The Quenching of the Fluorescence of Anthracene Gas.

By W. S. Metcalf.

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The rates of reaction of various substances with excited anthracene molecules increase with falling temperature as would be expected if quenching collisions were increased in number by van der Waals attractive forces.

THE quenching of the fluorescence of anthracene gas by oxygen, sulphur dioxide, hydrogen iodide, and methyl, ethyl, and pentyl iodides can be described by the scheme :

$$\begin{array}{lll} A + h\nu \longrightarrow A^* & \dots\dots\dots\dots & \textit{Absorption} \\ A^* \xrightarrow{} A + h\nu' \overset{k_f}{} & \dots\dots\dots & \textit{Fluorescence} \\ A^* + Q \longrightarrow \text{unknown} \overset{k_Q}{\text{products}} & \dots\dots & \textit{Quenching} \end{array}$$

which leads to the Stern–Volmer equation : $(f_0/f - 1)/[Q] = k_f/k_Q = k$, where f_0 and f are the fluorescence intensities without and with the quencher present at a concentration [Q] moles/l. The quenching constants observed at 200° and 300° at an anthracene pressure of 1·2 mm. in hydrogen at 1 atm. pressure given in the Table were obtained over a range of quencher concentration up to the quoted value at which $f_0/f \sim 2$ from zero. In no case did k, the quenching constant, vary significantly with quencher concentration. Determinations were retained if the values of f_0 found before and after the measurement of f were consistent. Temperature coefficients, measured at the best quencher concentrations for accuracy in separate experiments in which only the temperature was altered, are significant to the number of figures given. They cannot be so accurately deduced from the quenching constants given which include measurements throughout the range of concentration quoted.

Quencher	Concn. moles/l.	Quenching constant, k 200°	300°	k_{200}/k_{300}	E
SO_2	0·0005	2180 ± 60(9) *	2210 ± 14(2)	1·020	630
O_2	0·001	932 ± 3(4)	917 ± 4(2)	1·013	590
HI	0·002	291 ± 10(8)	—	—	—
MeI	0·012	77·4 ± 2(7)	59 ± 0(2)	1·30	1940
EtI	0·012	104 ± 3(9)	79 ± 3(7)	1·29	1900
$C_5H_{11}I$	0·007	182 ± 10(4)	139 ± 2(3)	1·28	1860
$C_6H_5NH_2$	0·009	90 ± 6(7)	47 ± (1)	1·9	4000

* Values quoted are the unweighted mean and standard deviation. The figure in parentheses are the number of determinations made.

Self-quenching of anthracene reduces the quenching constants as the anthracene pressure increases. Preliminary measurements over a range of anthracene pressures showed that the k values extrapolated to zero anthracene concentration differed by about 2% from those quoted. Recent direct measurements of the self-quenching of anthracene (Bowen and Stevens, personal communication) show that the k values in the Table are 3% low on this account.

In the last column are given the values of E required to fit the equation $k = AT^{1/2}e^{+E/RT}$ to the observed temperature coefficients. E, the work done (cal./mole) by the forces of attraction as the excited anthracene and quencher molecules approach the point where energy degradation occurs, requires a value of 516 cal./mole to produce a zero temperature coefficient between 200° and 300°, because of the term $T^{1/2}$ in the equation above. The small but definite negative temperature coefficients of quenching by oxygen and by sulphur dioxide indicate the slightly higher attractive energies shown. The more complex quenchers show a very marked decrease in efficiency with rising temperature, with a correspondingly high negative value of the " activation energy." k_f is assumed to be independent of temperature.

The values of E may be compared with the following values calculated from the temperature coefficient of the viscosity of various gases (cf. " Handbook of Chemistry and Physics," Chemical Rubber Publ. Co., Cleveland, 1944) by the equation $\eta = \eta_0 T^{1/2} e^{-E/RT}$ (Loeb, "The Kinetic Theory of Gases," McGraw-Hill, New York, 1934, p. 225), in which E is the work done (cal./mole) by the attractive forces as the molecules approach the collision distance: O_2, 170; HI, 354; SO_2, 380; C_6H_6, 470; $Me{\cdot}CO_2Bu^i$, 1250 cals./mole. These values increase with molecular weight and boiling point. It seems therefore that the negative temperature coefficients of quenching are no greater than can be attributed to the attractive forces expected between anthracene and quencher molecules.

Increase in the length of the alkyl group of alkyl iodides enhances the quenching without increasing the negative temperature coefficient. This behaviour is doubly curious in that the larger alkyl groups would be expected to decrease the quenching by obstructing the iodine atom, which effect might be somewhat offset by an increased van der Waals attraction and a correspondingly larger negative temperature coefficient. As this is not so, the enhancement appears to be due to the increase in the collision diameter of the quencher which behaves as a whole rather than as an active iodine atom with an inactive "tail." By contrast, quenching by hydrogen iodide is high, as is expected if the unhindered approach of the iodine atom to the excited anthracene molecule is the essential part of the quenching process.

EXPERIMENTAL.

The photometer has already been described (*J.*, 1954, 976).

Hydrogen, freed from oxygen, was saturated with quencher in three successive bubblers of thin glass in a temperature-controlled water- or oil-bath. In the cases of oxygen, sulphur dioxide, and hydrogen iodide, mixtures with hydrogen were stored in reservoirs. The mixture, kept hot electrically to prevent condensation, passed through a series of eight bulbs containing pure anthracene heated externally by the condensing vapour of anisole (b. p. 155°). The mixed gases entered a Pyrex tube (4" × 1") surrounded by an aluminium block regulated at 200° or 300° as required. Double windows at right angles admitted the exciting light (3650 Å) to the tube and passed the fluorescence to the photocell. The reference photocell observed a similar tube, in the same aluminium block, containing anthracene maintained at a steady pressure by a side arm in a second aluminium block whose temperature was set for maximum fluorescence. For the determination of f_0, the hydrogen by-passed the quencher saturator.

The flow-rate and the total pressure were controlled. The fluorescence intensity and the quenching constant were independent of flow-rate over a considerable range, and about two min. were normally required to reach a steady value. In no case did the partial pressure of carrier gas affect the fluorescence intensity or the quenching constant. With sulphur dioxide the same constant is found when either hydrogen or nitrogen is used as carrier gas. Values for sulphur dioxide obtained in the absence of carrier gas are less accurate because flow rates are difficult to control at low pressures, but they do not differ significantly from the results quoted. The discrepancy with the value of 1000 given by Bowen and Metcalf (*Proc. Roy. Soc.*, 1951, *A*, **206**, 437) obtained in a static apparatus has not been resolved.

Oxygen and sulphur dioxide were obtained from cylinders and were not purified further. Hydrogen iodide was prepared by combination of the elements over hot platinum, and fractionated in liquid air traps. As hydrogen iodide attacks mercury its pressure was measured by a spoon gauge.

Methyl iodide, ethyl iodide, and aniline were fractionally distilled (20 plates). Their vapour pressures were measured in an isoteniscope immersed in the bath used for the saturators, thus avoiding thermometric errors. When the stem correction was applied the vapour pressures agreed with those quoted by Timmermans ("The Physico-Chemical Constants of Pure Organic Compounds," Elsevier, 1950). The vapour pressure of pentyl iodide (d_4^{20}, 1·5170) similarly purified was as follows:

p_{mm}	20	30	40	60	80	100	150
$T°$ (corr.)	53·7	62·5	68·9	78·6	85·6	91·5	102·7
p_{mm}	200	300	400	500	600	700	760
$T°$ (corr.)	111·4	123·8	133·3	141·0	147·4	153·0	156·0

VICTORIA UNIVERSITY COLLEGE,
WELLINGTON, NEW ZEALAND.

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