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Primary Isotope Effects on Excited State Hydrogen Atom Transfer Reactions. Activated and Tunneling Mechanisms in an *ortho*-Methylanthrone[1]

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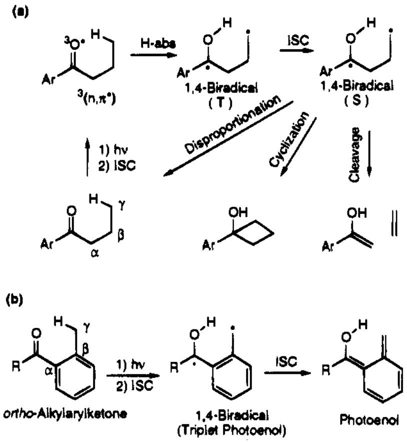
Abstract: Phosphorescence intensities and lifetimes of 1,4-dimethylanthrone (1,4-MAT) and 1,4-dimethylanthrone-d_8 (1,4-DMAT) were measured to determine the involvement of activated and quantum mechanical tunneling mechanisms (QMT) in their hydrogen and deuterium atom transfer reactions. The thermal-dependence of the radiative and thermal decay of the anthrone chromophore and the effect of methyl substitution were evaluated by using anthrone (AT), 2,3-dimethylanthrone, (2,3-MAT), and 10,10-dimethylanthrone (10,10-MAT). Measurements were carried out in methylcyclohexane (MCH) glasses between 18 and 80 K. The unreactive molecules AT, 2,3-MAT, and 10,10-MAT present phosphorescence parameters typical of diarylketones with $^3n,\pi^*$ configurations and show a relatively small temperature dependence changing from monoexponential at 77 K to nonexponential at the lowest temperature values. The phosphorescence intensity from 1,4-DMAT was extremely weak and highly temperature-dependent. In contrast, no phosphorescence was detected in 1,4-MAT at all temperatures studied. Differences between deuterio and protio compounds were analyzed in terms of a large isotope effect on the hydrogen atom transfer reaction. A quantum mechanical tunneling mechanism was confirmed from nonlinear Arrhenius plots constructed with the average deuterium transfer rates of 1,4-DMAT. A temperature-independent quantum mechanical tunneling reaction with a rate of 2×10^3 s^{-1} was calculated between 30 and 18 K. The involvement of reaction was confirmed by accumulation and detection of the photoenol product in ethanol glasses at all the temperatures studied. Changes in phosphorescence intensity observed even under conditions where the triplet lifetimes remain constant (18−30 K) were analyzed in terms of an avoided crossing mechanism predicted by orbital and state symmetry considerations.

Introduction

The intramolecular γ-hydrogen abstraction by electronically excited carbonyl groups, also known as the Norrish type-II reaction, is one of the most studied and best understood organic photochemical processes.[2,3] The reaction involves the transfer of a hydrogen atom from the γ-carbon to the carbonyl oxygen to produce a 1,4-biradical (Scheme 1a). In the case of arylalkylketones, the nature of the reactive excited state, its multiplicity, and a variety of structural, steric, electronic, and solvent effects have been evaluated.[2] Much attention has also been given to reactions involving *ortho*-alkyl-substituted ketones where an analogous process leads to formation of *ortho*-quinodimethanes in a reaction commonly referred to as photoenolization.[4−15] Both reactions share hydrogen abstraction as the first step, but they differ in the following parts of the mechanism. The Norrish type-II reaction produces a triplet 1,4-biradical, while the corresponding species in the photoenolization reaction is identified as the triplet excited state of the photoenol product (Scheme 1b).

Scheme 1



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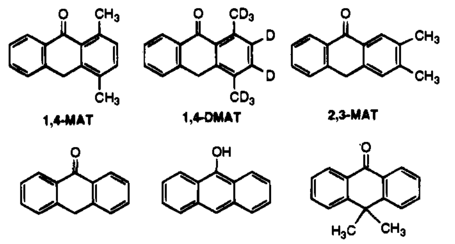
It is well-known that rapid and efficient intersystem crossing results in triplet state reactivity and that reaction is promoted by the singly occupied n-orbital in the $^{3}n,\pi^*$ state. The effects of structure, solvents, and substituents on the relative energies of closely lying n,π^* and π,π^* excited states and how they relate to the reaction have been also analyzed in detail.[16] Hydrogen abstraction is sensitive to structural factors relating to the distance and orientation of the target hydrogen relative to the oxygen n-orbital. Several theoretical analyses support this argument and suggest possible reasons for the advantage of a six-membered transition state, as required in a γ-H transfer.[17-22] Experimentally, the structural dependence of the hydrogen abstraction step has been established through elegant conformational analysis,[3] by carefully designed rigid molecules[23-25] and by studies carried out in the crystalline solid state.[26-28] The reactivity of the resulting 1,4-biradicals and their products have also been the subject of numerous investigations.[2,12-14] Biradicals are initially formed in a triplet state (T) and must intersystem cross to the singlet manifold (S) before forming closed-shell products (Scheme 1). The three most important reaction modes for the 1,4-biradical are cyclobutanol formation, cleavage of the α,β-bond, and disproportionation by reverse hydrogen atom transfer to regenerate the starting ketone. In contrast, the triplet enol in Scheme 1b intersystem crosses to the ground state photoenol in the last step of what constitutes an adiabatic triplet state overall transformation.

In spite of abundant information on several aspects of the reaction, very few studies have addressed an expected primary isotope effect.[29] These few reports on various types of ketones give results that vary from no isotope effect[30] to fully developed primary kinetic isotope effects (i.e. $k_H/k_D = 6-8$, at 300 K)[31,32] and to propositions of quantum mechanical tunneling.[14,15] Excited state barriers suggested by state correlation diagrams[33-36] and quantum mechanical tunneling arguments proposed by Formosinho and Arnaut[37] both suggest that significant isotope effects should be observed in the reaction. Among these reports currently available, there is a range of structural variations, electronic configurations, and excited state spin multiplicities that may contribute to those widely different observations.

Chart 1



Additionally, there are some difficulties in the determination of primary isotope effects of photochemical reactions. For instance, isotope effects on radiationless pathways other than reaction are well documented and are expected to obscure the results of the hydrogen abstraction step.[38,39] Most studies have relied on relative or absolute rate measurements over relatively restricted temperature ranges in conventional solvents, when in fact lower temperatures would increase the magnitude of a kinetic isotope effect and would help determine whether quantum mechanical tunneling is indeed involved.[40,41] An ideal methodology would involve direct detection of the reacting triplet state over the widest temperature range and at the lowest possible temperatures. A survey of reported activation parameters for arylketones with n,π^* excited states ($E_a = 2-4$ kcal/mol; $\log A = 9-11\ s^{-1}$)[30,32,42,43] suggests that intramolecular hydrogen abstraction may occur with measurable quantum yields at temperatures as low as *ca.* 50-80 K if certain conditions are fulfilled. Both kinetic and quantum mechanical tunneling isotope effects would be unambiguously and distinctively manifested at these temperatures. However, high solvent viscosity at such low temperatures would result in technical problems that may be further complicated by the fact that the rate determining step for reaction may change from hydrogen abstraction to conformational dynamics.[3,5,44,45] If conformational restrictions prevent the substrate from freely exploring numerous geometries, reactions will only proceed if there is a strong structural similarity between the reactant, the transition state, and the final products.[10,23-27,46] It is in fact reasonable to expect that most reactions should not occur at cryogenic temperatures simply because reactive conformers may not be reached in highly viscous environments. This limitation may be circumvented by studying rigid molecular structures such as those found in *ortho*-methyl substituted anthrones such as 1,4-dimethylanthrone (1,4-MAT) and 1,4-dimethylanthrone-d_8 (1,4-DMAT) where conformational motions to reach the transition state are largely minimized (Chart 1 and Scheme 2).

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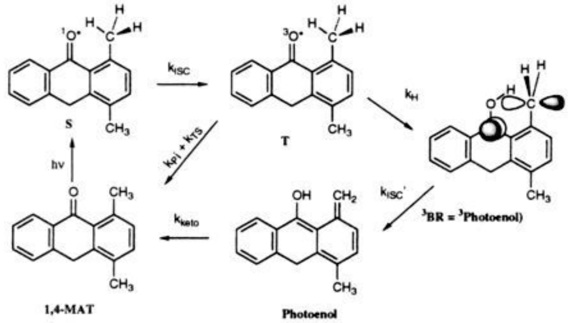
Scheme 2



If the structural requirements for a reaction are met at all temperatures, activated abstraction rates will become slow enough at sufficiently low temperatures to allow for radiative decay of triplets to compete with the reaction. We report the use of phosphorescence to monitor triplet state populations for a convenient determination of kinetic isotope effects and to analyze the reaction temperature dependence.[1] Phosphorescence measurements are ideally suited for the study of solid samples at ultralow temperatures and have the potential of neatly separating triplet state reactivity from that of the singlet state while removing interference from ground state transients. A triplet state reaction should reduce phosphorescence quantum yields and shorten triplet lifetimes in *ortho*-methyl-substituted anthrones as compared to analogous compounds with no reaction pathway (Scheme 3). To isolate photophysical processes particular to the anthrone chromophore, we have analyzed AT, 2,3-MAT, and 10,10-MAT (Scheme 2). With anthrone we address the general properties of the unsubstituted chromophore. Methyl substituents are known to affect the rates of hydrogen transfer of arylketones by modifying the relative energies of n,π^* and π,π^* states as compared to unsubstituted compounds. It has been proposed that the effect of *ortho*- and *meta*-substituents should be similar to one another and about half as large as that of the *para*-substituent.[5] It has also been shown that the effects of multiple substituents are additive and quite pronounced in arylalkylketones.[6] However, the effect of methyl substituents should not be nearly as dramatic in diarylketones with larger n,$\pi^*-\pi,\pi^*$ energy gaps, and we qualitatively address the effect of the methyl substituents with 2,3-MAT.[47] One may expect that 2,3-dimethyl (*para, meta*) substitution should have a comparable effect on the relative n,π^* and π,π^* state energies of anthrone as compared to the 1,4-dimethyl compound (*ortho, meta*) so that the former should be a proper qualitative control for the effect of methyl groups on the photophysical properties of the parent chromophore. It is also known that anthrone and anthranol may exist in a solvent-dependent tautomerization equilibrium that we may need to address in this study. While the ketone is largely favored in nonpolar solvents such as methylcyclohexane (MCH),[48] the possibility of analytical interference from fluorescence by small quantities of 9-anthranol derivatives may be addressed by analyzing the nonenolizable 10,10-MAT.[49] Finally and most importantly, the involvement of a hydrogen atom transfer reaction, its kinetic isotope effect, and the possibility of quantum mechanical tunneling are analyzed by comparing 1,4-DMAT with 1,4-MAT.

In this paper, we present phosphorescence measurements in dilute methylcyclohexane (MCH) glasses over a large temperature range. We compare results from anthrone (AT), 2,3-dimethylanthrone (2,3-MAT), and 10,10-dimethylanthrone (10,10-MAT), with those from the *ortho*-methyl substituted compounds (1,4-MAT and 1,4-DMAT). We also present strong evidence for a hydrogen abstraction reaction at temperatures as low as 18 K and an isotope effect that is well beyond the dynamic range of our measurements (*ca.* $>10^6$). Triplet decay rates as a function of temperature are analyzed in terms of concurrent activated and tunneling mechanisms. Evidence of singlet state temperature-dependent deactivation mechanism is analyzed in terms of a singlet state hydrogen atom transfer reaction and the possibility of an avoided crossing effectively leading to an internal decay mechanism is considered. The formation and accumulation of the photoenol over the entire temperature range is also demonstrated in polar solvents.

Experimental Section

Materials. All the solvents employed in this study were of the highest purity commercially available and were used as received. Anthrone (AT), 2,3-dimethylanthrone (2,3-MAT), 1,4-dimethylanthrone (1,4-MAT) and 1,4-dimethylanthrone-d_8 (1,4-DMAT) were prepared by Sn·HCl reduction of the corresponding anthraquinones in acetic acid as reported by Meyer.[50] 10,10-Dimethylanthrone was prepared from anthrone as reported by Curtin *et al.*[51] 1,4-(d_6)-Dimethylanthraquinone-*2,3-d_2* was prepared by two sequential Friedel–Crafts reactions from phthalic anhydride and *p*-xylene-d_{10}. Samples were purified by repeated recrystallization and column chromatography.

Emission Measurements at 77 K. Fluorescence and phosphorescence spectra and phosphorescence decays were measured on a SPEX-Fluorolog spectrometer equipped with an R 928 PMT detector and a 1943D phosphorimeter. Solutions of anthrone and anthrone derivatives were freshly prepared in methylcyclohexane at a concentration of *ca.* $3-10 \times 10^{-5}$ M. These low concentrations were used to avoid aggregation or microcrystallization of the samples. Excitation was carried out at 309 nm. Measurements at 77 K were carried out in 5 mm o.d. Pyrex tubes placed inside the cold finger of a transparent Pyrex Dewar filled with liquid nitrogen. Glasses of high optical quality were obtained, and data collection was carried out by front-surface excitation and detection. Phosphorescence emission spectra were shown to be independent of the excitation wavelength. Decay curves were measured point-by-point by changing the delay in 10–50 μs steps after the 10 μs lamp pulse. Between 10 and 300 pulses per point were accumulated, and 500 data points were typically collected per decay. When possible, signal intensities were collected for as many as four decades and then fit to single or double exponentials. The signal intensities of reactive samples were much lower than those of the nonreactive compounds and curve fitting quality was primarily judged by visual comparison and at this point our fitting parameters should be viewed with caution and considered qualitative.

Variable Temperature Measurements. For variable temperature measurements between 18 and 100 K, refrigeration was achieved by means of a closed cycle two stage helium refrigerator manufactured by Air Products which consists of a compressor, an expander, and flexible high pressure hoses.[52] For glassy samples, a copper rod with a flat polished surface was connected to the second stage of the refrigerator. The samples were injected into the sample compartment through a septum opening in the outer shroud and adhered to the copper rod by cryopumping. Quartz windows on the sides of the vacuum shroud of the expander allowed for excitation and detection to be carried out at right angles with the sample placed at 45 degrees for front-surface excitation and detection. Alternatively, connected at the bottom of the shroud was a quartz tube through which the sample was accessed frontally. The temperature of the samples was varied with the help of a small resistive heater wrapped around the lower part of second stage of the refrigerator. The heater and a 0.07% iron-doped gold vs chromel

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Table 1. Phosphorescence Parameters of Several Anthrone Derivatives in Methylcyclohexane

compd	lifetime (ms) 17K[a]	lifetime (ms) 77 K[a]	λ_{max} (0−0)	E_T[b]	Φ_P[c]
AT	$\tau_1 = 1.6$ (75%) $\tau_2 = 4.4$ (25%)	$\tau = 1.7$	403	71.0	1.0
2,3-MAT	$\tau_1 = 1.75$ (90%) $\tau_2 = 0.50$ (10%)	$\tau = 1.6$	400	71.5	0.44
10,10-MAT		$\tau = 1.9$	404	70.8	0.64
1,4-DMAT	$\tau_1 = 0.48$ (76%) $\tau_2 = 0.087$ (24%)	$\tau_1 = 0.23$ (75%) $\tau_2 = 0.03$ (25%)	414[d]	69.1	<0.0013
1,4-MAT[e]	[e]	[e]	[e]	[e]	[e,f]

[a] The contribution of each component from double exponential fittings is included in parentheses. [b] Estimated from the spectra in Kcal/mol. [c] Values measured at 77 K are relative to anthrone and have an estimated 5% error. [d] Measured at 18 K. [e] No emission detected. [f] An upper quantum yield limit of $\ll 10^{-4}$ at 18 K was estimated by comparison with 10^{-3} parts of anthraquinone which has a quantum yield of 1.0.

thermocouple were connected to a digital temperature indicator/controller manufactured by Scientific Instruments, Inc. The necessary vacuum was maintained with an oil diffusion pump (Edwards Vacuum Components Limited Model EO2) that was backed by a mechanical fore pump (Welch Duo Seal Model 1402).[52]

Transparent glassy films of about 1 mm thickness were obtained when samples were deposited at 18 K. Measurements were carried out by front-surface excitation and detection. To account for possible matrix annealing effects that may indirectly affect triplet decay or reaction rates, samples were heated up to *ca.* 100 K and allowed to stand at this temperature for about 30 min before starting data acquisition at 18 K. In order to minimize sample sublimation, measurements with a given sample were carried out within a period of several hours. To prevent systematic errors in intensity readings and decay measurements, data collection were carried out by alternating temperatures at the high and low ends of the temperature range studied. Once a selected temperature was reached, the sample was allowed to equilibrate for 15 min before starting data collection. Intensity readings at 18 K at the beginning and at the end of an experimental session with a given sample showed a total decrease of no more than 5% which may be ascribed to either sample sublimation or matrix deterioration. Intensity measurements by front surface illumination and detection are very sensitive to geometric factors and our control over sample thickness is at present limited. From these two factors, intensity measurements when deposition of a sample was repeated showed significant variations. In contrast, decay data obtained at a given temperature were found to be highly reproducible from sample to sample and, for a given sample, after temperature changes and or at the beginning and the end of the experiment.

Photoenol Detection. Samples of 1,4-MAT and 1,4-DMAT (0.1 M) in ethanol or in EPA were irradiated with a 250 W Hg•Xe lamp at 77 or at 18 K for 15 min when the formation of a deep yellow color was clearly evident. Fluorescence emission and excitation spectra were recorded, and the transient nature of the yellow species was demonstrated by warming the samples to room temperature. Emission spectra were recorded by excitation at 470 nm and excitation spectra were recorded by emission at 575 nm (Figure 3). Proton exchange experiments were carried out by irradiation of 1,4-MAT and 1,4-DMAT in EtOD, MeCN:D_2O = 9:1, and in deuterated EPA. The extent of deuteron (or proton) exchange was measured by ^1H NMR and by EI-MS analysis. Only limited exchange was observed under a wide variety of experimental conditions.

Computational Details. Molecular mechanics calculations were carried out with MacroModel V3.5X and BatchMin V3.5.[53] The MM3[54] and Amber [55] force fields were used with default settings in MacroModel. The Monte-Carlo facility of the program was used to search for the lowest energy conformer of 1,4-MAT. Lowest-energy conformers located by MM3 were submitted to energy optimization by the AM1[56] and PM3 semiempirical RHF SCF-MO methods as implemented by the program Spartan V3.0.4 (Wavefunction Inc.).[57]

Results

Phosphorescence Measurements at 77 K. The photophysical and photochemical properties of unsubstituted anthrone (AT) have been studied in great detail. Anthrone is known to possess properties that are typical of arylketones with lowest n,π^* triplet excited state[58,59] with a phosphorescence quantum yield of 0.55 and a lifetime of 1.5 ms in ethanol.[60] Our measurements in methylcyclohexane (MCH) are in qualitative agreement with those reports and set the benchmark by which the triplet state properties for the other anthrone derivatives may be analyzed (Table 1).

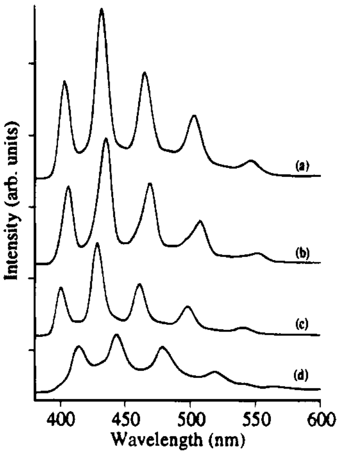

Figure 1. Phosphorescence spectra of optically matched 10^{-4} M solutions of (a) AT, (b) 10,10-MAT, and (c) 2,3-MAT at 77 K. Spectrum (d) corresponds to 1,4-DMAT at 18 K and is not at scale with the other three.

The normalized phosphorescence spectra of AT, 2,3-MAT and 10,10-MAT in dilute MCH glasses at 77 K are shown in Figure 1 along with that of 1,4-DMAT at 18 K (the latter is not to scale). The relative phosphorescence yield values at 77 K in MCH are 1.0, 0.44, and 0.64 for AT, 2,3-MAT, for 10,10-MAT with an upper limit of 0.0013 obtained for 1,4-DMAT (Table 1). As per expectations, the relative intensities of the three anthrone derivatives with no intramolecular H-abstraction possibilities compare to each other within a factor of two and are much stronger than that of 1,4-DMAT by a factor of at least 400. The spectra shown in Figure 1 have a vibronic structure characteristic of excited states with n,π^* configurations. The 0−0 bands in the spectra of AT, 2,3-MAT, and 10,10-MAT occur at 403, 400, and 404 nm, while the corresponding

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transition in the spectrum of 1,4-DMAT is red shifted to 414 nm (Table 1). The red shift observed in the *ortho*-methyl compound may come from a perturbation to the carbonyl by the *ortho*-methyl group. This is manifested in the IR spectra in terms of a 10 cm^{-1} shift in the C=O stretching frequencies of the *ortho* compounds as compared to the other anthrone derivatives. Stretching frequencies vary from 1660, 1659, and 1658 cm^{-1} for AT, 2,3-MAT, and 10,10-MAT, to 1648 cm^{-1} for 1,4-DMAT and 1,4-MAT (at 2 cm^{-1} resolution).

The phosphorescence decays of the three highly luminescent anthrone derivatives are consistent with expectations from an n,π* lowest triplet state. Lifetimes of 1.7, 1.6, and 1.9 ms were estimated for AT, 2,3-MAT and 10,10-MAT, respectively. Phosphorescence decays at 77 K are well described by a single exponential. In contrast, a significant kinetic heterogeneity was observed at 18 K and values from double exponential fits (*vide infra*) at the lower temperature are also included in the table. The decay of 1,4-DMAT was fit to double exponentials at both temperatures. A relatively weak signal at 77 K was fit to lifetime values of $\tau_1 = 0.23$ and $\tau_2 = 0.03$ ms with relative contributions of 75 and 25%, respectively. We estimate that errors due to low signal to noise ratio are about 20–25% at this temperature although they become smaller in the lower temperature experiments.

Conspicuous in Figure 1 and Table 1 are the lack of data for 1,4-MAT for which no phosphorescence could be observed with our detection system even under conditions of highest sensitivity. The lack of phosphorescence of 1,4-MAT and the relatively low intensity and shortened triplet lifetimes of 1,4-DMAT suggest that depletion of the triplet state does not occur only by radiative and/or nonproductive thermal T_1-S_0 decay but by internal hydrogen abstraction. A very large isotope effect on the phosphorescence intensity was indeed realized. The proximity of the *ortho*-methyl group to the carbonyl oxygen should facilitate the reaction which would compete directly with phosphorescence and thermal decay. Intramolecular hydrogen abstraction gives a triplet state enol with the methylene-centered radical orthogonal to the ring π-system (Scheme 3). The triplet photoenol decays to the singlet ground state *ortho*-quinodimethane-1-ol structure of the photoenol by intersystem crossing and bond rotation. The photoenol is a transient with a solvent-dependent lifetime determined by a proton-transfer reaction that regenerates the starting ketone.[7,10,61,62] Ketonization is known to be fastest in nonpolar solvents such as MCH which ideally serves the purpose of this study.

Measurements at 18 K. The remarkably large isotope effect observed on the phosphorescence intensity of the *ortho*-methyl substituted compound,[1] and the reduced triplet yield and lifetime of 1,4-DMAT as compared to AT, 2,3-MAT, and 10,10-MAT, strongly support the involvement of an intramolecular hydrogen abstraction reaction. It is expected that the rate of the reaction (k_H, Scheme 3) should have a much larger temperature dependence than phosphorescence and nonradiative decay (k_{P^o} and k_{TS}). If the lowest activation energies (2 kcal/mol) and largest pre-exponential factors (10^{11} s^{-1}) reported in the literature are taken as the best case scenario for an activated reaction, one may calculate that reaction rates should become small compared to phosphorescence at temperatures below 40–45 K. At the point where activated hydrogen abstraction becomes unimportant, phosphorescence yields and triplet lifetimes in 1,4-MAT should become very similar to those of the nonreactive compounds. In the absence of other decay pathways, then, sufficiently low temperatures should result in sufficiently small hydrogen abstraction rates that spectral and lifetime measurements could be made for both isotopomers. With this in mind, a series of measurements were carried out at 18 K, well into the temperature regime where the rate of an activated reaction may be expected to be insignificantly small.

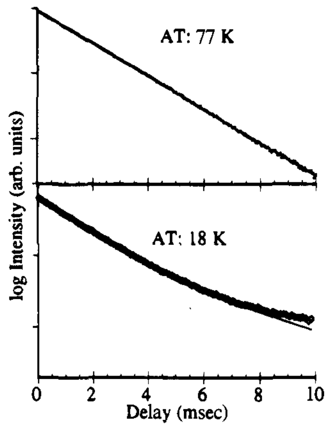

Figure 2. Phosphorescence decay of anthrone (AT) at 77 (top) and at 18 K (bottom) in methylcyclohexane. The line on top and bottom traces correspond to the fits to single and double exponentials, respectively.

Experimental evaluation of the temperature dependence of k_{P^o} and k_{TS} was carried out with AT and 2,3-MAT. Measurements at 18 K showed a relatively small spectral sharpening, and their decays were only slightly different from those recorded at 77 K. Sample decays of AT at 18 and 77 K are shown in Figure 2. The 18 K data could not be fit to single exponential functions, but double exponentials were satisfactory down to *ca.* 3.5% of original signal intensity. The decay of AT was fit to lifetimes of 1.6 ms and 4.4 ms with relative contribution of 75 and 25%, respectively. The decay of 2,3-MAT was fit to lifetimes of 1.75 and 0.5 ms with a 90% contribution by the former. The weighted average lifetimes of AT at 18 and 77 K are 2.3 and 1.7 ms, respectively, and the corresponding value in the case of 2,3-MAT is 1.6 ms at both temperatures. While nonexponentiality is common at cryogenic temperatures,[63,64] we wish not to emphasize the significance of the biexponential fit other than to stress the fact that a nonhomogeneous behavior is clearly evident from our data. The most important observation for the purposes of this study is that the lifetime values indicate a small temperature dependence associated with phosphorescence and with thermal T_1-S_0 decay rates. In agreement with lifetime measurements, intensity variations as a function of temperature for AT and 2,3-MAT were estimated to be no more than 5–15% when the temperature changed from 18 to 80 K.

Results with 1,4-DMAT and 1,4-MAT at 18 K were quite different from each other and from those of AT and 2,3-MAT. A large intensity increase at the lower temperature was evident only in the case of 1,4-DMAT. Even at 18 K, the decay of 1,4-DMAT was much faster than those of AT and 2,3-MAT with short and long-lived components of 0.96×10^{-4} and 4.8×10^{-4} s. The relative contributions of these components parallel those of AT with values about 70 and 30%, respectively. Surprisingly, no emission could be detected in the case of the protio-substituted compound (1,4-MAT). To estimate an upper quantum yield limit in the phosphorescence of 1,4-MAT, we co-deposited a sample with a small amount of anthraquinone (AQ). Anthraquinone has a phosphorescence quantum yield

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of 1.0[58] and has a spectrum that is quite distinct from that of diaryl ketones so that it may be used as an internal standard. The concentration of AQ for this experiment was adjusted to give an O.D. with a factor of 10^{-3} relative to that of 1,4-MAT at the excitation wavelength (i.e., 309 nm). Under conditions where the signal of AQ gave about 10^4 cps at a $\lambda_{max} = 490$ nm, no signal from 1,4-MAT could be observed between 400 and 500 nm when the noise level reached values of 10–50 cps. From these values, we may estimate an upper phosphorescence quantum yield of *ca.* $<10^{-6}$. If we assume a quantitative yield of triplet formation and exclusive triplet state deactivation by hydrogen atom transfer, we may calculate reaction rates of the order of *ca.* 10^9 s^{-1}. However, low emission yields may also arise from low triplet yields, fast T_1-S_0 thermal decay, or from exceedingly slow phosphorescence rates. The last two effects seem very unlikely, but indirect evidence suggesting low triplet yields due to singlet state reactivity is addressed below.

Photoenol Formation. Phosphorescence intensities and triplet lifetime measurements at 77 and at 18 K require the involvement of a strongly temperature-dependent triplet decay pathway in the case of 1,4-DMAT. The lack of emission of 1,4-MAT can be interpreted in terms of a remarkably large isotope effect for H-abstraction if the inherent uncertainty of a negative result may be removed. For this, the involvement of reaction at any temperature may be unambiguously demonstrated by formation of the photoproduct. The transient behavior of a large number of photoenols has been analyzed by several authors, and their solvent-dependent ketonization rates have been well documented.[4,5,8,10,12,14,15,65–72] Irradiation of 1,4-DMAT and 1,4-MAT with a high intensity (250 W) Hg•Xe lamp in MCH at 77 K gave no evidence of accumulation of a long-lived product. However, sample irradiation in polar protic solvents such as ethanol and EPA under otherwise identical conditions readily lead to bright yellow-orange discoloration both at 18 and at 77 K. Luminescence analysis of those samples revealed the presence of a species with fluorescence excitation and emission spectra consistent with those of several reported *o*-quinodimethanes.[73–75] Shown in Figure 3 are the excitation and emission spectra obtained in EtOH at 77 K for the deuterated compound. Similar emission spectra have been obtained in our laboratory by irradiation of several other *ortho*-alkyl substituted arylketones, and further studies are currently in progress.[76] The transient nature of both enols was easily demonstrated as the fluorescence signal and the color disappeared when the samples were annealed upon heating. Cycles of photoenol accumulation followed by thermal decay could be repeated without apparent changes in the sample.

Further evidence for the intermediacy of the enol formation in related systems is normally obtained by proton exchange in deuterated protic solvents.[5] However, irradiation of 1,4-MAT in MeOD or in MeCN:D_2O = 90:10 at normal temperatures fails to give significant deuterium incorporation by ^1H NMR analysis under conditions where prototype systems such as *ortho*-methylbenzophenone undergo quantitative exchange. In fact, it has been observed that proton exchange in geometrically-locked photoenols is an extremely inefficient process.[10,14] More sensitive mass spectral analysis revealed low incorporation values of *ca.* 2–3% after 2 h irradiation at 273 K. Experiments carried out with 10% D_2O in acetone, with the latter acting both as a solvent and as triplet sensitizer, also lead to inefficient deuterium incorporation. Attempts to catalyze the proton exchange with dilute acid led to formation of 1,4-dimethyl-9-anthranol in a ground state tautomerization process. Experiments carried out with 1,4-DMAT in the presence of protonated solvents gave complementary analogous results. Since formation of the enol has been observed spectroscopically by Baron *et al.*,[61] and by us in this work, these results suggest that intramolecular proton transfer must be more efficient than intermolecular proton exchange. A possible explanation for this result was suggested by PM3 semiempirical analysis of the photoenol and is based on an intramolecular O–H••π-face hydrogen[77–79] bonding interaction which will be discussed below.

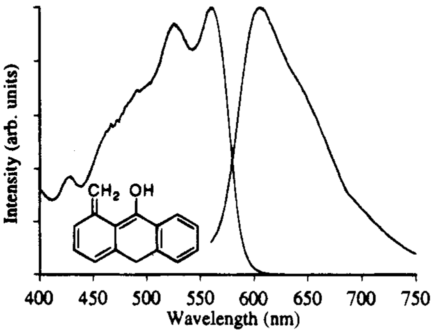

Figure 3. Excitation and emission spectra of the photoenol obtained upon irradiation of 1,4-DMAT in ethanol at 77 K.

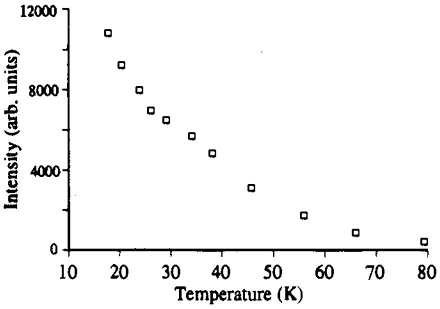

Figure 4. Plot of intensity vs temperature in 1,4-dimethylanthrone (1,4-DMAT).

Variable Temperature Studies. With the involvement of reaction and an isotope effect demonstrated, intensity and decay measurements were obtained for 1,4-DMAT between 18 and 80 K in order to analyze whether the reaction occurs by activated and/or tunneling mechanisms at cryogenic temperatures. Intensity values and phosphorescence lifetimes as a function of temperature are summarized in Figures 4 and 5 and in Table 2.

In contrast to the intensity of AT and 2,3-MAT which showed a modest temperature dependence, increasing the temperature from 18 to 80 K decreased the phosphorescence intensities of

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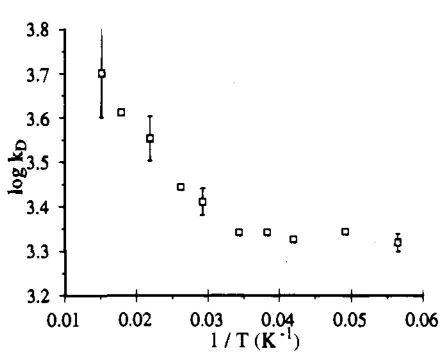

Figure 5. Arrhenius plot of the average deuterium transfer rate of 1,4-DMAT in MCH.

Table 2. Double Exponential Fitting Parameters from the Decay Data of 1,4-DMAT between 17.7 and 79.3 K[a]

T (K)	τ_1 (s, 10^{-6})	τ_2 (s, 10^{-6})	$\%\tau_1$[b]	$\%\tau_2$[b]
17.7	480	96.0	74.4	25.6
20.3	455	85.0	76.8	23.2
23.8	483	93.7	74.1	25.9
26.1	477	96.0	72.0	28.0
29.1	473	90.0	73.4	26.6
34.2	407	77.8	75.1	24.9
38.2	400	83.0	69.9	30.1
45.7	320	63.0	71.0	29.0
55.9	280	47.0	73.3	26.7
66.0	240	46.2	69.6	30.4
79.3	230	29.7	86.2	13.8

[a] From fitting function $I = I_1 \exp(t/\tau_1) + I_2 \exp(t/\tau_2)$. [b] The contribution from each component was obtained from their lifetime-weighted intensities: e.g., $\%\tau_1 = I_1\tau_1/(I_1\tau_1 + I_2\tau_2)$.

1,4-DMAT by a factor of *ca.* 20 (Figure 4). Phosphorescence decays were fit to double exponentials over the entire temperature interval (Table 2). A long component consistently contributed 70–77% of the total decay with values ranging between 480 and 230 μs, while a short component ranged between 96 and 30 μs with a temperature dependence similar to that of the longer one. While the nonexponential behavior of the decay data is analogous to that of the other anthrone derivatives (Table 1), contributions to nonexponentiality from heterogeneous reaction rates cannot be eliminated but would be difficult to draw from the data. Nonetheless, weighted average decay rates reflect the contributions from photophysical and photochemical processes that deplete the triplet excited state and should be useful in elucidating the temperature dependence of the reaction. If we assume that 1,4-DMAT has similar phosphorescence and thermal decay rates as AT and 2,3-MAT (e.g., $k_{P^o} + k_{TS} \approx 5 \times 10^2$ s^{-1}), we may calculate the rate of reaction (k_H) by subtracting those values from the temperature-dependent decay rate of 1,4-DMAT. Arrhenius plots constructed in this manner show the deuterium transfer rate of 1,4-DMAT to be temperature-dependent above *ca.* 30 K and temperature-independent below that value (Figure 5).

The average lifetime of 1,4-DMAT between 30 and 18 K is only 0.38 ms as compared to 1.76 and 2.3 ms for the reference compounds at 18 K. This lifetime difference at low temperatures is assigned to a triplet state tunneling reaction with an average reaction rate of $k_{QMT} \approx 2 \times 10^3$ s^{-1}. This assignment is supported by the fact that photoproduct formation is readily observed at these temperatures and by the fact that no lifetimes lower than 1 ms may be found on literature surveys of reported ^{3}n,π* diarylketones.[59,80] The lack of emission in the protio-compound (1,4-MAT) also adds weight to this interpretation (*vide infra*). Deuterium triplet state tunneling rates of $k_{QMT} \approx 10^3$ s^{-1} proposed by Al-Soufi *et al.* for 1,4-dimethyltetralone are also in excellent agreement with our result.[14]

Another important aspect about the results in Figures 4 and 5 and in Table 2 is the fact that total intensity of 1,4-DMAT decreases between 18 and 30 K under conditions where the triplet lifetime remains constant. In fact, the temperature dependence of the intensity values is significantly larger than the temperature dependence of the triplet lifetimes even under conditions where both lifetimes and intensities are affected (i.e., between *ca.* 30 and 80 K). A decrease in the quantum yield of triplet emission that is not paralleled by a decrease in the triplet lifetime requires that intensity losses occur before formation of the triplet state. It should be pointed out that intensity measurements for a given sample under the conditions of our measurements were shown to be reliable within *ca.* ±5%.

Changes in intensity between 18 and 30 K of *ca.* 60% demand a temperature-dependent singlet state process that competes with formation of the triplet state. It is known that anthrone undergoes quantitative intersystem crossing by virtue of rate of *ca.* 10^{12} s^{-1} at ambient temperatures,[81–83] and it is unlikely that this value should change drastically at low temperatures. A singlet state pathway competing efficiently with intersystem crossing requires rates of this magnitude. While there is no precedent for hydrogen atom transfer reactions to be this fast, the structure of dimethylanthrone may be an ideal candidate to support such a process and this possibility should be considered. A temperature-dependent singlet reaction at such low temperatures could only take place (with known pre-exponential factors) if sufficiently low activation barriers are granted. It is known that disproportionation of singlet biradicals to generate the starting ketone is an important biradical decay pathway in nonpolar solvents.[79] A singlet state hydrogen transfer may offer what amounts to a radiationless deactivation route whereby a hydrogen transfer to form a twisted biradical is followed by disproportionation back to the ketone ground state *if* the disproportionation is competitive with or faster than bond rotation. Alternatively, nonadiabatic decay to the ground state may occur if the energy surfaces are such that an orbital symmetry dictated surface crossing occurs partway along the path to the biradical.[33,36,84]

Discussion

Reports of isotope effects on hydrogen abstraction by excited carbonyl compounds are relatively limited. The structures of several molecules with well documented isotope effects (values in parenthesis) are shown in Chart 2. Included in the scheme are alkylketones, arylketones, enolizable *ortho*-methylarylketones and some examples involving intermolecular reactions. Isotope effects on these compounds at room temperature vary from the expected maximum of $k_H/k_D \approx 7$, to relatively small values such as 1.6. Early reports involving alkylketones by Coulson and Yang[85] and by Padwa and Bergmark[31] demonstrated different isotope effects from singlet and triplet states. Values of 6.7 and 5.2 were found in the excited triplet state of 2-hexanone (2-HEX) and 5-decanone-2,2-d_2 (d_2-DEC, Chart 2), respectively, while their corresponding singlets were shown to

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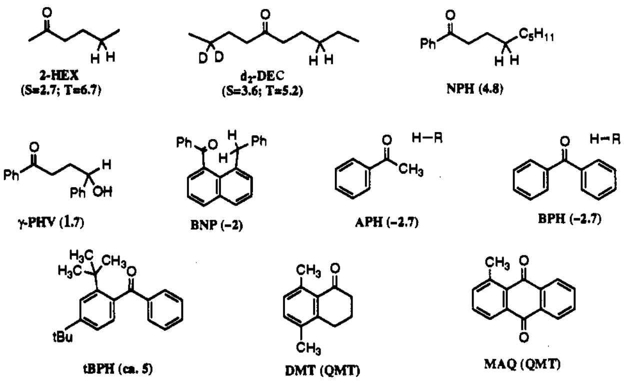
give isotope effects of only 2.7 and 3.6.[86] In the case of arylketones, exclusive triplet reactivity is normally assumed because of the high intersystem crossing rates. Studies by Lewis and by Wagner *et al.* involving γ-hydroxy-γ-phenylbutyrophenone (γHPB)[87] and nonanophenone (NPH),[88] respectively, have revealed relatively small isotope effects of 1.7 and 4.8. In the intermolecular version of the hydrogen atom transfer reaction, early work by Moore *et al.*[89,90] showed isotope effects of 2.7 with benzophenone as the triplet ketone acceptor. Consistent results were later obtained by Okamoto and Teranishi[91] who reported hydrogen abstraction by triplet benzophenone (BPH) from benzhydrol, methanol, isopropyl alcohol, and toluene at ambient temperatures, with isotope effect values of 2.7, 2.61, 2.69, and 1.80, respectively. In the reaction of triplet acetophenone (APH) with toluene and toluene-d_3 Wagner and Leavitt suggest an isotope effect > 5.[92]

A few temperature-dependence studies have also addressed the extent and nature of a primary isotope effect. Descriptions of a classic kinetic isotope effects due to zero point energy differences,[32] differences in pre-exponential factors,[30] and quantum mechanical tunneling effects have been proposed.[14,15] Two interesting instances involving δ-hydrogen abstraction have been reported by DeBoer *et al.* and by Wagner *et al.* In the first case, DeBoer *et al.* found that hydrogen atoms transfer about twice as fast as deuterium atoms in 1-benzoyl-8-benzylnaphthalene (BNP).[30] However, both reactions were shown to occur with identical activation energies and only differ in their pre-exponential factors. In contrast, Wagner *et al.* found evidence of a classic kinetic isotope effects with a small (*ca.* 1.1 kcal/mol) activation energy difference between hydrogen and deuterium methyl-substituted *o-tert*-butylbenzophenone (tBPH).[32] Finally, recent studies on the photoenolization reactions of 5,8-dimethyl-1-tetralone (DMT)[14] and 1-methylanthraquinone (MAQ),[15] and their respective d_3-methyl isotopomers, have suggested that tunneling may be an important contributor to the reaction at low temperatures. Triplet state tunneling was proposed in the case of 5,8-dimethyl-1-tetralone, while the singlet manifold was the suggested precursor for tunneling in the case of *ortho*-methylanthraquinone.

The wide variation in isotope effects on the compounds in Chart 2 probably reflects structural variations in the abstraction transition state and electronic state configuration differences. The possibility that isotopic substitution may significantly affect the rate of other photophysical steps in these compounds is unlikely, given our results and others. Furthermore, care must be taken in interpretation of the data. Primary isotope effects based on quantum yield measurements, for instance, reflect complex rate ratios. Absolute rate measurements must also be analyzed carefully as isotope effects may also occur on excited state processes other than reaction. Reaction rates of aryl ketones at normal temperatures are often large enough to make other triplet deactivation pathways nearly irrelevant. Nonetheless, low temperature studies such as that reported here will lead to reaction rates comparable to other triplet decay processes. Nonradiative T_1-S_0 transitions involve highly activated vibrational levels of S_0, and deuterium substitution can slow down intersystem crossing, thereby extending the lifetime of the triplet state, but these effects tend to be much more significant in large planar aromatics in $\pi\pi^*$ states. We expect that the effect of deuteration on the photophysical properties of the anthrone chromophore should be minimal. Triplet lifetimes of arylketones such as benzophenone and acetophenone are known to be insensitive to ring-deuteration at 77 K;[93,94] the effect of remotely located γ-hydrogens is likely to be negligible. Experiments supporting this assumption have been carried out with several benzophenone derivatives and will be published elsewhere.[95]

Chart 2



Because of its rigidity, all the gross structural features involving the relationship between the carbonyl and the methyl group in MAT should be preserved over a large temperature range. While ground state structural parameters do not bear directly on the transition state geometry of the triplet state surface, we expect that similarities between the ground state, the transition state, and the final product may be used as a qualitative guidelines to design and analyze our expectations of the reaction within an environmentally rigid medium. The positions of the two heavy atoms involved in the reaction and the position of the transferring hydrogen atom should be the most relevant structural parameters.

While we have not been able to obtain X-ray structural data for 1,4-MAT, molecules with *ortho*-methylbenzocyclohexanone fragments were searched for in the Cambridge Crystallographic Data Base.[96,97] Four suitable structures were found, including three with *ortho*-methyl substituted benzocyclohexanones and one with an *ortho*-isopropyl fragment. The nonbonded distance between the methyl carbon and the carbonyl oxygen (d_2: C···O) and the nonbonded distance between the closest hydrogen atom in the *ortho*-methyl group and the carbonyl oxygen (d_1: CH···O=C) are very short (see Chart 3 for definitions). Because of the unique steric arrangement, these distances fall within the range suggested for intramolecular C−H···O hydrogen bonding interactions.[78] While hydrogen positions are uncertain in X-ray measurements due to their low diffraction power, the separation between the two heavy atoms, d_2, is quite reliable, and varies between 2.77 and 3.03 Å for the sampled

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(86) An interesting observation in the case of alkyl ketones is that deuterated samples give higher quantum yields of reaction in spite of their lower reaction rates. This counterintuive observation may be understood in terms of deuteration slowing down the singlet state reaction relative to intesrystem crossing. A decrease in the yield of singlet biradicals reduces a pathway for reversible formation of the starting material. In contrast, slowing down the triplet state reaction does not reduce the triplet state yields.

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Chart 3

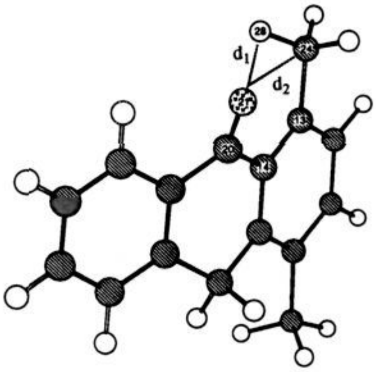

Table 3. Structure of 1,4-MAT by Molecular Mechanics and by Semiemprical Methods

method	d_1 (CH···O) Å	d_2 (C···O) Å	$O_{21}-C_{20}-C_{14}-C_{13}$ (deg)
amber*[a]	2.54	2.76	23
MM3*[a]	2.54	2.76	18
AM1[b]	2.39	2.66	15
PM3[b]	2.65	2.91	35
X-ray[c]	2.22−2.49	2.77−2.80	12−43

[a] Amber and MM3 force field as implemented in MacroModel. [b] AM1 and PM3 as implemented in Spartan. [c] Range of values from X-ray structures reported in refs 85 and 86.

compounds.[98−100] These distances are substantially less than the sum of the van der Waals radii of carbon and oxygen (i.e., 3.2 Å)[26] and only 0.23 to 0.49 Å longer than the C···O distance of a UHF/3-21G ab initio transition state model involving γ-hydrogen abstraction in hexanal calculated by the Houk group, 2.54 Å .[18,19]

Not surprisingly, analysis of 1,4-MAT with molecular mechanics and semiempirical methods also suggests short C···O and C−H···O distances. Structural parameters from minima obtained by a Monte Carlo conformational search using the MM3 and Amber force fields (MacroModel), and from optimized semiempirical RHF AM1 and PM3 structures, are summarized in Table 3. While there are significant variations in these models, they share several structural features with each other which also suggest a favorable ground state geometry. As shown in Table 3, the calculated C···O and C−H···O distances compare relatively well with those obtained with the X-ray models. The most important differences come from the $O_{21}-C_{20}-C_{14}-C_{13}$ dihedral angle that relates the plane of the carbonyl to the plane to the aromatic ring. It should be noted that a close to collinear C−H···O orientation suggested by the X-ray structures is not observed in structures of 1,4-MAT as calculated by molecular mechanics or by semiempirical methods, which predict structures in which the C···O vector bisects the corresponding H−C−H angle. However, one may expect that methyl group rotation is rapid under all of our experimental conditions.

The photophysical properties of anthrone (AT), the benchmark for the current study, have been studied in great detail over the last several years. Picosecond measurements at room temperature have demonstrated an efficient intersystem crossing with time constants between 10−50 ps that results in a quantitative population of the triplet excited state.[81,83,101] Nanosecond laser flash photolysis has been used to demonstrate efficient *intermolecular* hydrogen abstraction reactivity with suitable hydrogen atom donors.[102−105] AT has been reported to have efficient phosphorescence with a quantum yield of 0.55 and a lifetime of 1.5 ms in ethanol.[58,59] The vibronic structure and its relatively short triplet lifetime are diagnostic for a lowest triplet state with an n,π^* configuration. The lack of detectable product formation at 77 K suggests that anthrone triplets decay exclusively by phosphorescence and by T_1-S_0 thermal decay. The current results in methylcyclohexane are in good agreement with those in EtOH and with expectations from its lower polarity. Relative phosphorescence yields measured at 77 K give the highest value for AT, and values that are about half as large for 2,3-MAT and 10,10-MAT. As expected, *meta*-methyl and *para*-methyl substitution in 2,3-MAT do not significantly alter the phosphorescence decay of the anthrone nucleus. Neither were significant differences observed in the case of 10,10-MAT.

In contrast, the triplet state properties of the anthrone chromophore are profoundly affected by the methyl substituents in 1,4-MAT and 1,4-DMAT (Table 1). A preliminary analysis is based on Scheme 2. A triplet state reaction with rate k_H (or k_D for 1,4-DMAT) competes with phosphorescence (k_{P^o}) and thermal decay (k_{TS}) reducing both the phosphorescence yields (Φ_P) and phosphorescence lifetimes (τ_P), compared to those of the nonreactive compounds. The latter values depend inversely on the magnitude of the hydrogen atom transfer rate, k_H, as indicated in eqs 1 and 2. In agreement with expectations and in keeping with Scheme 2, an efficient triplet deactivation pathway is indicated for 1,4-DMAT, based on its low phosphorescence yields and reduced lifetime. 1,4-MAT appears to have chemistry so dominated by hydrogen atom transfer that its phosphorescence is below the limit of our detection.

$$\tau_P = 1/(k_H + k_{TS} + k_{P_o}) \tag{1}$$

$$\Phi_P = \Phi_T k_{P_o} \tau_P \tag{2}$$

The lack of emission from 1,4-MAT, even at 18 K, appears to constitute an enormous isotope effect. However, a primary kinetic isotope effect fully consistent with a hydrogen atom transfer, arising from differences on the zero-point energies of the breaking σ bonds, may be quite large at sufficiently low temperatures. Assuming stretching frequencies of 3000 and 2100 cm^{-1} for C−H and C-D, respectively, isotope effects of 6−8 at room temperature correspond to values $>10^3$ and $\gg 10^{10}$ at 77 and at 18 K.[106] While our observations are consistent with such large ratios, and it is difficult to anticipate any other available process which could show effects of this magnitude, a more detailed analysis shows that there is an upper limit to the observable intensity ratios and direct interpretations must be made with care.

Arguments based on activation energy differences from zero point energy values predict that isotope effects become larger as reaction rates become smaller at lower temperatures.[106] In

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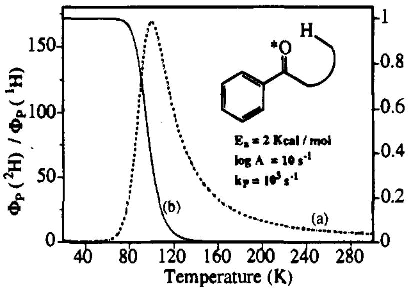

Figure 6. (a) Simulated phosphorescence intensity ratio as a function of temperature for model arylketone decaying exclusively by phosphorescence and by H-transfer reaction. Assumed reaction parameters are $E_a = 2$ kcal/mol, log $A = 10$, $k_{P^0} = 10^3$ s^{-1} and $\Phi_{ISC} = 1$. The phosphorescence rate (k_{P^0}) is assumed to be isotope and temperature-independent. (b) Phosphorescence quantum yield of the ^{1}H-donor compound with scale on the right.

contrast to ground state processes where reactions may be slowed down to hours, days, months, etc., the time scale for photochemical reactions is inherently limited, and *reactions will not be observed when the rate falls significantly below that of radiative decay.* Isotope effect values of 10^3 or 10^{10} would not only be experimentally difficult to quantitatively determine but will not have an opportunity to manifest themselves once reaction rates become sufficiently slow. If isotope effects are measured through phosphorescence yields, limitations occur both when reaction is too fast or when it is too slow as compared to the rate of phosphorescence.

In general, the phosphorescence intensity ratio for deuterated and protonated compounds is expected to follow a behavior such as that simulated in Figure 6a where a model system with typical ketone phosphorescence rates (10^3 s^{-1}) and hydrogen abstraction activation parameters ($E_a = 2$ kcal/mol, log $A = 10$ s^{-1}) is considered. The position of the maximum will be displaced to lower temperatures and to greater $\Phi_P(D)/\Phi_P(H)$ values as the activation energies become smaller and the pre-exponential factors become larger. It is assumed in the figure that the phosphorescence rate (k_{P^0}) is isotope and temperature independent and that the reaction is susceptible to a full primary isotope effect with $\nu_H = 3000$ and $\nu_D = 2100$ cm^{-1}. It is also assumed for simplicity that only reaction and phosphorescence contribute to the depletion of the excited state and that reaction occurs exclusively by an activated mechanism. The quantum yield of phosphorescence ranges from near zero to unity within the temperature range simulated (line b), and it is easy to see that reaction dominates the triplet decay at temperatures higher than *ca.* 120 K for the set of parameters assumed. As shown in the figure, when the temperature of our model system is lowered below approximately 70 K, the quantum yield of phosphorescence for both isotopomers asymptotes to unity, and the observed isotope effect disappears. The maximum observable isotope effect obtainable from phosphorescence measurements occurs at about 100 K at a point where the rate of reaction of both isotopomers has been slowed down but is still comparable to k_P. A reaction rate ratio $k_H/k_D \sim 420$ expected at this temperature does not have an opportunity to fully develop giving rise instead to a maximum of observable of *ca.* $\Phi_P(D)/\Phi_P(H) \sim 90$.

Results with 1,4-MAT and 1,4-DMAT do not fit the expectations of the simplified model implied in Scheme 2 and Figure 6, where phosphorescence and an activated reaction compete for deactivation of the triplet excited state and triplet formation is quantitative at all temperatures. For a large isotope effect not to disappear at 18 K under those assumptions it would be necessary for triplet 1,4-MAT to have an extremely favorable triplet state reaction. If one assumes that intersystem crossing yields are isotope-independent, a phosphorescence quantum yield of $\Phi_P(H) \ll 10^{-6}$ estimated for 1,4-MAT at 18 K would imply a reaction rate of *ca.* $>10^9$ s^{-1}. At 18 K, such a rate requires activation energies of *ca.* <0.050 kcal/mol if a large pre-exponential factor is available (e.g., log $A \approx 12$). This possibility may be viewed as unlikely and further insights may be obtained by analyzing the triplet decay rates and the temperature-dependence of the phosphorescence intensities and the phosphorescence lifetimes of 1,4-DMAT in order to modify Scheme 2.

Nonexponentiality of low temperature phosphorescence decays as observed here is common in heterogeneous and glassy media and is usually assigned to conformational or matrix effects. The current results do not demand an alternate interpretation. Reasonable fits were obtained from a double exponential function for all the compounds in Table 1. The relatively small difference between the fast and slow components and the consistency of the contributions suggest that the double exponential fit provides an excellent qualitative, if not quantitative, description of the behavior.

More importantly, lifetime variations for AT and 2,3-MAT at 77 and 18 K are small, indicating that the temperature dependence of k_{P^0} and k_{TS} is very small. By contrast, the phosphorescence intensity of 1,4-DMAT (Figure 4) decreases as the temperature rises from 18 to 80 K. A systematic increase in the triplet lifetimes as a function of temperature was observed between 80 and 30 K followed by a region where the triplet lifetime remained constant below 30 K. The Arrhenius plot shown in Figure 5 was obtained from the triplet decay rates of 1,4-DMAT by subtracting the nonreactive contributions to decay, estimated form the AT and 2,3-MAT. It clearly shows a baseline of temperature-independent reactivity, which is dominant at temperatures below about 30 K. This treatment supports a quantum mechanical tunneling reaction and suggests that a tunneling correction to the triplet state hydrogen atom transfer rate in eq 1 and Scheme 2 should be implemented. Moreover, the apparent deuterium tunneling rate of $k_{QMT} \approx 2 \times 10^3$ s^{-1} compares remarkably well with the triplet state deuterium tunneling rate of $3 \pm 2 \times 10^3$ s^{-1} proposed by Al-Soufi *et al.* for the structurally related 1,4-dimethyltetralone (DMT, Chart 2).

The possibility that a change in slope in Figure 5 may be the result of a temperature dependence in the pre-exponential factor as suggested by rate expressions from transition state and collision theory also needs to be considered at ultralow temperatures.[107,108] Plots of log $k_D/T^{1/2}$ and log k_D/T vs $1/T$ were found to deviated considerably from linearity, which makes this alternate explanation for the data significantly less tenable.[108]

Further examination of the data shows that even the triplet tunneling correction is not sufficient to account for all the intensity and lifetime trends. A qualitative mismatch between the phosphorescence intensity and lifetime of 1,4-DMAT, compared to AT and 2,3-MAT at 18 K, is observed. Though the lifetime of 1,4-DMAT is about one-fifth that of 2,3-MAT, its phosphorescence intensity is attenuated by a much larger factor (ca. 100). There is no reason to believe that widely deviant k_{TS} and k_{P^0} values could account for this, based on the similarity of AT, 2,3-MAT, and 10,10-MAT. Further, the weighted lifetime of 1,4-DMAT changes only by a factor of 2−3 over the 18−80 K, interval while the intensity values change by a factor of *ca.* 24. A significant intensity variation

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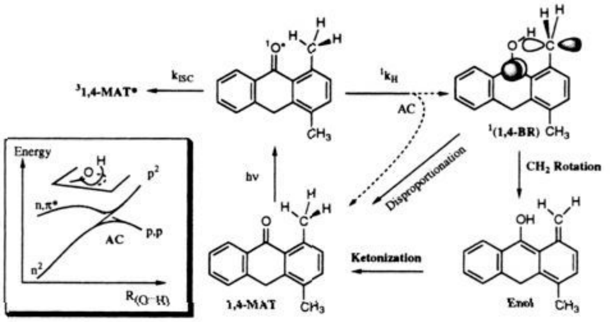
Scheme 3



is observed between 18 and 30 K, in spite of this being a region where the triplet lifetime remains constant. Intensity changes between 18 and 30 K are particularly clear and experimentally unambiguous and require a temperature-dependent deactivation pathway that precedes formation of the triplet state. In this study, this behavior is unique to the compounds with an *ortho*-methyl group, and it is reasonable to associate it with a singlet deactivation mechanism which depends critically on the presence of the *ortho*-methyl substitution (Scheme 3).

As indicated in Scheme 3, a singlet state hydrogen atom transfer reaction may form a singlet 1,4-biradical which proceeds to the ground state enol by simple bond rotation or regenerates the starting ketone by very rapid disproportionation. Orbital and state symmetry considerations predict that a vibrationally activated process capable of breaking the reaction symmetry plane or a trajectory where the target hydrogen is not co-planar with the carbonyl group (*i.e.*, any real system) will result in an avoided crossing (AC). As shown in the inset in Scheme 3, an AC occurs between the excited singlet state surface leading to the biradical and a surface correlating a zwitterion with the ground state ketone.[33,109] Such an AC occurs at some point prior to formation of the 1,4-biradical along the reaction coordinate which may be visualized mainly by the O···H distance in Scheme 3. Depending on its exact location and the shapes of the surfaces, the avoided crossing may lead to partitioning between formation of the twisted biradical and non-adiabatic return to the ground state without formation of an intermediate. The efficiency of an avoided crossing depends on the extent of interaction between the two surfaces. This should be affected by motions that alter the reaction plane of symmetry and should therefore be thermally activated. Thus ^1k_H may compete with intersystem crossing (k_{ST}) to reduce the quantum yield of triplet formation (Φ_{ISC}), affecting phosphorescence intensities even under conditions where the triplet lifetime remains constant, fully consistent with eqs 1, 2, and 3.

$$\Phi_{ISC} = k_{ST}/(^1k_H + k_{ST}) \qquad (3)$$

Singlet state deactivation by photoenolization reactions has been previously proposed in *ortho*-methylacetophenone and in 1,4-dimethyltetralone to account for the low yields of triplet formation. It is known, however, that *ortho*-methylbenzophenone does not react from the singlet state but instead undergoes a quantitative intersystem crossing.[5] By analogy, one may speculate that singlet state reactions in diarylketones should be unlikely, therefore questioning the validity of this suggestion.[2] To compete with excited state intersystem crossing ($k_{ST} \sim 10^{12}$ s^{-1}), a singlet state reaction requires a large pre-exponential factor ($\log A > 12$ s^{-1}) and negligible activation barriers ($E_a \sim 0$ kcal/mol). However, differences between *ortho*-methylbenzophenone and 1,4-MAT may be explained if one postulates that activation barriers for singlet state reactions are intrinsically small, but that reaction will only occur under conditions of precise orbital alignment in a highly preorganized structure, that is, when large *A*-factors are available. It is reasonable that *ortho*-methylbenzophenone should have a much lower pre-exponential factor than 1,4-MAT and conformational motions in methylbenzophenone may be too slow for a singlet reaction to compete with intersystem crossing of the excited state. The propeller conformation expected for *ortho*-methylbenzophenone[110] may change to coplanar structures much too slowly for singlet state reactivity to occur. In contrast, *ortho*-methylacetophenone may exist in nearly planar syn-conformers which may also have smaller rotational barriers. Finally, while our evidence for a singlet state reaction in the case of 1,4-DMAT and 1,4-MAT is only indirect, it is indicative of an activated process. We have no experimental indications of a singlet state H- or D-atom tunneling but certainly cannot rule it out as a parallel, but unobserved, pathway.

The reluctance of the photoenol to undergo proton exchange under several conditions is consistent with literature reports on other rigid photoenols. An avoided crossing path or a singlet state biradical undergoing a rapid disproportionation reaction would contribute to proton exchange inefficiency by preventing formation of the photoenol. One may speculate that the high temperature behavior may be dominated by singlet state processes that ultimately prevent the formation of the triplet excited state ketone and the photoenol. However, high temperature (up to 293 K) flash photolysis detection of several photoenols by Baron *et al.*[61] indicates that their formation is not the limiting factor. Reketonization rates were studied as a function of temperature in EPA (ether:isopentane:ethanol = 5:5:2), and the importance of quantum mechanical tunneling in this reaction was reported. The ketonization rates of photoenols from 1,4-MAT and 1,4-DMAT were shown to have different temperature dependences as compared to each other and to photoenols from *ortho*-methylbenzophenone.[61] However, reketonization rates at high temperature were found to be quite similar (1,4-MAT: $k_{\text{enol-ketone}} \approx 10^6$ s^{-1}; *ortho*-methylbenzophenone: $k_{\text{enol-ketone}} \sim 5 \times 10^5$ s^{-1}). Since *ortho*-methylbenzophenone proton-exchanges extremely efficiently, the reluctance of 1,4-MAT and other related ketones is surprising and suggests that the hydroxyl hydrogen is not free to exchange during the lifetime of the photoenol. A possible explanation for this behavior comes from a strong intramolecular interaction between the OH group and the π-face of the *ortho*-quinodimethane-1-ol. Support for this interpretation was obtained from a PM3 structural optimization of the photoenol structure which clearly reveals a favorable interaction between the *exo*-methylene π-system and the O−H bond in the corresponding *ortho*-quinodimethane structure (Chart 4). Hydrogen bonding interactions between OH and π-faces have been increasingly documented and accepted.[77,78,111] A recent study by Rzepa *et al.* revealed several compounds with OH···π-face bonding documented in the Cambridge crystallographic data base.[77] It was also shown in this study that semiempirical methods (AM1 and PM3) tend to underestimate this interaction. It is interesting that the PM3 structure of the photoenol of 1,4-MAT shows C···O and C−H···O distances characteristic of an intramolecular hydrogen bond with coordinates that clearly suggest a tunneling mechanism for the reketonization reaction (Chart 4). This type of interaction was also observed in a recent theoretical study

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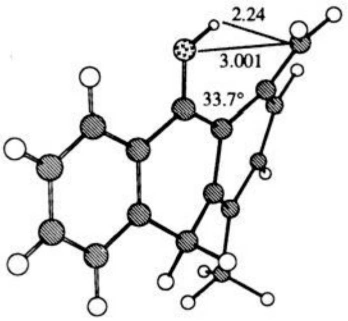
Chart 4



on the ketonization of 1,4-dimethyltetralone by Smedarchina *et al.* where both the AM1 and PM3 Hamiltonians reveal a gas phase photoenol structure consistent with a distorted skeleton and close O—H$\cdots\pi$-face interaction as that shown in Chart 4.[7] Solvation effects analyzed by these authors suggest an interaction with three water molecules which do not disrupt the structure of (syn) photoenol where the O—H bond points to the *exo*-methylene group. We suggest that a similar, entropically favored intramolecular OH$\cdots\pi$-face interaction in the rigid structure of 1,4-MAT may be responsible for the lack of efficient exchange. The strength of this interaction should be much smaller in the photoenol derived from *ortho*-methylbenzophenone and other compounds where a prospective O—H$\cdots\pi$-face hydrogen bond may be disrupted by intramolecular rotation.

A large primary isotope effect and a complex interplay of singlet and triplet state processes has been demonstrated for the *ortho*-methylanthrones reported in this study. From the literature reports addressing an excited state primary isotope effect, the work by Al-Soufi *et al.*[14] and by Gritsan *et al.*[15] suggest several interesting comparisons. Dimethyltetralone (DMT) was investigated between 80 and 270 K[14] and *ortho*-methylanthraquinone (MAQ) between 120 and 350 K.[15] Our measurements were carried out by phosphorescence in a nonpolar solvent (MCH) and covered inverse temperature limits much greater than those studied before with temperature values as low as 18 K. Studies with dimethyltetralone (DMT) and *ortho*-methylanthraquinone (MAQ, Chart 2) were carried out by transient absorption methods in polar solvents, and extensive deconvolution of the data was required to separate the kinetics of temperature-dependent transients which included the triplet ketones, triplet enols, and ground state enols. The main limitation in our study is given by the rapidly disappearing phosphorescence signals even at relatively low temperatures (*e.g.*, 80 K). Long enol lifetimes at low temperatures present serious analytical problems in polar solvents (EtOH, EPA) but were shown not be a problem in MCH. Considering that hydrogen abstraction occurs from equilibrium populations of n,π^* triplet states,[2] it is interesting that triplet state tunneling occurs in the case of tetralone which has a π,π^* lowest state configuration. If thermal population of the n,π^* state is required for reaction, additional contributions to the reaction temperature dependence may be expected in lower temperature studies. Tunneling rates of 10^3 and 10^5-10^6 s^{-1} were proposed, respectively, for deuterium and hydrogen transfer,[14] and the former is in full agreement with our own observations.

Results from *ortho*-methylanthraquinone (MAQ), which is a well established n,π^* triplet, also raise several interesting questions and comparisons. An activated triplet state reaction and a singlet state quantum mechanical tunneling process are the most remarkable conclusions reported from that study.[15] The lack of observable triplet state tunneling in MAQ may be related to the higher temperature range analyzed (120 to 350 K), and it is possible that future work may show its occurrence at lower temperature values. However, should the lack of triplet state formation be confirmed at lower temperatures, it will be interesting to analyze possible reasons for this behavior including its ditopic nature and its lower triplet energy. It is interesting to comment that evidence for a singlet state reaction in the case of MAQ was based on "instantaneous" flash photolysis detection of a fraction of the singlet photoenol. However, no evidence for a tunneling mechanism was presented, and the possibility of a thermally activated singlet state reaction was not considered. Evidence for a singlet state reaction in the present study is also indirect and is based on phosphorescence intensity changes that occur even when the triplet lifetime remains constant. While we interpret this observation in terms of a thermally activated singlet state process, we have no means of eliminating a concurrent singlet state tunneling mechanism. We also propose that a temperature-dependent singlet state process capable of competing with intersystem crossing at temperatures as low as 18 K is very likely associated with an avoided crossing adiabatic pathway as proposed sometime ago by Salem.[109]

Conclusions. The use of phosphorescence measurements to study hydrogen atom transfer reactions of triplet ketones has been demonstrated. The method is ideally suited to analyze solid state systems with reaction rates similar to those of radiative decay and was utilized here to address the involvement, the extent, and the mechanism of a primary isotope effect in an *ortho*-methylanthrone (1,4-MAT and 1,4-DMAT) at cryogenic temperatures. Our results confirm the existence of a very large primary isotope effect and demonstrate a triplet state reaction with contributions from both thermally activated and quantum mechanical tunneling mechanisms. While no phosphorescence could be detected for the protio-substituted compound (1,4-MAT), phosphorescence intensities and phosphorescence lifetimes showed deuterium quantum mechanical tunneling to be the dominant triplet state mechanism below 30 K in the case of 1,4-DMAT. Indirect evidence for activated singlet state reactivity was also obtained in the deuterated compound from phosphorescence intensity measurements. A singlet state deactivation process was analyzed in terms of an avoided crossing (AC) mechanism. Further studies are in progress and are aimed to delineate the structural requirements for reaction by using substrates with variable structures and in different solid state media.

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