

Effect of Solvents on the Photoenolization of *o*-Methylanthrone at Low Temperatures. Evidence for H-Atom Tunneling from Nonequilibrating Triplets

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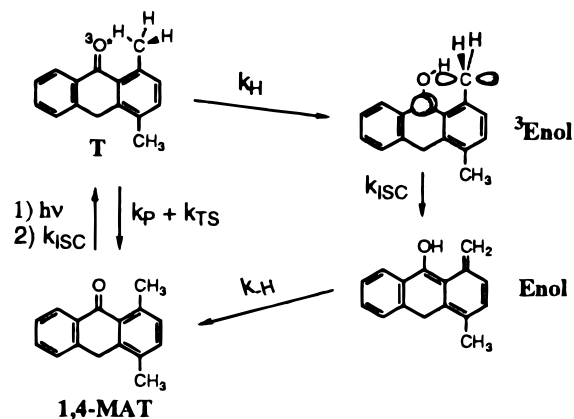
The reactivity of 1,4-dimethylanthrone (1,4-MAT) and 1,4-dimethylanthrone-*d*₈ (1,4-DMAT) toward hydrogen transfer was investigated in methylcyclohexane (MCH), ethanol (EtOH), and 2,2,2-trifluoroethanol (TFE) by comparing their triplet-state emission spectra and lifetimes with those of compounds without the *o*-methyl substituent. A predominantly n,π^* lowest triplet state in nonpolar solvents such as MCH changes toward a less reactive π,π^* configuration in polar solvents such as EtOH and TFE. In EtOH, 1,4-DMAT exhibits a temperature-dependent dual emission while the corresponding protio compound (1,4-MAT) decays by reaction at all temperatures analyzed (ca. 15–90 K). Although compounds without the *o*-methyl group also presented dual emission, their relative intensities and lifetimes were shown to be temperature-independent, indicating the lack of thermal equilibration between the two triplets below 90 K. In the case of 1,4-DMAT in EtOH, an Arrhenius plot based on the data from the short-lived component (mainly n,π^*) and detection of the enol between 19 and 80 K revealed that deuterium transfer occurs by quantum-mechanical tunneling (QMT). In agreement with results in MCH where a short-lived n,π^* state predominates, the D-tunneling rate constant was estimated to be ca. $(1.5\text{--}7.5) \times 10^3 \text{ s}^{-1}$. The phosphorescence of anthrone derivatives in TFE was long-lived, with a strong π,π^* character, and highly heterogeneous, but not dual. A large isotope effect on phosphorescence is assigned to the isotope-dependent tunneling reaction from a predominant π,π^* state.

Introduction

The photoenolization of *o*-methylaryl ketones has been studied in detail by several authors.^{1–15} The reaction occurs adiabatically on the triplet surface^{5,12,14–16} by transfer of a hydrogen atom from the *o*-methyl group to the carbonyl oxygen (k_H), and it is completed by intersystem crossing to the ground-state enol (k_{ISC} , Scheme 1).^{2–4,6–8,17–21} The photoenol is a thermodynamically unstable *o*-quinodimethane that rearomatizes to the starting ketone in a proton-transfer reaction (k_{-H}) to complete an overall cyclic process.²² Although much of the initial interest in the reaction came from the complex kinetic behavior of conformationally flexible compounds such as *o*-methylacetophenone^{3,5–8,12,14,15} and *o*-methylbenzophenone,^{1,2,4,9–11,13} recent studies by us^{23–25} and others^{26,27} with conformationally locked compounds have shown that both H-transfer reactions may occur by quantum-mechanical tunneling mechanisms.

Work from our group has focused on the excited-state H-atom transfer of *o*-methyl-substituted benzocycloalkanones such as anthrone and tetralone. In contrast to other studies where reaction rates as a function of temperature were determined by analysis of the spectra of overlapping laser-flash-photolysis transients,^{26,27} we determined the rates of triplet reaction (k_H) by emission spectroscopy at very low temperatures.^{23–25,28} We calculated reaction rates (k_H , eq 1) from the total triplet decay rate (k_{dec}) by subtracting contributions from radiative (k_P) and thermal processes (k_{TS}), which were assumed from model compounds lacking the *o*-methyl group.²⁹ It was shown that deuterium transfer (k_D) in *d*₈-1,4-dimethylanthrone (1,4-DMAT) and in *d*₈-5,9-dimethyl-1-tetralone (DMT) at very low temperatures (ca. 15–90 K) is slow enough to compete with radiative and thermal decay [i.e., $k_D \geq 10^2\text{--}10^3 \text{ s}^{-1}$ and $k_D \leq (k_P + k_{TS})$].

SCHEME 1



The involvement of quantum-mechanical tunneling was unambiguously established by curved Arrhenius plots, by detection of the photoenol at temperatures as low as 15–20 K, and, in the case of deuterated DMT, by excellent agreement between flash-photolysis results published by El-Soufi et al.²⁷ and emission results from our laboratory.²⁵

$$k_{dec} = k_H + (k_P + k_{TS}) \quad (1)$$

In the non-deuterated compounds, ¹H transfer ($k_H \geq \sim 10^7$) dominates the triplet decay at all temperatures analyzed ($k_{dec} \approx k_H \gg k_P$) and no emission has been observed.²⁷ It is known that an increase in polarity slows the rate of hydrogen abstraction in Norrish type-II^{30–33} and photoreduction^{34,35} reactions of triplet aryl ketones. The same effect may be expected in the photoenolization of the *o*-methyl-substituted compounds. Since

SCHEME 2

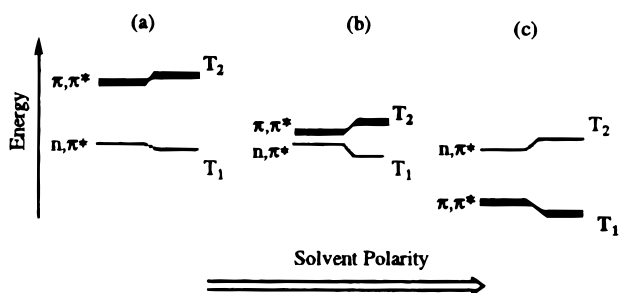
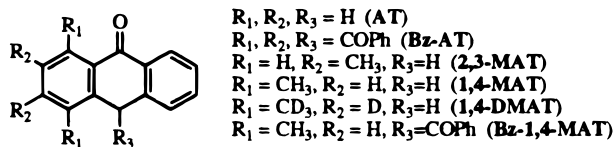


CHART 1



the effect of solvents on the photophysical behavior of aromatic carbonyls at low temperatures has been extensively investigated,^{36–43} a correlation between photophysical measurements and photochemical behavior would be highly informative. Changes in the rate of hydrogen transfer reflect perturbations along the reaction coordinate, and the identification of activated and tunneling processes may give valuable insights into the reaction potential. To accomplish this, the effect of solvents can be analyzed in terms of changes in the electronic configuration of the lowest triplet surface, which may be given in terms of zero-order n, π^* and π, π^* configurations (Scheme 2). It is known that polar solvents stabilize the relatively polar π, π^* triplet (in heavy lines in Scheme 2)^{32,37,44} while the close-lying n, π^* state is either destabilized³⁷ or unaffected. It is also known that n, π^* states are much more reactive than π, π^* states toward hydrogen-transfer reactions, and their energetic proximity results in interesting kinetic behavior. A strong vibronic interaction between the zero-order states may result in the formation of mixed states, T1 and T2 (Scheme 2), which may display hybrid properties.^{31,45} It has been suggested that ketones with a lowest triplet state that has a dominant π, π^* configuration (Scheme 2c) may owe their reactivity to their residual n, π^* character.^{46,47} However, Wagner has shown,^{48–52} and others confirmed,^{33,34,45} that reaction occurs in most cases from equilibrium populations of the state with greater, and often nearly pure, n, π^* character. In rare examples, reactions from a T1 with a predominant π, π^* character have been documented, suggesting the validity of the former model.^{48,53} The case of naphthyl ketones, where activation barriers are smaller than the energy required to populate the n, π^* -rich T2, reported by Hammond and Leermakers⁴⁸ and by DeBoer et al.,⁵³ are among the best-documented examples. Rates of hydrogen abstraction in those cases are 100–1000 times slower than those observed in ketones with n, π^* states.

In this paper we explore the effect of solvents on the photophysical properties and chemical reactivity of 1,4-DMAT and 1,4-MAT (Chart 1). It is expected that the lowest triplet of the anthrone chromophore may be switched from a predominantly n, π^* configuration in MCH to a T1 that is richer in π, π^* character in polar solvents such as EtOH and TFE (Scheme 2).

We compare results from anthrone (AT), 2,3-dimethylantrone (2,3-MAT), 1,4-dimethylantrone (1,4-MAT), and 1,4-dimethylantrone-*d*₈ (1,4-DMAT) in ethanol (EtOH) and 2,2,2-trifluoroethanol (TFE) to those previously reported in methylcyclohexane (MCH). We have also analyzed 10-benzoyl-

anthrone (Bz-AT) and 10-benzoyl-1,4-dimethylantrone (Bz-1,4-MAT). From the compounds selected for this study only 1,4-MAT, 1,4-DMAT, and Bz-1,4-MAT can undergo a photoenolization reaction. AT and 2,3-MAT have no hydrogen-donating *o*-methyl groups and were analyzed to evaluate the effect of solvents on the photophysical properties of the chromophore. The benzoyl group in Bz-1,4-MAT was introduced as an intramolecular triplet sensitizer to address the possibility of singlet-state deactivation in 1,4-MAT. The effect of the benzoyl group in the anthrone chromophore was explored with Bz-AT. Measurements were carried out between 15 and 80 K.

Experimental Section

Methylcyclohexane, ethanol, and acetone were of the highest quality commercially available and were used as received. 2,2,2-Trifluoroethanol was filtered through calcium sulfate and sodium bicarbonate prior to use. The syntheses of anthrone (AT), 2,3-dimethylantrone (2,3-MAT), 1,4-dimethylantrone (1,4-MAT) and *d*₈-1,4-dimethylantrone (1,4-DMAT) were previously described.^{23,54} 10-Benzoylantrone and 10-benzoyl-1,4-dimethylantrone were prepared by the method of Camaioni and Alnajjar.⁵⁵ Fluorescence and phosphorescence spectra and phosphorescence decays were obtained as previously reported for MCH glasses.^{23,54} Solutions of anthrone and anthrone derivatives were freshly prepared in MCH, EtOH and TFE at concentrations of ca. $(3–10) \times 10^{-5}$ M. Excitation was carried out at 309 nm. Solutions of 1,4-MAT and 1,4-DMAT in 10% acetone/ethanol had concentrations of ca. 0.1 M. Excitation was carried out at 295 nm. Glasses of high optical quality were obtained for EtOH, EtOH/acetone mixtures, and MCH. Frozen TFE solutions appeared polycrystalline. Phosphorescence emission spectra were shown to be independent of the excitation wavelength. Decay spectra of TFE samples were obtained point by point by changing the delay in 0.01, 0.1, 0.5, or 10 ms steps, with detection windows similar to the step size. Between 50 and 300 pulses per point were accumulated and 50–100 data points were typically collected per decay. Our system for low-temperature measurements has been described before.⁵⁴ Transparent glassy films of about 1 mm thickness were obtained when ethanolic samples were deposited at 19 K.

Results

The phosphorescence emission of several anthrones in methylcyclohexane has been reported before.^{23,54} The spectra of all compounds in the nonpolar solvent are well resolved and possess vibrational structure and lifetimes characteristic of nearly pure n, π^* states ($\tau < 3$ ms). Spectra obtained in ethanol and trifluoroethanol were more complex. A summary of spectral data obtained at 20 K is shown in Table 1. Phosphorescence decays were fit to monoexponential functions, as described in eq 2, or to biexponential functions as described in eq 3. In the latter case, average lifetimes were calculated according to eq 4 with $\tau_1 = 1/k_1$ and $\tau_2 = 1/k_2$:

$$I = I_0 \exp(-k_0 t) \quad \text{where } k = 1/\tau \quad (2)$$

$$I = I_1 \exp(-k_1 t) + I_2 \exp(-k_2 t) \quad (3)$$

$$\tau_{\text{ave}} = \tau_1 [I_1 \tau_1 / (I_1 \tau_1 + I_2 \tau_2)] + \tau_2 [I_2 \tau_2 / (I_1 \tau_1 + I_2 \tau_2)] \quad (4)$$

Phosphorescence of AT, 2,3-MAT, 1,4-MAT, and 1,4-DMAT in Ethanol (EtOH). The phosphorescence emission of all anthrones in EtOH at 19 K is blue-shifted by 2–6 nm

TABLE 1: Phosphorescence Parameters of Anthrone and Derivatives in Methylcyclohexane (MCH), Ethanol, and 2,2,2-Trifluoroethanol (TFE)

compound	solvent	$\lambda_{(0-0)}$, nm	other maxima, nm	lifetime 20 K, ms
AT	MCH	403	431, 465, 503, 546	$\tau_1 = 1.6$ (75%) $\tau_2 = 4.4$ (25%)
AT	EtOH	397	424, 456, 492, 534	$\tau = 2.0$
AT	TFE	398	423, 453, 491, 529	$\tau_1 = 2.1$ (19%) $\tau_2 = 44$ (81%)
2,3-MAT	MCH	400	429, 462, 498, 541	$\tau_1 = 1.75$ (90%) $\tau_2 = 0.50$ (10%)
2,3-MAT	EtOH	396	423, 456, 490, 531	$\tau_1 = 13$ (75%) $\tau_2 = 2.1$ (25%)
2,3-MAT	TFE	<i>c</i>	<i>c</i>	$\tau_1 = 169$ (99%) $\tau_2 = 9$ (1%)
1,4-DMAT	MCH	413	443, 479, 518, 565	$\tau_1 = 0.46$ (77%) $\tau_2 = 0.085$ (23%)
1,4-DMAT	EtOH ^a	411	439, 473, 511, 556	$\tau_1 = 0.61$ (77%) $\tau_2 = 0.13$ (23%)
1,4-DMAT	EtOH ^b	<i>c</i>	<i>c</i>	$\tau_1 = 35$ (11%) $\tau_2 = 330$ (89%)
1,4-DMAT	TFE	<i>c</i>	<i>c</i>	$\tau_1 = 31$ (14%) $\tau_2 = 413$ (86%)
1,4-MAT	MCH	<i>d</i>	<i>d</i>	<i>d</i>
1,4-MAT	EtOH	<i>d</i>	<i>d</i>	<i>d</i>
1,4-MAT	TFE	<i>d</i>	<i>d</i>	<i>d</i>

^a Short-lived component (acquisition 0–2 ms). ^b Long-lived component (0–500 ms). ^c Broad spectrum with no vibrational resolution. ^d No emission detected.

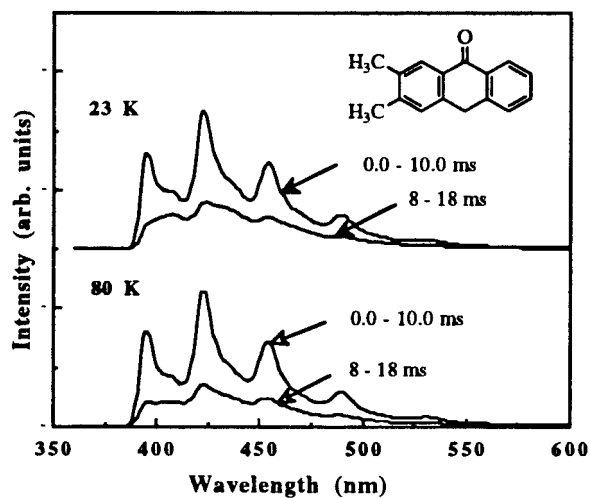


Figure 1. Phosphorescence emission spectra of a 10^{-4} M solution of 2,3-MAT in ethanol at 23 and 80 K detected between 0 and 10 ms and between 8 and 18 ms. Excitation was carried out at 309 nm.

from its emission in MCH. The spectra present the vibrational progression characteristic of an n,π^* electronic configuration, but are broader than in MCH. The decay of AT was fit to a monoexponential function with a constant triplet lifetime of 2.0 ms between 19 and 79 K. The spectra of the 2,3-MAT displays dual phosphorescence with a broader and red-shifted component remaining at the later times (Figure 1). It is noteworthy that the spectra and decays of 2,3-MAT are temperature-independent. The decays were fit to a double exponential with lifetimes of 2.1–2.4 ms (25–29%) and 11–13 ms (71–75%), respectively (see Figure 1).

The phosphorescence emission of 1,4-DMAT in EtOH is also dual. The shape of the emission collected at early times is well resolved and typical of a state with predominant n,π^* configuration (Figure 2, top frame). Spectra collected at longer decay times were structureless (Figure 2, lower frame). Unlike the emission of 2,3-MAT, the shape of the phosphorescence

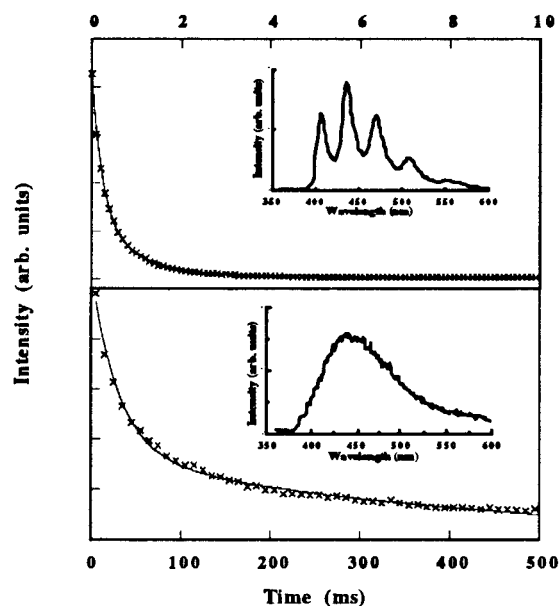


Figure 2. Phosphorescence decay of a 10^{-5} M solution of 1,4-DMAT in ethanol at 22 K: (top) maximum delay time is 10 ms, and increment and detection windows are 0.1 ms (top inset, corresponding emission); (bottom) maximum delay time is 500 ms, and increment and detection windows are 10 ms (bottom inset, corresponding emission).

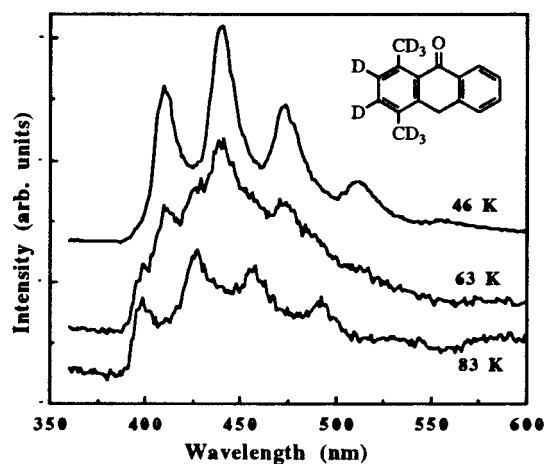


Figure 3. Phosphorescence emission of a 10^{-5} M solution of 1,4-DMAT in ethanol at 46, 63, and 83 K detected between 0 and 10 ms after the excitation pulse.

emission of 1,4-DMAT depended not only on the delay after the flash but also on temperature (Figure 3). Emission spectra detected with a 10.0-ms window between 19 and 83 K are fairly intense and well resolved at low temperatures (ca. 19–50 K) and are significantly weaker and with a greater contribution from the long-lived component at higher temperatures.

As suggested by the data shown in Figures 2 and 3, the experimental acquisition of decay curves of 1,4-DMAT in ethanol was not straightforward. Decays were collected point by point with pulsed excitation and gated acquisition after the 10- μ s lamp pulse. Proper acquisition of the fast components ($\tau < 2$ ms) requires small delay increments (e.g., 0.01 ms), short detection times, and multiple experiments per data point to accumulate a reasonable intensity. However, if the same acquisition parameters were used to collect data for the long-lived components ($\tau \approx 100$ ms), the large number of data points required (up to 10^5 points) would make the experiment prohibitively long. As a reasonable compromise, we decided to collect data with two different sets of acquisition parameters.

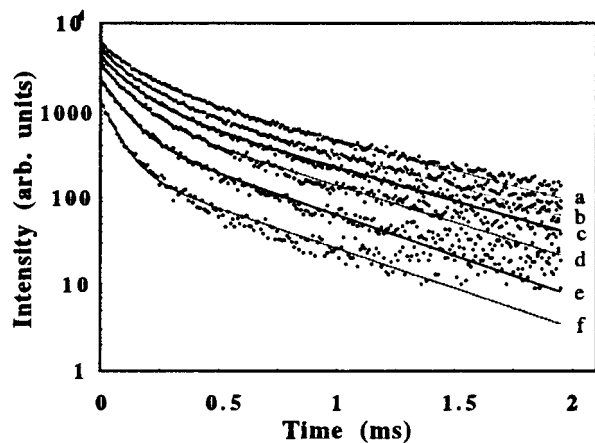


Figure 4. Decays of 1,4-DMAT in EtOH with a maximum delay time of 2 ms and with increment and detection windows of 0.01 ms at (a) 18.8, (b) 28.3, (c) 33.3, (d) 39.3, (e) 45.8, and (f) 53.9 K. The fits corresponds to $I = I_1 \exp(-k_1 t) + I_2 \exp(-k_2 t)$.

TABLE 2: Double-Exponential Fitting Parameters from the Decay Data of 1,4-DMAT in EtOH Obtained with a Maximum Delay Time of 2 ms and an Increment of 0.01 ms in the 18.8–72.4 K Temperature Range^a

<i>T</i> (K)	τ_1 (ms)	τ_2 (ms)	% τ_1^b	% τ_2^b
18.8	0.613	0.125	76.6	23.4
19.3	0.623	0.128	74.7	25.3
21.1	0.612	0.127	74.4	25.6
23.9	0.601	0.126	73.1	26.9
28.3	0.582	0.122	72.4	27.6
33.3	0.564	0.118	68.7	31.3
39.3	0.512	0.105	65.7	34.3
45.8	0.462	0.088	62.4	37.6
53.9	0.473	0.069	58.5	41.5
59.1	0.583	0.064	56.1	43.9
63.1	1.041	0.061	61.3	38.7
72.4	1.167	0.046	81.8	18.2

^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., % $\tau_1 = I_1 \tau_1 / (I_1 \tau_1 + I_2 \tau_2)$.

The first set emphasized the faster component with a small increment of 0.01 ms and a maximum delay of 2 ms for a total of 200 data points per decay. The second set of parameters was optimized to capture the long-lived component with a 5-fold greater number of flashes per point to improve the signal-to-noise ratio, an initial delay of 5 ms to eliminate the short-lived component, a maximum delay of 500 ms, and an increment between data points of 10 ms. Although the first set of parameters produced complex decays, the number of data points obtained was insufficient for analysis by complex fitting models and double-exponential fits were employed as rough estimates for triplet lifetimes. The limitations of these fits, as illustrated in Figure 4, become more severe when the short-lived emission is weaker at the higher temperatures. Table 2 summarizes these results. The second set of acquisition parameters provided essentially temperature-independent, but complex, data, which were fit to a double-exponential function with lifetimes of 31 ms (14%) and 413 ms (86%). In contrast to 1,4-DMAT, neither 1,4-MAT nor Bz-1,4-MAT showed any phosphorescence emission in ethanol.

Phosphorescence of AT, 2,3-MAT, 1,4-MAT, and 1,4-DMAT in 2,2,2-Trifluoroethanol (TFE). Although the specific interactions between triplet ketones and TFE are still controversial, broad spectra and longer lifetimes are indicative of a substantial increase in the π, π^* character of T1.^{56–58} The emission and decay of AT in TFE has dual character (Figure

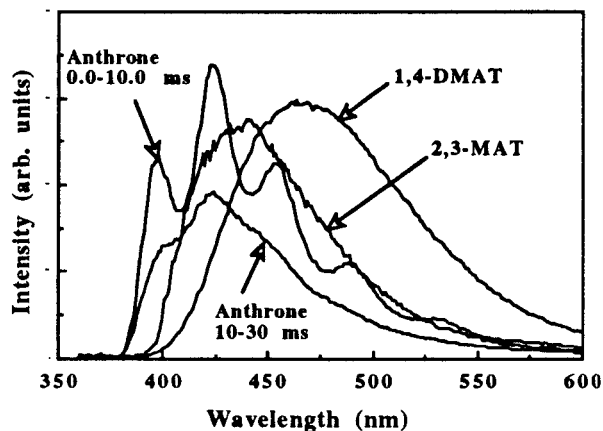
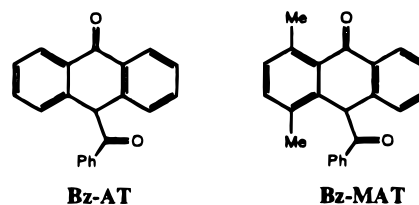


Figure 5. Phosphorescence spectra of 10^{-4} M solutions of anthrone in TFE at 77 K detected between 0 and 10 ms and between 10 and 30 ms and of 2,3-MAT and 1,4-DMAT in TFE at 77 K detected between 0 and 10 ms.

SCHEME 3



5). Spectra detected between 0 and 10 ms have an n, π^* vibrational progression but are significantly broader than those observed in MCH and EtOH. Detection between 10 and 30 ms reveals a very broad emission (Figure 5). Triplet decay was fit to a double exponential with lifetimes of 2.1 ms (19%) and 44 ms (81%), suggesting states with predominant n, π^* and π, π^* character, respectively. Also shown in Figure 5, the spectra of 2,3-MAT and 1,4-DMAT are broad and featureless, but we do not consider their emission as being dual. The phosphorescence decay of 2,3-MAT was fit to a double-exponential function with $\tau_{\text{short}} = 9$ ms and $\tau_{\text{long}} = 169$ ms, but the long-lived component was clearly the dominant one (96%). The phosphorescence emission of 1,4-DMAT in TFE was also broad and featureless with its λ_{max} displaced to the red and with lifetimes of 330 ms (89%) and 35 ms (11%). Samples of 1,4-MAT in TFE exhibited a very weak emission signal indistinguishable from that of an otherwise insignificant impurity and are considered nonemissive.

Enol Formation. The formation of enols as a result of hydrogen transfer could be easily monitored because of their bright-orange color and their characteristic fluorescence excitation and emission.^{59,60} Enols were readily observed in all the *o*-methyl-substituted compounds. Of the three solvents studied, enols could be accumulated only in ethanol. They are known to be very short-lived in nonpolar MCH^{22,61} and in relatively acidic media like TFE.^{62,63}

Sensitization Studies. Attempts to sensitize the triplet state of 1,4-MAT with acetone in ethanolic glasses were unsuccessful. Intramolecular sensitization was carried out in 10-benzoyl-1,4-dimethylanthrone (Bz-MAT, Scheme 3). The keto form of Bz-AT gives a single-exponential anthrone-like emission in ethanol.⁶⁴ In contrast, Bz-MAT yielded no phosphorescence in any solvent even though the corresponding photoenol could be rapidly accumulated in ethanol.

Discussion

Effect of Solvent Polarity and Methyl Substitution on Triplet State Configurations. The effect of substituents and

solvents on triplet emission and reactivity of aryl ketones has been the subject of much work.^{30,31,65–68} Although the spectra and decays measured in this study are generally complex, we may reach some qualitative conclusions by considering their vibrational structure, whether their lifetimes are dual, and their temperature dependence. We will assume that solvents and methyl substituents affect the energy difference between the two lowest triplets of a common anthrone chromophore.

The phosphorescence of AT in MCH and EtOH reflects a triplet state with a dominant n,π^* configuration. The spectra have the characteristic vibrational progression and short-lived decay that deviates little (MCH) or not at all (EtOH) from monoexponentiality. The small effect observed when the solvent changes from MCH to EtOH suggests that an increase in polarity in this case is not enough to affect the behavior of the lowest triplet, which remains with a dominant n,π^* character. In contrast, when measurements are carried out in TFE, a solvent significantly more polar and acidic than ethanol, one observes a dual emission with short- and long-lived components. The spectrum changes from a relatively broad but vibrationally resolved n,π^* emission at early times to a nearly featureless one as the detection window is delayed (Figure 5). The two components have lifetimes of 2.1 and 44 ms, respectively, which are consistent with concurrent emission from states with predominant n,π^* (short-lived) and π,π^* (long-lived) configurations. Although good overlap between the two spectra suggest an energetic proximity, neither the lifetimes nor the spectra change as a function of temperature between 17 and 80 K, indicating that no state equilibration occurs at those temperatures.^{69,70}

In agreement with observations suggesting that methyl groups stabilize the π,π^* states and/or destabilize the n,π^* triplets,^{31,36,44,71} the effect of increasing solvent polarity on the emission of the methyl-substituted compounds is more pronounced. The dimethyl-substituted anthrones 1,4-DMAT and 2,3-MAT display dual phosphorescence in EtOH under conditions where pure n,π^* emission was detected in AT. Temperature-independent spectra and lifetimes in the case of 2,3-MAT are also consistent with a static model with two nonequilibrating states giving rise to two types of emission. The temperature-dependence of 1,4-DMAT relates only to the short-lived component and is associated with an H-transfer reaction (vide infra). A further increase in polarity in TFE gave rise to broad and long-lived emissions with lifetimes suggestive of π,π^* triplets (Figure 5). Decays in TFE are not monoexponential, and average lifetimes of 300 and 170 ms for 1,4-DMAT and 2,3-MAT, respectively, are significantly longer than the π,π^* component of AT in TFE (44 ms).

A small heterogeneity and similar lifetimes observed for the n,π^* emissions of AT and 2,3-MAT in MCH and EtOH indicate a small conformational and solvent-site sensitivity by this state. The n,π^* spectra measured in MCH and EtOH, and which are absent in TFE, have lifetimes in the 2–3 ms range. This is in great contrast with the widely different lifetimes and kinetic heterogeneity observed for the long-lived components in EtOH and TFE, which suggests a mixed state with various degrees of aromatic (3L_a)^{37,41} π,π^* character. The average lifetimes of AT, 2,3-MAT, and 1,4-DMAT in TFE change from 36 to 170 to 300 ms. These may correlate with decreasing amounts of n,π^* character mixed in a predominantly π,π^* lowest state. The spectra and lifetimes of the longer-lived component of a given ketone are also very sensitive to the medium. For instance, a broad but resolved long-lived component from 2,3-MAT in EtOH (Figure 2) changes to a completely unresolved spectrum

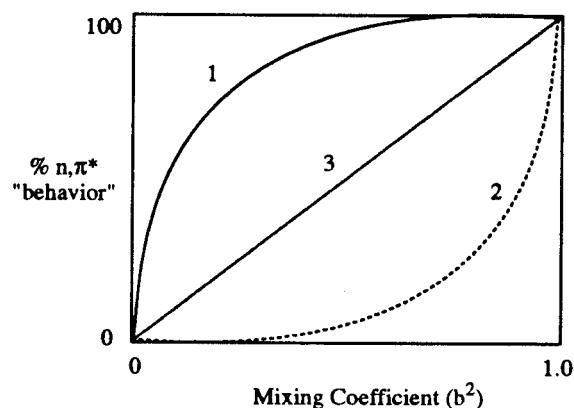


Figure 6. Hypothetical variations of % n,π^* behavior in a given triplet state as a function of its n,π^* character.

in TFE (Figure 5) while the corresponding average lifetimes change from 13 to 170 ms. The high heterogeneity observed in TFE probably reflects longer triplet lifetimes sampling hydrogen-bonding interactions, conformations, and site effects more sensitively. The lack of temperature dependence in AT, 2,3-MAT and the long-lived component of 1,4-DMAT indicate that there is no equilibration between the two emitting states. It is not clear what determines the relative populations of the two emitting states when dual emission is observed, but one possibility put forth by Rauh and Leermakers³² is that they may be determined by specific but heterogeneous environmental interactions such as hydrogen bonding.^{32,72–74}

To account for the concurrence of what appear to be nearly pure n,π^* states and π,π^* states having widely different degrees of mixing, one may suggest that the kinetic and spectral behavior of aryl ketone triplets is disproportionately influenced by their n,π^* character.⁶⁴ A qualitative representation of this model is shown by line 1 in Figure 6 where the percentage of n,π^* behavior (e.g., vibrational structure, lifetime, reactivity etc.) is plotted against a measure of n,π^* mixing as given by the coefficient b^2 from the corresponding triplet wave function, $\Psi_T = a\Psi(\pi,\pi^*) + b\Psi(n,\pi^*)$. States with a dominant n,π^* configuration ($b^2 > 0.5$) behave essentially as the zero-order state with very short lifetimes and well-resolved carbonyl vibrational frequencies. Complementarily, states with a dominant π,π^* character ($b^2 < 0.5$) may draw much of their behavior from the n,π^* character that is mixed in. For instance, polarity changes from MCH to EtOH to TFE in the case of AT do not affect the lifetime of the short-lived component despite stabilization of the π,π^* state suggested by the appearance of the long-lived component in the more polar solvent. Accordingly, the short-lived component of methyl-substituted compound 3,4-MAT remains unaltered in the MCH and EtOH despite variations in the lifetime of the long-lived component in going from EtOH (13 ms) to TFE (169 ms). This model implies that experimental observables may be determined by the state primarily responsible for the dynamics of the triplet state (i.e., single-electron density at the oxygen n orbital and spin-orbit coupling) rather than a linear contribution from each state. This interpretation may account for a very narrow distribution of n,π^* lifetimes, while the π,π^* lifetimes expand over 2 orders of magnitude, for long-lived π,π^* emissions with spectral shapes showing “residual” n,π^* vibrational structure and for dual emission displaying nearly “pure” n,π^* states along with highly heterogeneous and long-lived π,π^* triplets.

A nonlinear dependence of hydrogen-abstraction reactivity on the amount of n,π^* state character mixed on a π,π^* -rich T1 was critically analyzed by Wagner et al.³¹ as a possible

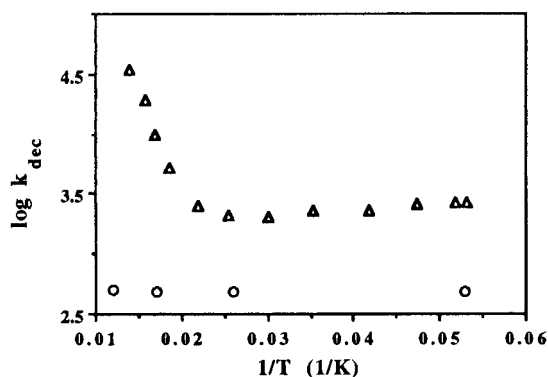


Figure 7. Arrhenius plots of triplet decay rate of the short-lived component of 2,3-MAT (circles) and 1,4-DMAT (triangles) in 10^{-5} – 10^{-4} M EtOH solutions.

explanation for the reduced reactivity of *p*-methoxyaryl ketones. In that model, it was required that the π, π^* state character had a larger influence on chemical behavior than the n, π^* state for any given mixing values (Figure 6, line 2). This model was found incorrect after it was shown that Boltzman populations of an n, π^* -rich T2 clearly dominate photochemical behavior under conditions of kinetic preequilibrium.³¹ A mixing model analyzed by Berger et al.⁴⁵ assumes that the chemical behavior of a given state may be linearly associated with its fractional n, π^* character as given by its mixing coefficient values (Figure 6, line 3). Their model was refined to account for the thermal population of energetically close states and for higher reaction barriers in the case of reaction from π, π^* states. In agreement with Wagner's observations, it was suggested that reactivity could be dominated by a higher state that is richer in n, π^* character. In the nonequilibrating cases presented here, when variations in spectral shapes and lifetimes are considered in terms of trends suggested by methyl substitution and solvents, a situation such as that depicted by line 1 accounts for our results without conflicting with data obtained at high temperatures.

Effect of Solvent Polarity on Hydrogen Transfer and Quantum-Mechanical Tunneling of 1,4-DMAT and 1,4-MAT. The emission spectra of 1,4-DMAT in MCH possess the vibrational progression expected for an n, π^* ketone at all temperatures analyzed. The lifetime of 1,4-DMAT at 18 K is much shorter than those of compounds with no *o*-methyl group, suggesting that deuterium tunneling contributes to the decay of the n, π^* triplet. Contributions to triplet decay from a thermally activated process occur above ca. 30–40 K, although formation of the product is observed over the entire temperature range. In TFE, 1,4-DMAT behaves as a π, π^* ketone. The emission spectrum is featureless and does not change as a function of delay, and its lifetime is 3 orders of magnitude greater than that in MCH. As mentioned above, lifetimes of 35 (11%) and 330 (89%) ms may reflect the site-heterogeneity that gives rise to emitting states possessing different extents of π, π^* character. In EtOH, where both π, π^* and n, π^* states were observed (Figure 2), the decay of 1,4-DMAT was too complicated to be described properly by a double-exponential function. Heterogeneity in this case may be assigned mainly to contributions from the two emissive states and concurrent chemical reactions and, second, to conformational and matrix effects. Given the limitations of our data acquisition, a strict analysis of the total decay rates as a function of temperature is essentially impossible. To carry out a qualitative analysis of the reaction, we analyzed data obtained with acquisition parameters that emphasize the shorter-lived n, π^* -rich component (Table 2 and Figure 7).

An Arrhenius plot constructed with the short-lived component

of the 2-ms acquisition data of 1,4-DMAT and the short-lived component of 2,3-MAT in ethanol glasses from ca. 18–80 K is shown in Figure 7. The short-lived component of 2,3-MAT has the same decay value as the monoexponential decay of anthrone, which is also temperature-independent over the same temperature range. The temperature dependence of the decay rate of 1,4-DMAT (triangles) above ca. 40–50 K is unique to the *o*-methyl-substituted compound and is assigned to thermally activated deuterium transfer. The single-exponential decay rates of nonphotoenolizable AT and the short-lived component of 2,3-MAT below 40 K are smaller than the short-lived component of 1,4-DMAT. The difference may be assigned to contributions from a quantum-mechanical tunneling reaction.

In EtOH, 1,4-DMAT emits from π, π^* and n, π^* states and at temperatures higher than 40 K the contribution of the π, π^* remains nearly unchanged while the n, π^* triplet is depleted by the deuterium-transfer reaction. Keeping in mind the fact that the complex phosphorescence decay of 1,4-DMAT in EtOH was fit with limitations to a double-exponential function, we can only estimate a tentative rate of tunneling for 1,4-DMAT in EtOH. The rate of triplet decay of AT, which is the same as the short-lived component of 2,3-MAT ($5 \times 10^2 \text{ s}^{-1}$), can be subtracted from the rate of decay of 1,4-DMAT in the tunneling region between 18 and 40 K. From the two components of the short-lived acquisition parameters we can bracket this rate between ca. $2 \times 10^3 \text{ s}^{-1}$ and $8 \times 10^3 \text{ s}^{-1}$. The resulting tunneling rate constant falls between 1.5×10^3 and $7.5 \times 10^3 \text{ s}^{-1}$, which compares reasonably well with the rate constant of deuterium transfer calculated for triplet DMAT in MCH between 18 and 30 K, i.e., $2 \times 10^3 \text{ s}^{-1}$.²⁴

It is significant that no temperature dependence was observed in the decay of 1,4-DMAT in TFE where population of π, π^* -rich triplet states is postulated. This is consistent with a slow deuterium transfer reaction that proceeds by quantum-mechanical tunneling up to very high temperatures or with no reaction at all.⁵³ In contrast, the absence of emission in 1,4-MAT suggests that hydrogen transfer in the protio compound is still too fast to allow for phosphorescence to compete with triplet decay.^{23,24} Since equilibration of π, π^* and n, π^* states may be ruled out by analogy with the other compounds, reaction in this case must occur with a very high isotope effect from a π, π^* triplet. An alternative explanation would be that singlet-state deactivation and low triplet yields are responsible for the lack of triplet emission. This explanation requires a deactivation mechanism capable of competing with intersystem crossing at a rate of about 10^{11} s^{-1} .^{75,76} It has been suggested that singlet deactivation involving an avoided surface crossing along the H-transfer reaction^{77,78} may be fast enough.^{24,79,80} To test this possibility, we analyzed Bz-1,4-DMAT as a compound with a built-in triplet sensitizer (Scheme 3).⁸¹ Light absorption in this compound should occur at the benzoyl and anthrone chromophores with similar probabilities. Fast intersystem crossing and triplet-energy equilibration⁸² would be expected to compete with singlet-state deactivation pathways unique to the *o*-methylanthrone chromophore. The fact that no phosphorescence was observed in this compound under conditions where Bz-AT emits strongly suggest that the π, π^* triplet of *o*-methylanthrones may be efficiently deactivated by a quantum-mechanical H-transfer tunneling reaction. Results in progress in our laboratory with indanones and benzosuberones also suggest the involvement of quantum-mechanical tunneling from triplets with predominant π, π^* configurations.⁸³ We hope that further studies will help obtain a better understanding of the

factors that control aryl ketone reactivity and quantum-mechanical processes.

Conclusions

We have analyzed the effect of three solvents of different polarity on the emission and reactivity of several anthrone derivatives as a function of temperature between 15 and 90 K. The effect of methyl substitution and solvents manifests itself on the presence of short- and long-lived components assigned to states with predominant n,π^* and π,π^* character. Temperature-independent spectra and lifetimes, which include several cases with dual emission, suggest that the two states do not equilibrate at the temperatures analyzed. It is suggested that the spectral and kinetic behavior of a given triplet state may be disproportionately influenced by its n,π^* character. Evidence for quantum-mechanical tunneling from n,π^* and π,π^* states was presented. Future studies are desirable to build a database that may help confirm our observations and may help make correlations between tunneling probabilities and the corresponding energy surfaces.

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