On the Mechanism of Quenching of Singlet Oxygen by Amines

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Abstract: The rate constants for the quenching of singlet oxygen by diazobicyclooctane (Dabco) and triethylamine were compared with the rate of quenching of the singlet states of some aromatic compounds. The experimental results from the quenching experiments indicate that there is a relationship between the mechanism of quenching of the singlet oxygen and the quenching of the fluorescence of the other compounds. A good correlation was obtained between the log of the rate constant for quenching and a measure of the electron affinity of the singlet states including singlet oxygen. Results in both methanol and 1-butanol for Dabco were obtained but almost no solvent effect was observed.

Recently Ogryzlo has shown that the rate of quenching of the first singlet state of oxygen by a series of amines is related to the ionization energy of the amines in the gas phase.[1] Although diazobicyclooctane (Dabco) was also shown to quench singlet oxygen, the absence of its ionization potential at the time prevented comparison with the other amines. Ogryzlo suggested the mechanism for quenching is *via* charge-transfer states of an intermediate complex. Others have also suggested that Dabco quenching of singlet oxygen proceeds through a charge-transfer species.[2,3]

We were interested in learning more about the quenching mechanism of Dabco and other amines in solution as it is a practical singlet oxygen quencher. It can be used in most cases as evidence for the presence of singlet oxygen which may be an intermediate in certain oxidation reactions.

There has been earlier evidence that the quenching mechanism of some singlet states could be *via* charge-transfer species.[4] More recently Nakajima has shown that the quenching of aromatic compounds is related to the electron affinity of electron-accepting quenchers and related to the ionization energies of electron-donating quenchers (amines).[5] In addition Evans has postulated charge-transfer intermediates in order to explain the quenching of acridine by a series of amines.[6]

We decided to see if there was any correlation between the mechanism for the quenching of singlet oxygen ($^1\Delta_g$, $^1O_2$) in solution and the quenching of other singlet states by amines.

Experimental Section

The reactivity ($\beta = k_d$ (decay of singlet oxygen)/k_q (quenching of singlet oxygen)) of the various amines in quenching singlet oxygen was determined by a variation of a competitive method recently developed by ourselves.[7] Rose Bengal was used as the dye sensitizer and no triplet quenching by the amines was found as determined by comparisons of reactions in air-saturated and oxygen-saturated solutions. In addition no singlet quenching of the dye sensitizer was observed at the concentration of the amine used as determined by checking the fluorescence of Rose Bengal. Complete details for the quenching of singlet oxygen by amines will be given in a later paper.

As the rate constant for the decay of singlet oxygen in methanol (9.0 (±0.5) × 10^4) and 1-butanol (5.2 (±0.8) × 10^4)[8] is known, the rate constant for the quenching of singlet oxygen by the amines can be calculated from experimental β values. This was done for diazobicyclooctane (Dabco) and triethylamine and the results are recorded in Table I.

Table I. Quenching Results of Singlet Oxygen by Amines

Amine	$(k_d/k_q) \times 10^2$	$k_q \times 10^{-6}$
Dabco (CH_3OH)	1.23	7.3
Dabco (1-butanol)	1.15	4.5
Triethylamine	0.76	12

The rate constants for the quenching of fluorescence for a series of aromatic compounds were obtained using a Perkin-Elmer, a Ferrand Mark I, and/or Aminco-Boman spectrophotofluorometer.[9] These rate constants were determined from typical Stern–Volmer quenching plots, the slope of which gave a value for k_q(amine) × τ_{air} (lifetime of excited singlet state in an air-saturated solution). The lifetimes of the single states, τ_{air}, were calculated from Stern–Volmer quenching plots for the quenching of fluorescence in nitrogen-, air-, and oxygen-saturated solutions. The slope of these plots yielded $k_q(O_2) \times \tau_{N_2}$. From an estimated rate constant for quenching (assumed to be diffusion controlled)[10] the value for τ_{air} was calculated. From this value, the rate constants for quenching of the single state for all of the compounds by the amines were obtained. The log of these rate constants are recorded in Table II.

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(1) E. A. Ogryzlo and C. W. Tang, *J. Amer. Chem. Soc.*, **92**, 5034 (1970).

(2) G. O. Schenck, *Ann. N. Y. Acad. Sci.*, **171**, 67 (1970).

(3) C. Ouannes and T. Wilson, *J. Amer. Chem. Soc.*, **90**, 6527 (1968).

(4) D. Kuman and S. Basu, *J. Chem. Phys.*, 33, 1191 (1960); G. H. Schenck and N. Radke, *Anal. Chem.*, 37, 449 (1965); D. Rehm and A. Weller, *Israel J. Chem.*, 8, 259 (1970); A. Weller, "Fast Reactions and Primary Processes in Chemical Kinetics," S. Claesson, Ed., Wiley-Interscience, New York, N. Y., 1967, pp 413 ff.

(5) A. Nakajima and H. Akamatu, *Bull. Chem. Soc. Jap.*, **41**, 1961 (1968); *ibid.*, **42**, 3030 (1969).

(6) T. R. Evans, *J. Amer. Chem. Soc.*, **93**, 2081 (1971).

(7) R. H. Young, K. Wehrly, and R. L. Martin, *J. Amer. Chem. Soc.*, **93**, 5774 (1971).

(8) New values for the rate constant of decay of singlet oxygen are given here which deviate slightly from those given in ref 7. These new values were recently determined through the use of a direct method by ourselves in collaboration with Dr. R. Keller of the National Bureau of Standards, experiments being carried out at the National Bureau of Standards. Complete details of these results will be presented in a later paper.

(9) In addition to carrying out all the quenching experiments ourselves, a number of them (with Dabco) were checked in a laboratory experiment carried out at Georgetown during a Food and Drug Administration Fluorescence and Phosphorescence training course.

(10) Although various rates of diffusion (k_q) for oxygen in solution for different compounds are known, there seemed to be only small variations and no definite trends for the different aromatic compounds. For this reason only one value was used for $k_q(O_2)$ for all of the aromatic compounds reported in this paper. Actual quenching constants (differing solvents) can be obtained from the following references. W. R. Ware, *J. Phys. Chem.*, **66**, 455 (1962); B. Stevens and B. E. Algar, *ibid.*, **72**, 2582 (1958); L. K. Patterson, G. Porter, and M. R. Topp, *Chem. Phys. Lett.*, **7**, 612 (1970). For methanol, a value of 2.9 × 10^{10} was used as an average, and for 1-butanol a value of 2.1 × 10^{10} was used, the difference being due to a viscosity difference and the 1-butanol value was estimated from the data given in Ware's paper.

Table II. Quenching of Excited Singlet States by Amines

Compound	Reduction[b] potential	Singlet energy (0–0), eV	Weller function, eV	$\tau_{air} \times 10^9$, sec	Log k_q Dabco (CH_3OH)	Log k_q Dabco (n-BuOH)	Log k_q Et_3N (CH_3OH)
Benzene	−2.30	4.54	2.24	7.7	9.77		
Naphthalene[a]	−2.54[c]	4.13	1.59	12.4	9.44	9.30	9.98
1-Chloronaphthalene[a]	−2.10[c]	4.04	1.94	1.38	9.95	10.23	10.81
2-Methoxynaphthalene[a]	−2.60[d]	3.83	1.23	6.46	8.89	9.15	9.43
2,6-Dimethoxynaphthalene[a]	−2.60[d]	3.57	0.97	6.25	8.29	8.58	8.80
2-Aminonaphthalene[a]		3.43		8.15	7.91	7.84	8.20
Anthracene	−1.92[c]	3.31	1.39	3.3	9.68	9.42	
Pyrene	−2.09[c]	3.50	1.41	16.2	9.11		
Phenanthrene	−2.44[c]	3.75	1.15	9.6	8.88		
1,2,3,4-Dibenzanthracene	−1.53[c]	3.43	1.90	11.8	9.3		
1,3-Diphenylisobenzofuran	−1.92[c]	2.91	0.99	4.07	8.50		
Tetracene	−1.58[c]	2.63	1.05	3.66	8.65		
Rubene	−1.45[c]	2.35	0.90	3.02	8.47	7.95	
Oxygen	−0.75[c]	0.96[e]	0.21	11,000[f]	6.86	6.66	7.08
Hammett ρ[a]					2.24 ± 0.11	2.4 ± 0.4	2.5

[a] Hammett ρ for the substituted naphthalenes. [b] From E. S. Pysh and N. C. Yang, *J. Amer. Chem. Soc.*, **85**, 2124 (1963). [c] From C. K. Mann and K. K. Barnes, "Electrochemical Reactions in Nonaqueous Systems," Marcel Dekker, New York, N. Y., 1970. [d] From A. Zweig, A. H. Maurer, and B. G. Roberts, *J. Org. Chem.*, **32**, 1322 (1967). [e] Singlet–triplet energy used. See C. S. Foote, *Accounts Chem. Res.*, **1**, 1041 (1968). [f] See ref 8.

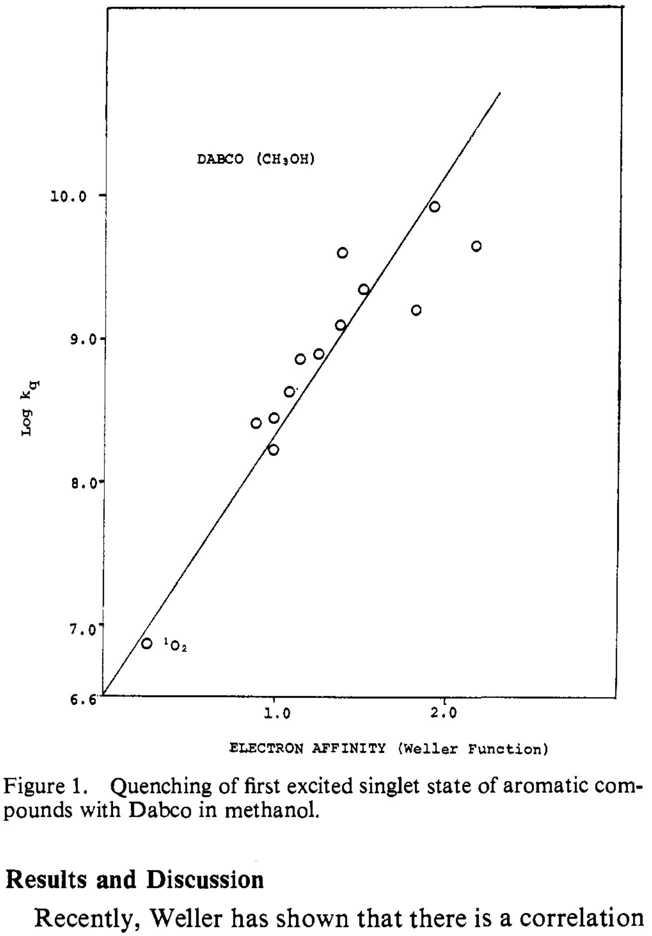

Figure 1. Quenching of first excited singlet state of aromatic compounds with Dabco in methanol.

Results and Discussion

Recently, Weller has shown that there is a correlation between the log of the rate of fluorescence quenching of aromatic hydrocarbons by quadricyclene and a function proportional to the electron affinity of the excited singlet state of the aromatic compound.[11] He suggested that the free energy (ΔF) of the reaction between a donor and an acceptor in an electron-transfer process was dependent upon the ionization potential of the donor (D), the singlet excitation energy of the acceptor (A) ($^1\Delta E_A$), the electron affinity of A, and the coulombic energy gained from the interaction of the ionic species.

$$\Delta F \approx -{}^1\Delta E_A + IP_D - EA_A - C$$

Although the electron affinities are not generally known accurately, they are related to reduction potentials ($\epsilon(A_s^-/A_s)$). Thus, Weller suggests that

$$\Delta F = \text{constant} - [{}^1\Delta E_A + \epsilon(A_s^-/A_s)]$$

when the donor is constant for a series of acceptors.

We have obtained the singlet energy (ΔE_{0-0}) for a series of compounds in methanol.[12] These values, along with reduction potentials obtained from the literature, are recorded in Table II.

A good correlation between the log of the rate constant for quenching (k_q) of the singlet states by diazobicyclooctane (Dabco) in methanol and a measure of the electron affinity (Weller function) was obtained.[13] This correlation is illustrated in Figure 1. It is worthwhile noting that the value obtained for the quenching of singlet oxygen correlates well with the resulting plot. This suggests strongly that there is a correlation between the mechanism for the quenching of the singlet excited states of some aromatic compounds and that for singlet oxygen. This would agree well with previous work which showed that quenching involves charge-transfer states in all cases.[1,4–6,14]

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(11) B. S. Solomon, C. Steel, and Z. Weller, *Chem. Commun.*, 927 (1969).

(12) E_{0-0} was obtained from absorption and/or uncorrected excitation spectra in conjunction with uncorrected fluorescence spectra. See D. M. Hercules, "Fluorescence and Phosphorescence Analysis," Interscience, New York, N. Y., 1966, p 126.

(13) We wish to thank one of the referees for pointing the applicability of Weller's results to our own work.

(14) We have recently obtained a good correlation between the quenching of singlet oxygen by a large number of amines with the ionization potential of the amines in methanol solvent. This work was reported at the 162nd National Meeting of the American Chemical Society, Washington, D. C., Sept 1971. R. H. Young, R. L. Martin, K. Wehrly, and D. Feriozi, *Amer. Chem. Soc., Div. Petrol. Chem. Prepr.*, **16**, A89 (1971). Details will be given in a later paper.

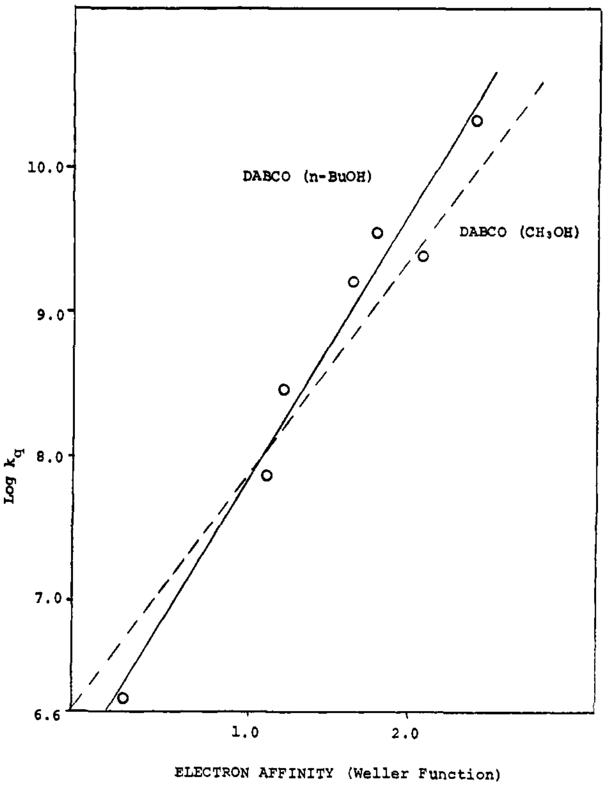

Figure 2. Quenching of the first excited singlet states of aromatic compounds with Dabco in 1-butanol as compared with methanol.

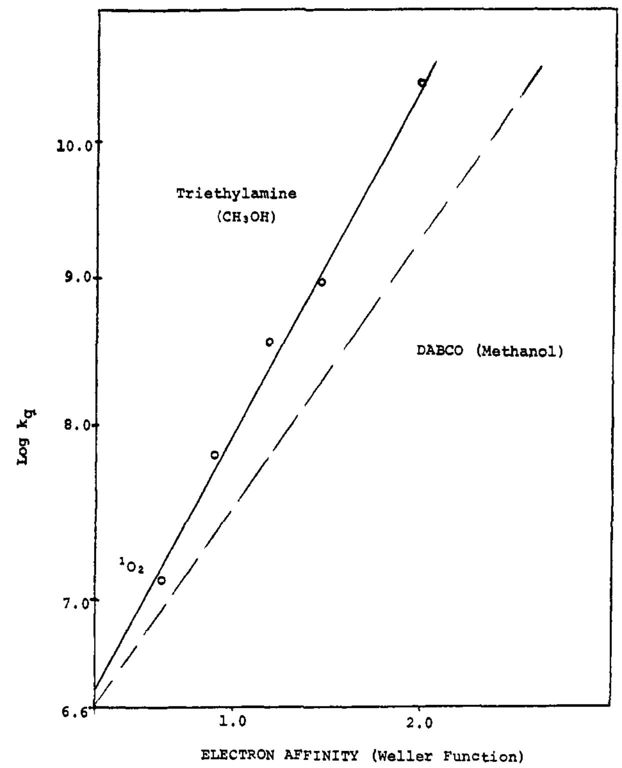

Figure 3. Quenching of the first excited singlet states of aromatic compounds with triethylamine and Dabco both carried out in methanol solution.

In addition, we have obtained similar results for the quenching by Dabco in 1-butanol solvent. The results, given in Table II and illustrated in Figure 2, show a very small solvent effect from the results obtained in methanol. This indicates that there may only be a partial charge-transfer intermediate formed in these quenching reactions.

Quenching by triethylamine was found to give similar results to those obtained for Dabco (Table II, Figure 3).

We have also obtained Hammett substituent ρ values for the quenching of a number of substituted naphthalenes for each of the amines. The ρ values were found to be 2.24 for Dabco and 2.5 for trimethylamine. These ρ values indicate only a moderate charge development in the limiting step of the quenching reaction in agreement with only a partial charge-transfer intermediate.

In all of these cases, the results for singlet oxygen quenching agree very well with the quenching results of the aromatic compounds by all of the amines used. This substantiates our claim that similar mechanisms are involved. A reasonable mechanism would involve a charge-transfer state contributing to the intermediate complex. The contribution of such a state would perturb the singlet state so as to cause increased singlet–triplet interaction and hence enhanced intersystem crossing. The extent of the charge-transfer contribution would be reflected in the quenching rate and be affected by changes both in the ionization potential of the donor (the amine) and the electron affinity of the acceptor.

The method applied to the quenching of the fluorescence of the aromatic compounds by the amines does suffer from some experimental limitations. Amines which are poor quenchers are difficult to use. This is not the case for the quenching of singlet oxygen by amines using the methods recently developed.[7,8] The correlation between singlet oxygen quenching and fluorescence quenching now means that information obtained by the quenching of singlet oxygen may be extended by inference to the quenching of other singlet states. We are continuing our efforts to further elucidate the mechanism of quenching of singlet oxygen.

Acknowledgments. We would like to acknowledge the Research Corporation for partial support of this work, and to thank Perkin-Elmer Corp., Ferrand Optical Co., and American Instrument Co. for the loan of instruments.[9]