J. Am. Chem. Soc. 1994, 116, 5005–5006

Temperature Dependence of Oxygen Quenching of Aromatic Hydrocarbon Triplet States in Viscous Solution

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Received February 15, 1994

Recently, several publications reported temperature dependencies for reactions between triplet states and oxygen which indicate that these reactions proceed via exciplexes formed between the triplet states and molecular oxygen.[1] In this report, further thermodynamic evidence for the involvement of exciplexes is presented in reactions where a charge-transfer, CT, state exists with an energy, E_{CT}, lower than that of the localized triplet state, E_T. Two temperature-dependent behaviors are apparent depending on the magnitude of $E_T - E_{CT}$. When E_{CT} is substantially lower than E_T, the activation energy for the oxygen quenching reaction is equal to the energy for viscous flow of the solvent, i.e., the reaction is diffusion controlled. However, when the gap between E_{CT} and E_T is smaller, the activation energy for the reaction is significantly less than that for viscous flow, implying that these triplet states are quenched via a rate-determining step which is not associated with molecular diffusion.

Reactions between triplet states and oxygen are described by the following pathways:[2-4]

$$^3A^* + {}^3O_2 \rightleftarrows {}^1(A\cdots O_2)^* \rightarrow {}^1A + {}^1O_2^* \qquad (a)$$

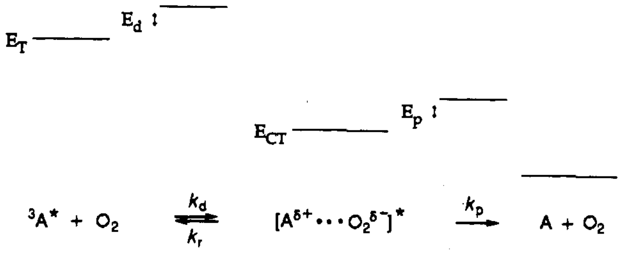
$$^3A^* + {}^3O_2 \rightleftarrows {}^1(A\cdots O_2)^* \rightarrow {}^1A + {}^3O_2 \qquad (b)$$

$$^3A^* + {}^3O_2 \rightleftarrows {}^5(A\cdots O_2)^* \qquad (c)$$

Kinetic and singlet oxygen measurements[2,5,6] have shown that path b, which involves a CT stabilized exciplex, is important for triplet states with high energies and/or relatively low oxidation potentials, E_{D/D^+}. In these cases, energies of the charge-transfer exciplexes with oxygen, $E_{CT} = E_{D/D^+} - E_{O_2^-/O_2} - C$, where $E_{O_2^-/O_2}$ is the reduction potential of oxygen and C is the stabilization energy associated with ion pair formation, are lower than those of the locally excited triplet states.

By studying the temperature dependence of the rate of oxygen quenching of the triplet states of a number of aromatic ketones and hydrocarbons over the temperature range 190–360 K, McLean and Rodgers[1] recently obtained thermodynamic evidence that, at the higher temperatures, some of these reactions do proceed through an exciplex state with an energy lower than that of the triplet state, as represented by the reaction coordinate shown in Scheme 1, where the rate constant for the overall quenching reaction, k_Q, is given by

Scheme 1



$$k_Q = k_d k_p/(k_r + k_p) \qquad (1)$$

In this report, further rate constants for the oxygen quenching of selected aromatic hydrocarbon triplet states are presented which show temperature dependencies expected from reactions which involve CT stabilized exciplexes. In the present work, triplet-state quenching reactions were studied in a highly viscous environment, viz., in 3-methylpentane (3MP) solvent, from 90 to 115 K, which is just above this solvent's glass transition temperature. k_Q was determined as a function of temperature for naphthalene and 4-, 7-, and 5-methylbenz[*a*]anthracenes by measuring the rates of decay of phosphorescence from the triplet states of these molecules in degassed and in oxygen-saturated solutions. Over the limited temperature range studied in this work, the concentration of oxygen in solution is assumed to be independent of temperature. The gradients, G_{AR}, of the Arrhenius plots of $\ln 1/k_Q$ vs $1/T$ together with $(E_T - E_{CT})$ for each molecule studied are given in Table 1.

Table 1. Gradients, G_{AR}, of the Arrhenius Plots of $\ln 1/k_Q$ vs $1/T$ for the Oxygen Quenching of the Triplet States of Various Aromatic Hydrocarbons with Energies, E_T, from Refs 8 and 9[a]

	G_{AR}, kJ·mol^{-1}	$(E_T - E_{CT})$, kJ·mol^{-1}
naphthalene	67 ± 4	22.0
4-methylbenz[*a*]anthracene	30 ± 2	8.95
7-methylbenz[*a*]anthracene	36 ± 3	9.1
5-methylbenz[*a*]anthracene	36 ± 2	9.0

[a] The charge-transfer exciplex energies, E_{CT}, were calculated from the equation $E_{D/D^+} - E_{O_2^-/O_2} - C$, where C is 0.06 eV,[10] the reduction potential of oxygen in acetonitrile is –0.82 eV,[10] and the oxidation potentials of the hydrocarbons are taken from ref 11.

E_d, the activation energy for viscous flow in 3MP from 80 to 95 K, is reported[7] to be 66.7 kJ·mol^{-1}. The activation energy for oxygen quenching of the triplet state of naphthalene in 3MP over the same temperature range is 67.0 ± 4 kJ·mol^{-1}, in excellent agreement with E_d. Therefore, it is concluded that this reaction is diffusion controlled. However, the gradients of the Arrhenius plots (activation energies) for oxygen quenching of the methylbenz[*a*]anthracene triplet states in 3MP are substantially lower than those for a diffusion-controlled reaction.

All of these observations can be explained in terms of involvement of charge-transfer exciplexes in the rate-determining steps and the thermodynamics of the reaction coordinate represented in Scheme 1.

Equations 2 and 3 express the temperature dependencies of the rate constants for the two competing reactions associated

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with decay of the charge-transfer exciplex $^{1,3}[A^{\delta+}\cdots O_2^{\delta-}]^*$ in Scheme 1. For naphthalene, $(E_T - E_{CT})$ is large, i.e., the charge-transfer state lies well below the locally excited triplet state. If, as a result, $(E_T - E_{CT}) + E_d$ is sufficiently greater than E_p, such that $k_r \ll k_p$, it follows from eq 1 that $k_Q \approx k_d$, i.e., the reaction is diffusion controlled. However, for the methylbenz[*a*]anthracenes, $(E_T - E_{CT})$ is smaller than that for naphthalene (see Table 1).

$$k_r = A_r \exp[-E_d/RT] \exp[-(E_T - E_{CT})/RT] \quad (2)$$

$$k_p = A_p \exp[-E_p/RT] \quad (3)$$

In 3MP solvent at all temperatures studied, k_d (as determined for the rate constant of quenching of the triplet state of naphthalene) is at least an order of magnitude greater than k_Q for the methylbenz[*a*]anthracene triplet states, i.e., $1/k_Q \gg 1/k_d$. When $1/k_Q \gg 1/k_d$, from eq 1–3 it follows

$$1/k_Q \approx (A_r/A_pA_d) \exp[E_p - (E_T - E_{CT})]/RT$$

The plots of ln $1/k_Q$ vs $1/T$ for the benz[*a*]anthracenes shown in Figure 1 are linear, with gradients less than E_d. This indicates that the rate-determining step for these compounds is not the diffusive, encounter pair formation process but instead the decomposition of the CT stabilized exciplex. The activation energies for decomposition of these exciplexes to give stable products, E_p, derived from these plots are 39, 45, and 45 kJ·mol^{-1} for the 4-, 7-, and 5-methyl derivatives of benz[*a*]anthracene, respectively.

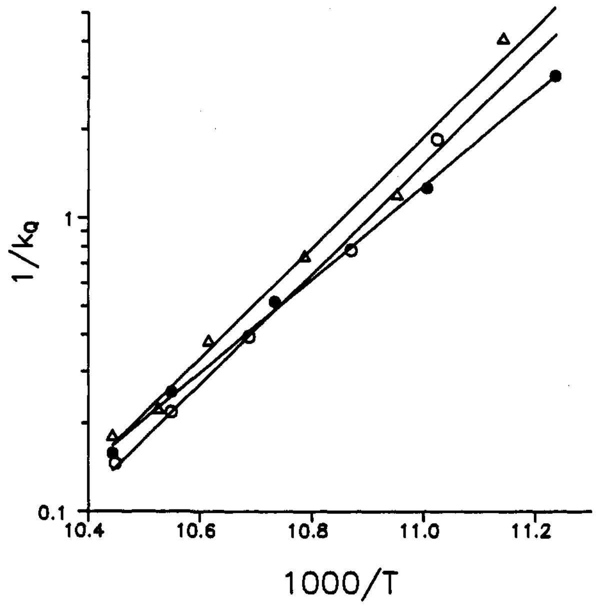

Figure 1. Plots of the reciprocals of bimolecular rate constants for the reactions between oxygen and the triplet states of methylbenz[*a*]anthracenes in 3MP solvent against reciprocal temperature. ●, 4-Methyl-, ○, 7-methyl-, and △, 5-methylbenz[*a*]anthracene.

Acknowledgment. The author thanks the New Zealand Foundation for Research Science and Technology, Contract C08222, and the Australian Wool Research and Development Corporation for financial support of this work.