

The Pennsylvania State University

The Graduate School

Department of Chemistry

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

A Thesis in

Chemistry

by

Lewis Reynolds

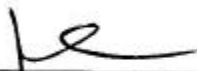
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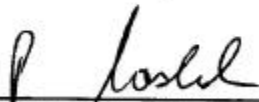
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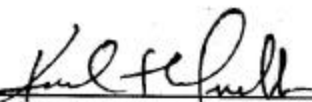
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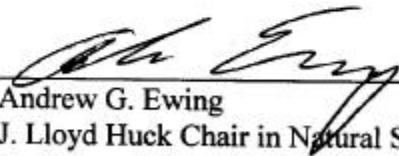
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ABSTRACT

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 $k_{PT} = (1.5 \pm 0.5) \times 10^{12} \text{ s}^{-1}$. Nuncatalytic 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 excited-state 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 nuncatalytic 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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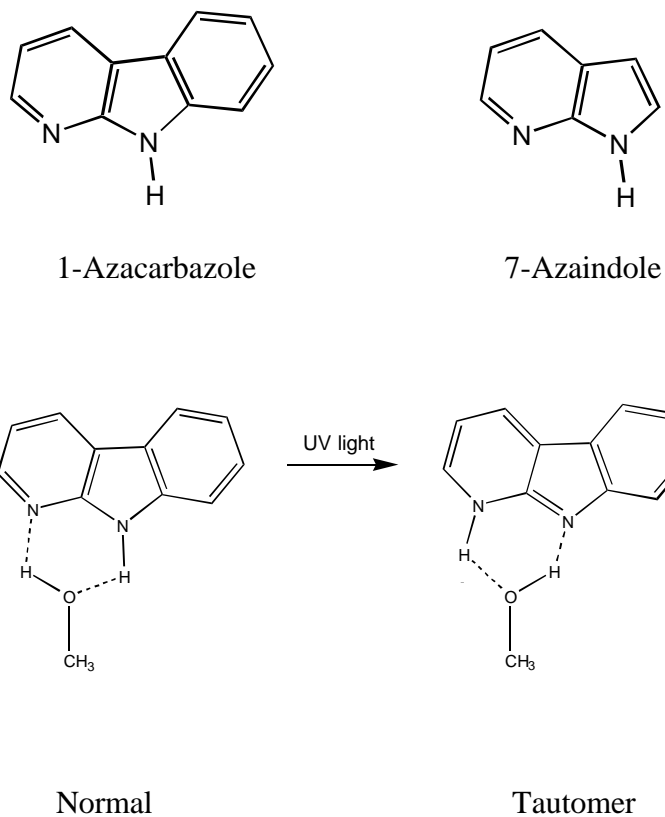
research. The time away from the contents of the dissertation was very helpful, for good progress was made in furthering my understanding of the subject of solvent catalyzed, excited-state proton transfer when unproductive ideas had been left behind.

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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, hydrogen-bonded 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 excited-state 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:

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

The observed rate depends on some function of the intrinsic proton transfer and on some function of the solvent. The decomposition of one rate into two 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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