

Deuterium Tunneling in Triplet 5,8-Dimethyl-1-tetralone by Phosphorescence Detection between 80 and 15 K

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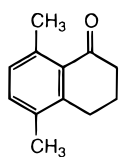
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Phosphorescence measurements with 5,8-dimethyl-1-tetralone (DMT) and 5,8-dimethyl-1-tetralone-*d*₈ (DMT-*d*₈) in methylcyclohexane were carried out between 15 and 80 K to analyze their triplet-state hydrogen- and deuterium-transfer reactions. As expected for a decay process displaying a very large isotope effect, emission could be observed only for the deuterated compound. Phosphorescence intensities and decay measurements in the case of DMT-*d*₈ were analyzed to determine the rates of deuterium transfer which were used to build an Arrhenius plot where tunneling can be readily identified. A temperature-independent triplet state reaction rate ($k_D(\text{QMT}) = (5 \pm 1) \times 10^2 \text{ s}^{-1}$) below 40 K was assigned to quantum mechanical tunneling. Detection of the photoproduct after irradiation at 77 and 15 K was accomplished by fluorescence and by FTIR spectroscopy. Results obtained in this study are in excellent agreement with laser flash photolysis results reported by Al-Soufi et al. (Al-Soufi, W.; Eychmuller, A.; Grellmann, K. H. *J. Phys. Chem.* **1991**, *95*, 2022–2026).

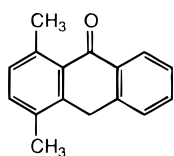
Introduction

Recent studies have demonstrated the involvement of excited-state hydrogen atom tunneling in rigid *o*-methyl-substituted arylketones with favorable transfer geometries.¹ Large isotope effects and nonlinear Arrhenius plots have been observed,^{2–5} and some theoretical studies have followed.^{2,6} It has been proposed that tunneling occurs from n,π^* excited states when the transferring hydrogen is favorably positioned relative to the singly occupied *n*-orbital. While both singlet³ and triplet^{4,5} H-atom tunneling have been invoked, the most convincing evidence has been in the case of triplet precursors such as 5,8-dimethyl-1-tetralone (DMT),² and 1,4-dimethylanthrone (MAT).^{4,5}

In the case of DMT, hydrogen- and deuterium-transfer rates as a function of temperature were calculated from laser flash photolysis data.² In contrast, phosphorescence decays were used to calculate reaction rates in the case of MAT.^{4,5} Flash photolysis studies were carried out between 270 and 80 K while phosphorescence measurements in the case of MAT were carried out between 80 and 17 K. Experimental values of deuterium tunneling rates were obtained with both techniques, but complications and/or limitations in both cases prevented the determination of hydrogen tunneling which was estimated to be 3–4 orders of magnitude larger. The rates of D-tunneling obtained from the two techniques and with the two compounds are remarkably similar with $k_D(\text{QMT}) = (1 \pm 2) \times 10^3 \text{ s}^{-1}$ for DMT and $k_D(\text{QMT}) = 2 \times 10^3 \text{ s}^{-1}$ for MAT.



DMT



MAT

In this paper, we report a variable-temperature phosphorescence analysis of dimethyl-1-tetralone (DMT) and deuterium-labeled 5,8-dimethyl-*d*₆-6,7-tetralone-*d*₂ (DMT-*d*₈) between 18 and 80 K. Our goal is to confirm the validity of phosphorescence

measurements in determining the rates of H-transfer reactions at ultralow temperatures and to complement the laser flash photolysis results by carrying measurements to much lower temperatures.

Experimental Section

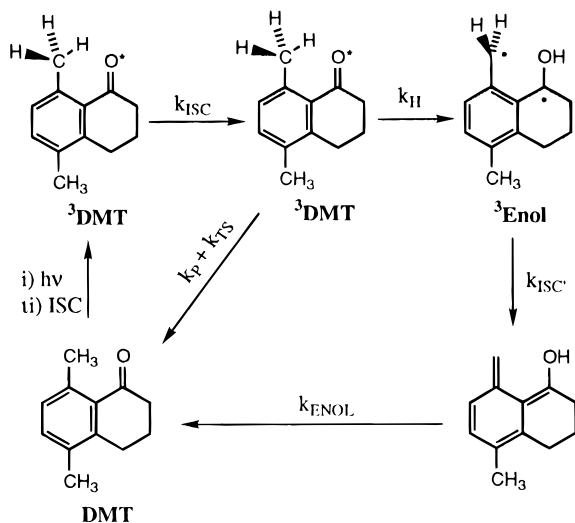
All solvents used were of the highest purity commercially available and were dried by distillation from CaH₂. 5,8-Dimethyl-1-tetralone (DMT) and 5,8-dimethyl-*d*₆-1-tetralone-6,7-*d*₂ (DMT-*d*₈) were synthesized as previously described by Barnett and Sanders from *p*-xylene and *p*-xylene-*d*₁₀ and maleic anhydride.⁷ Tetralone was obtained from Aldrich Chemical Co. All compounds were purified immediately before use by chromatography and/or distillation. Low-temperature phosphorescence measurements of optically dilute samples with excitation at 340 nm were taken between 15 and 88 K as described previously.⁵ Accumulation of the photoproduct at 14 K in ethanol and in methyltetrahydrofuran (MTHF) was accomplished by irradiation with a 250 W mercury lamp until a yellow discoloration assigned to the trapped photoenol was readily evident. Evidence for the photoproduct was obtained in MTHF by FTIR and in EtOH by fluorescence spectroscopy. Photoenol fluorescence was obtained as described before.⁸ Infrared spectra were obtained with a 60SX Nicolet spectrometer. A cesium iodide probe was placed into a copper holder that was attached to the second stage of the refrigerator. Methyltetrahydrofuran solution samples were injected into the chamber of the refrigeration system where they adhered to the probe as a transparent thin film. Quartz and potassium bromide windows were fitted onto opposite sides of the vacuum shroud of the refrigerator expander making it possible to photolyze the samples with the output from UV source and to obtain FTIR transmittance spectra.

Results and Discussion

Phosphorescence spectra and decay measurements were carried out with tetralone, 5,8-dimethyl-1-tetralone (DMT) and 5,8-dimethyl-*d*₆-1-tetralone-6,7-*d*₂ (DMT-*d*₈) in methylcyclohexane glasses (MCH) between 15 and 80 K. MCH glasses

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SCHEME 1



were chosen to prevent the accumulation of the photoproduct which is known to be long-lived only in polar solvents.⁹ Since unsubstituted tetralone cannot undergo intramolecular hydrogen atom transfer, it was analyzed as a standard to compare the properties of the *o*-methyl compounds. The reaction mechanism commonly accepted in the case of DMT is shown in Scheme 1.⁹⁻¹³ To detect the triplet state by phosphorescence, it was an important requirement of this work that the rate of reaction could be slowed down sufficiently for radiative processes to contribute significantly to the total decay rate.

As with most aryl ketones, intersystem crossing to ³DMT is expected to occur within a few picoseconds.¹⁴⁻¹⁶ Although triplet yields close to unity are usually assumed, experimental evidence for singlet-state deactivation competing with intersystem crossing has been recently analyzed in the literature and should be considered in this case.^{3,5,17} However, for the sake of clarity, this possibility is not indicated in Scheme 1. Decay of the triplet ketone occurs radiatively (k_p), by intersystem crossing (k_{TS}), and by an adiabatic hydrogen atom transfer (k_H) that yields a triplet-state enol (³Enol). The triplet enol intersystem crosses to the ground state product¹ which has an *o*-quinodimethane structure that reketonizes back to the starting ketone via a proton-transfer mechanism susceptible to quantum mechanical tunneling effects.¹⁸ We analyze the hydrogen (deuterium) atom transfer step (i.e., k_H or k_D) by measuring the decay of the triplet ketone (k_{dec}), as given by the rates of reaction, phosphorescence, and thermal decay ($k_{dec} = k_H + k_p + k_{TS}$).

Since large primary isotope effects are expected, measurements with deuterated and nondeuterated samples were carried out to confirm the contribution of reaction to triplet decay. The spectrum of DMT- d_8 in methylcyclohexane glasses (MCH) at 15 K is weak and relatively broad as compared to that of unsubstituted tetralone (Figure 1). In agreement with an expected and dominating isotope-dependent decay pathway, no emission could be observed from samples of DMT. On the basis of signal-to-noise levels, we estimate a conservative lower limit of $\Phi_D/\Phi_H > 10^3$ even at 18 K. The spectrum of DMT- d_8 is characteristic of triplet n,π^* aryl ketones¹⁹ and it is red-shifted by ca. 15 nm as compared to the spectrum of tetralone. Interestingly, a similar shift was observed in *o*-methylantrone but not in *m*- and *p*-dimethyl-substituted compound.⁵ On the basis of the fact that a 10 cm^{-1} red shift was observed in the C=O stretch of the *o*-methyl compound, it was speculated that this shift may be associated with an intramolecular C-H...O bond.^{20,21} Similarly, a 5 cm^{-1} red shift was also observed in

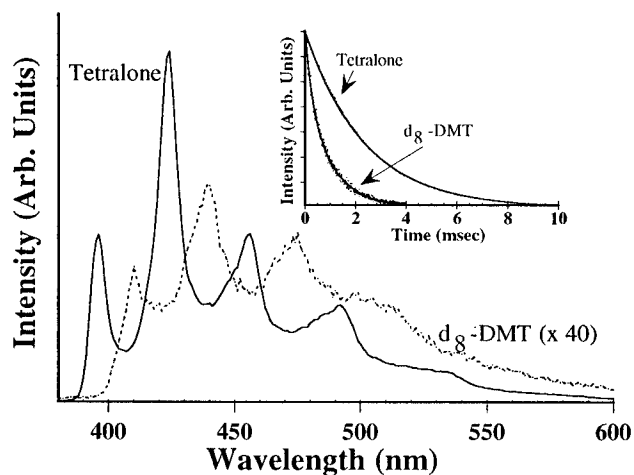


Figure 1. Phosphorescence emission spectra of tetralone and DMT- d_8 at 18 K in methyl cyclohexane. Inset: decay traces with single (tetralone) and double (DMT- d_8) exponential fits.

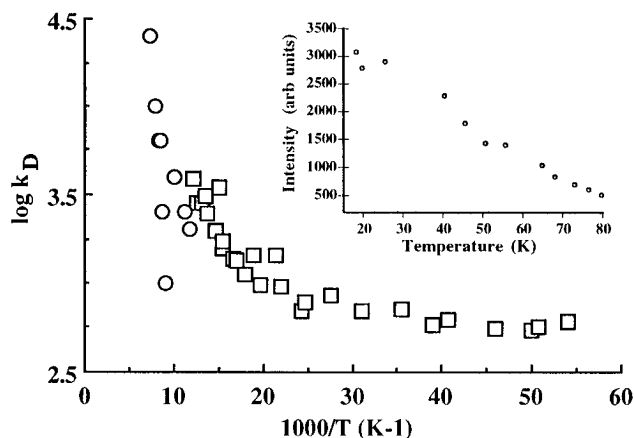


Figure 2. Arrhenius plot of deuterium-transfer rates in excited DMT- d_8 . Squares represent rates from phosphorescence measurements, and circles represent flash-photolysis data adapted from ref 2. Inset: intensity changes as a function of temperature for one of two experimental runs.

the C=O stretch of DMT as compared to that of tetralone with bands occurring at 1678 and 1685 cm^{-1} , respectively.

Phosphorescence intensities and decay measurements were obtained in MCH between 18 and 82 K to evaluate the temperature dependence of the reaction rate (Figure 2). The phosphorescence intensity and lifetime of unsubstituted tetralone remained essentially constant while those of DMT- d_8 presented a large decrease until emission almost disappears near 82 K (Figure 2, inset). Intensity and decay data for DMT- d_8 was collected in two different experiments at 27 different temperatures between 18 and 82 K. Data from tetralone was collected at five different temperatures spanning the same temperature range. The phosphorescence decay of tetralone in MCH was fit to a single-exponential function with a triplet decay rate, $k_{dec} = 440 (\pm 50) \text{ s}^{-1}$ which is attributed to the sum of phosphorescence and thermal decay ($k_{dec} = k_p + k_{TS}$). The decays of DMT- d_8 were fitted to double-exponential functions with fast and slow components varying by factors between 3 and 5 along the temperature range. Representative decay curves and fits of tetralone and DMT- d_8 at 18 K are shown in the inset of Figure 1.

Since the nonexponentiality of the triplet decay of DMT- d_8 in MCH is not paralleled by that of tetralone, we propose that it may be due to small conformational and/or environmental heterogeneity capable of affecting the rate of reaction but not the rates of thermal and phosphorescence decay.⁸ Hydrogen-

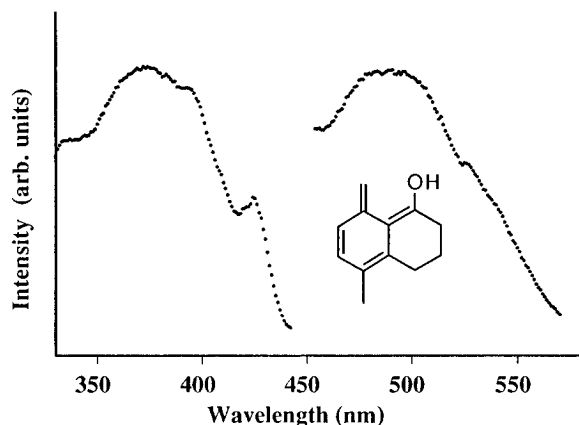


Figure 3. Fluorescence excitation and emission spectra of the photoenol in EtOH at 77 K.

transfer rates may be expected to be sensitive to relatively small structural differences affecting the distance and orientation between the transferring hydrogen and the target carbonyl oxygen. Given the limited number of data points (250–500) and intensity range per decay, rather than emphasizing the meaning of the two components (which may be a representation for a complex distribution of lifetimes), we calculated average decay rates, k_{ave} , as indicated in eq 1. The τ_i and I_i represent

$$k_{\text{ave}} = (I_1\tau_1 + I_2\tau_2)/(I_1\tau_1^2 + I_2\tau_2^2) \quad (1)$$

$$k_{\text{ave}} = k_{\text{D}} + (k_{\text{TS}} + k_{\text{P}}) \quad (2)$$

each of the two lifetimes and their corresponding preexponentials.^{22,23} To estimate the D-transfer rates, it was assumed that triplet decay rates (k_{ave}) of DMT- d_8 contain terms associated with thermal (k_{TS}) and radiative (k_{P}) decay and a term associated with the deuterium-transfer reaction (k_{D}). It also was assumed that nonreactive decay rates in DMT- d_8 are the same as those of tetralone [$k_{\text{dec}} = 440 (\pm 50) \text{ s}^{-1}$]. We expect that this assumption may give a systematic error on the magnitude of the calculated D-transfer rates but should not affect conclusions drawn from their temperature profiles. The reaction rates calculated in this manner are summarized in Figure 2 in the form of an Arrhenius plot along with some of the values reported from flash photolysis measurements by Al-Soufi et al.²

The agreement between flash photolysis data shown in circles and phosphorescence data shown in squares is excellent and strongly argues in favor of our interpretation in terms of a triplet state reaction. The scattering around 80 K is more severe in the flash photolysis results and is probably due to complications occurring when the solvent changes from a viscous fluid to an amorphous solid. Reaction rates calculated from phosphorescence measurements in MCH are slightly higher than those obtained by flash photolysis in EtOH as expected for a solvent effect. It is known that less polar solvents favors the more reactive n,π^* configuration of the triplet excited state.^{1,24} Assuming that the rate of reaction had become temperature independent by 100 K, Al-Soufi and co-workers proposed a temperature-independent deuterium tunneling rate, $k_{\text{D}}(\text{QMT})$ of $(3 \pm 2) \times 10^3 \text{ s}^{-1}$.² However, the curvature in the Arrhenius plot in Figure 1 at these temperatures suggests contributions from a thermally activated reaction. In fact, quantum mechanical tunneling becomes the only mechanism at temperatures below ca. 30–40 K with a tunneling rate, $k_{\text{D}}(\text{QMT}) = (5 \pm 1) \times 10^2 \text{ s}^{-1}$.

That deuterium tunneling is an important component of the decay when triplet lifetimes become temperature independent

is suggested by the relatively high decay rate and is also supported by the accumulation and detection of the photoproduct. Irradiation of DMT and DMT- d_8 in 10^{-2} M ethanol glasses at 77 K resulted in a yellow discoloration assigned to the enol. A relatively weak fluorescence spectrum consistent with those of other known *o*-quinodimethanes was observed with a λ_{max} at 480–500 nm (Figure 3).^{20–22} With the goal of detecting the O–H stretch of the photoenol, FTIR experiments were also carried out in concentrated methyltetrahydrofuran (MTHF) glasses deposited at 14 K and irradiated with $\lambda > 300 \text{ nm}$. The growth of signals assigned to the enol and depletion of signals assigned to the ketone were observed along with the characteristic yellow discoloration of the product. Signals assigned the enol include a broad band centered at ca. 3300 cm^{-1} (O–H), two strong signals at 1597 and 1625 cm^{-1} (C=C). These were accompanied by a large decrease in the C=O and C=C stretches of the starting ketone at 1675 and 1576 cm^{-1} .

As in previous low-temperature work with 1,4-dimethylantrones,^{4,5} we noticed that phosphorescence intensities increase with decreasing temperatures even when the triplet lifetimes remain constant. This observation suggests a temperature-dependent deactivation pathway that precedes the formation of the triplet state. We have tentatively assigned this to an intramolecular atom-transfer deactivation mechanism where an avoided crossing along the path to the primary product allows for return to the ground-state ketone.^{25–28} Experimental observations have been documented suggesting singlet deactivation by hydrogen transfer when reaction may compete with intersystem crossing.^{5,17,29,30} It has also been recently shown that product formation from the singlet state is in fact very inefficient.¹⁷ While indirect evidence in the case of DMT suggests an activated process, it has been speculated that a singlet state reaction observed in *o*-methylantraquinone by laser flash detection may occur via quantum mechanical tunneling.³ However, to compete with intersystem crossing, a state reaction in aryl ketones requires rate constants on the order of 10^{12} s^{-1} .^{14–16} Such a high rate may be satisfied in an activated process at temperatures as low as 15–20 K when a high preexponential factor and a nearly barrierless reaction may be granted. In contrast, singlet-state tunneling would have to be 10 orders of magnitude faster than tunneling in the triplet state. Since both are adiabatic processes, such a difference in tunneling probabilities would seem rather intriguing and unlikely.

Conclusions

Phase changes and spectral interference due to accumulation of the photoenol limit flash photolysis measurements to relatively high temperatures (ca. $> 80 \text{ K}$).^{2,3} In contrast, phosphorescence measurements with dilute samples in rigid media can be carried out only at very low temperatures ($T < 80 \text{ K}$) under conditions where reaction is slow enough for radiative decay to compete efficiently.^{4,5,8} Because of the large H-transfer rates, phosphorescence techniques did not allow us to obtain rates for the nondeuterated compound (DMT). However, phosphorescence results with DMT- d_8 agree well with those reported by Al-Soufi et al. and support the validity of this method of analysis. By going to much lower temperatures, we have established that the curved region of the Arrhenius plot extends to temperatures that are lower than previously anticipated (i.e., down to ca. 30 K). Small differences between our results and those of Al-Soufi et al. in the region 80–90 K are near experimental error and may be due to the different solvents used. Further studies addressing structural effects on hydrogen and deuterium tunneling and the role of singlet state are currently in progress in our laboratory.

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