Oxygen Quenching of the Aromatic Excited Singlet State

Sir:

The quenching of excited aromatic singlet states by the ground state of O_2 ($^3\Sigma_g$) is exceedingly efficient. Both gas- and liquid-phase studies indicate that quenching occurs on every collision.[1-4] (Of course, the calculated number of collisions is based on an assumed cross section and lifetime, which may introduce considerable error.) The nature and the products of this process are by no means well understood. The possible reactions are[5]

$$O_2(^3\Sigma_g^-) + {}^1A^* \longrightarrow {}^3A + O_2(^3\Sigma_g^-) \tag{1}$$

$$\longrightarrow {}^3A + O_2(^1\Delta_g^-) \tag{2}$$

$$\longrightarrow {}^3A + O_2(^1\Sigma_g^-) \tag{3}$$

$$\longrightarrow A + O_2(?) \tag{4}$$

The minimum energy transfer necessary for eq 2 to be operative is 0.98 eV, and for process 3 the energy needed is 1.64 eV. These conditions are both easily met in most aromatics. Several investigators[6-8] have detected $O_2(^1\Delta_g)$ in aromatic–oxygen systems stimulated by ultraviolet radiation. In addition, both Comtet[9] and Cventanović[2] have found that oxygen quenching of the aromatic singlet state leads to the formation of the aromatic triplet. From these data process 2 seems the most likely mechanism. However, $O_2(^1\Delta_g)$ is formed from an interaction with the aromatic triplet state[10] and thus process 1 cannot be eliminated.

Berlman[11] reported, in his laser studies of the O_2–pyrene system, that at high intensities oxygen is involved in the quenching process for less than 2×10^{-10} sec. Since this is much shorter than the lifetime of $O_2(^1\Delta_g)$, a short-lived charge-transfer mechanism was invoked. Mulliken[12] also gives strong evidence, based on absorption studies, for a weak-contact charge-transfer complex between aromatic molecules and oxygen in solution.

To shed more light on the possibility of contact-charge-transfer species in aromatic–oxygen systems, Stern–Volmer quenching studies were carried out on several aromatic compounds with differing ionization potentials. Although Stern–Volmer studies could be carried out on a large number of molecules, the alkyl- and fluorobenzenes have the advantages of a minimal amount of photochemistry, only one easily obtainable electronic transition, relatively small fluorescent yields, and well-known lifetimes. The results of this study are shown in Figure 1. The figure illustrates the large difference in slopes of the alkyl- and fluoro-substituted benzenes. The fluorescent quenching rate constants are tabulated in Table I along with the radiative lifetimes used to calculate them. Although a large error may exist in the absolute values of k_q owing to the uncertainty of the lifetimes, the trend is obvious. As the ionization potential increases from *tert*-butylbenzene to *m*-difluorobenzene, the rate of quenching decreases. The importance of the ionization potential in determining the quenching rate constant is quantatively shown by the straight line obtained in Figure 2.[13] The quenching rate also parallels the trend found for electrophilic substitution reactions in aromatic systems except that the *tert*-butyl group offers no steric hindrance. Thus, the data tend to support the contact-charge-transfer complex mechanism of fluorescence quenching by oxygen. However, it should be noted that the data offer no evidence on the nature of the final states of the aromatic and of the oxygen after collision. Conceivably, any of the forementioned

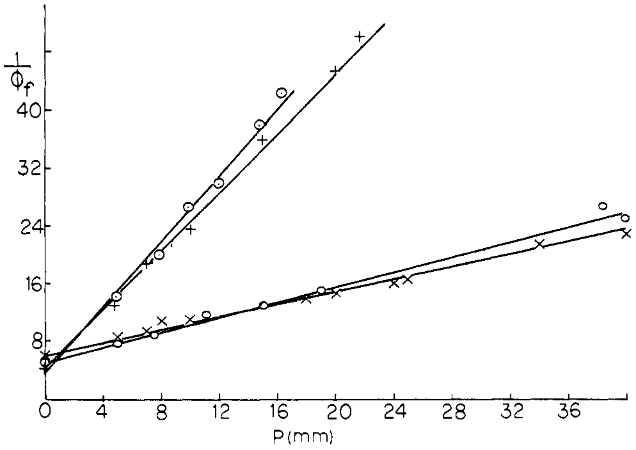

Figure 1. Oxygen quenching of the fluorescence of *m*-difluorobenzene (×) (pressure 1 Torr), fluorobenzene (○) (pressure 1 Torr), ethylbenzene (+) (presure 5 Torr), and *tert*-butylbenzene (⊙) (pressure 2 Torr); irradiated at 266 nm.

Table I. The Rate Constants for Oxygen Quenching of the Aromatic Singlet State

	k_q[f]	τ, nsec	Φ_f
tert-Butylbenzene[a]	4.2×10^{-10}	155[d]	0.25 ± 0.05
Ethylbenzene[a]	3.7×10^{-10}	155[d]	0.28 ± 0.03
Toluene[b]	3.88×10^{-10}	145	0.3 ± 0.01
Benzene[c]	$2.1–1.4 \times 10^{-10}$	407	0.18 ± 0.03
Fluorobenzene[e]	1.3×10^{-10}	100	0.21 ± 0.02
m-Difluorobenzene[a]	1.1×10^{-10}	97	0.16 ± 0.02

[a] Irradiated at 2640 Å. [b] See ref 4. [c] See ref 2. [d] These lifetimes are derived from Berlman (I. B. Berlman, "Handbook of Fluorescence Spectra of Aromatic Molecules," Academic Press, New York, N. Y., 1965) by multiplying them by the ratio of Burton and Noyes' lifetime of toluene to that of Berlman's. [e] K. Nakamura, *J. Chem. Phys.*, **53**, 998 (1970). [f] In units of cubic centimeters per molecule per second.

---

(1) H. Ishikawa and W. A. Noyes, Jr., *J. Chem. Phys.*, **37**, 583 (1962).

(2) A. Morikawa and R. J. Cvetanović, *ibid.*, **52**, 3237 (1970).

(3) I. B. Berlman and T. A. Walters, *ibid.*, **37**, 1888 (1962).

(4) C. S. Burton and W. A. Noyes, Jr., *ibid.*, **49**, 1705 (1968).

(5) E. K. C. Less, M. W. Schmidt, R. G. Shortridge, Jr., and G. A. Haninger, Jr., *J. Phys. Chem.*, **73**, 1805 (1969).

(6) K. Kawaoka, A. U. Khan, and D. R. Kearns, *J. Amer. Chem. Soc.*, **91**, 1039 (1969).

(7) D. R. Snelling, *Chem. Phys. Lett.*, **2**, 346 (1968).

(8) E. Wasserman, U. J. Kuck, W. M. Delavar, and W. A. Yager, *J. Amer. Chem. Soc.*, **91**, 1040 (1969).

(9) M. Comtet, Dissertation, 1970, University of Texas, Austin, Texas.

(10) K. Gollnick, *Advan. Photochem.*, **6**, 11 (1968).

(11) I. B. Berlman, C. R. Goldschmidt, G. Stein, Y. Tomkiewicz, and A. Weineb, *Chem. Phys. Lett.*, **4**, 338 (1969).

(12) H. Tsubomura and R. S. Mulliken, *J. Amer. Chem. Soc.*, **82**, 5966 (1960).

(13) The ionization potentials used were all determined by the same method (photoionization) to keep the results consistent.[14] For *tert*-butylbenzene the photoionization data were not availabile, so data for *n*-butylbenzene were used. The actual value for *tert*-butylbenzene should be slightly higher than for *n*-butylbenzene and would give even a better fit in Figure 2.

(14) V. I. Vendeneyev, L. V. Gurich, V. N. Kondrat'yev, V. A. Medvedev, and Y. L. Frankevich, "Bond Energies, Ionization Potentials, and Electron Affinities," Edward Arnold, London, England, 1962.

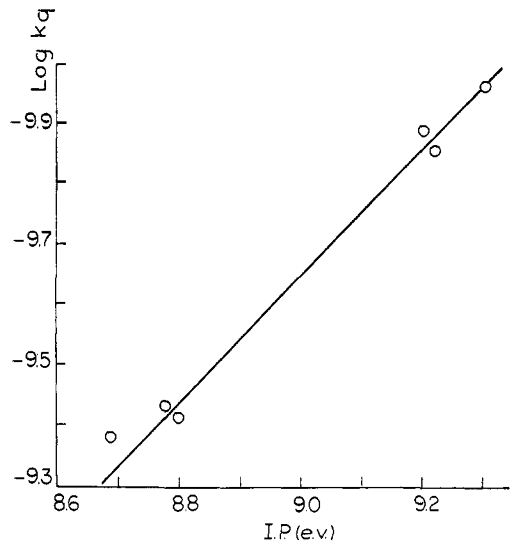

Figure 2. The ionization potential dependence of the oxygen quenching rate constants for several simple aromatic molecules.

processes could involve a contact-charge-transfer intermediate. Extrapolation of the present data to other systems may prove useful. As an example, the lack of observed oxygen quenching of the singlet state of many ketones may be due to their high ionization potentials.

Acknowledgment. I wish to thank Dr. W. A. Noyes, Jr., for many helpful comments. This work was supported by grants to Dr. W. A. Noyes, Jr., from the Robert A. Welch Foundation and from the Camille and Henry Dreyfus Foundation.

Terry Brewer
Chemistry Department, University of Texas
Austin, Texas 78712
Received October 19, 1970

Acid-Catalyzed Solvolysis Reactions of Zinc Porphyrins Having Various Basicities and Zinc *N*-Methylporphyrins[1]

Sir:

The study of acid-catalyzed solvolysis reactions of metal chelates has mainly been confined to flexible multidentate ligand complexes where the possibility exists for the ligand to uncoil from around the coordinated metal ion.[2] With rigid macrocyclic ligands, however, the unraveling mechanism is inapplicable, and some recent work has been directed to this problem,[3] especially with porphyrin molecules.[4-9] A variety of mechanisms have been advanced to explain the differing kinetic behavior found in the acid-induced dissociations of Cu, Zn, Mn(II), and Mg porphyrins in various solvents. To this end, we present results on the kinetics of the acid-catalyzed dissociations of (A) zinc etioporphyrin(III) in methanol, (B) zinc *N*-methyletioporphyrin(III), and (C) 2,4-disubstituted zinc deuteroporphyrins of differing basicities.

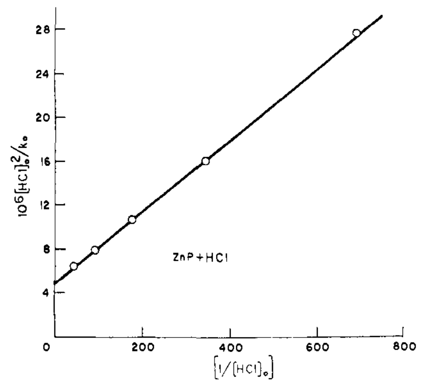

Figure 1. $[HCl]_0^2/k_{obsd}$ *vs.* $1/[HCl]_0$ for the reaction of zinc etioporphyrin with HCl in methanol, 25°.

The porphyrin and zinc complexes were prepared and purified by literature methods.[9,10] The kinetics were run at 25° in methanol acidified with HCl, using a Durrum stopped-flow apparatus or Cary 14, under pseudo-first-order conditions in porphyrin (*ca.* 10^{-5} *M*). Such rates were independent of water concentration below 0.2 *M*, but decreased by a factor of 10 to a limiting value at about 0.7 *M* H_2O. The dissociation of the zinc porphyrins into their acid forms was complete under the reaction conditions, and no reincorporation of Zn was observed.

At constant HCl concentrations, the additions of a two-, four-, or sixfold excess of NaCl or $(Et_4N)Cl$ each increased the rate, with respect to the absence of added chloride, by the same amount of *ca.* 20%. Thus no rate term in chloride is evident in HCl-methanol. With 0.02 *F* $HClO_4$ the observed rate constant was approximately 500-fold lower than that with the same concentration of HCl. Both 0.02 *F* and 0.12 *F* $(Et_4N)Cl$ in 0.02 *F* $HClO_4$-methanol showed the same solvolysis rate as produced by 0.02 *F* HCl-methanol itself. The observed rates with either HCl or $HClO_4$ were unaffected by a fivefold formal excess of $(Et_4N)ClO_4$. These observations can be rationalized by assuming that HCl in methanol exists predominantly in an undissociated ion-pair form.[11] The following results were obtained for the HCl-catalyzed solvolysis reactions in methanol.

For zinc etioporphyrin(III) [ZnP], Figure 1 shows the linear plot of $[HCl]_0^2/k_{obsd}$ *vs.* $1/[HCl]_0$. This is consistent with the rate law

$$k_{obsd} = k_a[HCl]_0^3/(\rho_a + [HCl]_0) \qquad (1)$$

for which $k_a = (2.0 \pm 0.1) \times 10^{+5}\ F^{-2}\ sec^{-1}$ and $\rho_a = (6.6 \pm 0.2) \times 10^{-3}\ F$.

With zinc *N*-methyletioporphyrin(III) [Zn-*N*-MeP], Figure 2 shows the linear graph of $[HCl]_0/k_{obsd}$ *vs.*

---

[1] Abstracted from the M.S. Theses of B. Shears and B. Shah, Howard University, 1971.

[2] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," Wiley, New York, N. Y., 1967, Chapter 3.

[3] D. K. Cabiness and D. W. Margerum, *J. Amer. Chem. Soc.*, **92**, 2151 (1970).

[4] W. S. Caughey and A. H. Corwin, *ibid.*, 77, 1509 (1955).

[5] R. Snellgrove and R. A. Plane, *ibid.*, **90**, 3185 (1968).

[6] D. G. Davis and J. G. Montalvo, Jr., *Anal. Chem.*, **41**, 1195 (1969).

[7] P. Hambright and E. B. Fleischer, *Inorg. Chem.*, **9**, 1757 (1970).

[8] B. Shah and P. Hambright, *J. Inorg. Nucl. Chem.*, **32**, 3420 (1970).

[9] J. E. Falk, "Porphyrins and Metalloporphyrins," Elsevier, Amsterdam, 1964.

[10] B. Shears and P. Hambright, *Inorg. Nucl. Chem. Lett.*, **6**, 679 (1970).

[11] Such ion pairing is in accord with the interpretation of the kinetics of cis–trans isomerization of azobenzene in HCl–ethanol solutions: S. Ciccone and J. Halpern, *Can. J. Chem.*, **37**, 1903 (1959).