242. *Absorption Spectra of Substances containing the Carbon–Iodine Bond. Part I.*

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The ultra-violet absorption spectra of the vapours of many compounds containing the carbon–iodine bond are continuous. This is interpreted in terms of photo-dissociation of the C–I linkage. Photochemical reactions of iodobenzene and iodoacetic acid support this interpretation. New experimental observations include measurements on the absorption spectra of iodobenzene vapour, which confirm the view that the continuous absorption band obtained in solutions is not due merely to the influence of the solvent molecules. Experimental results are also recorded on the ultra-violet absorption spectra of iodoacetic acid, sodium iodoacetate, ethyl β-iodopropionate, and 3-iodopropaldehyde.

The near ultra-violet absorption spectra of many molecules containing the carbon–iodine bond are continuous, which corresponds to dissociation of the molecules, the iodine atom invariably splitting off. They cannot be compared with spectra of similarly constituted substances which have one of the other halogens attached to the carbon, or some other feature of photochemical importance, and show vibrational structure.

The saturated hydrocarbons like methane and ethane show absorption only in the far ultra-violet. The bands are usually diffuse, or only continuous absorption is evident, so that a pre-dissociation process may be operative (Mulliken, *J. Chem. Physics*, 1935, **3**, 518). Substitution of a hydrogen by a halogen atom shifts the absorption in to the near ultra-violet region; the photochemical process following the light absorption starts from the splitting-off of the halogen atom (Hukumoto, *ibid.*, p. 164). In the case of the iodides, at least, a series of bands begins below 2000 A., comparable with the far ultra-violet spectra of molecules which exhibit a Rydberg series leading to ionization (Herzberg and Scheibe, *Z. physikal. Chem.*, 1930, **7**, *B*, 390; Price, *J. Chem. Physics*, 1935, **3**, 365; Mulliken, *ibid.*, p. 513).

The molecule of ethylene begins to absorb below 2000 A., which is interpreted by Price and Tutte (*Proc. Roy. Soc.*, 1940, *A*, **174**, 207) as a so-called $N \longrightarrow V$ transition, in which one π electron is in an anti-bonding orbital and the other remains in the bonding orbital. Substitution of hydrogen by iodine produces a new band in the 2600-A. region, resembling the continuous absorption of an alkyl iodide. It cannot be attributed to a bathochromic shift of the $N \longrightarrow V$ band. Vinyl iodide, like ethyl iodide, liberates iodine by light absorption in the 2600-A. region (Emschwiller, *Compt. rend.*, 1931, **192**, 799; Rollefson and Burton, "Photochemistry," Prentice-Hall, 1942, p. 206). There is no evidence to suggest, among other things, that absorption of a light quantum by vinyl iodide results in a rotation about the double bond.

In the aromatic series substitution of hydrogen by halogen produces bathochromic shifts, but here the vibrational structure lends itself to a more quantitative treatment. The theoretical treatment of this problem of light absorption by the symmetrical benzene molecule and its simpler derivatives has been very successful (Sponer, *Rev. Mod. Physics*, 1942, **14**, 224; Sklar, *ibid.*, p. 232). The fluoro-, chloro-, and bromo-benzenes behave normally, and show a vibrational structure similar to that of benzene, but iodobenzene shows mainly continuous absorption, in this way resembling the alkyl iodides in its photo-chemical behaviour.

Aldehydes and ketones possess characteristic absorption, ascribed to the C=O group, in a region extending in the simpler cases from 3500 to 2400 A. Any discrete vibrational structure is usually masked by a continuous background, so that here substitution of hydrogen by iodine produces a result which is not so easy to interpret, although such compounds in their photochemical behaviour resemble the alkyl iodides (Mulliken, *J. Chem. Physics*, 1935, **3**, 564; McMurry, *ibid.*, 1941, **9**, 241).

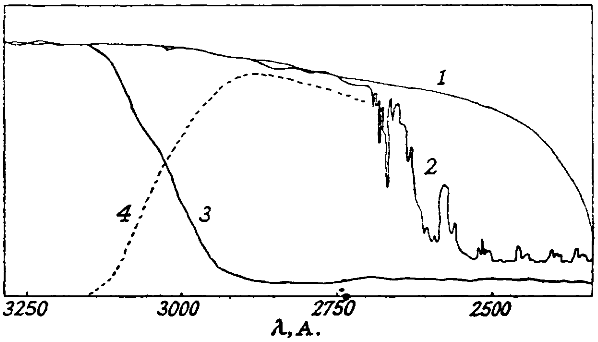
The characteristic absorption of carboxylic acids (other than formic acid which shows some structure in its spectrum) and esters begins with a continuous band at 2400 A., having a maximum at 2100 A. (Ley and Arends, *Z. physikal. Chem.*, 1932, **17**, *B*, 177). It is ascribed to the carboxyl group. Substitution of hydrogen by iodine in methyl, *e.g.*, formation of iodoacetic acid, produces the characteristic alkyl iodide band in the 2600-A. region. The characteristic carboxyl band, however, is also present, and is more intense than in acetic acid and has suffered a bathochromic shift. Here we have an example of strong absorption due to a particular group (the C–I bond) preceding the normal absorption of the parent molecule, acetic acid.

Where the C–I bond exists in a molecule separated far from another chromophoric feature, *e.g.*, the resonating benzene structure, Hillmer and Paersch (*Z. physikal. Chem.*, 1932, **161**, *A*, 46) found that additive relations are sometimes possible, in agreement with Henry's law

(" Etudes de photochimie," Paris, 1919, p. 174; Braude, *J.*, 1949, 1903). They found that the extinction coefficient of iodopropylbenzene was nearly equal to the sum of the extinction coefficients of propylbenzene and propyl iodide. No such agreement was possible in the case of iodobenzene compared with (benzene + alkyl iodide), and here we might expect some conjugation of the p electrons of the iodine atom with the electrons of the benzene ring. There is evidence, as Hillmer and Paersch have shown, of a banded structure, as well as of continuous absorption, for solutions of the iodopropylbenzene. Some molecules absorb one way by excitation of the C–I bond, others by excitation in the benzene ring, according to their respective transition moments given by the equation $M = \int\psi_0 r\psi' \mathrm{d}\tau$.

Almost all studies of absorption spectra have been made on substances dissolved in appropriate solvents. In this way important features of the absorption process have sometimes been lost. The rotational fine structure is in every case absent, and often the individual vibration bands have been merged into a continuous spectrum in the liquid phase. In some cases, for purposes of identifying structure, these features are not important; in others they are. When the continuous absorption appears for the vapour phase of the compound at low pressures, it will not always be comparable with the band of another substance in the same region, which shows vibrational structure in the vapour phase and continous absorption in the liquid phase.

FIG. 1.



Densitometer tracings: (1) *Hydrogen arc;* (2) *Benzene absorption;* (3) *Iodobenzene absorption;* (4) *Difference in density between* (1) *and* (3), *showing absorption maximum.*

We have studied absorption spectra of substances both in solution and in the vapour state.

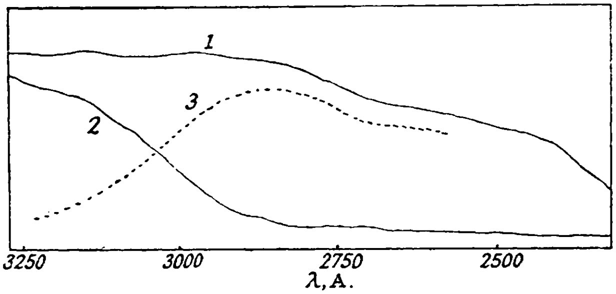
Iodobenzene.—We found the absorption spectrum of the vapour of this substance to be entirely continuous (cf. Purvis, *J.*, 1911, 2318). The photographic plate (negative) was examined with the aid of a densitometer. The density curve of the iodobenzene continuous absorption compared with the benzene structure is shown in Fig. 1. Owing to the decrease in sensitivity of the plate towards the shorter wave-lengths, a true appreciation of the absorption maximum cannot be obtained from this curve. By plotting the difference between the densities of the hydrogen-arc spectrum and the iodobenzene-absorption spectrum (dotted curve) a broad maximum is discovered in the region 2800 A.

Our absorption measurements on iodobenzene in hexane corroborate those of previous investigators (Hillmer and Paersch, *loc. cit.*). The first absorption band has a maximum at 2560 A., $\varepsilon = 665$, and the second at 2320 A., $\varepsilon = 10{,}000$. The second band may correspond to the 2100-A. band (${}^1A_{1g} \longrightarrow {}^1B_{1u}$) of benzene (Sklar, *loc. cit.*). In hexane under the influence of nitric oxide, which inhibits the back reaction $C_6H_5 + I = C_6H_5I$ by the side reaction $C_6H_5 + NO = C_6H_5{\cdot}NO$, a quantum yield of approximately unity has been found for the photo-decomposition of iodobenzene by light of wave-lengths 2500—2800 A. (Durie, Iredale, and Kingsbury, *Nature*, 1949, **164**, 786). Practically all the light-affected molecules must have absorbed by way of the C–I bond and not in the benzene ring by the π electrons, as it is very unlikely that NO would have reacted at room temperature with excited molecules.

Iodoacetic Acid.—The absorption spectrum of the vapour of this substance is continuous. There is a broad maximum at ~2800 A. (Fig. 2). In different solvents the well-known C–I band appears with maximum at 2600—2780 A.:

Solvent.	λ (max.).	λ (min.).	ε (max.).	ε (min.).
Water	2610	2500	455	388
Alcohol	2730	2480	452	340
	2240	—	510	—
Hexane	2708	2440	330	157
Aqueous soln., pH 1	2680	2420	306	228
N/20-NaOH	2600	2520	384	375
Soln. of sodium iodoacetate	2600	2580	317	314
	2240	—	1800	—

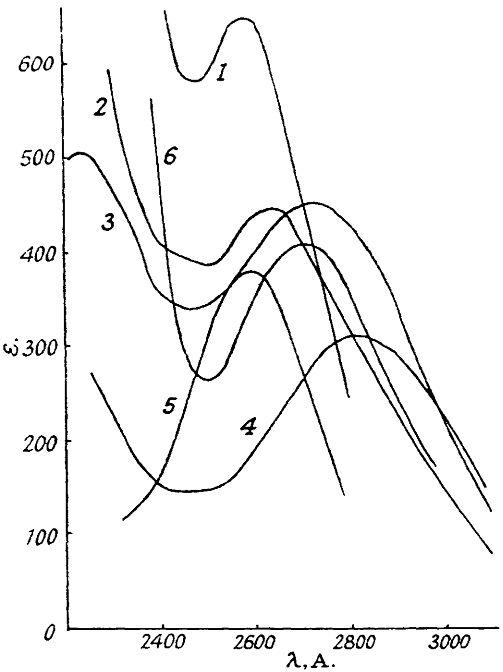
FIG. 2.



Densitometer tracings: (1) *Hydrogen arc;* (2) *Iodoacetic acid absorption;* (3) *Difference in density between* (1) *and* (2), *showing absorption maximum.*

On the short-wave side of the minima another absorption band commences, and this is the characteristic feature of the acetic acid absorption. In general, the maxima of this band are in a region not suited to measurement by the Beckman instrument, but for sodium iodoacetate a second maximum was found at 2240 A., ε = 1800, also with the alcoholic solution of the acid.

FIG. 3.



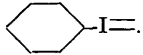
Light absorption by: (1) *iodobenzene in hexane;* (2) *iodoacetic acid in water;* (3) *iodoacetic acid in alcohol;* (4) *iodoacetic acid in hexane;* (5) *ethyl β-iodopropionate in heptane;* (6) 3-*iodopropaldehyde in heptane.*

The influence of the solvent on the disposition of the C–I band might be related to ionization, together with hydration of the ion. But we have found no evidence that the spectrum is indicative of an electron transfer, as is sometimes the case with anions (Rabinowitsch, *Rev. Mod. Physics*, 1942, **14**, 112). The iodoacetate ion definitely shows an absorption shift towards the shorter wave-lengths, when compared with the molecule. As iodine is liberated under conditions where the back reaction I + $\cdot CH_2\cdot CO_2H = CH_2I\cdot CO_2H$ cannot occur (experiments to be described shortly), we must assume that decomposition of the molecules follows on instability caused by excitation in the C–I region.

The same kind of absorption is found with iodopropionic acid (Levene and Rothen, *J. Biol. Chem.*, 1934, **107**, 538).

Ethyl β-*Iodopropionate.*—In heptane this substance shows the characteristic C–I band, with a maximum at 2595 A., ε = 381. Methyl β-iodopropionate shows similar absorption (Kuhn and Biller, *Z. physikal. Chem.*, 1935, **29**, *B*, 256).

3-*Iodopropaldehyde.*—The typical C–I band has a maximum at 2700 A., ε = 403, which is shifted towards the shorter wave-lengths relative to the propaldehyde absorption, which has a maximum at 2880 A., ε = 23. The intensity of the iodide absorption is much higher than that of the aldehyde itself. In the 2700-A. region iodopropaldehyde in solution in hexane is unstable to light, and liberates iodine, as do the alkyl iodides.

A quantitative treatment of these results based on theoretical considerations of the interaction of the iodine atom with the π-electron system of the benzene, or with the carboxyl and other groups, will not be essayed at present. Of this we may be certain : in its state of univalent combination iodine can sometimes exhibit a degree of unsaturation surpassing that of the other halogens. The formula for iodobenzene might be written .

Further work is to follow, involving a study of the iodides of more extensively conjugated systems such as naphthalene and phenanthrene, where we have found that the C–I spectrum is not so strongly in evidence. The experimental difficulties associated with these investigations are very great. They involve a recognition of an underlying continuous absorption where the vibration band system is strong, and the detection of an underlying band system where the C–I continuous absorption is strong. Bands can only be detected at low pressures, and where the utmost precaution is taken to prevent formation of a condensate on the end windows of the absorption cell.

The results we have obtained serve to emphasise certain features of light absorption which have not been highly developed, at least, not on the theoretical side. For it is evident that a molecule may absorb in the same spectral region in one or more ways, and in one or other of different groups, to an extent dependent on the transition moments in these groups and on the influence these groups have on one another. Some nitro-compounds, *e.g.*, nitrobenzene, are similar to the iodides. The vapours show only continuous absorption, which is localized in the nitro-group and leads to photo-dissociation in this region (Hastings and Matsen, *J. Amer. Chem. Soc.*, 1948, **70**, 3514).

EXPERIMENTAL.

Measurements of absorption spectra in solution were carried out with the aid of a Beckman spectrophotometer. The wave-length scale was checked by the radiations of a mercury-vapour lamp, and the transmissions with a solution of alkaline potassium chromate (Hogness, Zscheile, and Sidwell, *J. Physical Chem.*, 1937, **41**, 379). The source of continuous radiation for measurements on the vapours was a modified form of the Allen hydrogen arc (Allen, *J. Opt. Soc. Amer.*, 1941, **31**, 268). The spectra were obtained with a Hilger 185 concave-grating spectrograph, and were photographed on Kodak super XX 10″ × 4″ plates, the sensitivity of which fell off rapidly towards the short-wave end of the spectrum. The plates were examined with the aid of a Baird Associates densitometer (Baird, *ibid.*, p. 179). Iron and copper arcs were used for comparison spectra. The substance examined was distilled into a quartz tube with plane quartz ends, evacuated, sealed off, and supported in an air-thermostat, heated in a way designed to prevent condensation on the end windows.

Materials.—Hexane. Hilger's pure, spectroscopic.

Heptane. This was purified, after fractional distillation of a commercial sample, by passage through a column of silica gel, 120 cm. in length, and re-distillation. Transmission of the purified sample was 27% of 2200 A. and 67% of 2300 A.

Alcohol. 95% Ethanol was used for general purposes; it had a high transmission (35%) of 2200A., and no selective absorption anywhere.

Iodobenzene. Purified by distillation under reduced pressure. It was colourless, boiling at 188°/759 mm.

Iodoacetic acid. This was made by interaction of chloroacetic acid and potassium iodide at 50°. The iodoacetic acid was extracted with ether, and the small flat crystals recovered on evaporation of the ether. The material was carefully recrystallized at low temperatures from water, and also from light petroleum; it had m. p. 83°.

Sodium iodoacetate. This was prepared from the acid by the addition of sodium carbonate to the solution until there was no more evolution of carbon dioxide. The solution was then added to alcohol, and the crystalline product filtered off.

Solution of pH 1. A Clark and Lubs buffer, made with potassium chloride and hydrochloric acid.

Ethyl β-iodopropionate. The material was freed from iodine by shaking it with sodium sulphite solution, washed, dried, and distilled under reduced pressure; it had b. p. 200°/760 mm.

3-*Iodopropaldehyde.* 30 G. of propaldehyde were mixed with 85 c.c. of 90% alcohol and 41·5 g. of iodine, and finally 16·5 g. of iodic acid were added. The mixture was allowed to remain with frequent shaking at about 20° for 14 days. Water was added. A heavy oil which separated was removed, washed with very dilute sodium carbonate solution, and dried (Na_2SO_4). The product was distilled at 17 mm., and the fraction boiling at 83—84° collected.

We gratefully acknowledge financial assistance from the Commonwealth Science Grant to this University.

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