J. Am. Chem. Soc. **1993,** *115,* 4786–4792

Variable-Temperature Study of Aromatic Hydrocarbon Triplet-State Quenching by Molecular Oxygen in Solution

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Received October 27, 1992

Abstract: The temperature dependence of the bimolecular rate constant for $O_2(^3\Sigma_g)$ quenching of a series of aromatic hydrocarbon triplet states, k^T_{ox}, has been determined in toluene. Highly curved Arrhenius plots were obtained, indicating a change in rate-determining step over the available temperature range. At low temperatures, k^T_{ox} of all hydrocarbons approached a common limiting slope that was consistent with $^4/_9k_d$. At higher temperatures, low positive or negative activation energies were observed, indicating the involvement of exciplex intermediacy in the overall quenching process. In each case, the room temperature value of k^T_{ox} reflects the reversible formation of an exciplex where product formation is the rate-determining step. The temperature dependence of naphthalene k^T_{ox} was determined in an additional four solvents exhibiting a wide range of polarity. Again strong curvature was apparent in the Arrhenius plots, with k^T_{ox} consistently exceeding $^1/_9k_d$ at low temperatures. In all solvents the preequilibrium preexponential factors were identical within experimental error; variations in room temperature rate constants solely reflect solvent-dependent preequilibrium activation energies. These results lead to direct predictions of the temperature dependence of energy-transfer efficiencies when interpreted on the basis of the well-known spin-statistically derived scheme.

1. Introduction

The mechanism of quenching of the first excited triplet state of aromatic hydrocarbons by ground-state molecular oxygen, $O_2(^3\Sigma_g^-)$, first became the subject of intense theoretical[1] and experimental[2] investigation in the late 1960s and early 1970s due to the identification of singlet molecular oxygen, $O_2(^1\Delta_g)$, as the photosensitized species responsible for many photooxidation reactions.[3] Theoretical considerations[1] led to the development of Scheme I to account for the kinetics of aromatic hydrocarbon triplet quenching by $O_2(^3\Sigma_g^-)$.

On the basis of this scheme, the bimolecular rate constant for triplet-state quenching by $O_2(^3\Sigma_g^-)$, k^T_{ox}, is given by

$$k^T_{ox} = k_dk_1/9(k_{-1} + k_1) + k_dk_3/3(k_{-3} + k_3) \qquad (1)$$

where k_d is the diffusion-controlled bimolecular rate constant for both singlet and triplet complex formation, k_1 and k_3 are the unimolecular rate constants for singlet and triplet encounter complex dissociation forming products, respectively, and k_{-1} and k_{-3} are the unimolecular rate constants for singlet and triplet encounter complex dissociation forming reactants, respectively. The factors $^1/_9$ and $^1/_3$ in the first and second terms, respectively, of the right-hand side of eq 1, account for the relative statistical weights of the singlet and triplet configurations in the encounter complexes.

In what is widely regarded as the seminal work in this field, Porter and co-workers[2] showed experimentally that the value k^T_{ox} at room temperature for aromatic hydrocarbon triplets in solution fell into two groups: for aromatic hydrocarbons of triplet energy, E_T, between 30 and 42 kcal mol^{-1}, it was found that k^T_{ox} was limited to $^1/_9k_d$. However, where $E_T > 42$ kcal mol^{-1}, k^T_{ox} was often less than $^1/_9k_d$.[2] Such observations led to the suggestion that k^T_{ox} reflected quenching solely *via* channel Ia and was therefore limited to a maximum value of $^1/_9k_d$. Deviations to lower values were considered to arise as a consequence of both decreasing Franck–Condon factors with increasing triplet energy and hydrocarbon-dependent symmetry factors that effectively decreased the relative magnitude of k_1 with respect to k_{-1}.[1,2] Quencing *via* the triplet encounter complex was predicted[1] to be negligible due to the highly unfavorable Franck–Condon factors for the more exothermic process, giving ground-state products leading to $k_{-3} \gg k_3$. That k^T_{ox} was experimentally limited to $^1/_9k_d$ apparently confirmed the lack of involvement of channel Ib at room temperature, and as a result, eq 1 reduces to

Scheme I

$$\mathrm{Sens}(T_1) + O_2(^3\Sigma_g^-) \rightleftharpoons {}^1|\mathrm{Sens}\cdots O_2|^* \rightleftharpoons {}^1\mathrm{Sens}(S_0) + O_2(^1\Delta_g) \qquad (a)$$

$$\rightleftharpoons {}^3|\mathrm{Sens}\cdots O_2|^* \rightleftharpoons {}^3\mathrm{Sens}(S_0) + O_2(^3\Sigma_g^-) \qquad (b)$$

$$\rightleftharpoons {}^5|\mathrm{Sens}\cdots O_2|^* \qquad (c)$$

$$k^T_{ox} = {}^1/_9k_dk_1/(k_1 + k_{-1}) \qquad (2)$$

On this basis, Porter *et al.* successfully explained the relative magnitudes of room temperature k^T_{ox} values for a wide range of aromatic hydrocarbons in a series of low dielectric solvents.[1c,2] This interpretation, in agreement with that of Kearns,[1] led to the conclusion that the energy-transfer product, $O_2(^1\Delta_g)$, was formed with 100% efficiency upon hydrocarbon triplet-state quenching by $O_2(^3\Sigma_g^-)$.[4,5]

Later the focus on k^T_{ox} determinations was switched to measurement of the quantum yields of singlet oxygen formation (Φ_Δ). It immediately became clear that $O_2(^1\Delta_g)$ formation was not necessarily the only reaction responsible for sensitizer triplet-

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(1) (a) Kawaoka, K.; Khan, A. U.; Kearns, D. R. *J. Am. 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. II* **1973**, *69*, 721.

(2) (a) Patterson, L. K.; Porter, G.; Topp, M. R. *Chem. Phys. Letts.* **1970**, *7*, 612. (b) Gijzeman, O. L. J.; Kaufman, F.; Porter, G. *J. Chem. Soc., Faraday Trans. II* **1973**, *69*, 708.

(3) (a) Foote, C. S. *Acc. Chem. Res.* **1968**, *1*, 104. (b) *Singlet Molecular Oxygen*; Schaap, A. P., Ed.; Dowden, Hutchinson and Ross: Stroudsberg, PA, 1976. (c) *Singlet Oxygen Reactions with Organic Compounds and Polymers*; Ranby, B., Rabek, J. F., Eds.; Wiley: New York, 1978. (d) *Singlet Oxygen*; Wasserman, H. H., Murray, R. W., Eds.; Academic Press: New York, 1979. (e) *Singlet O_2*; Frimmer, A. A., Ed.; CRC Press: Boca Raton, FL, 1985.

(4) It has not been conclusively demonstrated that $O_2(^1\Delta_g)$ is the initial excited state produced; in the gas phase both $O_2(^1\Delta_g)$ and $O_2(^1\Sigma^+_g)$ have been observed from triplet-sensitized experiments.[5a] However, the decrease in quenching efficiency observed for $E_T > 40$ kcal mol^{-1} in the case of aromatic hydrocarbons has previously been taken to indicate that this excited state is formed in extremely low yields in solution.[1c,2]

(5) (a) Parmenter, C. S.; Rau, J. D. *J. Chem. Phys.* **1969**, *73*, 2242.

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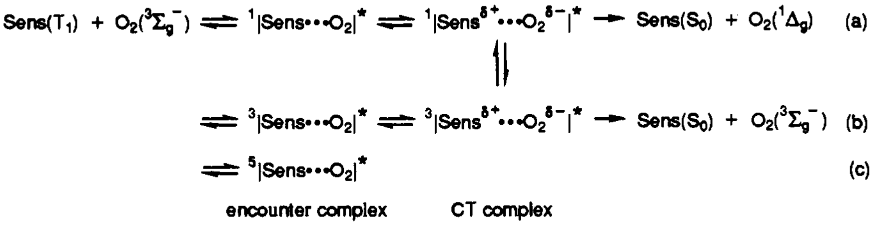
Scheme II



state deactivation by $O_2(^3\Sigma_g^-)$ in solution.[6] At present very few triplet sensitizers of any class have been found to form $O_2(^1\Delta_g)$ with 100% efficiency.[7] The efficiency with which T_1 yields $O_2(^1\Delta_g)$ *via* $O_2(^3\Sigma_g^-)$ quenching (S_Δ)[6a] has also been shown to be solvent dependent for several aromatic hydrocarbons.[8] The observation of S_Δ values of less than 1.00 are at considerable odds with the widely accepted and attractive treatments of Porter[2] and Kearns,[1a,b] both of which are routinely quoted in connection with the magnitude of k^T_{ox} regardless of the S_Δ value. In both of these earlier treatments, the possibility of charge-transfer (CT) processes influencing the rate of production of $O_2(^1\Delta_g)$ was recognized. It was argued that the matrix elements for CT perturbation would influence singlet and triplet product formation equally; however, the highly unfavorable Franck–Condon (FC) factors for the latter process always ensured $k_{-3} \gg k_3$.[1,2] Several more recent studies have proposed that CT interactions could lead to a loss of spin integrity of the singlet and triplet encounter complexes such that the partitioning of spin states strongly favors the triplet,[9] and as a result, singlet and triplet product formation are thought to become competitive. The CT-mediated scheme usually adopted is given in Scheme II.

Scheme II was originally introduced[9a] to explain the enhanced rate of triplet quenching of several aromatic ketones for which it was frequently observed that $^1/_9k_d \leq k^T_{ox} \leq {}^4/_9k_d$ while $S_\Delta < 1.0$. However, there are frequent exceptions to this combination; for example, in the case of triplet benzophenone quenching[6a] and for several aromatic hydrocarbons in benzene,[8] it is clear that $S_\Delta < 1.0$ even when $k^T_{ox} \leq {}^1/_9k_d$.[7] The possibility of CT-induced intersystem crossing (ISC) between the CT complexes was introduced to rationalize such observations, although this necessarily requires an as-yet-unexplained barrier to the triplet CT complex formation *via* the triplet encounter complex.[9c] Recently, the possibility of full, formal charge separation competing with energy-transfer quenching has been raised for triplet naphthalene quenching by $O_2(^3\Sigma_g^-)$ in acetonitrile.[9d]

The main barriers to general acceptance of CT-mediated S_Δ decreases lie in the lack of a reasonable explanation as to how the unfavorable FC factors for triplet-ground-state product formation are overcome or compensated for when $k^T_{ox} \leq {}^1/_9k_d$ and the further lack of any unambiguous experimental evidence for CT-solvated products arising from triplet sensitizer quenching. A second possibility is that of a *chemical* origin to low S_Δ values involving the formation of biradicals.[10] In this formulation, the eventual product distribution is dependent on the spin preferences of the biradical adduct between the sensitizer and $O_2(^3\Sigma_g^-)$.

With CT interactions so frequently postulated, the various encounter pairs could be viewed as exciplexes of different multiplicity.[7a,9a] It was therefore of interest to examine the possibility of exciplex intermediacy in such quenching processes in more detail. In particular, the observation of negative activation energies in excited-state bimolecular quenching processes has been taken to indicate exciplex intermediacy.[11] We could find only one report of variable-temperature studies on k^T_{ox} that employed media of very high viscosity.[12] In an effort to further the understanding of the situation, we have undertaken a thorough examination of the temperature dependence of k^T_{ox} for a wide range of triplet photosensitizers in different solvents. Our first efforts in this area were immediately rewarding, and we have recently presented strong evidence that triplet benzophenone quenching by $O_2(^3\Sigma_g^-)$ at room temperature in toluene proceeds *via* a reversibly formed exciplex. In this case, the rate-determining step at room temperature is exciplex dissociation forming products.[13] Furthermore, the low-temperature behavior of k^T_{ox} was fully consistent with a change in rate-determining step such that exciplex formation becomes rate determining and is limited to $^1/_3$ to $^1/_2$ k_d.

The work of Porter and Kearns and their subsequently derived mechanism[1,2] was specifically addressed to aromatic hydrocarbons. It was therefore of particular interest to determine whether aromatic hydrocarbons exhibit temperature-dependent behavior of k^T_{ox} similar to that of benzophenone and in so doing to determine whether the intermediacy of exciplexes in $O_2(^3\Sigma_g^-)$ quenching of triplet states is a general phenomenon.

In what follows we present our studies concerning the temperature-dependent behavior of k^T_{ox} of naphthalene (N) in toluene, methylcyclohexane, acetonitrile, acetone, and *n*-hexane and of anthracene (A), pyrene (P), coronene (C), and biphenyl (B) in toluene.

2. Experimental Section

2.1. Methods. All rate constants were determined by time-resolved laser flash photolysis methods[14] employing a variable-temperature cell similar to that designed by Wardman.[15] Sensitizer triplet lifetimes were determined by time-resolved absorbance and singlet lifetimes by monitoring the sample emission with the monitoring lamp shutters closed. In toluene, 355-nm excitation was employed in all cases; as a result, triplet naphthalene (N) and biphenyl (B) were generated *via* energy transfer from triplet benzophenone under conditions where all of the benzophenone triplet states were exclusively scavenged by the aromatic hydrocarbon (0.2 M) with 1 mM sensitizer. For the N experiments in all solvents

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(6) (a) Gorman, A. A.; Lovering, G.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1978**, *100*, 4527. (b) Garner, A.; Wilkinson, F. *Singlet Oxygen*; Ranby, B.; Rabek, J. F., Eds.; Wiley: New York, 1978; p 48. (c) Gorman, A. A.; Hamblett, I.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1984**, *106*, 4679.

(7) For comprehensive tables of S_Δ values, see: (a) Saltiel, J.; Atwater, B. W. In *Advances in Photochemistry*; Volman, D. H., Hammond, G. S., Gollnick, K., Eds.; Wiley: New York, 1988; Vol. p 1. (b) Gorman, A. A.; Rodgers, M. A. J. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, p 229.

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(10) (a) Gorman, A. A.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1986**, *108*, 5074. (b) Gorman, A. A.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1989**, *111*, 5557.

(11) (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.

(12) Osborne, A. D.; Porter, G. *Proc. R. Soc. A* **1965**, *248*, 9.

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

(14) The computer-assisted laser flash photolysis-kinetic spectrophotometry instrument has been described: Firey, P. A.; Ford, W. E.; Sounik, J. R.; Kenney, M. E.; Rodgers, M. A. J. *J. Am. Chem. Soc.* **1988**, *110*, 7626.

(15) Wardman, P. J. *J. Phys. E.* **1972**, *5*, 17. The variable-temperature cell consists of a quartz cell held against an aluminum heat sink. The temperature was controlled by balancing the flow rate of precooled N_2 gas through the block, and the rate of heating was controlled by a pair of cartridge heaters sunk into the aluminum block.

except acetone, 266-nm excitation was employed to excite N directly. In acetone, triplet N was again sensitized by energy transfer *via* benzophenone triplet. The monitoring wavelengths were at the triplet absorption of fluorescence emission maxima, respectively. Excited-state decay kinetics were strictly first order under all O_2 concentrations employed (see next section) and always returned to the base line. The temperature was varied over the entire solvent liquid range by controlling the rate of precooled N_2 gas flow and the heating rates of a pair of cartridge heaters in an aluminum temperature sink with which the reaction cell was in good thermal contact. Rate constants were determined at 5-deg intervals after at least 5 min equilibration time at any given temperature. Temperatures were determined using a copper constantin thermocouple that was placed in good thermal contact with the outside of the reaction cell. After each run, a plot of rate constant versus temperature was constructed and a line drawn through the points. The values of the rate constant at preselected values of temperature were read off these plots, and a new plot of rate constant versus O_2 concentration, with up to five O_2 concentrations being employed, was constructed. From the slopes the bimolecular rate constants were determined and Arrhenius graphs constructed.

2.2. Oxygen Concentrations. The basic procedure was that employed previously with benzophenone[13] and involved saturating a stock solution of aromatic hydrocarbon with a precisely known mixture of O_2/N_2 for 30 min at room temperature with a vapor space above the solution. The sample was then pushed into the reaction cell by saturating gas pressure. The O_2 concentration of the O_2/N_2 saturated solution was calculated on the basis of Henry's Law, assuming O_2-saturated concentrations of 8.55, 9.00, 14.8, 12.52, and 11.4 mM for toluene, acetonitrile, *n*-hexane, methylcyclohexane, and acetone, respectively.[16] Under our conditions, no vapor space was present in the reaction cell; as a result the sole correction for O_2 concentration temperature dependency was that due to solvent expansion and contraction. Solvent expansion coefficients were taken from Scaiano's compilation of solvent properties.[17]

2.3. Materials. All solvents were of spectroscopic grade and were from Fluka Chemika, Switzerland. The O_2/N_2 gas mixtures of precisely known composition were obtained from Liquid Carbonic, Findlay, OH. Naphthalene (Gold Label), benzophenone (Gold Label), coronene (sublimed), anthracene, and pyrene were obtained from Aldrich Chemical Company, Milwaukee, WI. Biphenyl (photosensitizer grade) was from Baker, Phillipsburg, NJ. All compounds were used as received except anthracene, which was recrystallized from ethanol 4 times, and pyrene, which was zone refined.

3. Results

3.1. Temperature Dependence of k^S_{ox}. It was desirable to have an experimental measure of the diffusional rate constant over the temperature ranges employed. An obvious candidate was the temperature dependence of k^S_{ox}—the bimolecular rate constant for oxygen quenching of S_1 which, in principle, is a diffusion-controlled process.[7a,18] The Arrhenius plots for k^S_{ox} of P in toluene and N in methylcyclohexane and acetonitrile are given in Figures 1, 2, and 3, respectively. In acetonitrile the k^S_{ox} values for N show linear Arrhenius behavior, but those for N in toluene and P in methylcyclohexane exhibit significant curvature over the broader temperature range accessible with these solvents. The Andrade equation,

$$\ln \eta = \ln A_\eta + E_a/RT \qquad (3)$$

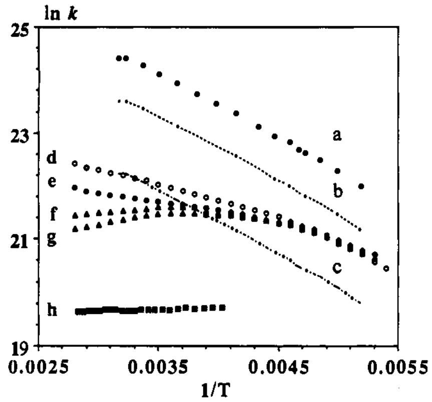

Figure 1. Arrhenius plots of bimolecular rate constants for $O_2(^3\Sigma_g^-)$ quenching of excited states in toluene. (a) k^S_{ox} pyrene, (b) ${}^4/_9k^S_{ox}$, (c) ${}^1/_9k^S_{ox}$, (d) k^T_{ox} anthracene, (e) k^T_{ox} pyrene, (f) k^T_{ox} naphthalene, (g) k^T_{ox} biphenyl, (h) k^T_{ox} coronene.

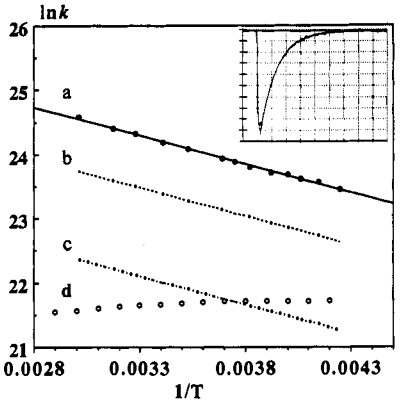

Figure 2. Arrhenius plots of bimolecular rate constants for $O_2(^3\Sigma_g^-)$ quenching of naphthalene excited states in acetonitrile. (a) k^S_{ox}, (b) ${}^4/_9k^S_{ox}$, (c) ${}^1/_9k^S_{ox}$, (d) k^T_{ox}. Insert: S_1 luminescence decay monitored at 350 nm, −32.1 °C, 4.96% O_2/N_2, 50 ns/div, 17 mV/div.

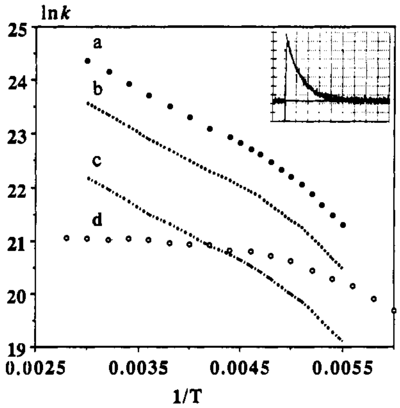

Figure 3. Arrhenius plots of bimolecular rate constants for $O_2(^3\Sigma_g^-)$ quenching of naphthalene excited states in methylcyclohexane. (a) k^S_{ox}, (b) ${}^4/_9k^S_{ox}$, (c) ${}^1/_9k^S_{ox}$, (d) k^T_{ox}. Insert: T_1 absorbance decay monitored at 415 nm, 40.2 °C, 4.96% O_2/N_2, 2 μs/div, 0.009 au/div.

expresses the temperature dependence of solvent viscosity, η, in terms of the activation energy of viscous flow, E_a. This expression often fails over very broad temperature ranges as a consequence of differing solvent binding forces having slightly different activation parameters.[7a,19] As can be seen in Table I, room temperature values of k^S_{ox} and the activation energies for solvent viscous flow agree well with literature values[7a,19] determined over comparable temperature ranges. It should also be pointed out that this agreement between our results and those in the literature for the temperature dependence of activation energies of viscous flow support the validity of our assumptions concerning the calculations of $[O_2]$ at different temperatures.[20] It is therefore clear that for toluene and acetonitrile the temperature dependence of k^S_{ox} reflects that of solvent viscous flow and as a result can be employed as an empirical measure of diffusion control in the solvents employed. The relatively high activation energy and

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(16) (a) Emmerich, W.; Battino, R. *Chem. Rev.* **1973**, *73*, 1. (b) *Oxygen and Ozone*; Battino, R., Ed.; Pergamon: Oxford, 1981; Solubility Data Series R, Vol. 7, p 257.

(17) Scaiano, J. C., in ref 7b, p 343.

(18) Ware, W. R. *J. Phys. Chem.* **1962**, *66*, 455.

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

(20) In ref 19, solvent viscosities were determined at different temperatures using a viscometer. Our results are in very good agreement with the Andrade equation parameters determined therein.

Table I. Room-Temperature k^S_{ox} Values and Arrhenius Parameters in Toluene, Methylcyclohexane, and Acetonitrile

solute/solvent	k^S_{ox} (M^{-1} s^{-1})	T, (K)	E_a (kcal/mol^{-1})	A (M^{-1} s^{-1})
P/toluene		190–220	2.68 ± 0.2 (2.73[b])	(39.5 ± 5) × 10^{11}
	3.42 × 10^{10}	220–310	2.28 ± 0.2 (2.17[b])	(16.2 ± 3) × 10^{11}
N/MH[a]		180–220	3.47 ± 0.5	(266 ± 100) × 10^{11}
	2.60 (2.67[c]) × 10^{10}	220–335	2.03 ± 0.3	(8.0 ± 3) × 10^{11}
N/acetonitrile	3.36 (3.60[d]) × 10^{10}	240–345	1.77 ± 0.2 (1.63[b])	(6.6 ± 2) × 10^{11}

[a] Methylcyclohexane. [b] Activation energies for viscous flow.[7a] [c] For N in cyclohexane.[7a] [d] For methylnaphthalene in acetonitrile.[9d]

Table II. Room Temperature (298 K) Values fof k^T_{ox} and High-Temperature Limiting Arrhenius and Activation Parameters for Aromatic Triplet States in Toluene

hydrocarbon	k^T_{ox} (M^{-1} s^{-1})	E_a (kcal/mol^{-1})	A (M^{-1} s^{-1})	$\Delta H^\ddagger$ (kcal/mol^{-1})	$\Delta S^\ddagger$ (cal mol^{-1} K^{-1})
anthracene	3.96 × 10^9	1.16 ± 0.20	(2.8 ± 0.7) × 10^{10}	0.59 ± 0.20	–12.7 ± 0.5
pyrene	2.79 × 10^9	0.64 ± 0.20	(8.3 ± 1.0) × 10^9	0.07 ± 0.20	–15.1 ± 0.6
coronene	2.35 × 10^8	0.12 ± 0.20	(2.9 ± 0.7) × 10^8	0.45 ± 0.20	–21.8 ± 0.7
naphthalene	2.33 × 10^9	–0.41 ± 0.20	(1.2 ± 0.5) × 10^9	–0.98 ± 0.20	–18.9 ± 0.6
biphenyl	1.93 × 10^9	–0.88 ± 0.20	(2.9 ± 0.7) × 10^8	–1.45 ± 0.20	–21.8 ± 0.6

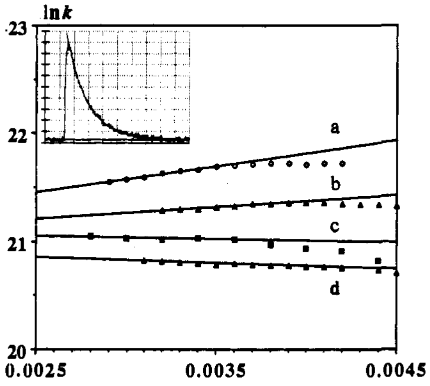

Figure 4. Arrhenius plots of bimolecular rate constants for $O_2(^3\Sigma_g^-)$ quenching of naphthalene(T_1). (a) Acetonitrile, (b) acetone, (c) methylcyclohexane, (d) *n*-hexane. Insert: T_1 absorbance decay monitored at 410 nm in *n*-hexane, –33.4 °C, 20% O_2/N_2, 500 ns/div, 0.009 au/div.

preexponential factor obtained for N in methylcyclohexane over the 180–220 K temperature range is of some concern in the absence of literature values for comparison over the equivalent temperature range. However, the k^S_{ox} values for N in methylcyclohexane were determined under the same conditions as those for k^T_{ox} and are being used to estimate the $^1/_9$- and $^4/_9k_d$ limits. It therefore seems reasonable that we employ them for purely comparative purposes.

3.2. Temperature Dependence of k^T_{ox} in Toluene. In Figure 1, the temperature dependence of k^T_{ox} in toluene is expressed in Arrhenius form for each of the hydrocarbons studied. The dashed lines in Figure 1 represent $^1/_9$- and $^4/_9k_d$, taking k_d as being equal to k^S_{ox} of P (shown as the uppermost data set in Figure 1). The derived Arrhenius and activation parameters are given in Table II.

3.3. Solvent-Dependent Behavior of k^T_{ox} of Naphthalene. The Arrhenius plots of k^T_{ox} and k^S_{ox} for N in toluene, methylcyclohexane, and acetonitrile are given in Figures 1, 2, and 3, respectively. The Arrhenius plots obtained for k^T_{ox} of N in all of the nonaromatic solvents employed are given in Figure 4, and the derived activation parameters are given in Table III.

4. Discussion

The most striking feature of all of the Arrhenius plots of k^T_{ox} is the high degree of curvature apparent. As shown in Figures 1 and 3, at low temperatures k^T_{ox} follows typical Arrhenius form, indicating a positive activation energy for the quenching process. At higher temperatures, marked deviation from the Arrhenius form is noted, with the temperature dependence exhibiting positive slopes in some cases. These observations are consistent with a change in rate-determining step over the accessible temperature range. The energy profile of a reaction involving an intermediate of lower energy than that of reactants is given in Figure 5. The energy barrier to formation of the intermediate is that of the activation energy of solvent viscous flow, E_d, while unimolecular decay forming products is given by E_p and that of reactant regeneration, E_{-d}. The general scheme can be summarized as follows[11b]

$$A + B \rightleftharpoons C \rightarrow \text{products}$$

and the bimolecular rate constant is given by

$$k_q = k_d k_p/(k_{-d} + k_p) \qquad (4)$$

where k_d is the bimolecular diffusion-controlled rate constant and k_{-d} and k_p are the unimolecular rate constants for exciplex breakdown forming reactants and products, respectively. It can be seen from Figure 5 that the temperature dependence of k_p is less than that of k_{-d} by virtue of E_{-d} being greater than E_p. If the preexponential factor of k_{-d} is greater than that of k_p, then the Arrhenius plots for these two rate constants must cross at some specific temperature, T_s. At temperatures less than T_s, k_{-d} is less than k_p and the reaction is diffusion controlled:

$$k_q = k_d \qquad (5)$$

and

$$\ln k_q = \ln A_d - E_d/RT \qquad (6)$$

At temperatures greater than T_s, k_{-d} is much larger than k_p, and the reaction rate is given by

$$k_q = k_d k_p/k_{-d} \qquad (7)$$

and

$$\ln k_q = \ln (A_d A_p/A_{-d}) - (\Delta E + E_p)/RT \qquad (8)$$

where $\Delta E = E_d - E_{-d}$. Due to unfavorable entropic/preexponential factors, the rate-determining step is the breakdown of the intermediate to form products, and the reactants are in equilibrium with the intermediate. It is therefore possible to have overall *negative* activation energies for the reaction, simply because $\Delta E + E_p$ may be negative. In cases where a photochemical process is involved, a negative activation energy has been taken to imply the existence of an enthalpically stable intermediate, an exciplex, lying along the quenching coordinate.[11] The key point is that if T_s falls somewhere in the middle of the available temperature range, then strong curvature in Arrhenius plots would be observed, and, in principle, both low-temperature (diffusion) and high-temperature (preequilibrium) limiting forms of the rate constant temperature dependence can be obtained.[11c]

Table III. Room Temperature (298 K) $k^{\rm T}_{\rm ox}$ Values and Preequilibrium Arrhenius and Activation Parameters for Naphthalene as a Function of Solvent

solvent	$k^{\rm T}_{\rm ox}$ (M^{-1} s^{-1})	E_a (kcal mol^{-1})	A (M^{-1} s^{-1})	$\Delta H^{\ddagger}$ (kcal mol^{-1})	$\Delta S^{\ddagger}$ (cal mol^{-1} K^{-1})
n-hexane	1.07×10^9	0.11 ± 0.1	$(1.3 \pm 0.5) \times 10^9$	-0.46 ± 0.1	-18.6 ± 0.5
methylcyclohexane	1.38×10^9	0.06 ± 0.1	$(1.5 \pm 0.5) \times 10^9$	-0.51 ± 0.1	-18.5 ± 0.5
acetone	1.78 ± 10^9	-0.21 ± 0.1	$(1.2 \pm 0.5) \times 10^9$	-0.78 ± 0.1	-18.9 ± 0.5
acetonitrile	2.70×10^9	-0.47 ± 0.2	$(1.1 \pm 0.5) \times 10^9$	-1.04 ± 0.2	-19.1 ± 0.6
toluene	2.33×10^9	-0.41 ± 0.2	$(1.2 \pm 0.5) \times 10^9$	-0.98 ± 0.2	-18.9 ± 0.6

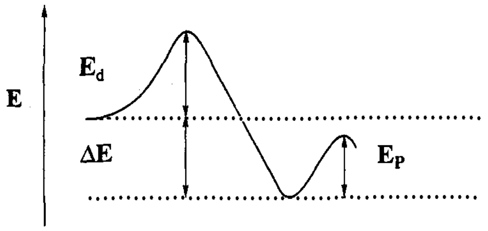

Figure 5. General energy profile for a bimolecular reaction involving an energetically stable intermediate.

Exciplexes are stabilized by CT interactions,[21] and as already mentioned in the Introduction, such interactions have been repeatedly invoked to explain sensitizer-dependent S_Δ values.[9,22] The involvement of CT interactions does not imply that full charge-separated species are involved; however, it does indicate that a polar intermediate is present along the quenching coordinate between the nonpolar reactants and products. The wave function, ${}^m\Psi_{\rm ex}$, of the exciplex of multiplicity m can be expressed as a linear combination of zero-order wave functions of the localized excited state ${}^m(SO_2)^*$ and the fully charge-separated CT state ${}^m(S^{\bullet+}O_2^{\bullet-})$:

$$m\Psi_{\rm ex} = a\Phi_0{}^m(SO_2)^* + b\Phi_0{}^m(S^{\bullet+}O_2^{\bullet-}) \qquad (9)$$

where a and b are coefficients describing the degree of local excited-state character and formal CT states, respectively, contributing to the exciplex function.[9d,23,24] It is expected that at low triplet energies $E_{\rm T}$, the a term should dominate, whereas at high values of $E_{\rm T}$ the b term should become more significant due to IP − $E_{\rm T}$ decreasing as $E_{\rm T}$ increases,[25,26] where IP is the sensitizer ionization potential. Effectively, the degree of CT stabilization of the exciplex is expected to increase as triplet energy increases, i.e., in the sequence A, P, C, N, to B.[2b,26]

4.1. Low-Temperature Behavior. Figure 1 shows that the measured bimolecular rate constant for triplet-state quenching by $O_2(^3\Sigma_g)$ in toluene consistently *exceeds* the expected $^1/_9k_d$ limit at temperatures less than −60 °C. Unfortunately, the liquid range of toluene is too small to allow us to establish accurate values for the low-temperature limiting slope and corresponding preexponential factors. However, it appears that the aromatic hydrocarbon $k^{\rm T}_{\rm ox}$ values are tending toward common limiting behavior that is consistent with the expectations of eqs 4, 5, and 6. This suggests that steric factors governing the rate constant for intermediate formation are independent of the size of the aromatic hydrocarbon. Such a situation seems reasonable given that the diffusion coefficient of $O_2(^3\Sigma_g)$ is some 3–4 times greater than that for aromatic hydrocarbons,[18] and, as a result, diffusion rates will be controlled by O_2 diffusion rather than that of the hydrocarbon. As indicated in Figure 2, the values of $k^{\rm T}_{\rm ox}$ for N at the low-temperature end of the liquid range of acetonitrile are not limited to $^1/_9k_d$. In methylcyclohexane (Figure 3), the low-temperature limiting value of $k^{\rm T}_{\rm ox}$ is *at least* $^4/_9k_d$.

4.2. High-Temperature Limiting Behavior. As can be seen in Figure 1, the values of ln $k^{\rm T}_{\rm ox}$ are all linear with $1/T$ at $1/T < 3.5 \times 10^{-3}$ K^{-1}. The slopes of these lines provide activation energies, E_a, and enthalpies, $\Delta H^{\ddagger}$, and their intercepts at $1/T = 0$ provide preexponential factors, A, and activation entropies, $\Delta S^{\ddagger}$. These parameters are listed in Table II. We can see that both E_a and A are dependent on aromatic hydrocarbon. In each case the activation energies and enthalpies are lower than those for diffusion control and in the cases of triplet N and B are negative. In terms of the scheme outlined in Figure 5, this behavior is consistent with preequilibrium control where the product-forming step becomes rate limiting on account of unfavorable activation entropies. The negative activation energies observed for the quenching of N and B triplets in toluene are consistent with exciplex intermediacy. The observed hydrocarbon-dependent and solvent-dependent activation enthalpies and energies (Tables II and III) may reflect increasing CT stabilization of the activated complexes for product formation as triplet energy is increased from A to B.

It is difficult to interpret the high-temperature preexponential factors of Table II in terms of CT-induced solvation changes because the magnitudes of the preexponential factors almost certainly reflect hydrocarbon-dependent symmetry factors and triplet energy-dependent Franck–Condon factors.[1c] In general, the preexponential factors listed in Table II decrease with increasing triplet energy, $E_{\rm T}$. The interaction of these symmetry and Franck–Condon effects was previously invoked to explain the very low $k^{\rm T}_{\rm ox}$ value of C.[2b]

The preequilibrium activation entropies of N at room temperature are strikingly independent of solvent (Figure 4 and Table III). In fact, the observed preequilibrium A factors are extremely close to those ($(1–2) \times 10^9$ M^{-1} s^{-1}) reported for the gas-phase quenching of triplet N by $O_2(^3\Sigma_g^-)$.[27] The activation entropies listed in Table III reflect the differences in solvent ordering in the product-forming transition state with respect to that of the solvated reactants. That the values listed are insensitive to the nature of the solvent suggests that there are no profound solvent reorganization changes on going from solvated reactants to the product-forming transition state in any of the solvents studied. Neither triplet N nor $O_2(^3\Sigma_g)$ is a highly polar species, and it seems unlikely that a *transition state* for product formation that contains a high degree of charge separation between exciplex partners could be formed in these solvents without observing significant changes in $\Delta S^{\ddagger}$ values. Such changes in $\Delta S^{\ddagger}$ should arise due to electrostriction effects on the solvation of a transition state associated with the formation of charge-separated products.[28] In agreement with such indications, we could find no spectroscopic evidence for the formation of N radical cation *via* triplet-state

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(26) (a) A definite relationship between ionization potential, IP, and oxidation potential, $E_{\rm ox}$, has been established for aromatic hydrocarbons in acetonitrile.[26b] For the sensitizers employed in this study, $\Delta G_{\rm et}$, the free energy of CT-state formation *via* ground-state quenching, systematically varies from approximately 1.8 to 2.5 V in acetonitrile for A and B, respectively (employing $E_{\rm red} = -0{,}78$ V for O_2)[22] and can be contrasted with the $E_{\rm T}$ values ranging from 1.8 to 2.8 V, respectively. It is therefore clear that the CT-state energy lies extremely close to the hydrocarbon triplet state, ranging from slightly above to below the $E_{\rm T}$ value. (b) Pysh, E. S.; Yang, N. C. *J. Am. Chem. Soc.* **1964**, *85*, 2124.

(27) Porter, G.; West, P. *Proc. R. Soc., Ser. A* **1964**, *279*, 302.

(28) *Chemical Kinetics*, 3rd ed.; Laidler, K. J., Ed.; Harper and Row: New York, 1987.

quenching by $O_2(^3\Sigma_g)$ in any of the solvents examined. Our failure to observe radical cations contrasts with the recent suggestion that charge-separated products are formed from N triplet quenching by $O_2(^3\Sigma_g)$ in acetonitrile.[9d]

The solvent dependence of room temperature k^{T}_{ox} values of N arise solely as a consequence of solvent-dependent activation energies in the preequilibrium region (Figure 4, Table III). It is interesting to note that preequilibrium is attained at a slightly higher temperature in methylcyclohexane than in the lower viscosity, similarly nonpolar solvent *n*-hexane, whilst ΔH^* and ΔS^* are essentially unchanged. Such behavior is predicted simply because the barrier to k_{-d} ($\Delta H_0 + \Delta H_d^*$) is slightly greater for the more viscous solvent. The viscosities of *n*-hexane, acetone, and acetonitrile are all around 0.3 cp[17] at room temperature, and therefore the increasingly negative ΔH^* values must arise due to either ΔH_0 becoming more negative or ΔH_p^* decreasing or both as a function of solvent polarity. It is far from firmly established that ΔH_0 is in fact a simple function of solvent polarity in the general case of exciplex formation.[24] If anything, exciplex stability, as measured by ΔG_0, arises primarily because of solvent-dependent ΔS_0 values.[24] It is possible that the lack of systematic solvent effects on ΔS^* of triplet N arise due to either or both of the following reasons. (1) Close contact between reactants in the product-forming transition state causes the absence of any solvent separating the reactants. The use of eq 9 implies strong coupling between the hydrocarbon triplet state and $O_2(^3\Sigma_g)$ in the exciplex and therefore requires that the encounter distance be of van der Waals magnitude.[29] Or, (2) there may be a decrease in solvation enthalpy associated with the solvation of two nonpolar reactants as compared to that for one nonpolar product-forming transition state on going to progressively more polar solvents. Increasingly negative ΔH^* values would, in the latter case, reflect the lower solvation volume of the product-forming transition state with respect to that of the free solvated reactants.

Whatever the detailed nature of intraexciplex forces and interactions with the solvent, our results are most consistent with the formation of an encounter stabilized by configuration interaction with the local CT state, in which the product-forming step (for N exciplex collapse) is characterized by a transition state requiring specific reactant geometrical interactions that are independent of solvent and similar to those in the gas phase. The recent results of McGarvey *et al.* clearly demonstrate that CT energies can influence room temperature k^{T}_{ox} values,[22] and the rate variations observed by them are consistent with exciplex involvement in the quenching process.

4.3. General Considerations. The results obtained from this study indicate that quenching of aromatic hydrocarbon triplet excited states by $O_2(^3\Sigma_g)$ at room temperature involves the formation of reversibly formed complexes. The formation rate of these complexes is independent of the aromatic hydrocarbon and consistently exceeds $^1/_9k_d$ in all cases in toluene and, for N, in all of the solvents examined. Scheme I demands that exciplexes of three distinct multiplicities (singlet, triplet, and quintet) be considered as intermediates in $O_2(^3\Sigma_g)$ quenching of aromatic hydrocarbon triplet states. By analogy with the simplified scheme in Figure 5 and eqs 4–8, k_1 and k_{-1} of eq 1 can be equated to k_p and k_{-d}, respectively, and likewise for the rate constants associated with the triplet exciplex, k_3 and k_{-3}. Thus the interpretation of temperature-dependent behavior of k^{T}_{ox} on the basis of Scheme I quickly becomes very complex. However, using the generalized argument arising from Figure 5, inspection of eq 1 shows that k^{T}_{ox} values of greater than $^1/_9k_d$ can arise only when the second term becomes significant, that is, when quenching takes place through both singlet and triplet exciplexes. Ultimately, Scheme I predicts a limit of $k^{T}_{ox} = {}^4/_9k_d$ when $k_1 \gg k_{-1}$ and $k_3 \gg k_{-3}$. This spin-statistical limit arises due to the fact that the quintet encounters do not lead to removal of reactants, and since singlet and triplet exciplex formation is rate limiting at low temperatures, a maximum of 4 in 9 reactant encounters can lead to triplet hydrocarbon quenching. A similar situation is frequently encountered in radical recombination reactions,[7a,19,30] a situation that leads to a $^1/_4k_d$ quenching limit. The data shown in Figure 1 and for N in methylcyclohexane in Figure 3 may be consistent with a low-temperature limiting rate of $^4/_9k_d$. In the absence of definitive evidence to the contrary, we shall assume that the low-temperature limiting rate constant corresponds to $^4/_9k_d$.[31] If Scheme I is applicable and no ISC takes place between exciplexes of different multiplicity,[32] then S_Δ values should limited to 0.25 for *all* hydrocarbons in *all* solvents, providing that the rate-determining step or steps are exciplex formation.

Clearly, the temperature at which the triplet and singlet exciplexes turn over from diffusion to preequilibrium control will depend on the balance between the ΔH^* and ΔS^* factors for both singlet and triplet exciplexes. This should also affect the S_Δ value at any given temperature. Given that preequilibrium k^{T}_{ox} values are determined by entropic or preexponential factors, it is reasonable to expect that high-temperature limiting values of k^{T}_{ox} should eventually reflect the form of the singlet exciplex decay, since the Franck–Condon factors for the latter should be 50–100 times greater than those for triplet exciplex collapse.[33] Consequently, in the absence of ISC between singlet and triplet exciplexes, S_Δ values of 1.00 would be expected at extreme full preequilibrium. It may be that the solvent-independent ΔS^* values of triplet N arise because of such a situation.

It is in the temperature region between these extremes that S_Δ values of anywhere between 1.00 and 0.25 could arise. It is not possible to determine whether ΔG_0 for singlet and triplet exciplex formation will be the same. However, exciplex involvement will clearly alter the ratio of rate constants of product formation to those of reactant regeneration with respect to the situation where no CT stabilization can take place. Again the results of McGarvey *et al.* indicate that S_Δ and k^{T}_{ox} in benzene at room temperature are related through ΔG_0.[22] In our case, room temperature S_Δ values range from 0.75 (A) to 0.45 (B)[34] in benzene, and the changes in both ΔH^* and ΔS^* in toluene are consistent with increasing enthalpic stabilization of the product-forming transition state derived from an exciplex intermediate. In cyclohexane and acetonitrile it has been demonstrated that S_Δ has a value of 1.00 at room temperature,[35] whereas in benzene values of between 0.55[8] and 0.62[22] have been reported. It would appear that benzene acts on the exciplexes such that either ΔG_0 is more negative at room temperature or the reorganization energy is greater than in nonaromatic solvents. At present we have no satisfactory explanation for the anomalous nature of these effects in benzene.[36]

Finally, we must recognize the possibility that the irreversible rate-determining breakdown of the exciplexes might involve processes other than formation of $O_2(^3\Sigma_g)$ and -($^1\Delta_g$). The solvent independent ΔS^* values observed in triplet N quenching might reflect the irreversible formation of a common second intermediate

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(29) Weak coupling demands that the CT complex be formed as a discrete species, if it is formed at all, and substantial changes in solvent reorganization energies should result in profoundly different ΔS^* values for its formation on proceeding from *n*-hexane to acetonitrile—the lack of any systematic solvent effect on ΔS^* of N would appear to rule out such a possibility.

(30) Schuh, H. H.; Fischer, H. *Helv. Chim. Acta* **1978**, *61*, 2130.

(31) It would be desirable to determine the temperature dependence of k^{T}_{ox} of a sensitizer triplet state that has a large room temperature k^{T}_{ox} value. It may then be possible to determine the limiting low-temperature behavior over a broader temperature range, allowing a more convincing determination of the exciplex formation rate constant. Preliminary experiments with *p*-methoxyacetophenone ($k^{T}_{ox} = 8 \times 10^9$ M^{-1} s^{-1} at room temperature) in toluene suggest that $^4/_9k_d$ is the low-temperature limiting rate constant.

(32) Darmanyan, A. P.; Foote, C. S. *J. Phys. Chem.* **1992**, *96*, 3723.

(33) Kearns[1] estimates that the Franck–Condon factor for $O_2(^1\Delta_g)$ formation is favored over ($^3\Sigma_g$) by a factor of approximately 10^2 for triplet sensitizers of energy between 42 and 75 kcal mol^{-1}.

(34) The S_Δ values for A, P, N, and B in benzene are 0.75,[6c] 0.65,[9b] 0.55,[8] and 0.45,[8] respectively, at room temperature.

(35) It has been reported that N has an S_Δ value of 1.00 in cyclohexane and acetonitrile.[8] This has been confirmed using photoacoustic techniques (private communication from R. W. Redmond).

(biradical?) in competition with either $O_2(^3\Sigma_g)$ and -$(^1\Delta_g)$. The rapid partitioning of this species into singlet and/or triplet products would then be responsible for the ultimate product distribution. There is precedent for such a possibility in aromatic ketone[10a] and olefinic[10b] triplet quenching by $O_2(^3\Sigma_g)$ and also in the photooxidizing intermediates proposed by Schenck some 30 years ago.[37] Biradicals have frequently been postulated as products of exciplex collapse in other systems, notably in excited triplet ketone quenching by simple alkenes.[11b,38] However, our results do not demand that such intermediates exist, and in principle the known product distribution (at room temperature) can be accounted for in a qualitative way without invoking them.

5. Conclusions

We have demonstrated that $O_2(^3\Sigma_g)$ quenching of aromatic hydrocarbon triplet states at room temperature proceeds *via* a rapidly and reversibly formed exciplex. The rate parameters for exciplex formation are independent of aromatic hydrocarbon in toluene and exceed $^1/_9k_d$ in all of the solvents employed.[39] It is difficult to establish whether or not the limiting rate is $^4/_9k_d$—an important point since such a limit would vindicate the use of the widely accepted spin-statistically based interpretation of room temperature $k^T{}_{ox}$ values (Scheme I), albeit with the provision that room temperature triplet hydrocarbon quenching proceeds through the reversible formation of singlet and triplet *exciplexes*. The intermediates involved of multiplicity *m* can be represented as

$$^m[S\cdots O_2 \leftrightarrow S^{\delta+}\cdots O_2{}^{\delta+}]^*$$

with the balance between polar and nonpolar contributions dictated by the *a* and *b* coefficients of eq 9.

Whether Scheme I adequately describes the temperature dependence of $k^T{}_{ox}$ or not, the high-temperature limiting behavior seen for N is not consistent with the formation of charge-separated products from triplet N quenching by $O_2(^3\Sigma_g)$ in the more polar solvents, as indicated by the lack of polarity dependence of the N preequilibrium entropies of activation. The only apparent experimental difference in preequilibrium behavior in the various solvents studied appears to be small changes in the magnitude of the preequilibrium activation enthalpy.

The observed temperature dependence of $k^T{}_{ox}$ of aromatic hydrocarbons leads to verifiable, although qualitative, predictions as to the temperature dependence of S_Δ values when interpreted in terms of CT stabilization of exciplexes. Clearly, variable-temperature determinations of S_Δ are required before we can determine the general applicability of Scheme I and whether or not exciplex intermediacy alone can successfully account for solvent dependency of both $k^T{}_{ox}$ and S_Δ values. S_Δ values are expected to be temperature dependent in all solvents, providing that the $k^T{}_{ox}$ Arrhenius plots over the same temperature range exhibit some curvature.[41] Whatever the ultimate satisfactory explanation for variation in S_Δ values as a function of aromatic hydrocarbon, it is clear that the overall triplet quenching process proceeds *via* exciplex intermediacy.

Acknowledgment. This work is supported in part by NIH Grant GM 24235 and the Center for Photochemical Sciences, Bowling Green State University. We would also like to thank Drs. Stephen L. Logunov and Anthony A. Gorman for useful discussions.

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(36) (a) In a recent report by Darmanyan and Foote,[34b] a series of experiments in which triplet flouranil is quenched by $O_2(^3\Sigma_g)$ are described. In acetonitrile S_Δ was 1.00, however, in aromatic solvents where a triplet fluoranil/solvent exciplex was present, S_Δ values of considerably less than 1.00 were observed. No detailed explanation of these observations has emerged. It is possible that weakly bound solvent/aromatic hydrocarbon triplet exciplexes exist in benzene and that low S_Δ values observed in benzene are a result of similar mechanisms to responsible for fluoranil S_Δ. (b) Darmanyan, A. P.; Foote, C. S. *J. Phys. Chem.* **1992**, *96*, 6317.

(37) (a) Schenck, G. O. *Angew. Chem.* **1957**, *69*, 579. (b) Gollnick, K.; Schenck, G. O. *Pure Appl. Chem.* **1964**, *9*, 507.

(38) (a) Caldwell, R. A.; Gajewski, R. P. *J. Am. Chem. Soc.* **1973**, *95*, 2549. (b) Caldwell, R. A.; James, S. P. *Ibid.* **1969**, *91*, 5184.

(39) A study employing variable-pressure techniques reported that $k^T{}_{ox}$ of several anthracene derivatives in methylcyclohexane exceeded $^1/_9k_d$ and achieved a rate of at least $^4/_9k_d$ at 400 MPa in the case of dichloroanthracene.[38] These results were interpreted as being due to intersystem crossing from the triplet encounter complex to the singlet (Scheme I) on increasing pressure. It should be pointed out that these results can, in principle, be accounted for by similar arguments used here for N in the same solvent, namely the possibility that quenching proceeds *via* singlet and triplet exciplexes leading to lower S_Δ values.

(40) Yasuda, H.; Scully, A. D.; Hirayama, S.; Okamoto, M.; Tanaka, F. *J. Am. Chem. Soc.* **1990**, *112*, 6847.

(41) We are currently involved in S_Δ temperature-dependent experiments. In principle, the validity of Scheme I can be determined if the limiting low-temperature S_Δ of aromatic hydrocarbons is 0.25. In the absence of Scheme I, mechanisms involving either a single exciplex intermediate or biradicals could have S_Δ values from 0 to 1.00 independent of $k^T{}_{ox}$.