

Anomalous Absorption and Photolysis of Iodobenzene

IOBENZENE, as a vapour or in solution, is unstable to light, like the alkyl iodides, and lends itself to the same sort of photolytic study. Moreover, we have found that the presence of nitric oxide accelerates the decomposition, as is the case with methyl iodide¹. The alkyl iodides show continuous absorption spectra in the near ultra-violet; but it would not be expected from preliminary considerations that iodobenzene would do so. Benzene and its simpler derivatives have been subjected to a great number of absorption measurements. The bands in the 2600 Å. region found in benzene are considered to be due to a forbidden transition determined by symmetry considerations². Substitution of a hydrogen atom by a fluorine, chlorine or bromine atom alters the symmetry, the band system becomes stronger and shifts towards the red end of the spectrum. The red shifts³ in the case of fluoro-, chloro- and bromo-benzene for the $\nu(0-0)$ band are respectively -271 , $-1,037$ and $-1,093$ cm^{-1} . We might have expected the $\nu(0-0)$ band of the iodo-derivative to have displayed a red shift not very much larger than $-1,093$ cm^{-1} ; but substitution of the hydrogen by the iodine produces an anomalous result. There is still absorption in the 2600 Å. region; but the discrete bands have disappeared, and only a continuous absorption is observed⁴.

In order to confirm this, we carried out investigations on the absorption spectrum of pure iodobenzene vapour at different temperatures, using an Allen hydrogen arc⁵ as a background of continuous radiation, and a grating spectrograph (Hilger 185) to give ample dispersion. No discrete bands or fine structure of lines were observed in the 2600 Å. region, only continuous absorption, extending at high pressures from 2400 to 3000 Å., with a broad maximum at 2600–2800 Å. The absorption of iodobenzene in hexane solution shows a single band in the 2600 Å. region, with a maximum at 2568 Å. of molar extinction coefficient⁶ 600. The same type of absorption is shown by the alkyl iodides. As iodobenzene liberates iodine under the influence of light in the same way as the alkyl iodides, we are led to assume that absorption of the light quantum takes place, not by the π -electrons, but in the C—I bond, or by one of the iodine electrons. Excitation to the unstable A -level takes place, leading to the splitting off of an iodine atom, analogous to the case of methyl iodide discussed by Mulliken⁷. If the photochemical behaviour of iodobenzene follows closely that of the alkyl iodides, we might expect the quantum yield to be lowered by the back reaction: $\text{C}_6\text{H}_5 + \text{I} = \text{C}_6\text{H}_5\text{I}$. In the presence of nitric oxide in sufficient concentration, however, the reaction $\text{C}_6\text{H}_5 + \text{NO} = \text{C}_6\text{H}_5\text{NO}$ could take place, and the quantum yield for iodine formed (Φ_{I_2}) might be as high as unity.

The photolysis of iodobenzene dissolved in hexane in the presence of nitric oxide was carried out using previous techniques¹. In this two-phase system it is not very easy to maintain constant conditions of saturation; but the results we have obtained are of an order of accuracy sufficient to support the general conclusion. In one such series of runs we obtained for Φ_{I_2} : 1.2, 1.12, 0.91, 1.1, 0.96, 1.04. A value of Φ_{I_2} considerably lower than this would indicate some kind of deactivation of excited molecules, which evidently do not exist. A higher value of Φ_{I_2} would indicate a chain reaction, which seems very improbable.

A molecule of another kind, such as iodoacetic acid, has continuous absorption in the vapour state, and a separate band, ~ 2600 Å., analogous to the C—I absorption band of the alkyl iodides, some 400 Å. to the long-wave side of the first acetic acid band.

We are investigating a whole series of carbon-iodine compounds in order to find out to what extent the C—I bond determines the spectroscopic character and photochemical behaviour of these complex molecules.

R. A. DURIE
T. IREDALE
A. H. KINGSBURY

Physico-chemical Laboratories,
University of Sydney. May 27.

¹ Iredale and McCartney, *J. Amer. Chem. Soc.*, **68**, 144 (1946).

² Sponer, *Rev. Mod. Phys.*, **14**, 224 (1942). Sklar, *Rev. Mod. Phys.*, **14**, 232 (1942).

³ Herzfeld, *Chem. Rev.*, **41**, 249 (1947).

⁴ Purvis, *J. Chem. Soc.*, **99**, 2318 (1911).

⁵ Allen, *J. Opt. Soc. Amer.*, **31**, 268 (1941).

⁶ Hillmer and Paersch, *Z. phys. Chem.*, **A**, **161**, 46 (1932).

⁷ Mulliken, *Phys. Rev.*, **47**, 413 (1935).

Constitution of 'Pure' Cellulose

THE word 'cellulose' possesses two connotations: in a technical sense it denotes products obtained by certain processes from vegetable material; in a chemical sense it is commonly used for a linear high-molecular polysaccharide composed solely of glucose residues linked by α 1-4 glucosidic bonds. It is, however, not yet established with certainty that this polysaccharide is really the main constituent of natural cellulose fibres.

Haworth¹ suggests the possibility of pairs of chains being joined together by cross-links of an unknown nature; he bases this hypothesis on methylation experiments, from the results of which it seems that adjacent chains are fixed relatively to each other. The pre-existence of cross-links between pairs is, however, not in agreement with the X-ray evidence, which shows that, in any one plane parallel to the fibre axis, all chains of a cellulose crystallite are linked together in the same way. On the other hand, the fixation of adjacent chains during the methylation as postulated by Haworth is well explained by the action of residual valencies, which hold together the chains during the permutoid reactions of cellulose. Furthermore, the solubility of cellulose, for example, in cuprammonium hydroxide, is incompatible with the net-like structure which would result from irregular cross-links. The conclusions of Paesu² who postulates cross-links of a semi-acetal type are not sufficiently well grounded to be taken into consideration, especially since they were carried out on 'surgical cotton', a highly degraded cellulose. It is apparent that there is no valid evidence for the existence of primary valence cross-links, however disposed.

Raw cellulose contains carboxyl groups; several authors³ concluded that a small but definite number of these groups may be present in each molecule of the original cellulose. We have, however, found that both cotton and α -cellulose from wood pulp, if reprecipitated from cuprammonium solution, washed, acidified and electro-dialysed, are free from carboxyl groups. Samples of this highly swollen cellulose were shaken in a closed platinum dish with 0.6 N sodium chloride the pH of which had been adjusted to 6.2. After six days contact with the salt solution in order to establish the equilibrium, no change in pH was