Quenching of Triplet Benzophenone by Electron Donors

By JEAN-PIERRE BLANCHI
(*Laboratoire de Spectrometrie Physique C.E.R.M.O. Université Scientifique et Médicale de Grenoble, B.P. 53 Centre de Tri 38041, Grenoble Cedex, France*)
and ANDREW R. WATKINS*
(*Max-Planck-Institut für biophysikalische Chemie, 34 Göttingen-Nikolausberg, West Germany*)

Summary An unusual solvent effect has been found for the quenching of triplet benzophenone by aromatic and aliphatic amines.

THE quenching of triplet benzophenone by many organic compounds shows a tendency to increase with decreasing ionisation potential of the quencher. The quenching efficiency for a given ionisation potential depends on whether the quenchers used are aliphatic or aromatic,[1] but appears to depend little on the precise chemical construction of the quencher. We report a study of benzophenone triplet quenching in perfluoromethylcyclohexane (PFMCH), by following, in a conventional flash photolysis apparatus, the decay of the benzophenone phosphorescence at 520 nm in degassed solution as a function of quencher concentration. The resulting quenching rate constants k_q and corresponding ionisation potentials are listed in the Table for aliphatic and aromatic amines. The values of k_q stay virtually constant with changing ionisation potential for aromatic amines and, in the two cases studied, for aliphatic amines. In other solvents (benzene, cyclohexane) the value of k_q decreases by a factor of about 10^4 when the ionisation potential is increased through the same range.[1] It could be argued that the quenching mechanism in

PFMCH is a triplet–triplet energy transfer; however, the triplet energies given in the Table show that this cannot be the case for three of the amines studied here (benzophenone has a triplet energy of 2·99 eV) and this almost certainly also applies to *p*-toluidine,[2] and probably to the remaining amines. The constancy of the k_q values in PFMCH cannot be explained by assuming that the quenching reaction is diffusion controlled, since very much higher values of k_q have been found in benzene,[1] which has a viscosity (0·60 cP) similar to that of PFMCH (0·88 cP).

TABLE

Quenching rate constants for benzophenone in the presence of amines

Amine	IP[a]/(eV)	Triplet energy[b] (eV)	$k_q \times 10^{-8}$/ l mol^{-1} s^{-1}
p-Toluidine	8·14	—	4·4
Aniline	7·69	3·73	5·1
NN-Dimethyl-p-toluidine	7·33	—	3·0
Diphenylamine	7·25	—	5·3
NN-Diethylaniline ..	7·2	3·45	2·2
NN-Dimethylaniline ..	7·14	3·31	5·7
Triphenylamine	6·86	—	3·6
t-Butylamine	8·64	—	1·1
Triethylamine	7·50	—	0·65

[a] Ionisation potentials taken from ref. (9). [b] Triplet energies taken from ref. (10).

Quenching of triplet benzophenone by amines is usually assumed to proceed *via* an initially formed encounter complex,[3] where the two components have approached to within a critical distance at which the interaction leading to the observed quenching becomes important. This complex is loosely bound with respect to the separate components; the formation and dissociation steps are diffusional processes. In polar solvents a pathway for the disappearance of the complex is provided by electron transfer.[4] With decreasing solvent polarity electron transfer is no longer possible, and quenching appears to be due to mixing-in (in the complex) of the higher-lying charge transfer states (sometimes referred to as "partial charge transfer"[1]), [equation (1)] where B and A refer to benzophenone and the amine quencher, respectively; b and c are normally small with respect to a.

$$\psi(\text{complex}) = a\psi({}^3B^*\cdot A) + b\psi(B\cdot{}^3A^*) + c\psi(B^-\cdot A^+) \qquad (1)$$

The mixing-in of $\psi(B^-\cdot A^+)$, which induces a radiationless transition to the ground state,[5,6] depends on the magnitude of c. The coefficient c depends, among other things, on the inverse of the energy separation between the complex state and the charge-transfer state; this explains the observed dependence of k_q on ionisation potential.[6] In PFMCH solvent–solute interactions are unusually weak,[7] and the charge transfer state in this solvent could lie still higher than in benzene or cyclohexane.[1] This would produce a very small value of the coefficient c in (1), leading to the disappearance of any possible dependence on ionisation potential. In this case other effects, such as exchange interactions,[8] may be crucial in determining the fate of the complex.

We thank Mrs. S. Watkins and Miss U. Heine for help with the experiments, the Deutsche Akademische Austauschdienst (DAAD) for financial support for one of us (J-P.B.), and Dr. Kühnle for the purification of the solvent.

(*Received*, 14*th January* 1974; *Com.* 048.)

[1] J. B. Guttenplan and S. G. Cohen, *J. Amer. Chem. Soc.*, 1972, **94**, 4040.
[2] R. S. Davidson and M. Santhanam, *J. Chem. Soc.* (*B*), 1971, 1151.
[3] S. G. Cohen, A. Parola, and G. H. Parsons, *Chem. Rev.*, 1973, **73**, 141.
[4] K. H. Grellmann, A. R. Watkins, and A. Weller, *J. Luminescence*, 1970, **1/2**, 678; R. S. Davidson, D. F. Lambeth, J. F. McKellar, P. H. Turner, and R. Wilson, *Chem. Comm.*, 1969, 732.
[5] K. Kawaoka, A. U. Khan, and D. R. Kearns, *J. Chem. Phys.*, 1967, **46**, 1842.
[6] A. R. Watkins, *J. Phys. Chem.*, 1973, **77**, 1207.
[7] J. B. Birks, 'Photophysics of Aromatic Molecules,' Wiley-Interscience, London, 1970, p. 117.
[8] P. B. Merkel and D. R. Kearns, *J. Chem. Phys.*, 1973, **58**, 398.
[9] J. L. Franklin, J. G. Dillard, H. M. Rosenstock, J. T. Hesson, K. Draxl, and F. H. Field, 'Ionization Potentials, Appearance Potentials and Heats of Formation of Gaseous Positive Ions,' U.S. Department of Commerce, National Bureau of Standards, 1969.
[10] Y. Gondo and Y. Kanda, *Mem. Fac. Sci. Kyushu Univ. Ser. C*, 1964, **5**, 133.