

was epoxidized with *m*-chloroperbenzoic acid as before, to produce the epoxide VI in about 58% overall yield from benzaldehyde. Treatment of the epoxide with methanolic sulfuric acid (*vide supra*) produced cinnamaldehyde in about 70% yield.

Acknowledgment. We wish to acknowledge support of this investigation by the Petroleum Research Fund of the American Chemical Society.

Gilbert Stork,* Ernest Colvin

Department of Chemistry, Columbia University
New York, New York 10027

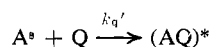
Received January 13, 1971

Singlet Quenching Mechanisms

Sir:

Charge-transfer interactions have been shown to be the predominant quenching mechanism for the singlet states of aromatic compounds with amines,¹⁻⁴ carbon tetrachloride,² and quadricyclene.⁵ The mechanism of fluorescence quenching of the azo compounds 2,3-diazabicyclo[2.2.2]oct-2-ene (DBO)^{6,7} and 2,3-diazabicyclo[2.2.1]hept-2-ene (DBH)^{6,7} and aromatic hydrocarbons⁸ has been described as exciplex-induced radiationless decay.^{7,8} We have found that minor modifications of the normal Stern-Volmer equation allow testing of the various mechanisms for singlet quenching. We would like to present evidence that the major quenching interaction for fluorescence quenching of the azo compounds and aromatic hydrocarbons is also charge transfer.

The usual scheme for fluorescence quenching reactions is written



in which k_q' is the apparent rate of quenching of the excited molecule A^s by the substrate Q . This mechanism leads to the normal Stern-Volmer equation

$$\phi_0/\phi = 1 + k_q'\tau_s[Q] \quad (1)$$

where ϕ_0 and ϕ are the quantum yields for fluorescence in the absence and presence of the quencher and τ_s is the lifetime of the singlet state of A . However, a slightly different scheme for diffusion-controlled reactions has been presented by North.⁹ It is, as written for fluo-

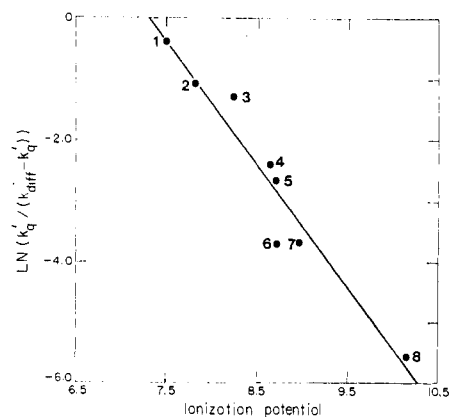
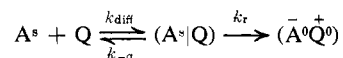


Figure 1. Fluorescence quenching of acridine: (1) triethylamine (IP = 7.50 eV^{11a}), (2) trimethylamine (IP = 7.82 eV^{11a}), (3) dimethylamine (IP = 8.24 eV),^{11a} (4) benzylamine (IP = 8.64 eV^{11a}), (5) *n*-butylamine (IP = 8.71 eV^{11a}), (6) isopropylamine (IP = 8.72 eV^{11a}), (7) methylamine (IP = 8.97 eV^{11a}), (8) ammonia (IP = 10.19 eV^{11a}). The least-squares procedure gives the empirical equation, $\ln [k_q' / (k_{diff} - k_q')] = 14.9 - 2.03IP$, with $k_{diff}(\text{water}) = 7.38 \times 10^9 \text{ l. mol}^{-1} \text{ sec}^{-1}$, with a correlation coefficient of 0.966.

rescence quenching by electron transfer



where k_{diff} is the rate constant for the diffusion of A^s and Q to form the proximity pair $(A^s|Q)$, k_{-q} is the rate constant for diffusion of the proximity pair out of the solvent cavity, and k_r is the rate constant for the quenching reaction. This leads to the Stern-Volmer equation

$$\phi_0/\phi = 1 + [k_{diff}k_r / (k_{-q} + k_r)]\tau_s[Q] \quad (2)$$

It can be seen from eq 1 and 2 that $k_q' = k_{diff}k_r / (k_{-q} + k_r)$. Since k_q' can be measured and k_{diff} calculated, the ratio k_r/k_{-q} , which is given by

$$k_r/k_{-q} = k_q' / (k_{diff} - k_q')$$

can be determined. If we assume that the rate constant for diffusion out of the solvent cavity, k_{-q} , is to the first approximation determined by only the properties of the solvent, then

$$\ln (k_r/k_{-q}) = \left(\ln \frac{k_q'}{k_{diff} - k_q'} \right) \propto \Delta G^\ddagger$$

where ΔG^\ddagger is the free energy of activation for the electron-transfer reaction. For a constant fluorescer and a series of quenchers,^{1,3,4,5,10} $\Delta G^\ddagger \propto IP + C$, where IP is the ionization potential of the donor and C is comprised of a series of terms related to the solvation of a pair of ions.

In Figure 1 the function $\ln [k_q' / (k_{diff} - k_q')]$ is plotted vs. ionization potential for the amine quenching of acridine,⁴ a known example of charge-transfer quenching. (IP values given in the figure captions are taken from ref 11.) The linear behavior indicates

(10) For a recent review, see D. Rehm and A. Weller, *Israel J. Chem.*, **8**, 259 (1970).

(11) (a) J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Herron, K. Droxl, and F. H. Field, "Ionization Potentials, Appearance Potentials, and Heats of Formation of Gaseous Positive Ions," NSRDS-NBS, No. 26, National Bureau of Standards, Washington, D. C., 1969; (b) D. A. Demeo and M. A. El-Sayed, *J. Chem. Phys.*, **52**, 2622 (1970); (c) J. L. Franklin and A. Mogenis, *J. Phys. Chem.*, **71**, 2820 (1967); (d) N. Bodor, M. J. S. Dewar, and S. D. Worley, *J. Amer. Chem. Soc.*,

(1) H. Knibbe, D. Rehn, and A. Weller, *Ber. Bunsenges. Phys. Chem.*, **72**, 257 (1968).

(2) S. Ander, H. Blume, G. Heinrich, and D. Schulte-Frohlinde, *Chem. Commun.*, 745 (1968); D. Schulte-Frohlinde and R. Pfefferkorn, *Ber. Bunsenges. Phys. Chem.*, **72**, 330 (1968).

(3) A. Weller, *Progr. React. Kinet.*, **1**, 192 (1961).

(4) A. Weller in "Fast Reactions and Primary Processes in Chemical Kinetics, Proceedings of the Fifth Nobel Symposium," S. Claesson, Ed., Interscience, New York, N. Y., 1967, p 413.

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

(6) B. S. Solomon, T. F. Thomas, and C. Steel, *J. Amer. Chem. Soc.*, **90**, 2249 (1968).

(7) A. C. Day and T. R. Wright, *Tetrahedron Lett.*, 1067 (1969).

(8) (a) L. M. Stephenson and G. S. Hammond, *Pure Appl. Chem.*, **16**, 125 (1968); (b) L. M. Stephenson, D. G. Whitten, and G. S. Hammond in "The Chemistry of Ionization and Excitation," G. R. A. Johnson and G. Scholes, Ed., Taylor and Francis, London, 1967, p 35; (c) L. M. Stephenson, D. G. Whitten, G. F. Vesley, and G. S. Hammond, *J. Amer. Chem. Soc.*, **88**, 3665, 3893 (1966); (d) S. Murov and G. S. Hammond, *J. Phys. Chem.*, **72**, 3797 (1968).

(9) A. M. North, *Quart. Rev., Chem. Soc.*, **20**, 421 (1966).

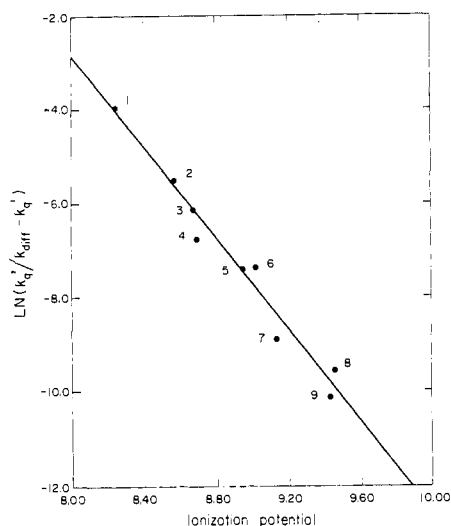


Figure 2. Fluorescence quenching of 2,3-diazabicyclo[2.2.2]oct-2-ene: (1) cyclohexadiene (IP = 8.25 eV,^{11b} 8.40 eV^{11a}), (2) cyclopentadiene (IP = 8.57 eV^{11a}), (3) 1,3-pentadiene (IP = 8.68 eV^{11a}), (4) quadricyclene (IP = 8.70 eV^{11a}), (5) cyclohexene (IP = 8.945 eV^{11a,b}), (6) cyclopentene (IP = 9.02 eV,^{11b} 9.01 eV^{11a}), (7) 2-butene (IP = 9.13 eV^{11a}), (8) 1-hexene (IP = 9.45 eV^{11a}), (9) 1-octene (IP = 9.43 eV^{11b}). The least-squares procedure gives the empirical equation $\ln [k_q'/(k_{diff} - k_q')] = 36.4 - 4.91IP$, with $k_{diff}(\text{isooctane}) = 13.9 \times 10^9 \text{ l. mol}^{-1} \text{ sec}^{-1}$, with a correlation coefficient of 0.9840.

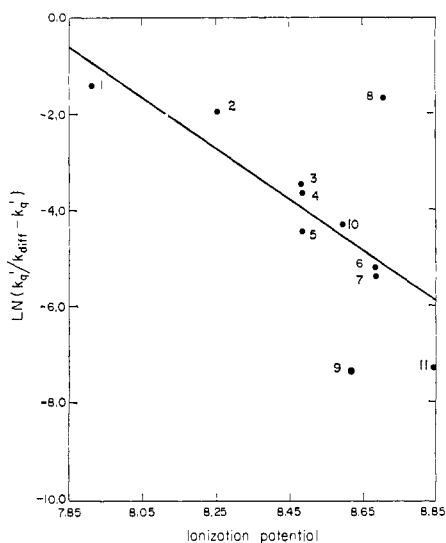


Figure 3. Fluorescence quenching of naphthalene: (1) 2,5-dimethyl-2,4-hexadiene (IP = 7.91 eV^{11c}), (2) 1,3-cyclohexadiene (IP = 8.25,^{11b} 8.40 eV^{11a}), (3) *trans,trans*-2,4-hexadiene (IP = 8.48 eV^{11c}), (4) *cis,trans*-2,4-hexadiene (IP = 8.48 eV^{11c}), (5) *cis,cis*-2,4-hexadiene (IP = 8.48 eV^{11c}), (6) *trans*-1,3-pentadiene (IP = 8.68 eV^{11a}), (7) *cis*-1,3-pentadiene (IP = 8.68 eV^{11a}), (8) quadricyclene (IP = 8.70 eV^{11a}), (9) norbornadiene (IP = 8.60 eV) [this is an average of reported values 8.45,^{11b} 8.62,^{11d} 8.69,^{11e} and 8.60 and 8.67 eV^{11a}], (10) cyclopentadiene (IP = 8.57 eV^{11a}), (11) isoprene (IP = 8.845 eV^{11a}). The least-squares procedure gives the empirical equation $\ln [k_q'/(k_{diff} - k_q')] = 47.93 - 6.13IP$, excluding the points for quadricyclene and norbornadiene; $k_{diff}(n\text{-hexane}) = 2.01 \times 10^{10} \text{ l. mol}^{-1} \text{ sec}^{-1}$. The correlation coefficient, excluding quadricyclene and norbornadiene, is 0.939.

that, to the first approximation, the assumptions of constant solvation terms and constant k_{-q} are valid.

92, 19 (1970); (f) P. Bishof, J. A. Hashmall, E. Heilbronner, and V. Hornung, *Helv. Chim. Acta*, **52**, 1745 (1969).

The data from the publications of Solomon, Thomas, and Steel⁶ and Solomon, Steel, and Weller⁵ on DBO fluorescence quenching are shown in Figure 2. Of the quenchers examined (the limiting factor is the availability of the ionization potentials), there is no clear evidence of any effects other than charge transfer operating on the quenching of DBO singlet state.

A linear relationship between $\ln [k_q'/(k_{diff} - k_q')]$ and ionization potential is also observed for the quenching of naphthalene fluorescence with several hydrocarbons, Figure 3. The linear relationship does not hold for some of the quenchers, notably quadricyclene and norbornadiene.¹² This anomalous behavior of quadricyclene is interesting because Solomon, Steel, and Weller⁵ have concluded that the quadricyclene interaction with aromatic hydrocarbon singlet states is charge transfer in character. We believe that all of the hydrocarbons are quenching by a charge-transfer mechanism, but other effects also seem to be operating.

Thus we conclude that the above kinetic method is useful for examination of photochemical reactions and that in spite of its simplifications it can be used to detect gross reaction mechanisms. Furthermore, we conclude that the major mechanism for fluorescence quenching of naphthalene and the bicyclic azo compounds is charge-transfer interaction.

(12) Neither 2,3-dimethyl-2-butene ($\Delta IP \cong 8.40 \text{ eV}$) nor 1,3-cyclooctadiene quenches the fluorescence of naphthalene¹³ and so these also fall into the class of compounds which do not obey the linear relationship. Quadricyclene shows "normal" behavior in the quenching of DBO fluorescence.

(13) L. M. Stephenson, Ph.D. Thesis, California Institute of Technology, 1968, p 17.

Ted R. Evans

Research Laboratories, Eastman Kodak Company
Rochester, New York 14650

Received January 6, 1971

Rhodium Complexes with the Molecular Unit P₄ as a Ligand

Sir:

Complexes in which a stable elementary molecule is bonded to a transition metal are quite rare. Only two types have been described in the literature: O₂ complexes, for example IrCl(O₂)CO[(P(C₆H₅)₃)₂]₂,¹ and N₂ complexes, for example IrCl(N₂)[P(C₆H₅)₃]₂.² An interesting candidate for use as an elementary molecular ligand is the tetrahedral P₄ molecule. P₄ has relatively strong internal π bonds and does not show perfect pairing in the ground state.³ It is therefore an unsaturated molecule, and the most favorable conditions for bonding to a transition metal atom should be those under which the metal can both accept and back-donate charge density to the P₄ molecule. We therefore examined the reactions of P₄ with low-valent, coordinatively unsaturated group VIII metal complexes. In the present communication we report the characterization of several monomeric, diamagnetic complexes which appear to contain an intact P₄ molecule bonded to a rhodium atom.

(1) L. Vaska, *Science*, **140**, 809 (1963).

(2) J. P. Collman, M. Kubota, F. D. Vastine, J. Y. Sun, and J. W. Kang, *J. Amer. Chem. Soc.*, **90**, 5430 (1968).

(3) R. R. Hart, M. B. Robin, and N. A. Kuebler, *J. Chem. Phys.*, **42**, 3631 (1965).