made with 2 nm resolution on a Spex 212E Fluorolog corrected for instrument response.² Timecorrelated single-photon counting was used to measure the time-resolved fluorescence emission.^{3,4} This spectrometer has been described earlier.⁵⁻⁷ Very briefly, picosecond light pulses (8-12 ps, 3.8 MHz, ~10 nJ / pulse) of wavelength 580-700 nm are generated by a cavity-dumped dye laser (modified Coherent 599) that is synchronously-pumped by the doubled output of a mode-locked Nd:YAG laser (Coherent Anteres 76). Most of the visible red light is frequency doubled to provide suitable UV excitation with vertical polarization, and it is focused into the sample cuvette maintained at constant temperature. Fluorescence emission is collected at a right angle, is passed through a polarizer set at the magic angle, and is focused onto the entrance slit of a 0.25-m single monochromator (Instruments SA, Inc., Model H-10). A Hamamatsu 3908U 6-µm MCP-PMT detects the fluorescence photons, and its amplified (Philips 6954-S100) and conditioned (Tennelec 454 Constant Fraction Discriminator, modified) signal provides the start pulse for the time-to-amplitude converter (Tennelec 864 TAC / Biased Amp). A portion of the visible red light from the dye laser is split to trigger a fast photodiode (Optoelectronics PD-30) whose conditioned signal (Tennelec 454, modified) is delayed and is used as a stop signal for the TAC. A multichannel analyzer (Oxford Nucleus PCA-II) organizes the TAC signal (<1% start/stop) into a fluorescence decay, which is fit iteratively to deconvolute the instrument response function generated by a scattering solution of non-dairy creamer in water (absorbance < 0.1). The fitting algorithm employed here is "upcvfit".⁸ Good fits satisfied the statistical test $c^2 < 1.2$ and displayed no significant ripples in the residuals.

For the experiments reported here, the spectrometer was operated with the following improvements. To minimize the dead-time of the time-to-amplitude converter [TAC] and thereby increase data acquisition rates, the experiment was run in the "reverse mode"³: the start signal for the TAC was provided by first fluorescence photon detected by a Hamamatsu 3908U MCP-PMT with Philips 6954-S100 preamplifier for the CFD, and the stop signal for the TAC was generated by an Optoelectronics PD-30 fast photodiode monitoring a portion of the cavity-dumped laser output. The 0.25-m singlemonochromator (Instruments SA, Inc., Model H-10) with 2 mm slits allowed bandpass of 20 nm. Fluorescence decays were recorded over time ranges of 7 ns [3.51 ps/channel], 14 ns [6.72 ps/channel], or 27 ns [13.33 ps/channel] selected to best capture the emission decay. The instrument response of the spectrometer is 50-60 ps (FWHM) on the shortest time base, providing lifetime resolution of 25-30 ps.⁹ The measured lifetime of a dilute solution of 2,5-diphenyloxazole [PPO] in methanol at 298 K is 1.52 ns and singleexponential, in acceptable agreement with 1.4 ± 0.2 ns¹⁰ and 1.61 ± 0.02 ns¹¹ noted for this reference compound in ethanol. The absolute uncertainty in the measured fluorescence lifetimes is 10%, although the precision of the experiment is better than 5%.

8.4 Sample Preparation

The dilute 1AC:complex solutions were prepared in a glovebag that was evacuated twice before the final nitrogen fill to ensure satisfactory removal of oxygen and moisture. All glassware, cuvettes, and pipette-capillary tubes were baked at 120 °C for several hours prior to use. This precaution was an especially important procedure in the formation of 1AC:AA-D. The nonpolar alkane solvent methylcyclohexane was chosen for this work to maximize the driving force for complex formation by minimizing extraneous interactions between the complexing agents and solvent.¹² Dilute solutions containing <18 μ M 1AC showed little tautomer emission from dimers prior to the addition of the complexing agents. Time-resolved tautomer emission from dimers was measured at higher concentrations [> 60 μ M] of 1AC in methylcyclohexane.

The preparation of 1AC complexes with deuterated acetic acid required considerable care since absorbed moisture on the surfaces of unbaked glassware, cuvettes, and pipette-capillary tubes was noted to reduce the observed kinetic isotope effect.¹³ Neat deuterated acid was added directly to the 1AC solution in methylcyclohexane to minimize the exchange between the deuterons and protons from contamination.

Complexes of 1AC with the lactams or with acetic acid were created by spectrophotometric titration using 0.02 M lactam stock solutions or neat acetic acid. Because the solid amides are insoluble in methylcyclohexane, these complexes were formed by sonicating a 15 μ M solution of 1AC in methylcyclohexane with excess amide. The remaining insoluble amide was separated in a closed polycarbonate tube spun in a centrifuge (4000 or 20000 r.p.m. for 20 minutes). The liquid amides are also insoluble in methylcyclohexane, and therefore sonication was applied to form a dilute emulsion from a mixture of 5% v/v N-methylformamide in methylcyclohexane. A dilute 1AC solution was then spectrophotometrically titrated with this emulsion. Since the 1AC fluorescence is quenched by oxygen, the samples were prepared in inert environments or were bubbled with nitrogen prior to measurements.

For studies in bulk protic solvents, the 1AC concentrations were less than 30 μ M to keep the absorbance below A=0.15 at the exciting wavelength for emission spectra. Fluorescence emission of 1AC in bulk protic solvents was excited in the region 305-335 nm, and these emission lifetimes were independent of the excitation wavelength. Solutions of 1AC in bulk protic solvents were typically prepared to have a peak absorbance of 0.3-1.0 for the absorbance measurements. Most data for the other bulk protic solvents was measured at least twice.

8.5 Quantum Yield Measurements

Quantum yields were determined with respect to quinine sulfate in 1.0 N $H_2SO_{4(aq)} [\phi_{ref}=0.546]^{14,15}$ or in 0.1 N HClO_{4(aq)} $[\phi_{ref}=0.59]^{15}$ and are estimated to have an uncertainty of ±10%. The quantum yields were calculated using the following expression, which corrects for differences in absorption between the solvents used for the quantum standard (A_{r,sol}) and for the sample (A_{s,sol}):

$$\boldsymbol{j}_{sample} = \boldsymbol{j}_{ref} \cdot \left(\frac{1 - 10^{-A_r}}{1 - 10^{-A_s}}\right) \cdot \left(\frac{1 - 10^{-A_{r,sol}}}{1 - 10^{-A_{s,sol}}}\right) \cdot \left(\frac{\int I_s(\boldsymbol{l}) d\boldsymbol{l}}{\int I_r(\boldsymbol{l}) d\boldsymbol{l}}\right) \cdot \left(\frac{n_s^2}{n_r^2}\right) \cdot (8.1)$$

In this expression, ϕ , A, n denote the quantum yield, absorbance, and index of refraction for the sample (s) and quantum yield reference (r), respectively. The absorbance of the sample and quantum yield standard at the exciting wavelength was measured with respect to their corresponding solvent blanks, while the absorbance of each solvent blank was determined with respect to air. The corrected fluorescence intensity was integrated over the entire emission range to calculate the total quantum yield for the 1AC samples, and the normal and tautomer quantum yields were estimated according to their relative areas in the dual fluorescence. Excitation of the 1AC and quinine sulfate was at 330 nm [bulk protic solvents] or 320 nm [1AC in methylcyclohexane]. Within experimental uncertainty, the quantum yields of 1AC in methylcyclohexane or in water were constant for excitation from the first S_1 or second S_2 absorption bands.¹⁶

Quantum yields of the relative tautomer emission from the complexes were estimated relative to the quantum yield 0.54 for 1AC in methylcyclohexane with 328 nm excitation and the estimated quantum yield 0.0038 for the tautomer emission of 1AC:acetamide with 328 nm or 348 nm excitation and assuming a complete reaction.

8.6 Fluorescence Measurements

8.6.1 1AC Complex Study

The 1AC complexes were excited on the red-edge of the first absorption band [348 nm] to excite fluorescence selectively from complexed species. Normal emission was monitored at 430-440 nm to avoid contributions from Raman scattering. Tautomer emission was recorded at 550-560 nm, which prevented contamination from the tail of

the normal emission.¹⁷ Solvent blanks were examined for fluorescent impurities. Values reported for the decay characteristics of most of the complexes discussed here represent an average of two or three independent measurements. (The 1AC:NMF emulsion experiment was completed once. A second experiment was attempted but failed due to difficulty in controlling the composition of the emulsion. The results of the first experiment are presented as interesting observations, but this an example of the difficulty in controlling the composition of hydrogen-bonded liquids in nonpolar alkane solvents.) The absorption and fluorescence emission were measured at room temperature, 295±2 K, and the fluorescence lifetimes were typically determined at 298 K.

8.6.2 Temperature Studies of 1AC in Diols, Benzyl Alcohol, Water and Amides

The temperature dependence of the 1AC reaction rate was examined in ethylene glycol and ethylene glycol-D₂ (EG; 1,2-ethanediol, m.p. -13 °C); propylene glycol (PG; 1,2-propanediol, m.p. -60 °C); benzyl alcohol (BzOH; m.p. -15 °C); water and deuterium oxide (m.p. 0 °C); and the amides formamide (FA; m.p. 2-3 °C) and N-methylformamide (NMF; m.p. -40 °C). Measurements over the temperature range 1 °C - 70 °C were repeated twice for ethylene glycol and once for the other solvents. The temperature was regulated to ± 0.5 °C by constant-temperature water flowing through a brass sample block. Experiments on 7AI in EG were repeated to provide a base of comparison with earlier results.¹⁷ Fluorescence in the temperature studies was excited at 290 nm for 7AI and 1AC in the diols and water, at 306 nm for 1AC in BzOH, at 328 nm for 1AC in FA, and at 331 nm for 1AC in NMF.

For some of the time-resolved emission in the EG samples, a wider bandpass was used to assist data collection. The sample cuvettes containing the EG samples also employed pieces of black glass to help reduce scatter in the photon-counting experiments. Later experiments found this black glass to be unnecessary. For the steady-state emission measurements in the diols, a Corning O-54 cutoff filter removed the 2nd-order diffraction of the 290 nm excitation while uniformly passing visible light above 340 nm. The deuterated ethylene glycol solvent was acidic which induced some protonation of the 7AI probe, as reflected in the steady-state temperature series. The temperature-dependence of the kinetics in BzOH, water, FA and NMF was measured directly without corrections from steady-state emission spectra.

8.6.3 1AC pH Study

The pH range 1-13 was examined roughly prior to focusing on the acidic-neutral range. Controlling the pH by addition of HCl or NaOH was found to produce unstable readings on VWR (Cat. No. 34100-674) and Beckman Φ 40 pH meters, especially near neutral pH values. Therefore, a ~2 mM buffer solution of MES (4-morpholine-ethanesulfonic acid, pK_a = 6.1) was used in these measurements to stabilize the pH measurements. Time-resolved emission measurements with 306 nm excitation were recorded at wavelengths 370 nm, 400 nm, 480 nm, and 560 nm in the normal and tautomer regions over the range pH=3-8. The experiment was repeated with excitation at the isobestic point at 331 nm to monitor the emission at 400 nm and 480 nm.

8.6.4 1AC in Methanol / Water Solvent Mixtures

Steady-state and time-resolved emission spectra of 1AC were measured in the series of mixtures 100:0, 90:10, 70:30, 50:50, 30:70, 10:90, and 0:100 [methanol:water, by volume]. Emission at 380-410 nm (normal) and 560 nm (tautomer) was monitored following excitation at 290 nm. The reported values represent an average of at least two measurements.

8.6.5 1AC in Methanol / Methanol-OD Solvent Mixtures

The time-resolved emission of normal 1AC in 7 mixtures of methanol and methanol-OD was recorded at 375 nm or 390 nm following excitation at 306 nm or 331 nm using the time-correlated single-photon counting spectrometer described here. The trueness of single-exponential fits and the reproducibility of the experiment were confirmed for independent measurements made over a two month period using the standard PPO in methanol ($\tau = 1.53$ ns at 25 °C). Time-resolved emission was recorded over a 13 ns window (6.72 ps/channel). The mixtures were prepared gravimetrically, and the solutions were saturated with nitrogen prior to fluorescence measurements.

ENDNOTES

¹ (a) L. Stephenson and W. K. Warburton, J. Chem. Soc. C, **1970**, 1355-1364.

(b) The synthesis was completed by S. J. Boryschuk, M.S. Thesis, The Pennsylvania State University, 1993.

² (a) The instrument correction files for the emission and excitation scans (mcorr896.spt, xcor0896.spt) were created by J. A. Gardecki and M. Maroncelli.

(b) Earlier instrument correction files (mcorr991.fin, xcorr991.fin) are discussed in R. S. Fee, Ph. D. Thesis, The Pennsylvania State University, 1994.

³ See, for example, J. R. Lakowicz, Ed., *Topics in Fluorescence Spectroscopy*. *Volume 1: Techniques*. (New York, Plenum Press, 1991).

⁴ A second introduction to TCSPC is G. R. Holtom, *SPIE Vol. 1204: Time-Resolved Laser Spectroscopy in Biochemistry II*, pp. 2-12 (1990).

⁵ C. F. Chapman, R. S. Fee, and M. Maroncelli, J. Phys. Chem., 94, 4929, (1990).

⁶ C. F. Chapman, Ph. D. Thesis, The Pennsylvania State University, 1993.

⁷ R. S. Fee, Ph. D. Thesis, The Pennsylvania State University, 1994.

⁸ This is an unpublished computer program written by M. Maroncelli.

⁹ (a) This resolution corresponds to HWHM of the instrument response function. It was confirmed by the measurements of the reaction in the 1AC: δ -valerolactam hydrogenbonded complex: the decay in the normal region of ~30 ps was resolved as a rise time of ~30 ps in the tautomer region. Simulations of emission decays using a measured instrument response function reveal that rise times greater than 20 ps and decay times greater than 10 ps may be reasonably resolved. (b) The instrument response of this spectrometer based on a cavity-dumped, single-jet dye laser synchronously pumped by a mode-locked Nd:YAG laser is limited in part by the electronic detection and in part by the width (~8-12 ps) of the excitation pulses. A similar spectrometer exploiting a Ti:Sapphire laser whose pulse widths are shorter (~1-2 ps) operates with an instrument response function of ~25-30 ps FWHM.

¹⁰ J. R. Lakowicz, *Principles of Fluorescence Spectroscopy* (New York, Plenum Press, 1983). pp. 88-89.

¹¹ D. J. S. Birch and R. E. Imhof in *Topics in Fluorescence Spectroscopy, Volume 1: Techniques.* [J. R. Lakowicz, Ed.] (New York, Plenum Press, 1991). p. 54.

¹² J. W. Walmsley, *J. Phys. Chem*, **85**, 3181-3187 (1981). This study on 7AI in several nonpolar solvents provides a discussion of complications with solvents such as benzene and carbon tetrachloride.

¹³ Other researchers have commented on the care required to form deuterated complexes. See, for example, T. Fiebig, M. Chachisvilis, M. Manger, A. H. Zewail, A. Douhl, I. Garcia-Ochoa, A. de La Hoz Ayuso, *J. Phys. Chem. A.*, **103**, 7419-7431 (1999).

¹⁴ J. N. Demas and G. A. Crosby, J. Phys. Chem., 75, 991 (1971).

¹⁵ R. A. Velapoldi and K. D. Mielenz, *NBS Special Publication 260-64*, pp. 50-52. (1980)

¹⁶ These preliminary measurements indicate the photophysical behavior of 1AC may be contrasted with the monophotonic ionization reported for indole and its derivatives. See, for example, F. Gai, R. L. Rich, J. W. Petrich, *J. Am. Chem. Soc.*, **116**, 735 (1994).

¹⁷ R. S. Moog and M. Maroncelli, J. Phys. Chem., **95**, 10359-10369 (1991).

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Overview

Since the excited-state tautomerization reactions of 7-azaindole and 1-azacarbazole are good representatives of intermolecular proton transfer, various aspects of these molecules have been extensively studied. The following bibliography is an effort to acknowledge the substantial body of published studies that consider topics that may be of additional interest to readers. The collection is arranged in alphabetical order based on the surname of the first author.

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VITA

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