

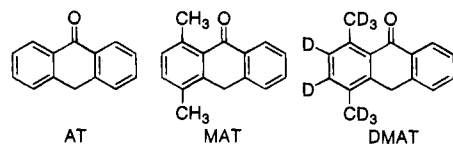
Excited State Intramolecular Hydrogen Atom Transfer at Ultralow Temperatures. Evidence for Tunneling and Activated Mechanisms in 1,4-Dimethylantrone

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In spite of a large number of reports on the Norrish type II reaction of excited aryl ketones,¹ there are only a few reports of a primary isotope effect on the hydrogen atom transfer step,² and the issue of quantum mechanical tunneling as a mechanism of hydrogen abstraction by triplet carbonyls has only begun to be addressed experimentally.³ Two recent studies on the related photoenolization reactions of 5,8-dimethyl-1-tetralone⁴ and 1-methylanthraquinone⁵ implicate tunneling as an important contributor to the reaction at low temperatures and in the triplet and singlet manifolds, respectively. One may also note that activation energies and pre-exponential factors, as reported in the literature, may allow for hydrogen abstraction to occur at cryogenic temperatures. However, thermally activated rates should be slow enough to allow for competitive radiative decay from the triplet state so that a temperature dependence and isotope effect analysis of phosphorescence yields and lifetimes should be valuable in establishing the importance of quantum mechanical tunneling and activated mechanisms. Here, we report evidence of hydrogen atom transfer at temperatures as low as 18 K in the case of geometrically locked 1,4-dimethylantrone (MAT) and 1,4-dimethylantrone-*d*₈ (DMAT).⁶ The data are consistent with concurrent activated and tunneling mechanisms.



Phosphorescence lifetimes and total intensity measurements of the methylsubstituted compounds in methylcyclohexane (MCH) glasses were compared with those of the well-studied parent compound, anthrone (AT), which serves as the benchmark by which to evaluate the other photophysical parameters. Methyl substitution and ring deuteration have relatively small

effects on the photophysical properties of benzophenone, and a similar trend may be expected in the anthrone series. Picosecond measurements of AT at room temperature have demonstrated an efficient intersystem crossing with time constants between 10 and 50 ps⁷ while nanosecond flash photolysis indicates an efficient *intermolecular* hydrogen abstraction reactivity.⁸

Placing AT in a MCH glass at 77 K results in phosphorescence parameters⁹ typical for diaryl ketones with $n\pi^*$ triplet configurations¹⁰ ($\tau = 1.7$ ms at 77 K).¹¹ An ortho-methyl group in the anthrone chromophore opens the possibility for a hydrogen atom transfer which will compete with phosphorescence and with other, nonradiative decays for excited state deactivation. In fact, no phosphorescence emission was observed from the protio compound (MAT), even at 18 K, while DMAT presented a weak, broadened, and red-shifted emission, compared with that of AT (Figure 1). The lack of a detectable emission in the protio compound is indicative of a large primary isotope effect and supports the γ -hydrogen abstraction reaction as the main deactivation mechanism in the methyl-substituted compounds.¹² Furthermore, the involvement of this reaction as a deactivation route at cryogenic temperatures in both DMAT and MAT was also shown by fluorescence detection of their corresponding photoenols, which were readily accumulated upon intense irradiation in EPA glasses not only at 77 K but also at 18 K (Figure 1c).^{13,14}

The rate of an activated hydrogen atom transfer should decrease with decreasing temperature, resulting in longer triplet lifetimes and higher phosphorescence intensities for DMAT. Thus, measurements were carried out between 18 and 80 K with samples deposited on the probe of a closed cycle liquid helium refrigerator.¹⁵ Relative to that observed at 77 K, the phosphorescence of AT at 18 K (Figure 1a) revealed some spectral sharpening and a small kinetic heterogeneity that was fit to a double exponential ($\tau_1 = 1.6$, 75%; $\tau_2 = 4.4$ ms, 25%).^{16,17}

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(9) Fluorescence and phosphorescence measurements were performed by front surface illumination and detection in a SPEX fluorolog spectrofluorimeter. Some data were collected using an Edinburgh FL900 spectrometer.

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(11) Unlike many phosphorescence decays at 77 K, that of AT could be satisfactorily fit to a single exponent.

(12) Kinetic isotope effect of 6–8 at room temperature corresponds to values of $>10^3$ and $>>10^{10}$ at 77 and 18 K, assuming stretching frequencies of 3000 and 2100 cm^{-1} for C–H and C–D stretches, respectively. See: Isaacs, N. S. *Physical Organic Chemistry*; John Wiley & Sons: New York, 1987; Chapter 7.

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(15) Refrigeration was achieved with an Air Products closed cycle two-stage helium refrigerator. The temperature was varied with the help of a resistive heater.

(16) Intensity data were fit to the function $I(t) = a \exp(-bt) + c \exp(-dt)$. The contribution from each component was calculated from the ratios ab/bd and c/d .

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(3) For an alternative view of tunneling in ketone photochemistry, see: Formosinho, S. J.; Arnaut, L. G. *Adv. Photochem.* **1991**, *16*, 67–117.

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(6) Samples of MAT and DMAT were synthesized according to standard procedures by Friedel–Crafts reactions of *p*-xylene and *p*-xylene-*d*₁₀ with phthalic anhydride followed by Sn/HCl reduction.

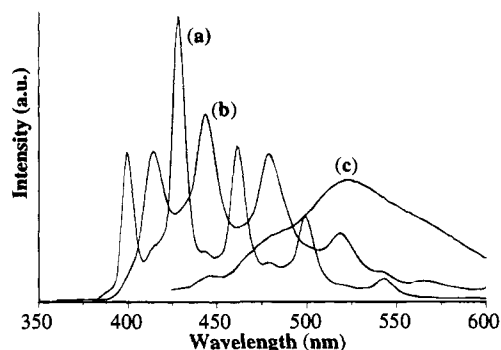


Figure 1. Phosphorescence spectra of (a) AT and (b) DMAT at 18 K in MCH. (c) Fluorescence spectrum of the DMAT photoenol accumulated at 77 K. Nearly identical photoenol spectra were obtained by irradiation of MAT at both 77 and 18 K (the spectra are approximately normalized for presentation).

Samples of DMAT at 18 K presented a spectrum nearly identical to but more intense than that observed at 77 K, while repeated measurements with MAT continued to give no detectable emission. Intensity measurements relative to 10^{-3} parts of codeposited anthraquinone ($\Phi = 1.0$) allow us to conservatively estimate an upper quantum yield limit of $\Phi_{\text{MAT}} \ll 4 \times 10^{-6}$. Even at 18 K, excited MAT is deactivated extremely efficiently by nonradiative processes. Intersystem crossing to the singlet ground state seems unlikely, and one may speculate whether a singlet state reaction more rapid than intersystem crossing or a triplet state reaction with rates greater than ca. $2.5 \times 10^8 \text{ s}^{-1}$ may contribute to this.

The intensity of DMAT phosphorescence showed a rapid decrease when the temperature was increased from 18 to 80 K. Phosphorescence decays were fit to double exponentials over the interval.^{17,18} A longer component consistently contributed 70–76% of the total decay, with values ranging between 4.8×10^{-4} and 2.3×10^{-4} s. The short component ranged between 9.6×10^{-5} and 3.0×10^{-5} s and had a temperature dependence similar to that of the long component. Arrhenius-type plots (Figure 2) constructed with the two components of the triplet decay of DMAT show a leveling in slope at about 30 K.¹⁸ The temperature-independent decay of DMAT (Figure 2) is almost an order of magnitude faster than that of AT which, at similar temperatures, gives $\tau_1 = 1.63 \times 10^{-3}$ s (75%) and $\tau_2 = 4.3 \times 10^{-3}$ s (25%). The effect of methylation on phosphorescence rates is usually trivial, and the fast decay below 30 K suggests an additional triplet deactivation pathway. As a control for

(17) We do not wish to emphasize the validity of a biexponential fit to these data. The observed trends and conclusions derived therefrom are unaffected by the exact method of data treatment.

(18) A possible temperature dependence in the pre-exponential factor as suggested by transition state and collision theory was not observed in plots of $-\log \tau/T^{1/2}$ and $-\log \tau/T$ vs $1/T$. See: (a) Carpenter, B. K. *Determination of Organic Reaction Mechanisms*; John Wiley & Sons: New York, 1984; Chapter 7, p 123; (b) McMahon, R. J.; Chapman, O. L. *J. Am. Chem. Soc.* **1987**, *109*, 683–692.

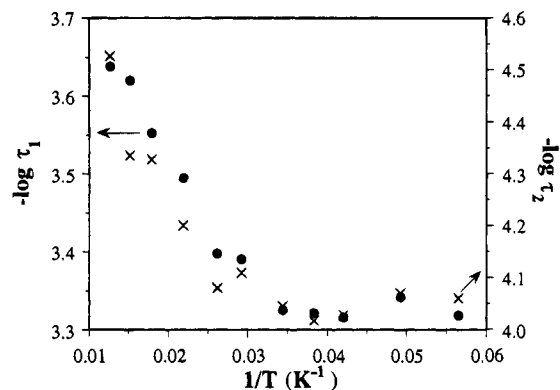


Figure 2. Arrhenius plot of the triplet decay of DMAT in dilute MCH glass. Scales on the right and left pertain to the short (x) and long (●) components, respectively.

effects of methylation on the radiative rate, 2,3-dimethylantrone was also investigated. Its decay parameters are very similar to those of AT and substantially slower than those of DMAT.¹⁹ Additionally, a survey of known triplet lifetimes of aromatic ketones without opportunity for intramolecular reaction at 77 K finds none below 1 ms.¹⁰ We suggest that deuterium atom tunneling dominates in DMAT at low temperatures (<30 K), while an activated process gains importance at higher values. The ability to accumulate the enol of DMAT at 18 K is also supportive of this conclusion.¹⁴

Phosphorescence intensity measurements from 18 to 30 K showed a ca. 40% decrease in intensity, despite the fact that the lifetimes remained constant over that region. This observation may suggest a very low barrier singlet state process in direct competition with intersystem crossing. A methyl group locked in the ortho position presents a hydrogen atom with a nearly ideal abstraction geometry, which may facilitate a very fast singlet state reaction.⁵ However, to compete with intersystem crossing, a singlet reaction requires a rate constant of the order of 10^{11} s^{-1} (assuming an ISC rate similar to that found at high temperatures),⁸ and the interpretation of this data should be viewed with caution. Studies in progress in our laboratories with DMAT and other geometrically locked *o*-methyl dibenzocycloalkanones are aimed to elucidate details of these processes as well as the potential energy surfaces involved.

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(19) The phosphorescence spectrum of 2,3-dimethylantrone in dilute MCH glasses has a 0–0 band at 401 nm. The lifetime at 77 K is 1.6 ms. At 18 K, a biexponential fit gives 1.75 (90%) and 0.5 ms (10%). Weighted average lifetimes at 18 K: AT, 2.3 ms; 2,3-dimethylantrone, 1.6 ms; DMAT, 0.38 ms.