processes in binary solvents are directly related to thermal diffusion processes.[24] Equation 3 may be sometimes more useful as it expresses the HMP for a system (a type III solvent)[15] directly in terms of the Soret coefficient and the activity factor, $\partial \ln a_1/\partial \ln c_1$, a function which indicates mixed solvent nonideality as does the heat of mixing, ΔH^M.

References and Notes

(1) Presented in part at The First Chemical Congress of the North American Continent; Abstract, Physical and Surface Chemistry No. 59, Nov 30–Dec 5, 1975, Mexico City. This paper represents the results of one phase of research carried out at the Jet Propulsion Laboratory, California Institute of Technology, under Contract No. NAS 7-100, sponsored by NASA.
(2) P. A. Carapellucci, *J. Am. Chem. Soc.*, **97**, 1278 (1975).
(3) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions", Wiley, New York, N.Y., 1963.
(4) F. Barat, L. Gilles, B. Hickel, and B. Lesigne, *J. Phys. Chem.*, **77**, 1711 (1973).
(5) F. Franks, Ed., "Structure and Transport Processes in Mixed Aqueous Solvents", Heineman Educational Books, London, 1967.
(6) O. I. Micic and B. Cercek, *J. Phys. Chem.*, **78**, 285 (1974).
(7) (a) L. Menninga and J. B. F. N. Engberts, *J. Phys. Chem.*, **77**, 1271 (1973); (b) J. F. G. Engbersen and J. B. F. N. Engberts, *J. Am. Chem. Soc.*, **96**, 1231 (1974).
(8) P. Warrick, Jr., J. J. Auborn, and E. M. Eyring, *J. Phys. Chem.*, **76**, 1184 (1972).
(9) K. Nakanishi and T. Ozasa, *J. Phys. Chem.*, **74**, 2956 (1970).
(10) R. Lumry and S. Rajender, *Biopolymers*, **9**, 1125 (1970).
(11) C. A. G. Brooks, K. M. C. Davis, and M. J. Blandamer, *J. Solution Chem.*, **3**, 247 (1974).
(12) M. J. Blandamer and J. Burgess, *Chem. Soc. Rev.*, **4**, 55 (1975).
(13) E. E. Tucker, T. R. Clem, J. I. Seeman, and E. D. Becker, *J. Phys. Chem.*, **79**, 1005 (1975).
(14) S. H. Koenig, K. Hallenga, and M. Shporer, *Proc. Natl. Acad. Sci. U.S.A.*, **72**, 2667 (1975).
(15) P. A. Carapellucci, *J. Phys. Chem.*, **79**, 2768 (1975).
(16) P. A. Carapellucci, submitted for publication.
(17) H. J. V. Tyrrell, "Diffusion and Heat Flow in Liquids", Butterworths, London, 1961, p 195.
(18) Y. Nishijima and G. Oster, *Bull. Chem. Soc. Jpn.*, **33**, 1649 (1960).
(19) B. Cercek, private communication.
(20) J. G. Aston and J. J. Fritz, "Thermodynamics and Statistical Thermodynamics", Wiley, New York, N.Y., 1959, p 156.
(21) Reference 17, p 44.
(22) Reference 17, p 256, 257.
(23) J. Van Dranen and F. Bergsma, *Physica* (*Utrecht*), **13**, 558 (1947).
(24) J. C. R. Turner, *Chem. Eng. Sci.*, **30**, 151 (1975). Here it is also stressed that a greater understanding of diffusion phenomena is to be had if the gradient of chemical potential, rather than concentration, is regarded as the "driving force" for diffusion.
(25) "International Critical Tables" Vol. 5, McGraw-Hill, New York, N.Y., 1929, p 157.
(26) C. S. Miner and N. N. Dalton, Ed., "Glycerol", Reinhold, New York, N.Y., 1953.

P. A. Carapellucci
Jet Propulsion Laboratory
California Institute of Technology
Pasadena, California 91103

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Nitroso Compounds and Azo Dioxides as Quenchers of Singlet Oxygen ($^1\Delta_g$) and Sensitizer Triplet States

Sir:

We recently reported that 3,3,4,4-tetramethyl-1,2-diazetine-1,2-dioxide (**1**) was a useful triplet quencher.[1] It absorbs at short wavelengths, efficiently quenches triplets of energies ⩾42 kcal/mol, and does not quench aromatic singlet states. We now describe some unexpected quenching properties of other azo dioxides and nitroso compounds.

Quenching of sensitizer triplets was monitored by the effect of quenchers on the rate of sensitized formation of O_2 ($^1\Delta_g$) in 95% ethanol. The reaction was followed by the disappearance of ~9 × 10^{-5} M 1,3-diphenylisobenzofuran (DPIF). Linear Stern-Volmer plots were obtained from which quenching rate constants were calculated.[2] The sensitizer triplet lifetimes required for these calculations were estimated from the product of the oxygen concentration in air-saturated ethanol (1.57 × 10^{-3} M)[3] and the rate constants for oxygen quenching of aromatic triplet states. The latter (1-3 × 10^9 M^{-1} s^{-1}) were either known or estimated from the triplet energies of the sensitizers.[4]

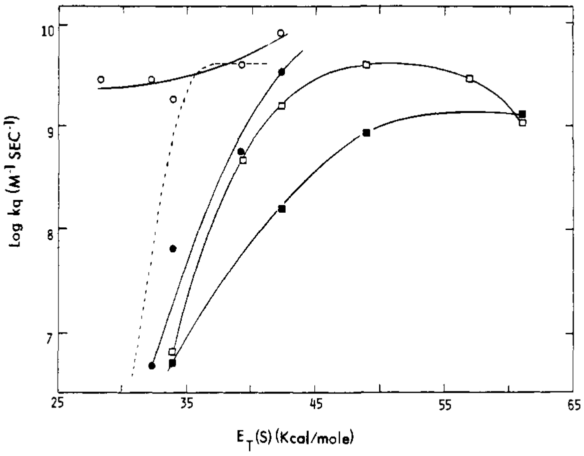
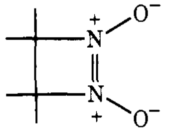


Figure 1. Rate constants for quenching sensitizer triplets by azo dioxides in ethanol: ■, **1**; □, **2**; ●, **4**; ○, apparent k_q for **5** ignoring possible quenching of O_2 ($^1\Delta_g$). Dashed line is calculated for a classical quencher ($E_T(Q)$ = 34 kcal/mol). Sensitizers, ascending order of $E_T(S)$, are chlorophyll a and b, methylene blue, rose bengal, anthracene, pyrene, chrysene, and naphthalene.

Representative quenching rate constants are compared in Table I with the longest wavelength absorption maxima of azo dioxides **1**-**6**.[5] The absorption maxima of the unchlorinated azo dioxides **1**-**4** decrease in energy as the quenching efficiencies increase. The accompanying structural changes suggest that the orbitals of the increasingly strained transannular 5,6-σ bonds in the series **1** (no bond), **2**, **3**, and **4**, may mix with the π*-azo dioxide orbitals and lower the excited state energies.



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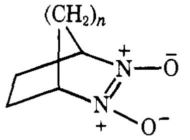

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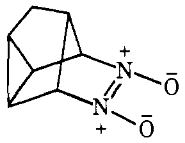
3, n = 1



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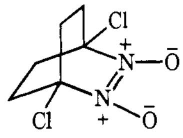

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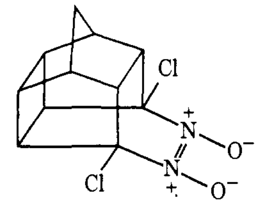

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The introduction of α-chlorine atoms in the azo dioxides should contribute to Coulombic destabilization of their ground states relative to their less polar excited states. Thus the absorption maxima of **5** and **6** are red-shifted relative to their unchlorinated analogues **2** or **3** and **4**, respectively. Although the greater quenching efficiencies of **5** and **6** suggest that Coulombic destabilization is also relieved in their lowest triplet states, significantly, the parallel relationship between absorption maxima and quenching rates found in the unchlorinated compounds was not observed.

The effect of sensitizer triplet energy on the azo dioxide quenching rate constants was compared with that expected in a classical energy transfer model (eq 1)

$$S^* + Q \underset{k_{-\mathrm{diff}}}{\overset{k_{\mathrm{diff}}}{\rightleftarrows}} |S^* + Q| \overset{K}{\rightleftarrows} |S + Q^*| \xrightarrow{k_{-\mathrm{diff}}} S + Q^* \qquad (1)$$

Table I. Absorption Maxima and Rate Constants for Quenching Sensitizer Triplets by Azo Dioxides in Ethanol

Quencher	λ_{max}^{EtOH} (nm)	$10^{-8}k_q$ (M^{-1} s^{-1}) Benzanthrone[a]	Anthracene[b]	Methylene blue[c]
1	255	14[d]	1.2,[d] 1.6[e]	0.052[e]
2	264		4.9[d]	
3	265		11,[d] 17[e]	0.066[e]
4	271		13[d]	0.12[e]
5	270		86[e,f]	19[e,f]
6	274		34[e]	0.64[e]

[a] $E_T(S) = 47$ kcal/mol. [b] $E_T(S) = 42.4$ kcal/mol. [c] $E_T(S) = 34$ kcal/mol.[12] [d] Determined by the previously reported method of quenching sensitized *trans*-stilbene isomerization in benzene; ref 1. [e] Determined by quenching sensitized formation of O_2 ($^1\Delta_g$). [f] Apparent k_q assuming no quenching of O_2 ($^1\Delta_g$), ref 2.

Table II. Quenching of $O_2(^1\Delta_g)$ Generated from $(C_6H_5O)_3PO_3$

Quencher	$10^{-9}k_q$ (M^{-1} s^{-1})	$10^{-4}k_d$ (s^{-1})	Solvent
7 (**5**)	12,[a] 0.080[b]	2.1	11:5 CH_2Cl_2/CH_3OH
8	5.3	1.9	11:5 CH_2Cl_2/CH_3OH
$(CH_3)_3CNO$	9.3	1.1	15:1 CH_2Cl_2/CH_3OH
β-Carotene[c]	20	4.2	C_6H_6
6	$\leqslant 2 \times 10^{-3}$		11:5 CH_2Cl_2/CH_3OH

[a] Calculated assuming **7** is the quencher. [b] Calculated assuming **5** is the quencher. [c] Reference 11a.

where energy transfer within the encounter complex is assumed to be rapid relative to diffusion. The triplet energies of the sensitizer $E_T(S)$ and quencher $E_T(Q)$ are then related by[6]

$$E_T(S) = E_T(Q) + RT \ln [k_q/(k_{diff} - k_q)] \qquad (2)$$

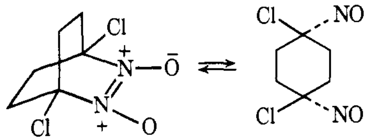
The thus calculated falloff in the quenching rate constant (k_q) with decreasing $E_T(S)$ exceeds that observed with every azodioxide (Figure 1). These results suggest a nonvertical energy transfer model in which the quencher triplet undergoes slow (relative to k_{-diff}) electronic excitation coupled with geometrical relaxation within the collision complex. Relaxation of azo dioxide triplets to low energy twisted planar or trigonal nitroxide biradicals appears probable.[1] It is noteworthy that azo dioxide **1** with its eclipsed geminal dimethyl groups has the greatest torsional strain at the N=N bond and shows the greatest deviation from classical behavior.

The exceptionally efficient quenching by azo dioxide **5** raises doubts about the assumption that O_2 ($^1\Delta_g$) is not quenched by this compound.[2] Indeed **5** was found to strongly inhibit the reaction of rubrene with O_2 ($^1\Delta_g$) (generated by adding 1 ml of 1×10^{-2} M $(C_6H_5O)_3PO_3$ in CH_2Cl_2 at −78° to 15 ml of 2.4×10^{-3} M rubrene in 2:1 CH_2Cl_2-CH_3OH at 25°).[7] By contrast, the other azo dioxides had little effect on this reaction. It was found from experiments in the absence of rubrene that, of the O_2 ($^1\Delta_g$) that was quenched, less than 0.36% led to destruction of **5**.

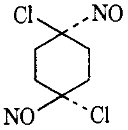
A linear quenching plot was obtained using the integrated rate expression[8]

$$k_r(P - R_0 + R)/\ln (R_0/R) = k_q[Q] + k_d \qquad (3)$$

where R is the final rubrene concentration, P is the initial ozonide concentration, and k_r (4×10^7 s^{-1})[9] and k_d are, respectively, the rate constants for reaction of O_2 ($^1\Delta_g$) with rubrene and for its decay in the absence of acceptors. Provided the quenching is actually due to **5**, the slope, k_q, was 8.0×10^7 M^{-1} s^{-1}. However, **5** displayed a weak absorption band at 645 nm (ε 0.32) in this solvent mixture, and an equilibrium with the bisnitroso isomer **7** was suggested by the temperature and solvent dependence of this peak. Based on the spectrum of the trans isomer **8**[5] (λ_{max} 645 nm, ε 46) about 0.7% of **7** is estimated to be in equilibrium with **5**.



5 **7**



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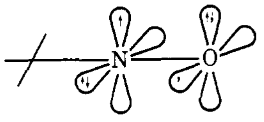

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Quenching studies with both **8** and 2-methyl-2-nitrosopropane demonstrated that nitroso compounds are efficient O_2 ($^1\Delta_g$) quenchers (Table II). Quenching by their azo dioxide dimers was excluded by the Beer's law dependence of these compounds at the quenching concentrations. At least part of the O_2 ($^1\Delta_g$) quenching by **5** is therefore due to quenching by **7**. Indeed the apparent quenching of low energy sensitizer triplets by **5** may be predominantly quenching of O_2 ($^1\Delta_g$) by **7**. Using this assumption k_q for this process was calculated as 9.2×10^9 M^{-1} s^{-1} with chlorophyll a (E_T = 28 kcal/mol) as sensitizer.[10] This compares favorable with 12×10^9 M^{-1} s^{-1} calculated when O_2 ($^1\Delta_g$) was formed chemically (Table II).

A comparison of the O_2 ($^1\Delta_g$) quenching constants with that of carotene, an efficient O_2 ($^1\Delta_g$) energy acceptor,[11] suggests that the nitroso compounds probably quench by an energy transfer mechanism. The exceptionally low effective triplet energy of these compounds (<23 kcal/mol) may result from coupling of energy transfer with relaxation of the bent (vertical) nitroso triplets to a low energy linear configuration **9**, isoelectronic with ground state oxygen.

References and Notes

(1) E. F. Ullman and P. Singh, *J. Am. Chem. Soc.*, **94**, 5077 (1972).
(2) Quenching of O_2 ($^1\Delta_g$) was shown to be negligible for all quenchers except **5** and was ignored when calculating sensitizer triplet quenching rate constants.
(3) C. B. Kretschmer, J. Nowakowska, and R. Wiebe, *Ind. Eng. Chem.*, **38**, 506 (1946).
(4) R. Benson and N. E. Geacintov, *J. Chem. Phys.*, **59**, 4428 (1973), and references cited therein.
(5) (a) P. Singh, *J. Org. Chem.*, **40**, 1405 (1975); (b) J. P. Snyder, M. L. Heyman, and E. N. Suclu, *Ibid.*, **40**, 1395 (1975); (c) O. Piloty and H. Steinbock, *Chem. Ber.*, **35**, 3101 (1902).
(6) An incomplete form of this equation was used by W. G. Herkstroeter and G. S. Hammond, *J. Am. Chem. Soc.*, **88**, 4769 (1966), to rationalize the rates of quenching by *trans*-stilbene. Equation 2 provides a better fit to their data.
(7) The reaction of rubrene in bromobenzene with O_2 ($^1\Delta_g$) generated by microwave discharge is also strongly inhibited by **5**, private communication from J. P. Guillory.
(8) Equation originally reported incorrectly, D. J. Carlson, G. D. Mendenhall, T. Suprunchuk, and D. M. Wiles, *J. Am. Chem. Soc.*, **94**, 8960 (1972).
(9) B. Stevens and S. R. Perez, *Mol. Photochem.*, **6**, 1 (1974).
(10) Calculated assuming $\tau(^1O_2) = (k_d + k_r[\mathrm{DPIF}])^{-1}$ where $k_d = 1.2 \times 10^5$ s^{-1} and $k_r = 8 \times 10^8$ M^{-1} s^{-1}.[11]
(11) (a) P. B. Merkel and D. R. Kearns, *J. Am. Chem. Soc.*, **94**, 7244 (1972); (b) C. S. Foote, R. W. Denny, L. Weaver, Y. Chang, and J. Peters, *Ann. N.Y. Acad. Sci.*, **171**, 139 (1970).
(12) Calculated value, R. W. Chambers and D. R. Kearns, *Photochem. Photobiol.*, **10**, 215 (1969).

Prithipal Singh, Edwin F. Ullman*
Contribution No. 62, Syva Research Institute
Palo Alto, California 94304

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