

## 27. The Photochemical Dimerisation of Acenaphthylene.

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The quantum efficiencies of the photodimerisation of solutions of acenaphthylene in blue and near ultra-violet light have been measured at various concentrations and temperatures. The results show that the limiting efficiency is only one-tenth of that expected if all activated molecules reacted, and that the mechanism of the dimerisation is probably not of a "collisional" type, but depends on the existence of van der Waals complexes in the solution.

ORGANIC substances containing an ethylene linkage show two types of behaviour photochemically, a unimolecular *cis-trans*-change and a bimolecular dimerisation to molecules containing a *cyclobutane* ring. Though the first type has been well studied (see Olson, *J. Amer. Chem. Soc.*, 1933, **55**, 1410; 1934, **56**, 1320; *J. Chem. Physics*, 1933, **1**, 418), little quantitative work has been done on the latter.

The substance chosen for this work was acenaphthylene (I) which has the advantage of being incapable of *cis-trans*-interchanges. The hydrocarbon is bright yellow, and when concentrated solutions are exposed to blue or near ultra-violet light a colourless dimeric product (II)



is produced, which is a mixture of two stereoisomeric forms (Dziewonski, *Ber.*, 1912, **45**, 2491; 1913, **46**, 1986; 1914, **47**, 1679).

The acenaphthylene was prepared by passing acenaphthene vapour through a red-hot silica tube in a stream of carbon dioxide, and purified by fractional crystallisation of the picrate from alcohol; m. p. 93°.

Solutions of the hydrocarbon were sealed in small glass tubes of equal diameter and exposed to the light from a 500-watt mercury-vapour lamp. The tubes were kept at constant temperature by a water-bath. Under these conditions the mercury lines 4360, 4050, and 3650 Å. were completely absorbed while all other lines played no part. The dimer is transparent to the first two lines but absorbs somewhat at 3650 Å. and is photochemically decomposed back to the monomer, but experiments with this line removed by a filter of acidified ferric alum solution showed that the reverse reaction was negligible under our conditions of measurement. The quantum efficiency was estimated by comparison reactions with the uranyl oxalate actinometer (Leighton and Forbes, *J. Amer. Chem. Soc.*, 1930, **52**, 3139; 1934, **56**, 2363). The amount of change was found by measuring the light absorption of the solution, suitably diluted, to the mercury 4360 Å. line, using a photoelectric cell. From a series of such measurements up to about 30% decomposition the initial rate of photochange for each solution was obtained. Check experiments showed that the rate was directly proportional to the light intensity and unaffected by the presence of dissolved oxygen. The table gives results for solutions in toluene, quantum efficiencies being expressed as moles of acenaphthylene removed per einstein.

Results for solutions in hexane, alcohol, and acetic acid gave figures within 20% of those for toluene.

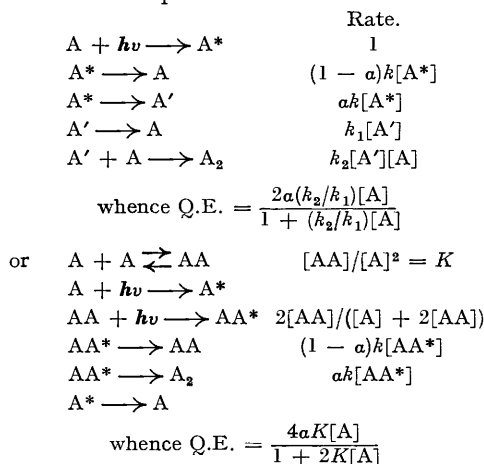
Temp. 11°	{	Molarity .....	0.163	0.221	0.269	0.326	0.432	0.618	1.13
		Q.E. ....	0.012	0.017	0.018	0.021	0.028	0.038	0.059
Temp. 31°	{	Molarity .....	0.158	0.222	0.316	0.423	0.628		
		Q.E. ....	0.011	0.016	0.019	0.024	0.035		
Temp. 52°	{	Molarity .....	0.163	0.218	0.270	0.320	0.434	0.614	1.13
		Q.E. ....	0.010	0.012	0.013	0.015	0.021	0.030	0.048

The experimental figures are fitted by an expression of the form :

$$\text{Quantum efficiency} = \frac{K_1 K_2 [A]}{1 + K_2 [A]}$$

$K_1$  representing the theoretical limiting value for high concentrations. The value of  $K_1$  found is 0.18 at each temperature, instead of the value 2 which would be found if every molecule physically activated reacted to give the dimer.

Two mechanisms give the above expression :



The constant  $K_2$  has a very different meaning in these two mechanisms; in the first it represents the ratio of the constants of a unimolecular deactivation process and a bimolecular dimerisation, while in the second it represents an "equilibrium constant". The second mechanism assumes strong van der Waals "dispersion" forces between the  $\pi$  electrons of the aromatic molecules giving complexes AA. The interaction is assumed to be not strong enough to give marked changes in the absorption spectrum, as has been noted for the more powerful complex formation in dye solutions (Vickerstaff and Lemin, *Nature*, 1946, **157**, 373), and the absorbed light is assumed to be divided between A and AA approximately in proportion to their concentrations. The two mechanisms closely resemble those put forward by Bowen, Barnes, and Holliday (*Trans. Faraday Soc.*, 1946, to appear) to explain two types of fluorescence quenching. It is there pointed out that the first mechanism is characterised by positive temperature coefficients and the rate is inversely related to the viscosity of the medium, while in the second, viscosity plays no part and the temperature coefficient is negative. The figures of the table and the results for other solvents indicate the second mechanism for the dimerisation on these criteria. If this is so, the temperature variation of  $K_2$  should be determined by the heat of formation of the complex AA. The value of this quantity so calculated is about 1.5 k.-cals./mole, which is comparable with other values for similar molecular interactions (cf. Bowen and Coates, preceding paper).