

Photochemistry Near Zero Kelvin - Quantum Mechanical Tunneling in the Photoenolization of *Ortho*-Alkyl-Arylketones

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Introduction

During the last few years, our group has been interested in taking advantage of the wealth of knowledge on aryl ketone photochemistry with the goal of developing functional solid state materials. We envision the use of robust crystalline solids with tunable photochromic properties and adjustable lifetimes as valuable elements for the construction of optical switches, information storage devices and display elements. To accomplish this, one will need to control the rates and yields of complex photochemical processes in solids, under conditions where molecular freedom is severely limited. It will be necessary to understand how the structure and environment of a solid will affect the rates and efficiencies of reactions, and how to exploit small amplitude motions and even zero point energy vibrations to accomplish desirable chemical transformations. It will also be essential to prepare materials with the required molecular order and environmental properties.

Although there is ample valuable information on the selectivity and feasibility of photochemical reactions in the solid state,^{1,2} structure-reactivity relations based on absolute rate constants remain a major challenge. With that in mind, we have recently analyzed the photoenolization of *ortho*-methyl-arylketones as a test case for the study of photochemical reaction rates in rigid media.³⁻⁶ We have found that properly selected substrates may provide a great deal of information that is valuable not only for a better understanding of solid state reactivity, but also to document and analyze challenging aspects of chemical dynamics. We discovered that the photoenolization of *ortho*-alkyl-arylketones constitutes an ideal system for the study of quantum mechanical tunneling.⁴

Photoenolization

The Norrish type-II reaction of ketones is one of the most interesting and best understood reactions in all of organic photochemistry.⁷ The reaction occurs via an intramolecular hydrogen atom transfer from a γ -carbon to the carbonyl oxygen. The nature of the reactive excited state, its multiplicity, and a variety of experimental variables have been studied in great detail over the last several years.⁷ In the case of *ortho*-alkyl-arylketones, excitation to the singlet state is followed by a rapid intersystem crossing to the triplet manifold ($k_{ISC} \approx 10^{12} \text{ s}^{-1}$). The lifetime of the triplet ketone under normal conditions is limited by a very fast hydrogen transfer reaction ($k_H \approx 10^9 \text{ s}^{-1}$) that dominates the slower decay by phosphorescence and internal conversion ($k_P + k_{IS} \approx 10^3 \text{ s}^{-1}$). The transfer of a hydrogen results in a triplet biradical corresponding to the triplet state of a quinodimethane enol-form ($^3\text{Enol}^*$) and, as shown in Scheme 1, a full cycle is completed by proton transfer to the original ketone (k_H) after the triplet enol intersystem crosses (k_{ISC}) to the ground state.

Interestingly, ground state photoenols absorb in the visible region of the spectrum and have relatively high fluorescence yields. Since their lifetimes depend on whether they are *syn* or *anti*, and on the polarity of the medium, the overall reaction constitutes a potentially useful reversible photochromic system.

From the Executive Director

D.C. Neckers, Executive Director, Center for Photochemical Sciences, Bowling Green State University

A few weeks ago, I came upon some statistics describing the mathematics performance of students enrolled in primary and secondary schools in a rather large geographic section of western New York State, specifically Chautauqua County. It's not coincidental that I should see such reports. Both my wife and I are natives of small towns in Chautauqua County, and we have a vacation home there.

What surprised me was that in many of the grade schools in this area of the U.S., less than 10% of the students were able to demonstrate mathematics mastery at the sixth grade level. In other words, fewer than 1 out of 10 12-year-olds performed "with distinction" in math on an examination that was standardized across the State of New York.

Of course one may choose to view such statistics with a grain of salt. Perhaps the persons collecting the data had an ulterior motive. Perhaps the statistics don't really mean what I think they mean. Perhaps the exams were written for students who go to urban schools rather than rural schools. Perhaps, perhaps, perhaps....

But whatever the excuses, the facts indicate that this group of American children are not very well prepared in math. I also suspect that Chautauqua County, New York, is the rule rather than the exception. For whatever reason, America's schools do not do a good job in preparing America's children in basic mathematics skills.

Poor math backgrounds in the grade schools preclude any potential for a career in the sciences for these young people. From another set of statistical data also from this county, I've been told that more than 50% of all Chautauqua County high school graduates continue their education. The question is what do they study?

Like many American colleges and universities, Bowling Green State University has seen a precipitous decline in the number of chemistry majors over the last decade. Yet, overall University enrollment remains at capacity; the campus is teeming with undergraduates taking courses. The question is what do they study?

It's easy to blame ourselves for the paucity of chemistry majors. Chemistry is hard; chemistry is old; chemistry is dirty, smelly, and dangerous. Chemistry isn't sexy. Chemistry isn't fun. Chemistry isn't computer graphics; that's fun. Chemistry isn't computer programming; that's fun. Chemistry isn't, isn't, isn't....

Perhaps the fault isn't all with chemistry. Perhaps the fault lies with a society that has greatly reduced its expectations of its younger generations. Then what?

What I think I hear from around the United States, and I know I hear at Bowling Green, is that one way to alleviate the lack of undergraduates taking chemistry is to reduce standards. I visited a technical university last week, and the lamenting conversation at lunch was all of their students expect A's and B's. However, the exams that one used to be able to give are just too hard for students in chemistry today. In short, I believe I am hearing that scientists—even scientists—have been trapped into reducing the expectations for university undergraduates in American universities.

American universities may be allowing American primary schools to get away with doing a poor job teaching math. Whom, I guess I must ask, does this serve?

Or, perhaps my observations about math are wrong; perhaps my assumptions about how universities have behaved as a result are wrong. Perhaps, perhaps, perhaps,

The fact remains, however, that many graduate schools in chemistry in America have more international students than Americans; the Americans just aren't there. Perhaps Americans should send selective grade school children to other countries to learn of their culture, and while they are at it, develop basic skills in mathematics.

Perhaps, perhaps, perhaps,

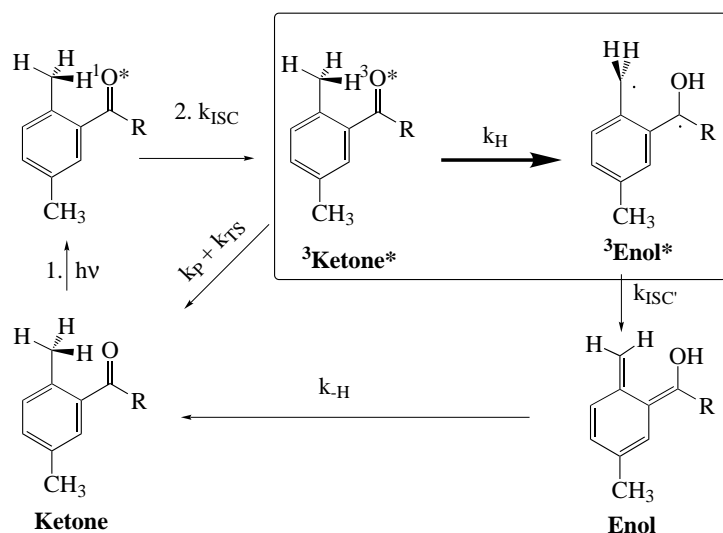
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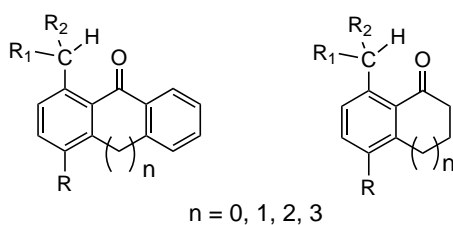
Structure-Reactivity Correlations

The main limitation to chemical reactions in the solid state is the lack of diffusion, rotation and conformational motions. If conformational restrictions prevent the substrate from exploring many structural alternatives, reactions



will require a strong structural similarity between reactant, transition state and final product. It is expected that most reactions will not occur in the solid state simply because no reactive conformers are kinetically accessible. In our group, we circumvent this limitation by studying rigid structures that position the transferring hydrogen and the carbonyl oxygen within close proximity of one another. Among these, *ortho*-substituted dibenzocycloalkanones and benzocycloalkanones of varying size ($n=0-3$) modify the dihedral angle between the planes of the aryl ring and the carbonyl oxygen. These changes affect the distance and orientation at the reactive center in relatively large increments (Scheme 2). More subtle structural variations can be accomplished by changing the nature of R_1 , R_2 and more remote substituents such as R . Our studies have included amorphous glasses, crystalline solids and polymer matrices. Scheffer suggested that

the feasibility of hydrogen transfer in the solid state should depend on the distance and orientation between the breaking $C-H$ bond and the singly occupied n -orbital in the ${}^3n,\pi^*$ carbonyl acceptor ($\cdot O=C$).⁸ Although we propose that a similar relationship should exist between reaction rates and structure, systematic structure-reactivity correlations in solids have been challenging. Some limitations come from the lack of models that relate structural and kinetic results, and some from the experimental challenges in the determination of absolute rate constants in solids. To address the first issue, we start from a simple representation of the reaction surface as a double well potential. The double well picture assumes that at a first approximation the extent of reaction can be represented by defining the position of the transferring hydrogen atom. The left portion represents the $C-H$ vibration in the triplet ketone while the right one corresponds to the $H-O$ vibration in the triplet enol product. As is illustrated for two different *ortho*-methyl-benzocycloalkanones in Scheme 3, this simplified reaction coordinate



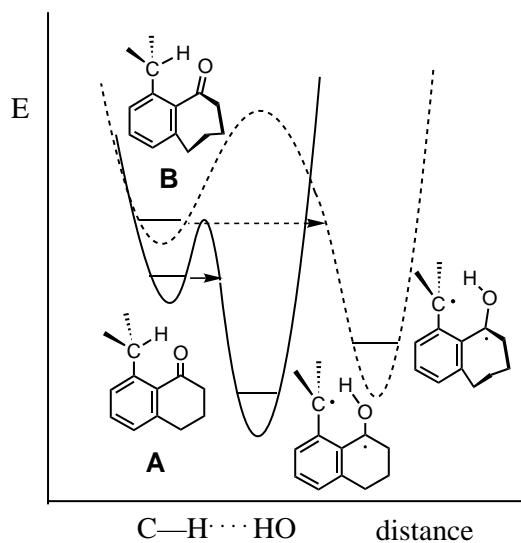
depends largely on the location of the heavy atoms C and O which are directly involved in the reaction. Compounds having the C -donor close to the carbonyl O -acceptor will give rise to reaction barriers that are small and narrow (Scheme 3, compound A). In contrast, compounds having a long distance between the two heavy atoms will give rise to reaction barriers that are high and wide (compound B). Although a double well model in Scheme 3 implies that the heavy atoms remain locked in place while the hydrogen displaces from reactant to product, a more accurate model will

include conformational motions and vibrational modes that alter the distance between the two reaction wells. The qualitative model suggest that some compounds may react with very little or no conformational motion. This is an important requirement for the reaction to occur in the solid state. The model also suggests a systematic approach to modifying the height and the width of the barrier, which is predicted to modulate the probability of a quantum mechanical tunneling reaction. Distances and orientations may be available from X-ray diffraction analysis in the case of the ground state reactant, and from computational methodologies in the case of the triplet excited states.

To determine the effect of structure and environment on the reaction coordinate, one needs information on the rate of the reaction as a function of temperature over a wide range. Activation energies and pre-exponential factors determined from Arrhenius plots reflect the energy and entropy of the transition state. Primary and secondary isotope effects are related to the extent of bonding at the transition state. And more interestingly, the occurrence of quantum mechanical tunneling gives information on the dynamics of the reactant and the product since it depends on the height and the width of the barrier separating one from the other.

Isotope Effects

Kinetic isotope effects result from the difference in zero point energies of the breaking C—H and C—D bonds and, as shown in Scheme 4, are expected to be exponentially dependent on temperature.⁹ Although intuitive isotope effects of $k_H/k_D \sim 7$ at ambient temperatures may reach values of $\sim 10^3$ at 77K and $>10^{10}$ at 20K, at lower temperatures the rate of reaction decreases. While ground state reactions may occur in days or months, the quantum yields of excited state reactions approach zero as temperature-independent decay pathways take over the consumption of the excited state. *It is expected that kinetic isotope effects of activated photochemical reactions should increase and then disappear as the temperature is decreased!*⁴

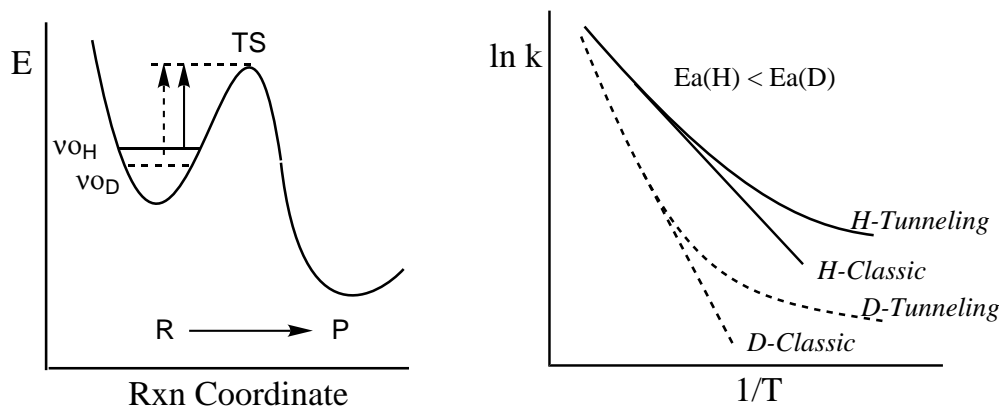


Scheme 3

Quantum Mechanical Tunneling^{9,10}

Experimentally, quantum mechanical tunneling is detected in terms of anomalous isotope effects (e.g., $k_H/k_D \gg 7$ at ambient temperatures) or in terms of deviations from the expected Arrhenius behavior. The name tunneling implies that the reactants may “tunnel” through the classical potential to reach the products without the thermal energy necessary to go over the barrier. Quantum mechanical tunneling originates from the fact that the location of the tunneling particle cannot be accurately represented by a classical potential. The wave function describing the location of the tunneling particle does not vanish at the turning points but it permeates through the barrier with a probability that is inversely proportional to its *mass* and to the *height* and *width* of the barrier.¹⁰

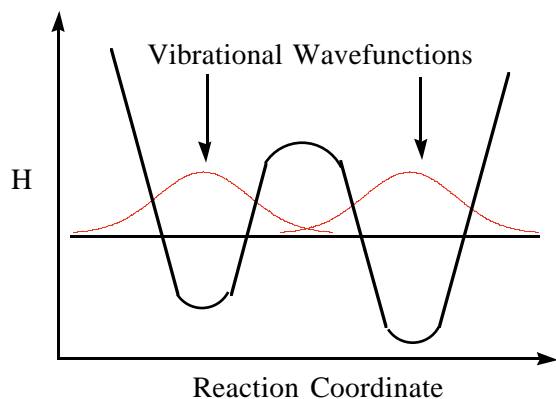
Tunneling corrections¹¹⁻¹³ to the rates predicted by transition state theory are larger for reactions with barriers that are small and narrow, and which involve the breaking and making of bonds with a small reduced mass (small tunneling particles). Tunneling is possible for light nuclei in lower vibrational states if there is a finite portion of the vibrational wave function beyond the classical limit which overlaps with a vibrational wave function in the product well (Scheme 5). Since the permeability of the wave function decreases with increasing particle size, tunneling is most common in reactions where a proton, hydride, or hydrogen atom transfer is part of the mechanism. Tunneling is detected by nonlinear Arrhenius plots as shown in Scheme 4 (right frame). Although tunneling may occur from all vibrational states, at high temperatures the activated reaction dominates the total rate. The Arrhenius plot is linear and the kinetic isotope effect k_H/k_D increases in an exponential fashion as a function of $1/T$. As the temperature decreases, reaction over the barrier is slowed down enough for tunneling to contribute significantly to the total rate. Tunneling rates of the lighter isotope are greater than those of the heavier isotope and the corresponding tunneling correction is larger. At the lowest temperatures, the thermally activated process may be completely arrested such that only tunneling contributes to the total rate. The Arrhenius plots initially bend and then become linear and flat until the isotope effect is nearly constant, and the rate of reaction nearly temperature independent.



Scheme 4

Absolute Rate Measurements in Solids

Although most kinetic studies on hydrogen transfer reactions have relied on absolute rate measurements carried out by laser flash photolysis in fluid media,¹⁴ similar measurements in the solid state are much more complicated.^{15,16}



Scheme 5

Fortunately, if conformational motions are not required, intramolecular hydrogen transfer is expected to occur with measurable yields at temperatures as low as *ca.* 50-80 K.⁴ With Arrhenius studies, isotope effects and quantum mechanical tunneling in mind, it is ideal to detect the reacting triplet state over the widest temperature range and to the lowest possible temperatures. One can measure changes in the concentration of triplet states by pulsed excitation and emission spectroscopy. For this reason, phosphorescence measurements are ideal for studying solid samples at very low temperatures with the added bonus of separating contributions from singlet state reactivity and with no interference from ground state transients. In our lab, we have carried out measurements on a spectrophotometer equipped with a pulsed phosphorimeter and a low temperature probe cooled by a closed-cycle liquid helium refrigerator which is temperature controlled between *ca.* 200 and 20 K.

As expected, ketones predisposed for reaction in non-polar rigid media have phosphorescence yields and lifetimes that are strongly dependent on the rate of reaction. In a typical experiment, one compares compounds with identical chromophore but with different reaction possibilities. For example, the phosphorescence yields and lifetimes of 2,3-dimethylantrone, 1,4-dimethylantrone-*d*₈, and 1,4-dimethylantrone are compared to determine the rate of radiative decay ($k_p + k_{TS}$), and contributions from deuterium transfer ($k_p + k_{TS} + k_D$), and hydrogen transfer ($k_p + k_{TS} + k_H$), respectively. In non-polar glasses at 77K, 2,3-dimethylantrone decays with a lifetime of 3 msec and a quantum yield of emission near unity (Figure 1). As the methyl groups are moved, the *ortho* methyl group is ideally positioned for reaction and it reacts so fast that it dominates the triplet decay with high reaction yields due to rates for transfer that are greater than $\sim 10^6 \text{ s}^{-1}$. When the hydrogens in the *ortho*-methyl group are substituted with deuteria, an expected isotope effect slows down the reaction enough for emission to compete. The yield of emission is lower than that of the model compound. Spectra obtained when the deuterated and protio compound are measured at 77K in Figure 1 reflect an large isotope of $k_H/k_D > 10^6$, even at temperatures as low as 20K. The fact that reaction can be observed at

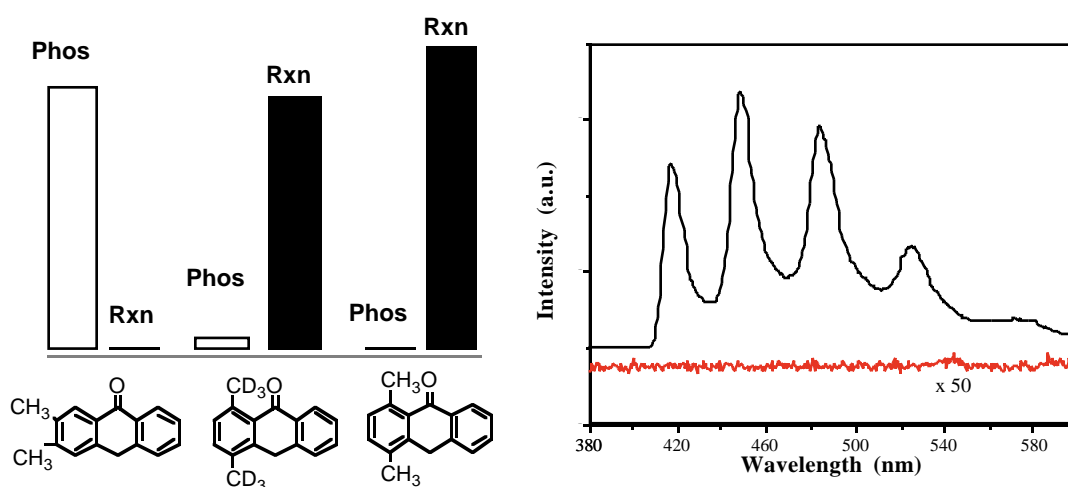
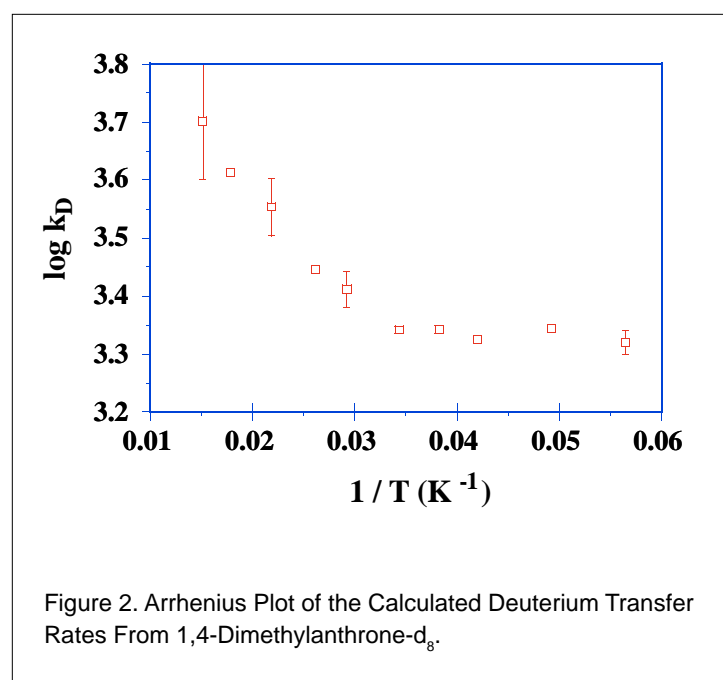


Figure 1. Relative Phosphorescence Intensities for 2,3- and 1,4-Dimethylantrones (left) and Phosphorescence Spectra Obtained from the Protio- and Deutero-1,4-Dimethyl Derivatives (right).

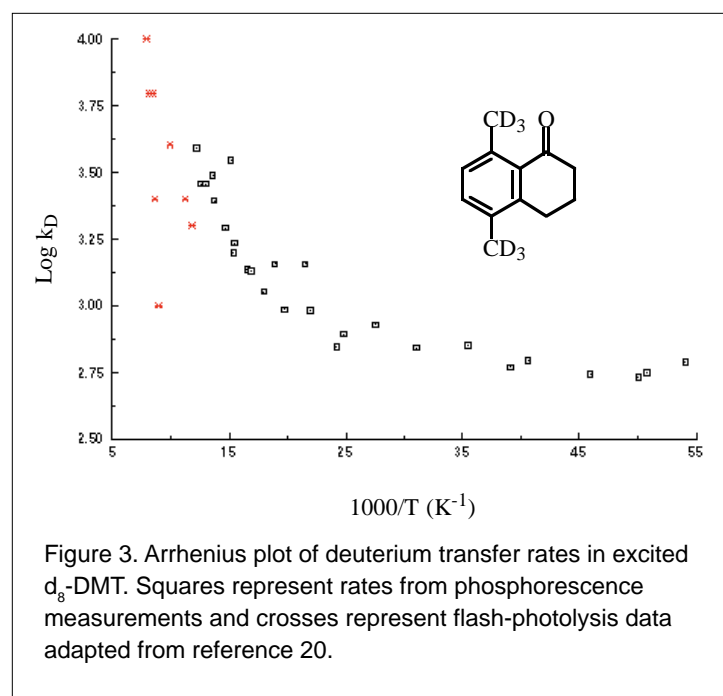
temperatures as low as 15-20K, and the fact that a very large isotope effect can be observed even at those temperatures strongly suggests that reaction occurs by quantum mechanical tunneling. This is confirmed by Arrhenius analysis of reaction rate data obtained from the triplet decay rates, k_{dec} after subtracting the contributions from photophysical pathways assumed from the model compound:

$$k_T = k_{\text{H(D)}} + k_P + k_{\text{TS}} \quad (2)$$

Deuterium transfer rates obtained for the deuterated methyl-anthrone in methyl cyclohexane glasses between 18 and 80K (Figure 2) reveal a nearly temperature independent reaction rate between 18 and 30 K that was attributed to deuterium tunneling at a rate of $2 \times 10^3 \text{ s}^{-1}$. The isotope effect $k_{\text{H}}/k_{\text{D}}$ is estimated to be *ca.* $>10^6$, even at 20K. It seems to be the largest isotope effect observed to date. The barrier for hydrogen abstraction has been estimated to be 2-4 kcal/mole¹⁷⁻¹⁹ so that no activated reaction may occur at the lowest temperatures. Little or no isotope effects would be observed if there were no tunneling. Photolysis of reactive anthrone derivatives in EtOH at 18 K yielded the expected photoenol which was characterized by its fluorescence excitation and emission spectra. We concluded that the observed decrease in triplet lifetimes and phosphorescence intensities, as well as the large isotope effects, are due to tunneling below 30 K.



factor of 10 faster than radiative and thermal decay processes, but become increasingly important as the rate of tunneling approaches those of photophysical decay processes. Based on triplet lifetimes obtained for several controls, we assign an upper error limit of about 20%. In order to test the validity and accuracy of phosphorescence measurements, reaction rates were determined for 5,8-dimethyltetralone-d₈ (DMT) in MCH. Our goal was to compare our results with those recently obtained by flash photolysis by Al Soufi and coworkers.²⁰



Although phosphorescence detection allows us to make accurate statements about tunneling in this system, there is a possibility of a systematic error in the calculated tunneling rates because of the assumption that the non-reactive decay processes are the same for reactive and non-reactive compounds. This error should be small for reaction rates that are more than a factor of 10 faster than radiative and thermal decay processes, but become increasingly important as the rate of tunneling approaches those of photophysical decay processes. Based on triplet lifetimes obtained for several controls, we assign an upper error limit of about 20%. In order to test the validity and accuracy of phosphorescence measurements, reaction rates were determined for 5,8-dimethyltetralone-d₈ (DMT) in MCH. Our goal was to compare our results with those recently obtained by flash photolysis by Al Soufi and coworkers.²⁰

Qualitatively, the same results were observed for the tetralones as for the anthrones. No emission was observed for the protio compound, and a weakened emission and shorter lifetimes were observed in the deuterated compound relative to unreactive tetralone. The enol was accumulated at 20K in both ethanol and methyl tetrahydrofuran, and it was detected by fluorescence and infrared spectroscopy.³ Reaction rates were obtained at various temperatures, and an Arrhenius plot (Figure 3) was constructed that showed excellent agreement with flash photolysis data. Data points obtained by flash photolysis by Al-Soufi et al. are shown in crosses and data points obtained by phosphorescence are shown in squares. Our results

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show that tunneling at a rate of $500 \pm 100 \text{ s}^{-1}$ is the dominant reaction mechanism below 40K. We concluded that phosphorescence was the preferred method for measuring tunneling rates at much lower temperatures.³

Our results demonstrate that *o*-methyl aryl ketones are an ideal system for a thorough study of quantum mechanical tunneling. Phosphorescence measurements are very promising for obtaining tunneling rates from zero-point energy states at ultra low temperatures. Flash photolysis will be the method of choice to obtain rates at higher temperatures and in cases where emission cannot compete with reaction. Since the two methods overlap at intermediate temperatures, systematic errors can be detected by comparing results. We are currently studying structure-reactivity relationships for tunneling by modification of the ketone structure, by studying isotope effects, and with computational studies. We are exploring the role of primary and secondary isotope effects on the observed tunneling rates by examining the CH_2D and CD_2H isotopomers. We are also investigating current theoretical models to calculate activated and tunneling rates for hydrogen and deuterium in several compounds. Our ultimate goal is to refine the current model to the point that it can be used to understand and predict more complex systems. The potential of quantum mechanical tunneling for materials applications is strongest in space technology, where chemical processes with predictable rates near zero Kelvin have to be developed.

Acknowledgment

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The Role of Acids in Excited State Reactions and Chemistry of Nitrosamines, Environmental Carcinogens

Yuan L. Chow

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This review was written in honor of and to celebrate the 80th birthday of Professor Sir Derek Barton. It is now dedicated to the memory of the man who even now continues to influence me as much as during my student days.

Introduction

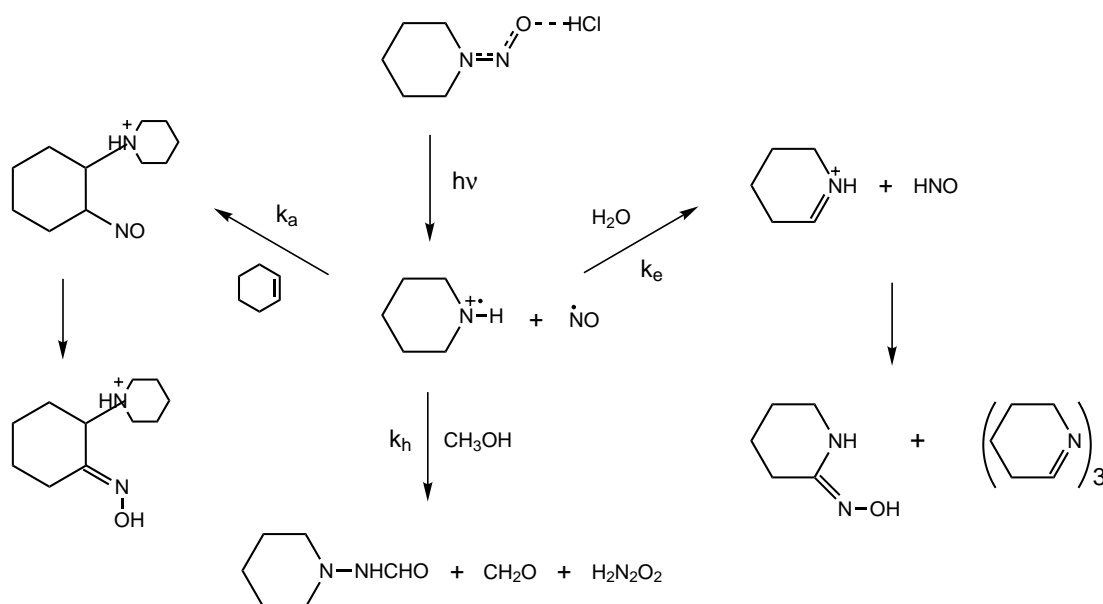
Established in the early 1960s, the Barton reaction exploits the photoreaction of organic nitrites to generate alkoxy and nitric oxide radical pairs under mild conditions¹ and is utilized to achieve specific functionalization of an ordinary alkane C-H bond. This reaction elegantly demonstrates the conformational driving force to discipline usually unruly radical H-abstraction to pin-point accuracy.¹ There is no doubt that many successful applications of this reaction have stimulated investigations into other radical-generating reactions in an endeavor to develop analogous processes.¹ The failure of *N*-nitrosamines to undergo a similar photoreaction in solution came as a surprise to many groups, including my own. The discovery that such nitrosamines in solution in the presence of a strong acid photolysed, with rarely encountered high efficiency,² was the source of further astonishment. In view of the fact that classic organic chemistry as we know it has evolved around acid catalysis, carbonium ions and related ionic reactions in the ground state, one may expect that there could be just as vast a role played by acid in the field of excited-state chemistry. This review uses *N*-nitrosamines as a model to explore the participation of acid catalysis in excited-state reactions. Needless to say, the reader should keep in mind that the multi-faceted potential of excited state acid participation in all probability goes beyond this single example.

Many nitrosamines, particularly simple ones such as *N*-nitrosodimethylamine (NDM) and *N*-nitrosopiperidine (NPP), are known to be animal and, by extrapolation, human carcinogens.³ This particular chemical health hazard is of global concern owing to the fact that these nitrosamines can be formed in the human digestive tract and in environmental samples under a wide variety of conditions with amazing facility.³ It must be emphasized that the uses of nitrosamines in the laboratory must be carefully controlled with respect to containment of the material and avoidance of physical contact.

Photolysis of *N*-Nitrosamines

In contrast to the resistance to photolysis in neutral solution, *N*-nitrosodialkylamines rapidly react in the presence of dilute acid to give the corresponding aminium and nitric oxide radical pairs as the primary intermediates^{2,4} that, depending on the conditions, undergo three major aminium radical reactions. This reaction commonly employs a medium consisting of methanol, water or a mixture thereof, and contains 0.1-0.001 N HCl, H₂SO₄ or trifluoroacetic acid (TFA). Using the piperidinium-NO radical pair as a model, Scheme 1 illustrates the reaction pattern and kinetic parameters obtained for this photoreaction.⁵ The hydrogen abstraction (k_h) process is followed by more than one radical reaction to give a mixture product. Among the three reactions, the most useful is the electrophilic addition (k_a) to simple olefins initiated by the aminium radical to give 1-piperidino-2-nitrosoalkanes and their rearrangement products. The photoaddition is efficient and gives good yields for olefins that do not carry an electron-withdrawing group (e.g., CN, NO₂ or CO₂R).⁴ Useful variations of this reaction are the intramolecular photoadditions that give caged amine-oximes and photolysis in the presence of oxygen to give vicinal amino-nitrates.⁴ It is significant that saturating amounts of oxygen do not quench the singlet state nitrosamine nor aminium radical (*vide infra*),⁵ but instead, quickly convert NO to NO₃ leading to the formation of nitrates. Also of note is the observation that aminyl radicals generated from tetrazenes or via other routes show no reactivity⁶ in Scheme 1 until they are protonated. For *N*-nitrosodipentyl amine, intramolecular abstraction of a δ -H atom generates the corresponding δ -nitroso derivative, a process that is analogous to the Barton and Hofmann-Löffler reactions.^{1,7}

The generation of the aminium radical from nitrosamines is established by comparison of the common transient absorption spectra and kinetics obtained from NPP and NDM to the results obtained from *N*-chloropiperidine and

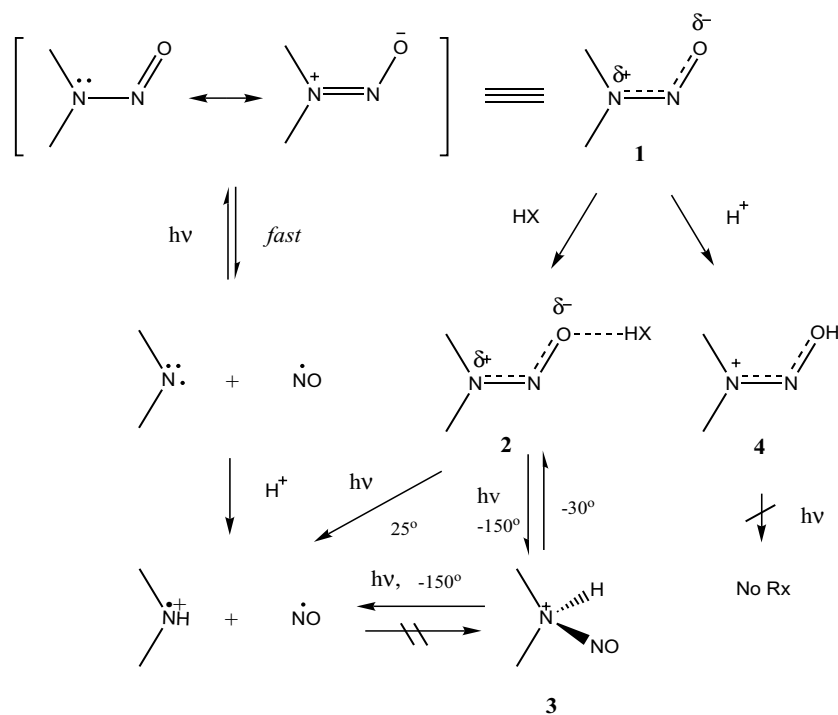


$$k_h = (2.4 \pm 0.3) \times 10^3 \text{ M}^{-1} \text{ s}^{-1}; \quad k_e = 9.1 \times 10^3 \text{ s}^{-1}; \quad k_a = (2.4 \pm 0.1) \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$$

Scheme 1

N-chlorodimethylamine following conventional flash photolysis conducted under comparable conditions.⁵ In the latter cases, the photolysis of the chloramines in strongly acidic conditions has been accepted to give aminium radicals^{5,7} (Hofmann-Löffler reaction). In aqueous solution at pH 2 under N_2 or O_2 , the piperidinium radical generated from NPP decays according to first order kinetics, with a lifetime of $110 \pm 4 \mu\text{s}$ regardless of acid concentration. Rate constants of other processes are shown in Scheme 1; those reactions with other substrates, and those from other aminium radicals are in the same order of magnitude as reported.⁵ Clearly, methanol can be used as a solvent for the photoaddition to most olefins since k_h is about 1000-times slower than the rate constant of addition processes (e.g., k_a). Recently, the more efficient laser flash photolysis (LFP) has been utilized to study aminium radicals from nitrosamines⁸ in acetonitrile in the presence of malonic acid (MA) or TFA. This study has revealed that the piperidinium-NO radical pair in acetonitrile has a lifetime of just $2.5 \mu\text{s}$, which is about two orders of magnitude shorter than the radical pair in water⁵; nevertheless it reacts with cyclohexene with $k_a = 1.2 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, a rate that is comparable with the analogous reaction in water. Apparently, the piperidinium radical pair has other reaction channels in this solvent system. The LFP of *N*-nitrosodiphenylamine under this system generates the aminyl radical signal, which slowly undergoes protonation at $6.8 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, a rate that is far below the diffusion controlled constant. Despite the use of the more efficient LFP, the generation of other aminyl radicals from *N*-nitrosodialkylamines has not as yet been observed as our ancient system has failed.⁸

What differentiates dialkylnitrosamines from nitrite esters is the contribution of the polar resonance form to the resonance hybrid (computed⁹ to be 48%). This contribution serves to pump high electron density into the oxygen atom that results in a partial double bond character for the N-N bond and low electron density at the amine nitrogen (1 in Scheme 2). The latter is confirmed by the dynamic temperature effect on signal exchanges in H-NMR spectroscopy, which gives an N-N bond rotational barrier of 23.3 kcal/mol for NDM.¹⁰ It has also been unambiguously demonstrated by NMR and X-ray spectroscopy that Lewis and Brønsted acids and metal ions coordinate with the nitroso oxygen.¹¹ The critical point is nitrosamine basicity, which has attracted investigation earlier.¹² Nitrosamines are shown to form association complexes **2** through H-bonding with protic acids in cyclohexane with a K_a of about 60 M^{-1} for NDM.¹² In an aqueous acidic solution of $\text{pH} < 2$, the association is extensive due to the H-bonding network. In contrast, at $[\text{H}_2\text{SO}_4] > 2 \text{ M}$, nitrosamines form protonated species **4** that are stable to photolysis.²



Why is it that acid-associated nitrosamines such as **2** are susceptible to photolysis when irradiated at the $n\text{-}\pi^*$ transition? NDM ($E_s = 73$ kcal/mol, $E_T = 59$ kcal/mol) gives no emission at all on excitation at 234 or 342 nm under a wide variety of conditions. NDM phosphorescence shows a maximum at 530 nm when excited from $S_0 \rightarrow T_1$ (at 440 nm, ϵ 0.064 M^{-1}), but its triplet state generated by sensitization or 440 nm excitation does not undergo chemical changes.¹³ By sensitization, the NDM-acid complex is shown to undergo irreversible chemical reactions from its singlet excited state, with quantum yields of 2-4 depending on NDM concentrations. The overall pattern indicates that the dissociation to aminium and NO radicals is the only deactivation channel available to the singlet excited state. In the gas phase, NDM is also shown to dissociate from the $n\text{-}\pi^*$ singlet state at $k > 10^{10} \text{ s}^{-1}$ with $\Phi = 1.03$ to generate the aminyl and NO radicals.

Significantly, they revert completely to NDM, a result that hints at the occurrence of ultra-fast recombination, even at the one Torr level.¹⁴ This agrees with a total lack of photoreactivity and of aminyl radical formation in flash photolyses that are conducted in neutral solution.^{2,5,8} Exceptions to the above are *N*-nitrosodiphenylamine and *N*-nitroso-*N*-alkylaniline,¹⁵ both of which undergo the Fischer-Hepp rearrangement, which involves a nitroso migration to form *p*-nitrosoaniline derivatives.

The function and movement of acids in the excited state NDM have been traced with low temperature photolysis.¹³ Photolysis of NDM-TFA in a transparent glass of EtOH-MeOH at -150° and at 313 nm gives the tautomer with a tetrahedral configuration (i.e., a keto-enol type tautomer), shown as the nitroso-dimethylammonium ion **3**, on the basis of UV peaks at 391, 375 and 362 nm showing regular vibration progressions from **2** (which is the enol-type tautomer). Significantly, under irradiation conditions no spectral change occurs in the absence of TFA. Intermediate **3** is irreversibly decomposed upon irradiation at 365 nm at -150° , but reverts completely to the original spectrum of **2** upon warming to -30° . The observation demonstrates that photolysis of NDM-TFA must be a consecutive two photon process in the frozen state in which the excess vibration energy is dampened. Of course irradiation at any wavelength of the $n\text{-}\pi^*$ band at room temperature results in spontaneous dissociation of the rearranged **3** as the result of residual vibration energy. An analogous low temperature photolysis of *N*-nitroso-*N*-methylaniline with TFA shows a similar spectral pattern¹⁵ which can be explained by the intermediary of tautomer **3**.

Some comments should be made on the processes in Scheme 2. In contrast to the ultrafast recombination of the aminyl-NO radical pair, reassociation of the aminium-NO pair to form **3** must be very slow and can be estimated from a lifetime of 110 μs in water to be $< 10^4 \text{ s}^{-1}$. The rapid recombination of the former pair undoubtedly reflects the enormous energy gain as the result of reversion to the resonance stabilized **1**. This would also explain why nitrosamine formation can occur easily and is ubiquitous in environments under ambient conditions, i.e. an environmental energy sink. The slow recombination rate of the latter aminium-NO pair arises from a high energy level for **3** due to the lack of resonance stabilization, a situation that allows aminium radicals to undergo competitive addition and H-abstraction processes. Secondly, owing to phenyl conjugations, *N*-nitrosodiphenylamine does not form acid complexes in dilute acidic acetonitrile; this probably results in giving the aminyl radical on LFP. Finally, we have assumed that the excitation and promotion of an electron to a π^* orbital should localize the electron cloud to the amine N atom, and that should pyramidize this N-atom as in **3**. In analogy to "the sudden polarization phenomena" in ethylene,¹⁶ the nitroso group may twist to avoid repulsion (or to gain an energy valley). This concept is similar to the well-documented "twisted intramolecular charge transfer" (TICT) of *p*-cyanoaniline,¹⁷ with the exception that the present

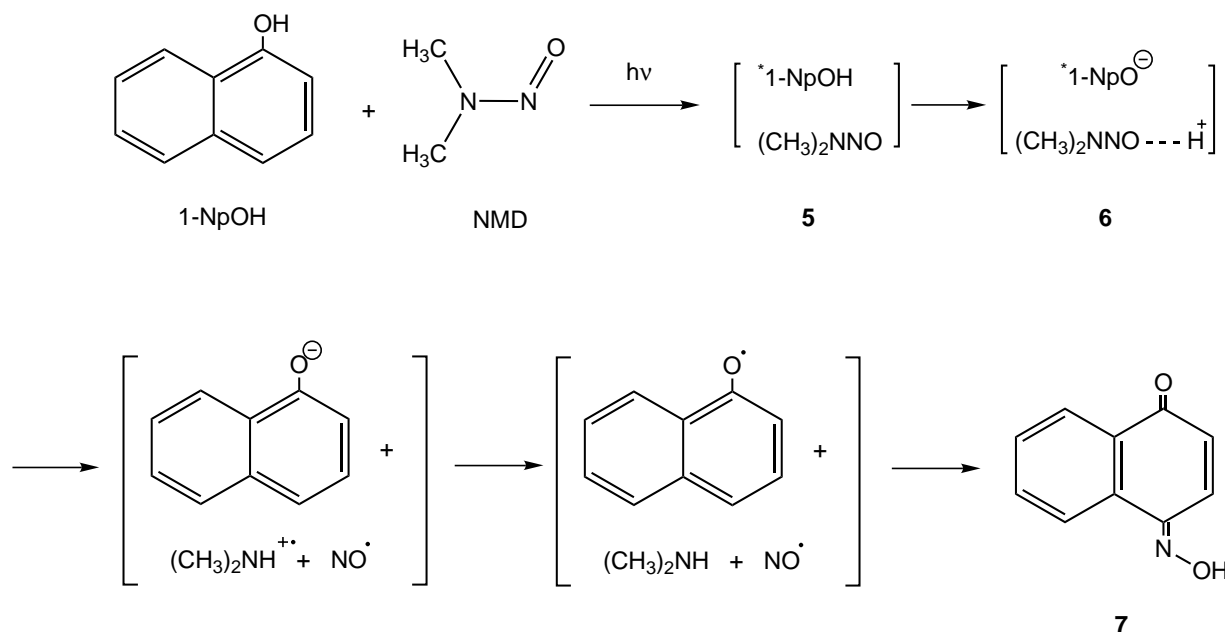
case involves a charge annihilation.

It can be speculated that the inherent stability of *N*-nitrosodialkylamines is the primary reason why these compounds can be transmitted through body matrix systems in an unchanged, intact form. However once they are accessible to an enzyme which possesses a cavity that is suitable to force an approximate configuration of **3**, they can become very reactive species. Indeed it is said that nitrosamines need an activation step to become carcinogenic.¹⁸

Sensitized Photodecomposition of Nitrosamines

Phenols in their singlet excited state exhibit enhanced acidity, a property that has been studied extensively,¹⁹ and that has been proven to be useful in a variety of special technical applications (e.g., polymerization, biological probes). Known as excited state proton transfer (ESPT),²⁰ this phenomenon is best illustrated by 1-naphthol showing pK_a^* of 0.4 ± 0.2 and lifetime of 10.6 ns; the corresponding data for 2-naphthol are 2.8 and 13.3 ns, respectively. The data imply that $^*1\text{-NpOH}$ provides a proton to the nearest H_2O cluster or base for the 10.6 ns lifetime, the duration of which is more or less modified by other dynamic processes. This proton transfer may be referred as kinetic acidity, and for the duration of this transfer, the process obviously provides an opportunity for the transient acidic effects to have an impact on a nearby base target. Considering this abbreviated lifetime, very few possibilities will exist for the occurrence of bond formation or scission processes, given that they would have to operate with a frequency in the order of $>10^8 \text{ s}^{-1}$. Despite this limitation, one consideration is the photodissociation of the NMD-acid complex, a process that is not only fast, but as is shown in Scheme 2, also requires both strong acid and excitation energy. This photodissociation provides an ideal model system to test the dual ability of tandem proton and energy transfer for $^*1\text{-NpOH}$.

For a solution containing NMD and a polycyclic phenol,²¹ the excitation of NMD at $>340 \text{ nm}$ does not bring about a chemical reaction; the ground state of a phenol is not adequately acidic enough to provide a proton to cause the NMD photodissociation. In contrast, when this solution is irradiated at the phenol absorption under suitable conditions, there is a rapid consumption of the phenol and the subsequent formation, in excellent to acceptable yields, of the corresponding *p*-quinone monoximes: 1-NpOH is converted to 1,4-naphthoquinone-4-oxime (**7** in Scheme 3), 2-naphthol to 1,2-naphthoquinone-2-oxime, 1-anthranol to 1,4-anthraquinone-4-oxime, and 9-anthranol to 9,10-anthraquinone-10-oxime. Photolysis under the conditions of similar mixtures containing the methyl ether of these phenols gives no chemical change, a result that shows that ESPT is not only the necessary but also the initiation step for the reaction. As the $^*1\text{-NpOH}$ singlet excited state has been extensively investigated and well documented,²⁰ this naphthol is used as the model compound for the ensuing discussion. Since this photo-nitrosation can not be driven by triplet sensitization or be quenched by the triplet quencher 1,3-cyclohexadiene, one can conclude that it is a singlet reaction. Additional support for the conclusion comes from the observation that NDM quenches $^*1\text{-NpOH}$ fluores-



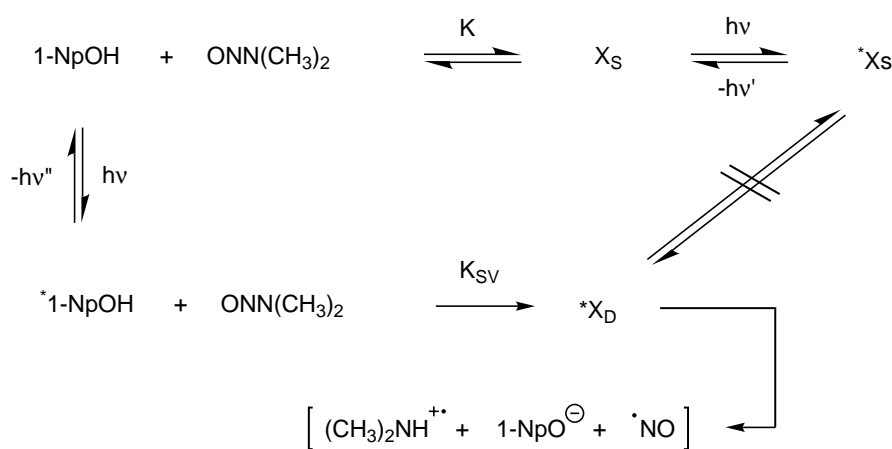
Scheme 3

cence, in various solvents, without a concomitant new emission ($K_{sv} = 120 \text{ M}^{-1}$ in dioxane).²²

However, the mechanism of this photonitrosation proves to be more complicated. In aprotic solvents 1-NpOH and NDM form a complex (X_s) that shows a new absorption at 360-450 nm, the excitation of which gives a broad exciplex ($*X_s$) fluorescence at 430-550 nm ($\lambda_{\text{max}} 480 \text{ nm}$) in acetonitrile. Fluorescence excitation spectra confirm that the origin of this weak emission is the ground state complex (X_s) but does not arise solely from 1-NpOH²² (Scheme 4). Unexpectedly, the excitation of X_s at $>380 \text{ nm}$ did not induce NDM decomposition or the formation of monoxime. In contrast, excitation of this solution at the 300 nm region caused dynamic quenching of $*1\text{-NpOH}$ fluorescence and rapid reaction, processes that should require another exciplex ($*X_d$) in view of the fast proton and energy transfer which would be required to occur in rapid succession (see below). It would then follow that broad band excitation ($>300 \text{ nm}$) of a solution of 1-NpOH-NDM would give two independent exciplexes that either emit or react faster, by at least an order of magnitude, than mutual isomerizations. The association constant K (7-8 and 30 M^{-1}) and the dynamic quenching rate constant K_{sv} (82 M^{-1}) in dioxane (see Scheme 4) have been determined.²² The dual presence of exciplexes and selective reaction pathways are both novel phenomena that show that ESPT in general requires stringent geometric arrangements. Two exciplexes must have different conformations that either allow ESPT to NDM or to a nearby target. It is conceivable that studies involving molecular mechanics coupled with NMR shift patterns will be able to

provide information on these molecular orientations.

In terms of the mechanism of self-photonitrosation of 1-NpOH and allied phenols, the stringent geometric requirements for ESPT to occur suggests that dynamic quenching should proceed through a finite exciplex $*X_d$ (as in Scheme 3) which would mediate a successful completion of the reaction. There is additional support in favor of exciplex participation in this dynamic process. First, the lack of deuterium isotope effects in the photonitrosation of 1-NpOH in quantum yield as well as K_{sv} measurements suggests a strong likelihood that ESPT occurs within a



Scheme 4

complex. Second, consecutive ESPT and energy transfer must occur very fast and in succession, as is hinted by a near diffusion-limited quenching rate constant and the lack of $*1\text{-NpO-}$ fluorescence. It would be more logical for these transfers to occur within an exciplex. Finally, the excited state phenolate anion must be in a complex, as only in this state can it cause the dissociation of NDM- H^+ through energy migration. Within $*X_d$, ESPT of $*1\text{-NpOH}$ to NDM must precede the energy transfer, as only in this sequence ($5 \rightarrow 6$) does the dissociation occur as in Scheme 3. The alternative order only creates $*\text{NDM}$ and does not lead to the aminium and NO radicals.⁵ The subsequent radical reaction to give monoxime **7** is straight-forward.²¹ While the efficiency of the $*X_d$ formation as represented by K_{sv} constants is comparable in many solvents, the limiting quantum yield of the oxime formation or NDM decomposition is higher in aprotic solvents. This observation suggests that in protic solvents, the ESPT may be partially wasted due to random protonation involving the hydrogen bonding network.

Supporting evidence for ESPT initiated decomposition of NMD is provided by the observation that, under comparable conditions, both $*1\text{-NpOH}$ fluorescence and the monoxime formation are quenched by water and triethylamine; both of which can quench $*1\text{-NpOH}$ through competing ESPT. The quenching rate constants by water have been determined in these two types of monitors and give excellent mutual agreement with values in the range of $4\text{-}6 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$, while those by triethylamine are reasonably good at 0.8, 2.1 and $1.6 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$.

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