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Exciplexes Involving Aromatic Ketone Triplet States and Molecular Oxygen. The Lack of a Spin-Statistical Effect on Exciplex Formation Rate Constants

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We have recently undertaken an extensive study of the temperature dependency of the bimolecular rate constant (k^T_{ox}) for sensitizer triplet-excited-state quenching by molecular oxygen in solution. In the case of benzophenone (Bp)[1] and several aromatic hydrocarbons,[2] the observation of a negative temperature dependence of k^T_{ox} at high temperatures (>20 °C) was a clear indication that quenching proceeds *via* a reversibly formed exciplex,[3] which provided an experimental basis for the suggestions[4,5] that the various singlet (S), triplet (T), and quintet (Q) encounter pairs of Scheme I[6] can be considered as exciplexes of different multiplicity.

Scheme I

$$\mathrm{Sens(T_1)} + \mathrm{O_2(^3\Sigma_g^-)} \rightleftharpoons \mathrm{S} \rightarrow \mathrm{Sens(S_0)} + \mathrm{O_2(^1\Delta_g)} \qquad \text{(a)}$$

$$\rightleftharpoons \mathrm{T} \rightarrow \mathrm{Sens(S_0)} + \mathrm{O_2(^3\Sigma_g^-)} \qquad \text{(b)}$$

$$\rightleftharpoons \mathrm{Q} \qquad \text{(c)}$$

As Q has no spin-allowed products, the bimolecular rate constant for triplet-state quenching by $O_2(^3\Sigma_g)$, k^T_{ox}, is given by

$$k^T_{ox} = k_d k_1/9(k_{-1} + k_1) + k_d k_3/3(k_{-3} + k_3) \qquad (1)$$

where k_d is the diffusion-controlled bimolecular rate constant for both S and T exciplex formation, k_1 and k_3 are the unimolecular rate constants for the dissociation of S and T to form products, respectively, and k_{-1} and k_{-3} are the rate constants for the unimolecular dissociation forming reactants, respectively. The factors $^1/_9$ and $^1/_3$ in the first and second terms, respectively, of (1) account for the relative statistical probabilities of S and T formation.[6] On the basis of eq 1, the largest possible value of k^T_{ox} is $^4/_9 k_d$ when S and T are both formed irreversibly, *i.e.*, when $k_1 \gg k_{-1}$ and $k_3 \gg k_{-3}$. For the photosensitizers referred to above,[1,2] a change in rate-determining step with temperature was observed, and the low-temperature limiting k^T_{ox} exceeded the frequently assumed $^1/_9 k_d$ limit.[6] Positive activation energies, E_a, were observed in toluene at temperatures lower than −50 °C. In the case of Bp, the limiting E_a value of 2.7 kcal mol^{-1} was consistent with that expected for a diffusion-controlled process,[1,2] and the preexponential factor was around one-third that calculated for full diffusion control.[1] The k^T_{ox} values of aromatic hydrocarbons tended toward a common limit at low temperatures which was between $^1/_9 k_d$ and $^4/_9 k_d$. We therefore suggested that the generally accepted spin-statistically derived scheme could describe the overall mechanism of aromatic hydrocarbon triplet-state quenching consistently, with the added proviso that on the basis of room temperature rate constants alone it is impossible to tell the degree to which breakdown of both S and T to form products (Scheme I a and b) contributes to the overall room temperature rate constant.

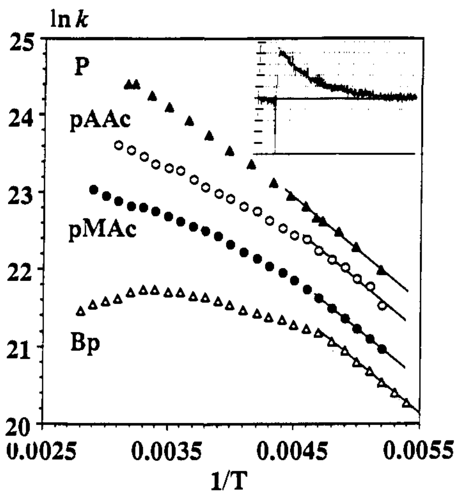

Figure 1. Arrhenius plot for bimolecular rate constants of $O_2(^3\Sigma_g)$ quenching of excited states in toluene. For **P** the plot is that for k^S_{ox}, while for the ketones, it is for k^T_{ox}. The low-temperature Arrhenius behavior leads to the following parameters; for **P**, $A = (3.8 \pm 0.5) \times 10^{12}$ M^{-1} s^{-1}, $E_a = 2.69 \pm 0.05$ kcal mol^{-1}; for pAAc, $A = (2.63 \pm 0.5) \times 10^{12}$ M^{-1} s^{-1}, $E_a = 2.61 \pm 0.10$ kcal mol^{-1}; for pMAc, $A = (1.3 \pm 0.5) \times 10^{12}$ M^{-1} s^{-1}, $E_a = 2.66 \pm 0.06$ kcal mol^{-1}; for Bp, $A = (8.9 \pm 0.8) \times 10^{11}$ M^{-1} s^{-1}, $E_a = 2.65 \pm 0.05$ kcal mol^{-1}. Inset: Triplet absorbance decay of pAAc in toluene at −64 °C, 0.463 mM oxygen. Time scale is 200ns/div, and absorbance scale is 3.1×10^{-3} units/div.

In light of our results involving triplet aromatic hydrocarbon quenching,[2] it became highly desirable to unambigously determine the exciplex formation rate constant and, in so doing, to determine the validity of Scheme I. While it has been generally assumed that spin-statistical effects are operative in triplet-state quenching by $O_2(^3\Sigma_g)$,[4–6] to our knowledge it has not been conclusively demonstrated that such processes do proceed *via* an intermediate or intermediates formed at $^4/_9 k_d$. In this communication we present evidence that exciplex formation rates of aromatic ketone triplet excited states are *not* controlled in a simple manner by spin statistics and, further, that exciplex formation rates can even *exceed* $^4/_9 k_d$.

The temperature dependence of sensitizers that possess large values of k^T_{ox} at room temperature can be examined in a solvent exhibiting a broad liquid range to determine the limiting low-temperature behavior of k^T_{ox}. We therefore examined the temperature dependence of k^T_{ox} of *p*-aminoacetophenone (pAAc) and *p*-methoxyacetophenone (pMAc) in toluene ($k^T_{ox} = 1.4 \times 10^{10}$ and 0.8×10^{10} M^{-1} s^{-1}, respectively, at room temperature) using laser flash photolysis techniques described fully in previous studies.[1,2] The Arrhenius plots obtained are given in Figure 1 along with those of k^T_{ox} for benzophenone[1] (Bp) and of the bimolecular rate constant for S_1 of pyrene (P) quenching by $O_2(^3\Sigma_g)$, k^S_{ox}, determined previously.[2] We have shown that the temperature dependence of k^S_{ox} provides an experimental measure of k_d.[2,4]

The most striking feature of the Arrhenius plots of k^T_{ox} is the strong curvature apparent in each case. As was discussed previously,[1–3] such behavior is indicative of a change in rate-determining step with temperature. At room temperature, quenching of triplet Bp lies close to the preequilibrium limit

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(1) McLean, A. J.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1992**, *114*, 3145.

(2) McLean, A. J.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1993**, *115*, 4786.

(3) (a) Giering, L.; Berger, M.; Steel, C. *J. Am. Chem. Soc.* **1974**, *96*, 953. (b) Winnik, M. A.; Maharaj, U. *J. Am. Chem. Soc.* **1981**, *103*, 2328. (c) Gorman, A. A.; Hamblett, I.; Lambert, C.; Spencer, B.; Standen, M. C. *J. Am. Chem. Soc.* **1988**, *110*, 8053.

(4) Saltiel, J.; Atwater, B. W. In *Advances in Photochemistry*, *Volume 14*; Volman, D. H., Hammond, G. S., Gollnick, K., Eds; Wiley: New York, 1988; p 1.

(5) (a) Garner, A.; Wilkinson, F. *Chem. Phys. Lett.* **1977**, *45*, 432. (b) McGarvey, D. J.; Szekers, P. G.; Wilkinson, F. *Chem. Phys. Lett.* **1992**, *199*, 314.

(6) (a) Kawaoka, K.; Khan, A. U.; Kearns, D. R. *J. Chem. Soc.* **1967**, *46*, 1842. (b) Kearns, D. R. *Chem. Rev.* **1971**, *71*, 395. (c) Gijzeman, O. L. J.; Kaufman, F. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 721. (d) Patterson, L. K.; Porter, G.; Topp, M. R. *Chem. Phys. Lett.* **1970**, *7*, 612. (e) Gijzeman, O. L. J.; Kaufman, F.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 708.

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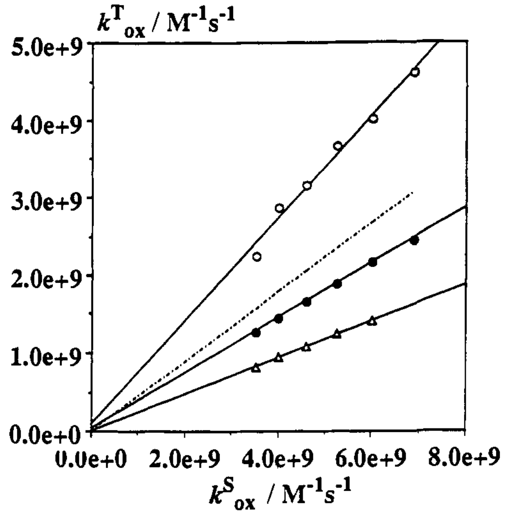

Figure 2. Pot of k^{T}_{ox} as a function of K^{S}_{ox} over the fitted temperature range in Figure 1. The plotted symbols correspond to those labeled in Figure 1. The dotted line is that expected for a spin-statistically controlled process (slope = 0.44). The slopes of the best straight lines are given by 0.64 for pAAc, 0.34 for pMAc, and 0.22 for Bp. The error in slopes of pMAc and Bp is ±10%; for pAAc, the slope of 0.64 should be regarded as a lower limit.

(exciplex decay rate limiting), while pAAc and pMAc are both closer to the diffusion limit (rate-limiting exciplex formation). It is expected that the pAAc and pMAc exciplexes are stabilized by CT interactions to a greater extent than Bp.[5a] Thus, the larger enthalpic barrier to k_{-1}, k_{-3}, and k_{-5} ensures that the product-forming steps are more rapid than reactant regeneration in the cases of pMAc and pAAc. For Bp, the corresponding enthalpic barrier to reactant regeneration is lower and can no longer offset the unfavorable preexponential factors for the formation of products.

The common low-temperature slopes of the Arrhenius plots for k^{T}_{ox} of the three ketones and k^{S}_{ox} of P (corresponding to an activation energy of between 2.6 and 2.7 kcal mol^{-1}) are a strong indication that exciplex formation is limited by solvent viscous flow at temperatures less than −60 °C.[7] The differences in exciplex formation rate constants therefore arise from differences in preexponential factors (A) for the three ketones. The key point is that the variation in A values in this series of aromatic ketones suggests that spin-statistical effects are not the sole factors controlling the exciplex formation rate constants of these compounds.

As further confirmation of these differences in A factors, the low-temperature values of k^{T}_{ox} are plotted as a function of k^{S}_{ox} in Figure 2. Given the identical E_a values, the slopes of the various plots should correspond to the ratio of A^{T}/A^{S} and have a intercept of zero.[8] If spin-statistical factors are operative, then the maximum possible value of k^{T}_{ox} should be $^{4}/_{9}k^{S}_{ox}$, leading to an expected value of 0.44 for the slope of the plots in Figure 2. A brief examination of Figure 2 shows that the requisite zero intercept is kept, however, the expected spin-statistically imposed limit has been exceeded by pAAc.[8b] Using the slopes of the lines in Figure 2, we find that the preexponential factors for exciplex formation are given by $0.22A^{S}_{ox}$, $0.32A^{S}_{ox}$, and $0.64A^{S}_{ox}$ for Bp, pMAc, and pAAc, respectively.

We therefore conclude that in the case of pAAc, quenching proceeds *via* **S**, **T**, *and* **Q** at low temperatures. This, in turn, implies that intersystem crossing (ISC) is operative between pAAc exciplexes of different multiplicity, since no products of quintet multiplicity can be generated. At low temperatures, the rate constant for ISC from the **Q** to **T** states of pAAc must be comparable to or exceed k_{-5}. The triplet excited states of Bp, pMAc, and pAAc vary from $n\pi^*$ to $\pi\pi^*$ to CT-type character, respectively. Perhaps of some significance is that aromatic hydrocarbons ($^{3}\pi\pi^*$) apparently exhibit common values for the exciplex formation rate constants,[2] although as mentioned earlier, the absolute formation rate constants are not known with any certainty for this class of compounds. It may be that the ketone A values reflect either or both of the following effects, both of which are expected to be solvent dependent. (a) Increasing charge separation in the triplet state (prior to exciplex formation) leads to less profound solvation shell geometry change associated with the formation of a polar intermediate (exciplex) and thus to larger A values. (b) From footnote 8, effective interaction radii (ρ) of 2.6, 3.9, and 6.1 Å can be estimated for Bp, pMAc, and pAAc, respectively, using the slopes determined by Figure 2 and assuming σ to be 1.00. These ρ values correspond to the required approach distance for unit quenching efficiency;[4,8c] in otherwords, spin-statistical effects are assumed to be absent in all cases.[8b,9] Only the value for pAAc corresponds to an interaction distance of approximately van der Waals contact, while that for Bp implies considerable overlap of the two "hard spheres" or simply that a small region of triplet Bp is reactive toward $O_2(^{3}\Sigma_g)$.[10] Such close approach is consistent with the idea of restricted access to the more localized electron pair in Bp being alleviated by the increasing electron delocalization from pMAc to pAAc. Thus, increasing electron delocalization ($n\pi^*$ to CT) may facilitate exciplex formation due to increasingly favorable overlap of ketone molecular orbitals and those of $O_2(^{3}\Sigma_g)$.

As far as we are aware, this is the first indication that spin-statistical factors are *not* solely responsible for controlling exciplex formation between triplet-excited-state ketones and $O_2(^{3}\Sigma_g)$ and that the predicted low-temperature limiting value for k^{T}_{ox} of $^{4}/_{9}k_d$ can be exceeded.[11]

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(7) Saltiel, J.; Shannon, P. T.; Zafirou, O. C.; Uriarte, A. K. *J. Am. Chem. Soc.* **1980**, *102*, 6799.

(8) (a) The slopes of the lines in Figure 2 are strictly given by[4] $\sigma(\rho_K/\rho_P)(D_K/D_P)$, where ρ and D are the interaction radius and mutual diffusion coefficients for the substrate and $O_2(^{3}\Sigma_g)$, respectively, σ is the spin-statistical factor (0.44), and the subscripts P and K refer to the pyrene and the ketone systems, respectively. Using the Stokes–Einstein equation either alone or with truncated microfriction correction factors[4] leads to a ratio of D_K/D_P values of no more than 1.06, assuming that the reactants and solvent can be treated as spherical and taking molecular radii as 2.0, 3.43, and 3.90 Å for $O_2(^{3}\Sigma_g)$, the ketones, and pyrene, respectively, and 3.15 Å for toluene. (b) Assuming that ρ_P = 12 Å, the same as that of anthracene,[8c] and taking σ = 0.44, then ρ_K = 18 Å for pAAc! This is obviously unreasonable for a diffusion-controlled reaction. We therefore conclude that σ = 1.00, and the slopes of the lines in Figure 2 are given by ρ_K/ρ_P. (c) Yasuda, H.; Scully, A. D.; Hirayama, S.; Okamoto, M.; Tanaka, F. *J. Am. Chem. Soc.* **1990**, *112*, 6847.

(9) The fact that $\sigma \geq 0.44$ for pAAc does not necessarily imply that this is also the case for Bp and pMAc. Our results do require that for a constant ρ value, spin statistics do not limit exciplex formation rates, and, similarly, assuming a constant σ value requires ketone-dependent ρ values. In either case, spin statistics are not the sole factors controlling exciplex formation rates.

(10) (a) The possibility of biradical formation between $O_2(^{3}\Sigma_g)$ and Bp and pMAc in competition to the exciplex decay pathways outlined in Scheme I has been suggested.[10b] Clearly such a possibility requires specific interaction between the carbonyl carbon atom and $O_2(^{3}\Sigma_g)$. It is interesting, therefore, that the low ρ values obtained for pMAc and Bp are qualitatively consistent with specific interactions between $O_2(^{3}\Sigma_g)$ and a single atom in the ketone during *exciplex* formation. (b) Gorman, A. A.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1986**, *108*, 5074.

(11) (a) A k^{T}_{ox} value of 1.7 × 10^{10} M^{-1} s^{-1} has been reported for *N*-methylindole in benzene at room temperature.[5a] This value is slightly greater than $^{4}/_{9}k_d$ (approx 1.3 × 10^{10} M^{-1} s^{-1}). We thank a referee for drawing our attention to this result.