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TRIPLET ENERGIES, REDUCTION POTENTIALS AND IONIZATION POTENTIALS IN CARBONYL-DONOR PARTIAL CHARGE-TRANSFER INTERACTIONS.

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We have recently proposed that eq. 1 describes interactions of carbonyl excited states with electron donors (1):

$$\log k_{ir} \sim \Delta G_c \approx -\Delta E_{o,o} + I.P._D - E(A^-/A) + C \qquad (1)$$

k_{ir} is the rate constant of a quenching interaction between an electron donor D, and an acceptor A, $\Delta E_{o,o}$ is the energy of the excited species, $I.P._D$ is the ionization potential of the donor, $E(A^-/A)$ is the reduction potential of the acceptor. For reaction of an acceptor with a series of donors $\log k_{ir} \sim I.P._D + C'$, and this was demonstrated for benzophenone triplet and a variety of donors (1). We now find that for fluorenone a linear relation between log k_{ir} and $I.P._D$ is found which differs from that of benzophenone in certain respects. Also, for a series of acceptors with a constant donor $\log k_{ir} \sim [-\Delta E_{o,o} - E(A^-/A)] + C''$, and we wish to report such a correlation.

Values of k_{ir} for fluorenone triplet with a series of donors were determined, as described previously (2,3). Values of k_{ir} are normalized to a diffusion rate constant of 6.3×10^9 M^{-1} sec^{-1} in benzene and to viscosity adjusted values of 4.0×10^9 and 1.1×10^{10} M^{-1} sec^{-1} in cyclohexane and acetonitrile respectively. Values of $-E(A^-/A)$, Table 2, are normalized against saturated calomel electrode, and where possible, are from work in basic solution, in which the ketone radical ion is formed (4). Such data were not available for biacetyl and p-aminobenzophenone. The value for biacetyl was estimated (1,5) by use of aromatic donors of known, graded oxidation potentials to quench its fluorescence; that for p-aminobenzophenone was obtained by using it as a quencher for a series of excited aromatic donors of graded oxidation potentials.

Some results for quenching of fluorenone triplet are summarized in Table 1.

The data are correlated by a single linear inverse plot of log k_{ir} vs. I.P. for both aromatic and aliphatic donors, Fig. 1, unlike the two line correlation for benzophenone (1). The slope, -0.135 mole/kcal, is higher than those for benzophenone, indicating a greater sensi-

TABLE 1

Quenching of fluorenone triplet by electron donors

Donor	k_{ir} $M^{-1}sec^{-1}$	I.P. e.v.[f]
1. N,N,N′, N′-Tetramethyl-p-phenylenediamine, TMPD.[a]	1.6×10^{10} [c]	6.54[g]
2. N,N-Dimethylaniline, DMA.[a]	6.0×10^{8} [c]	7.14[f]
3. 1,4-Diaza(2,2,2)bicyclooctane, DABCO.[a]	5.6×10^{8} [d]	7.2[h]
4. p-Chlorodimethylaniline.[a]	2.8×10^{8} [c]	7.39[f]
5. Triethylamine.[b]	3.2×10^{7} [e]	7.50[f]
6. 1-Aza(2,2,2)bicyclooctane, ABCO.[b]	$\sim 5 \times 10^{5}$	7.7[h]
7. N-Methyl-2-butylamine.[b]	2.9×10^{7}	8.02[j]
8. di-n-Butylsulfide.[b]	$\sim 5 \times 10^{4}$	8.30[k]
9. 2-Butylamine.[b]	$\sim 5 \times 10^{3}$	8.70[f]

[a] Value of k_{ir} determined in benzene. [b] Value of k_{ir} determined in cyclohexane. [c] S. G. Cohen and G. Parsons, J. Amer. Chem. Soc., 92, 7603 (1970). [d] Ref. 3. [e] Ref. 2. [f] From "Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions," J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Hesson, K. Draxl and F. H. Field, National Bureau of Standards. [g] Estimated from I.P. of DMA and difference in oxidation potentials of TMPD and DMA, Ref. 1 and A. Zweig, W. G. Hodgson and W. H. Jura, J. Amer. Chem. Soc., 86, 4130 (1964). [h] A. M. Halpern, J. L. Roebber and K. Weiss, J. Chem. Phys., 49, 1348 (1968). [j] Value for diethylamine. [k] Value for di-n-propylsulfide.

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tivity of fluorenone triplet to $I.P._D$. The value of k_{ir} for reaction of fluorenone triplet with triethylamine is 25 times greater in acetonitrile than in cyclohexane. This is nearly half the value, 54, observed for this solvent effect in the quenching of perylene excited singlet by N,N-dimethylaniline (6), which proceeds by full electron transfer, and relatively larger than those observed for benzophenone (1). The single line correlation and the large solvent effect indicate that fluorenone, with its low triplet energy and favorable reduction potential, undergoes quenching largely by an electronic interaction. The quenching of triplet benzophenone appears to involve other contributions, such as partial transfer of α-hydrogen.

Values of log k_{ir} for quenching of a series of acceptors with a constant donor, triethylamine, are given in Table 2, and the correlation between log k_{ir} and $[-{}^3\Delta E_{o,o} - E(A^-/A)]$ is given in Fig. 2.

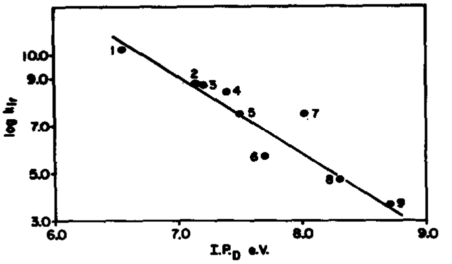

FIG. 1. Log k_{ir} for quenching of fluorenone triplet vs ionization potential of donor. Numbers refer to compounds of Table 1.

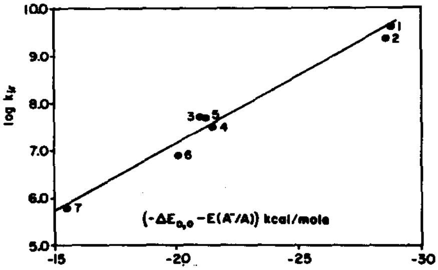

FIG. 2. Log k_{ir} for quenching of acceptor triplets by triethylamine vs triplet energy minus reduction potential. Numbers refer to compounds of Table 2.

TABLE 2

Quenching of triplet acceptors by triethylamine

Acceptor	${}^3\Delta E_{o,o}$ [a] kcal/mole	$-E(A^-/A)$ kcal/mole	$-{}^3\Delta E_{o,o}-E(A^-/A)$ kcal/mole	k_{ir} $M^{-1}sec^{-1}$	lowest triplet
1. Valerophenone	74.6 [b]	45.8 [d]	-28.8	4.2×10^9 [h]	n,π^*
2. Benzophenone	68.5 [a]	39.9 [d]	-28.6	2.3×10^9 [j]	n,π^*
3. p-Aminobenzophenone	67. [c]	46.	-21.0	5.4×10^7 [k]	π,π^*
4. Fluorenone	53.3 [a]	31.8 [e]	-21.5	3.2×10^7 [l]	π,π^*
5. Biacetyl	54.9 [a]	33.7	-21.2	5×10^7 [m]	n,π^*
6. 2-Naphthaldehyde	59.5 [a]	39.4 [f]	-20.1	8×10^6 [n]	π,π^*
7. 2-Acetonaphthone	59.3 [a]	43.8 [g]	-15.5	6×10^5 [n]	π,π^*

[a] Triplet energies from "Photochemistry", J. G. Calvert and J. N. Pitts Jr., John Wiley and Sons, N.Y. 1966, p.298. [b] Value of propiophenone. [c] S. G. Cohen and J. I. Cohen, J. Phys. Chem., 72, 3782 (1968). [d] "Electroanalytical Chemistry", M. Peover, Vol. 2, A. J. Bard, ed., Dekker, N.Y. 1967. For valerophenone value of acetophenone was used. [e] H. Berg and K. Kramarczyk, Ber. Bunsenges, Physik. Chem., 68 (3) 296 (1964). [f] R. W. Schmidt and E. Heilbronner, Helv. Chim. Acta., 37, 1453 (1954). [g] Calculated assuming $\Delta E(A^-/A)$ for (acetonaphthone-naphthaldehyde $\approx \Delta E(A^-/A)$ for (acetophenone-benzaldehyde). [h] P. J. Wagner and A. E. Kemppainen, J. Amer. Chem. Soc., 91, 3085 (1969); in benzene. [j] S. G. Cohen and A. D. Litt, Tetrahedron Lett., 837 (1970); in benzene. [k] S. G. Cohen and J. I. Cohen, loc. cit.; in cyclohexane. [l] Ref. 2; in cyclohexane. [m] N. J. Turro and R. Engel, J. Amer. Chem. Soc., 91, 7113 (1969); in benzene. [n] S. G. Cohen, G. A. Davis and W. D. Clark, ibid., 94, 869 (1972); in acetonitrile.

For compounds 1-3, in which the triplet energy is favorable, and for compounds 4 and 5 in which reduction potential is favorable, values of k_{ir} obtained in hydrocarbon solvent allow the correlation of Fig. 2. For compounds 6 and 7, in which unfavorable reduction potential is not compensated by high triplet energy, the larger values of k_{ir} in the polar solvent acetonitrile fit the linear correlation. The slope, -0.25 mole/kcal, is somewhat greater than that of Fig. 1, perhaps reflecting the low I.P. of triethylamine. The linear relation indicates that the function $(-{}^3\Delta E_{o,o}-E(A^-/A))$ may be a useful guide to values of k_{ir}, more sensitive than the triplet energies alone and than the triplet types.

In some cases correlations have been shown between relative disposition of n,π^* and π,π^* states and reactivity of triplets in hydrogen abstraction reactions (7). Substituent effects appear to be consistent with a dependence on reduction potential, but data are not available in these cases for test of correlation of log k_{ir} with $[-{}^3\Delta E_{o,o}-E(A^-/A)]$.

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