84. *The Quenching of the Fluorescence of Anthracene*

By W. H. Melhuish and W. S. Metcalf.

The quenching of the fluorescence of anthracene by alkyl and aryl bromides and by some other halides is enhanced by electron-attracting substituents in the quenchers.

Bowen and his collaborators [1,2,3,4,5] measured the quenching of the fluorescence of anthracene by many substances, in various solvents and over a wide range of temperatures, and examined the applicability thereto of various expressions based on diffusion theory.[2] Whereas quenching by many of the stronger quenchers is limited [1] by the rate of diffusion together of the excited anthracene and the quencher molecules,[4] quenching by the weaker quenchers is not so limited except in very viscous solvents such as medicinal paraffin or glycerol.[6]

In dilute solutions such weak quenching is sufficiently described [6] by the equation

$$(f_0/f - 1)/[\text{Q}] = k = \tau_0 k_3 K$$

where f_0 and f are the intensities of fluorescence of anthracene (A) with the concentration of quencher at zero and [Q] respectively, k is the experimental quenching constant, τ_0

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[1] Bowen and Norton, *Trans Faraday Soc.*, 1939, **35**, 44.
[2] Bowen, Barnes, and Holliday, *Trans. Faraday Soc.*, 1947, **43**, 27.
[3] Bowen and Coates, *J.*, 1947, 105.
[4] Bowen and Metcalf, *Proc. Roy. Soc.*, 1951, *A*, **206**, 437.
[5] Bowen, *Trans. Faraday Soc.*, 1954, **50**, 97.
[6] Melhuish and Metcalf, *J.*, 1954, 976.

is the average life of the excited molecules in the absence of quencher, K is the equilibrium constant describing the formation of A*Q pairs:

$$A^* + Q \underset{k_2}{\overset{k_1}{\rightleftharpoons}} A^*Q \quad ; \quad K = \frac{k_1}{k_2} = \frac{[A^*Q]}{[A^*][Q]}$$

and k_3 is the first-order rate constant of the quenching step

$$A^*Q \xrightarrow{k_3} \text{products}$$

k_3 and K, unlike k_1 and k_2, are independent of diffusion and viscosity.[4, 6]

The Table gives data for the calculation of the experimental values of k for a variety of weak quenchers in four solvents from 20° to 60°, and for values of [Q] from zero to about $1/k$. The concentration of anthracene was that required for maximum fluorescence in each solvent, namely, light petroleum $3{\cdot}26 \times 10^{-4}$M, *cyclo*hexane $4{\cdot}0 \times 10^{-4}$M, benzene $1{\cdot}85 \times 10^{-4}$M, ethanol $4{\cdot}0 \times 10^{-4}$M.

The values of k_0 at 20° for the series Pr^nBr (1·50), $BrCH_2{\cdot}CO_2Et$ (1·76), $BrCH(CO_2Et)_2$ (14·3), and $BrCH(CN){\cdot}(CO_2Et)$(63) show clearly what the remaining values suggest, namely that electron-attracting substituents in alkyl halides enhance their quenching power. Further examples of this effect are Me_3CBr (0·61), Me_2CHBr (0·83), Pr^nBr (1·32), $Me{\cdot}CHBr{\cdot}CH_2Br$ (2 × 1·8), $CH_2Br{\cdot}CH_2Br$ (2 × 2·6); $CHCl_3$ (3 × 0·03), CCl_4 (4 × 0·29), and $CCl_3{\cdot}CO_2Et$ (3 × 0·55). In each series the compounds are listed in the order of the electron-attracting power of the substituents inferred from the dipole moments.[7] It appears that electrons move toward the quencher in the quenching process.

$$k = k_0^{20}\,\{1 + a(T - 20) + b[Q]\}.$$

	Light petroleum			*cyclo*Hexane			Benzene			Ethanol		
Quencher	k_0^{20}	10^3a	b	k_0^{20}	10^3a	b	k_0^{20}	10^3a	b	k_0^{20}	10^3a	b
$CHCl_3$	0·095	—	0·036	—	—	—	0·085	−7	0·008	0·108	−2	0·046
CCl_4	1·17	19	−0·04	1·00	18	—	6·3	—	−0·095	10·9	13	−0·1
C_2Cl_6	1·58	19	+0·16	—	—	—	4·6	5	—	—	—	—
$CCl_3{\cdot}CO_2Et$	—	—	—	1·66	—	+0·72	—	—	—	—	—	—
p-$C_6H_4Cl_2$	0·37	−4	—	0·54	−6	−0·15	0·18	−1	—	0·38	−6	—
Me_3CBr	0·61	1	0·08	0·74	2	—	0·69	−1	0·0	—	—	—
Me_2CHBr	0·83	0	0·0	—	—	—	0·90	2	0·0	—	—	—
Pr^nBr	1·32	0	—	1·50	−2	—	1·25	−2	—	1·42	0	—
Bu^nBr	1·27	−2	0·0	—	—	—	—	—	—	—	—	—
*$BrCH_2{\cdot}CO_2Et$	—	—	—	1·76	—	0·14	—	—	—	—	—	—
*$BrCH(CO_2Et)_2$	—	—	—	14·3	—	−0·35	—	—	—	—	—	—
*$BrCH(CN){\cdot}CO_2Et$	—	—	—	63	—	—	—	—	—	—	—	—
PhBr	1·95	−3	0·03	2·15	−3	—	1·34	−3	—	2·12	−1	0·08
p-$Me{\cdot}C_6H_4Br$	2·33	−2	—	2·80	−4	—	1·65	−3	—	2·70	−1	—
p-$C_6H_4Br_2$	10·6	−5	—	10·6	−5	—	4·55	−2	0·0	8·9	−3	—
**p*-$MeO{\cdot}C_6H_4Br$	—	—	—	3·85	—	−0·13	—	—	—	—	—	—
**p*-$CO_2Me{\cdot}C_6H_4Br$	—	—	—	7·05	—	0·4	—	—	—	—	—	—
$Ph{\cdot}CH_2Br$	7·0	1	0·7	5·1	1	0·0	2·85	1	0·2	—	—	—
$MeCHBr{\cdot}CH_2Br$	3·69	−2	—	4·05	−4	—	2·97	−4	—	4·24	−1	—
$CH_2Br{\cdot}CH_2Br$	5·15	−4	0·0	—	—	—	3·72	−4	0·00	—	—	—
1 : 7-Dibromonaphthalene	42	1	—	—	—	—	16·6	—	—	—	—	—
HI	161	—	0·6	—	—	—	49	—	1	—	—	—
MeI	21·9	−2	0·02	—	—	—	—	—	—	22·4	+3	—
EtI	23·3	0	—	18·9	0	—	16·4	−1	0·03	21·4	0	—
n-$C_5H_{11}I$	—	—	—	—	—	—	16·0	—	0·7	—	—	—
PhI	32·3	0	—	—	—	—	17·5	4	—	—	—	—

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In the aromatic series the quenching constant of bromobenzene (2·15) is raised to

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[7] Sutton, *Proc. Roy. Soc.*, 1931, *A*, **133**, 668.

7·05 by the strongly electron-attracting group *p*-CO_2Me. The other substituents have smaller effects which are not simply in the order of the bond moments.

Only carbon tetrachloride [2] and hexachloroethane have definite positive temperature coefficients of quenching, and quenching constants very sensitive to the solvent. Quenching by carbon tetrachloride has been treated as diffusion-limited,[2] but is unaffected by viscosity [1, 6] and therefore cannot be diffusion-controlled. It is inferred that the quenching step in this case has an energy of activation which is sensitive to the nature of the solvent. The temperature-dependence of the other quenching constants is scarcely distinguishable from zero. In these cases there is thus no energy barrier to quenching which might be lowered by electron-attracting substituents. Such groups must enhance the probability of quenching in some other manner.

The lower quenching in benzene reflects the shorter lifetime τ_0 of anthracene in that solvent.

A more detailed analysis of the quenching processes [6] shows that the small dependence of k on [Q] is made up of a number of small terms which cannot be separated by experiment except in certain very favourable cases. We record this dependence to emphasise that it is very small but certainly detectable.

EXPERIMENTAL

Quenching was measured as described earlier.[6] The absorption of the exciting light (3650 Å) by the quenching substances was shown separately to be negligible.

The following substances were purified as recommended by Timmermans: [8] $CHCl_3$, CCl_4, C_2Cl_6, $C_6H_4Cl_2$, Me_3CBr, Me_2CHBr, Pr^nBr, Bu^nBr, PhBr, $Me{\cdot}C_6H_4Br$, $C_6H_4Br_2$, MeI, EtI, PhI.

The following were fractionally distilled: benzyl bromide, methyl trichloroacetate (b. p. 164—166°), ethyl bromoacetate ($d_4^{20} = 1{\cdot}5112$), ethyl bromomalonate (three fractions of identical quenching power), and ethyl bromocyanoacetate. The last decomposed slightly on distillation. The colourless fractions (presumed to be mixtures of ethyl bromocyanoacetate and ethyl cyanoacetate) were therefore analysed by adding them to acidified potassium iodide solution and titrating the iodine formed. Ethyl cyanoacetate does not quench.

Methyl *p*-bromobenzoate (m. p. 79·5—80·5°) and *p*-bromoanisole (m. p. 11·8—12·8°) were crystallised from methanol and fractionally frozen respectively.

Solutions of hydrogen iodide were estimated acidimetrically. *n*-Pentyl iodide was a sample described elsewhere.[9]

Benzene was treated with sulphuric acid to remove thiophen, which is a quencher. Light petroleum (b. p. 72—85°) and *cyclo*hexane were passed through a column of silica gel. The first liquid to come through is free from aromatic compounds as shown by the ultraviolet transmission.

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[8] Timmermans, " Physico-chemical Constants of Pure Organic Compounds," Elsevier, Amsterdam, 1950.

[9] Metcalf, *J.*, 1954, 2485.