208. *Electrolytic Dissociation Processes. Part V. The Solvolytic Ionisation of Molecular Iodine.*

By Fred Fairbrother.

The polarisation or ionisation of an iodine molecule by co-ordinate bond formation with a "basic" solvent molecule is discussed. Measurements have been made of the dielectric constants and densities of solutions of iodine in a number of solvents of zero or low polarity. Solvents with basic or electron-donor character give red or brown solutions with an enhanced dielectric polarisation: this group includes aromatic and ethylenic hydrocarbons, whose electron-donor character is attributed to the π electrons.

THE fact that solutions of iodine in non-aqueous solvents vary, according to the solvent, both in colour and in chemical properties has been known for a very long time: and although it has become generally recognised that the essential difference between a purple solution and a brown one lies in the presence in the latter of loose solvent–solute complexes, usually termed solvates, the structure of these complexes and the circumstances which determine their formation remain obscure.

The formation of an iodine–solvent complex is clearly not a matter of simple electrostatic solvation by polar solvent molecules, for it has little to do with the dielectric constant of the solvent, but rather does it appear to be a consequence, on the one hand, of the amphoteric nature of iodine and the electronic structure of the positive univalent iodine cation, and on the other hand, of the electron-donor characteristics of the solvent molecules.

It is well established that iodine can exist, not only as the more familiar negative iodide ion, but also as a univalent cation (cf. Gmelin, " Handb. d. anorg. Chem.", 8 Aufl., Nr. 8, 454 ff., Berlin, 1933). The first indication of the positive nature of iodine was given by Faraday (*Phil. Trans.*, 1833, 506), who showed that its liquid monochloride would conduct electricity and that iodide was liberated at the negative pole. Electrochemical investigations by later workers have confirmed completely the presence of the iodine cation in ICI, either in the fused state or when dissolved in polar inorganic solvent. Even dissolution of ICI in a non-polar solvent such as carbon tetrachloride or *cyclo*hexane will bring about an increase in the ionic character of the molecule (Fairbrother, *J.*, 1936, 847).

Iodide hydroxide, IOH, usually called "hypoiodous acid", is rather more basic than acidic: $K_a = [H^+][IO^-]/[IOH] = 2—3 \times 10^{-11}$ at 25° (Furth, *Z. Elektrochem.*, 1922, **28**, 57) and $K_b = [I^+][OH^-]/[IOH] = 3{\cdot}2 \times 10^{-10}$ at 25° (Murray, *J.*, 1925, **127**, 885). Cofman (*J.*, 1919, **115**, 1040) showed conclusively that this hydroxide is the active substance in the iodination of phenols, and clearly recognised that its properties showed it to be the hydroxide of a positive iodine ion.

Further, Carlsohn (*Angew. Chem.*, **45**, 580; 1933, **46**, 747), by treating the silver or mercurous salt of the appropriate acid with the calculated amount of iodine and a slight excess of pyridine or of one of its derivatives dissolved in some non-aqueous solvent, has prepared a whole series of crystalline oxy-acid salts of iodine; half the iodine in this reaction is precipitated as an insoluble iodide and the remainder forms a stable salt of a univalent iodine cation. Even from a solution of iodine in pyridine alone, an unstable compound PyI_2 may be precipitated by the addition of water (Waentig, *Z. physikal. Chem.*, 1909, **68**, 513).

It would appear that the formation of these compounds is a result of the strongly donor character of the basic nitrogen lone-pair of electrons, which stabilise the positive iodine ion, and although similar compounds do not appear to have prepared from other brown solutions of iodine, nevertheless it is not unreasonable to suppose that—parallel with the shift towards the violet of the visible absorption band—some polarisation may occur also in other basic solvents.

The mechanism by which such a process can occur may be understood by a consideration of the electronic structures of the iodine molecule and the iodine ions.

The wave function representing the single valence bond in a homonuclear diatomic molecule A–A can be written:

$$\Psi = a\psi_{A:A} + b\psi_{A^+A^-} + b\psi_{A^-A^+}$$

(Pauling, " The Nature of the Chemical Bond ", Cornell, 1940, p. 47), in which the squares of the coefficients *a* and *b* represent the contributions respectively of the purely covalent and of the ionic structures in which both valency electrons are associated with the same nucleus.

In the hydrogen molecule it is estimated that each of the two ionic structures H^+H^-, H^-H^+ makes a contribution of about 2% to the normal state of the molecule. There is, however, not much evidence as to the amount of ionic character of other single bonds between like atoms (Pauling, *op. cit.*), but although considerations of the energy required to convert, for instance, an extreme covalent Cl^-Cl pair into an ion-pair might make it appear that the ionic terms make very little contribution to the normal state of the chlorine, yet other considerations suggest that in some cases, especially in the case of iodine, the ionic contribution may be quite significant. Energy calculations show that it requires only about 15 kcals./mol. more to convert a gaseous iodine molecule into an ion-pair than to form an ion-pair from a gaseous ICl molecule, which undergoes solvolytic ionisation with relative ease.

Moreover, there is evidence to show that the valency electrons in the iodine molecule are relatively easily polarised, since the combination of two neutral iodine atoms to form a molecule is accompanied both by development of visible colour and by a marked increase in refractivity: atomic iodine is colourless, and only absorbs radiation of a shorter wave-length than 2300 A. (v. Angerer and Joos, *Ann. Physik*, 1924, **74**, 756), whilst the enhanced polarisability of the electrons in molecular iodine is shown by the work of Braun and Hölemann (*Z. physikal. Chem.*, 1936, *B*, **34**, 357). These authors made careful interferometer measurements of the refractivity of gaseous iodine from 150° to 1030° for the red hydrogen line ($\lambda = 6563$ A.) and found that the atomic refractivity was $13{\cdot}4 \pm 0{\cdot}2$ c.c. whilst the molar refractivity of the undissociated diatomic molecule was $32{\cdot}2 \pm 0{\cdot}2$ c.c. These measurements were necessarily carried out still in the region of absorption, for the bands extend far into the red, with the maximum absorption in the green (*ca.* 5000 A.), but the earlier work of Cuthbertson (*Phil. Trans.*, 1914, *A*, **213**, 1) on the refractivities of the halogens at a number of wave-lengths indicates that this high refractivity is not simply a matter of anomalous dispersion, for there appear to be no sudden changes of the refractivities of the halogens in passing through the absorption bands.

The refractivity of gaseous atomic iodine is closely similar to the atomic refractivity of iodine in an organic iodide (13·76 c.c. for H_α; Eisenlohr, *Z. physikal. Chem.*, 1911, **75**, 585), so that the refractivity of the iodine molecule is some 20% greater than the sum of the refractivities of the separated atoms or of two single electron-pair-bonded iodine atoms.

Two separate neutral iodine atoms together contain two 5*p* orbitals, each containing a single electron. When the two atoms come together to form a molecule, these two electrons may occupy a molecular orbital composed of the two 5*p* atomic orbitals to form a normal covalent bond or, somewhat less easily since the process is endothermic by nearly 2·5 e.v., to form an ion pair in which the two valency electrons occupy, with paired spins, a single 5*p* orbital leaving the other vacant, *i.e.*, I^+I^- or I^-I^+. The actual iodine molecule is a hybrid of these three structures.

Further, a molecule A, of a second substance, which possesses a sufficiently mobile pair of electrons, *e.g.*, a lone-pair, can form a co-ordinate bond with the atom which has a vacant 5*p* orbital, and thus its approach to the iodine molecule would stabilise one of the ionic structures. If the 5*p* orbital of the acceptor atom is wholly utilised in forming the co-ordinate bond, it will no longer be available for the iodine valency electrons, which will then pass to the 5*p* orbital of the further atom and the structure become wholly ionic : $A:I^+.I^-$. On the other hand, if the wave function of the donor electrons is such as to overlap the 5*p* orbital in question only to a limited extent, a new composite molecule will be formed in which the iodine is polarised by attachment to the donor molecule. This in terms of valence-bond theory may be described by saying that the relative contribution of one of the ionic forms had been increased. When iodine is dissolved in a medium which is both highly basic and polar, some actual electrolytic dissociation may occur, the energy necessary for the ionisation of the neutral molecule being supplied by the energy of co-ordinate bond formation and of solvation of the resulting ions.

It is suggested that the form of the iodine " acceptor " orbital is labile and that the iodine molecule adjusts itself to accommodate the donor electrons. Thus the degree of polarisation of the iodine and the strength of the solvent–solute bond will depend on the donor or " basic " (cf. Lewis, " Valence and the Structure of Atoms and Molecules ", New York, 1923, p. 142) character of the solvent. This in turn would account for the experimental observation that the visible absorption band is most displaced towards the violet (*i.e.*, the solution is browner) in basic solvents and hardly displaced at all in highly polar but non-basic solvents like the nitro-paraffins. Iodine forms an electrically conducting solution in dry pyridine (Audrieth and Birr, *J. Amer. Chem. Soc.*, 1933, **55**, 668) but a non-conducting solution in nitrobenzene unless a trace of moisture is present (Bruner and Galecki, *Z. physikal. Chem.*, 1913, **84**, 513). It seems very improbable that the solutions of iodine are of two distinct types only—purple and brown—as suggested by Lachman (*J. Amer. Chem. Soc.*, 1903, **25**, 50), rather that a more or less continuous series exists according to the basicity of the solvent. That the solvent–iodine bond is often of a weak nature is shown by the sensitivity of the colour of many solutions to a change of temperature, the colour becoming more purple or less brown with rise of temperature, and *vice versa*.

The ionisation and dissociation of iodine into *separate* positive and negative ions has been postulated by several authors to account for experimental observations. Lewis (*op. cit.*, p. 83) pointed out that the octet theory offered an explanation of this ionisation into an anion with a complete octet and a cation with six valency electrons which would account for the electrical conductivity of molten iodine; and Winther (*Z. physikal. Chem.*, 1929, *B*, **3**, 299) found it necessary to assume the existence of I^+ in aqueous solutions in order to account quantitatively for the distribution of iodine between carbon tetrachloride and water or aqueous potassium iodide or hydrochloric acid.

It has now been demonstrated, by means of dielectric-polarisation measurements, that when iodine is dissolved in a medium of zero or low polarity but possessing bonds or groups with electron-donor character, there results a polarisation of the iodine, which is accompanied by the formation of a red or brown solution. In *cyclo*hexane, which has no electron-donor character, the dipole moment is zero and the colour is purple.

The interpretation of measurements of dielectric polarisation in polar basic solvents, which also form red or brown solutions, is more difficult, and indeed such measurements may be impracticable on account of the electrolytic dissociation of the ionised iodine. In this connection may be cited the work of Higasi (*Sci. Papers Inst. Phys. Chem. Res. Tokyo*, 1934, **24**, 57), who found the moment of iodine in diethyl ether to be 0·7 D. but stated that the results were less reliable than for other solutes in ether because "the ether solution of iodine is found to be a little conductive".

Several more or less tentative suggestions have been put forward (*e.g.*, Williams, *Physikal. Z.*, 1929, **29**, 174; Dewar, *J.*, 1946, 406) inferring some degree of ionisation of iodine in benzene solution on the basis of its abnormal colour and dipole moment. The available evidence, however, regarding the magnitude or even the existence of such a dipole moment in benzene and other non-polar solvents is extremely unsatisfactory and conflicting.

Williams and Allgeier (*J. Amer. Chem. Soc.*, 1927, **49**, 246) measured the polarisation of iodine in benzene at 25° over the range of its solubility and gave the molar polarisation as 60·2 c.c. at each concentration. Estimating the electronic polarisation as 20 c.c., they ascribed to iodine a moment of 1·4 D. In a later paper, Williams (*Physikal. Z.*, 1928, **29**, 174) took the electronic polarisation as 28 c.c., giving (on the former polarisation figures) a moment of 1·2 D.; the same moment is given for carbon disulphide solutions on the basis of polarisation data obtained by Williams and Ogg (*J. Amer. Chem. Soc.*, 1928, **50**, 94).

The next investigation was by Müller and Sack (*Physikal. Z.*, 1930, **31**, 815) who, without giving any experimental figures, state that the moment in hexane and *cyclo*hexane is zero and in benzene 1·0 D. In a later paper (*ibid.*, 1933, **34**, 689) Müller gives the total polarisation figures—again without any details of individual measurements—as 20 c.c. in hexane, 20 c.c. in *cyclo*hexane, 39 c.c. in carbon tetrachloride, 50 c.c. in benzene, 32 c.c. in carbon disulphide, with a total molar refraction of 28·5 c.c. It may be observed that here the total polarisation in hexane and *cyclo*hexane is given as less than the refractivity, whilst the values in benzene and in carbon disulphide differ widely from those quoted by Williams.

Finally, from a study of the dielectric polarisation of iodine in benzene, in five concentrations measured over a temperature range of 50° (from 15° to 65°), Kaftanow Wassiliew, and Syrkin (*Acta Physicochim. U.R.S.S.*, 1937, **7**, 75) conclude that the dipole moment of iodine in benzene is zero and that their results "refute the hypotheses which were formerly made to the effect that the dipole moment is due to some kind of associated compounds".

A close examination of their experimental results, however, reveals a fallacy in the argument. They obtain an average molar polarisation of the iodine of 41·12 c.c., which does not differ greatly from the figure (38·5 c.c.) obtained in the present work. They argue that the moment calculated from this figure in the usual manner, assuming an electronic polarisation of 32 c.c., which would be 0·66 D., would mean in turn that the molar polarisation ought to diminish by 1·4 c.c. over the temperature range of measurement, and, which they state, they do not observe. This apparent temperature-independent polarisation, however, is obtained by averaging the polarisation *at each temperature* over all the concentrations. A rearrangement of the data to show the effect of change of temperature on polarisation *in each solution* reveals that the two most concentrated solutions, which are the most significant, actually do show a decrease of polarisation, of 1·16 and 2·24 c.c. respectively, and it is only the less significant results in the weaker solutions, where the effect of experimental error is greatly magnified, which give the impression, by this method of averaging, of a temperature-independent polarisation.

In Table I are given the results of measurements of the dielectric polarisation of iodine in a number of solvents of zero or low polarity and of varying "basic" character; f_2 is the mol.-fraction of iodine, ε and d respectively the dielectric constant and density of the solution, and P_2 the molar polarisation of the iodine calculated in the usual manner from the difference between the total polarisation and the fractional polarisation of the solvent.

The low solubility and low polarisation of iodine in *cyclo*hexane, coupled with the maximum attainable precision of measurement of ε and d, impose an uncertainty of about ± 1 c.c. in the value of P_2 in this solvent. It is noteworthy, however, that this value (31 c.c.), which corresponds to the refractivity at zero frequency, agrees much more closely with the refractivity of gaseous iodine than with the lower value appropriate to electron-pair-bonded atoms.

Measurements in *cyclo*hexene were made difficult by the photosensitivity of the solutions which rapidly faded even in diffused daylight. The solutions were therefore made up in black-painted flasks and exposed to light as little as possible. A further complication in the case of *cyclo*hexene is the slow spontaneous change undergone by the solvent itself, even under conditions of complete exclusion of moisture, though not of dry air. This results in a slow increase of both ε and d and necessitates blank determinations of the solvent polarisation each day.

In Table II are calculated the apparent moments of iodine in the several solvents. A large number of refractivity measurements were made on the solutions. The results were grouped

TABLE I.

Iodine in cyclo*hexane.*

f_2.	ϵ.	d.	P_2 (c.c.).
0·0000	2·0140	0·7732	—
0·001931	2·0151	0·7767	30·0
0·002938	2·0161	0·7786	32·3
0·003540	2·0164	0·7798	30·8
0·003780	2·0164	0·7802	30·7
		Average	31 c.c.

Iodine in benzene.

f_2.	ϵ.	d.	P_2 (c.c.).
0·0000	2·2727	0·8732	—
0·004723	2·2790	0·8839	37·1
0·007030	2·2823	0·8891	37·8
0·008982	2·2853	0·8934	38·3
0·01279	2·2913	0·9018	39·9
0·01919	2·3006	0·9162	39·7
		Average	38·5 c.c.

Iodine in p-*xylene.*

f_2.	ϵ.	d.	P_2 (c.c.).
0·0000	2·2596	0·8569	—
0·005201	2·2666	0·8654	46·3
0·006610	2·2689	0·8677	47·3
0·01442	2·2798	0·8803	47·4
0·01879	2·2861	0·8878	46·6
0·01985	2·2871	0·8893	46·6
		Average	47 c.c.

Iodine in cyclo*hexene.*

f_2.	ϵ.	d.	P_2 (c.c.).
0·0000	2·2200	0·8062	—
0·007355	2·2381	0·8219	55·3
0·01061	2·2470	0·8290	56·0
0·0000	2·2236	0·8064	—
0·01871	2·2716	0·8466	56·0
0·0000	2·2244	0·8065	—
0·007662	2·2435	0·8230	54·6
0·01431	2·2624	0·8372	57·7
		Average	56 c.c.

Iodine in 1 : 4-*dioxan.*

f_2.	ϵ.	d.	P_2 (c.c.).
0·0000	2·2118	1·0277	—
0·005368	2·2294	1·0395	65·8
0·007975	2·2385	1·0452	66·7
0·008049	2·2379	1·0452	65·7
0·01097	2·2492	1·0518	67·4
0·01350	2·2571	1·0572	66·8
		Average	66·5 c.c.

Iodine in di*iso*b*utylene.*

f_2.	ϵ.	d.	P_2 (c.c.).
0·0000	2·0908	0·7123	—
0·007133	2·1063	0·7221	75·6
0·009464	2·1114	0·7253	75·4
0·01047	2·1136	0·7268	74·9
0·01263	2·1182	0·7296	75·5
0·01723	2·1287	0·7361	75·4
		Average	75 c.c.

around an average value of about 29 c.c. for H_α (6563 A.), but owing to the opacity of the concentrated solutions, on the one hand, and the uncertainty which necessarily accompanies measurements on dilute solutions, on the other, this figure is probably not better than ± 1 c.c. Since, however, the total dielectric polarisation in *cyclo*hexane, which has no basic or donor properties, and in which the iodine dissolves to give a purple solution, presumably of symmetrical dipole-free iodine molecules, is 31 ± 1 c.c., this figure has been taken for P_{e+a} in the calculation of the apparent dipole moment. An error of ± 1 c.c. would not affect the moments as given, which are expressed only to the first decimal place.

TABLE II.

Solvent.	Colour.	P_2 (c.c.).	P_0 (c.c.).	μ (D).
*cyclo*Hexane	Purple	31	0	0·0
Benzene	Reddish purple	38·5	7·5	0·6
p-Xylene	Red	47	16	0·9
*cyclo*Hexene	Red-brown	56	25	1·1
1 : 4-Dioxan	Brown	66·5	35·5	1·3
Di*iso*butylene	Red-brown	75	44	1·5

It should be emphasised that these are only the apparent moments, since the polarisation includes also the effect of electronic shifts within the donor molecule. A quantitative correlation between the colour of the solution and the magnitude of the apparent dipole moment is therefore not to be expected. For instance, dilute solutions in 1 : 4-dioxan appear browner than solutions in *cyclo*hexene or in di*iso*butylene. The evidence for the formation of polar complexes in the red and the brown solutions is, however, unmistakable.

Of especial interest is the evidence of the bonding power of aromatic and ethylenic bonds. In these compounds the donor electrons are probably the π electrons, as suggested by Dewar (*loc. cit.*) for the case of benzene. It may be noted that a greater total electronic shift occurs in the case of ethylenic compounds, where the π electrons are less firmly bound than in the benzene ring.

EXPERIMENTAL

Materials.—cyclo*Hexane.* A commercial product was shaken with concentrated sulphuric acid, to which about 10% of " 10% oleum " had been added, for more than 12 hours : very little browning occurred. It was then washed, kept over potassium hydroxide pellets for a week, then set aside for several weeks in contact with phosphoric oxide, and fractionated through an efficient column in a stream of nitrogen, dried by passage through a coil immersed in liquid air; b. p. 81·1° ± 0·1°/757 mm.

Benzene. " AnalaR " Benzene was fractionally frozen three times to remove homologues, kept for several months over phosphoric oxide, and fractionated in dry nitrogen as above; b. p. 80·1° ± 0·1°/762 mm.

p-*Xylene.* A commercially pure product was dried by long contact with phosphoric oxide, and fractionated in dry nitrogen; b. p. 137·3° ± 0·1°/748 mm.

cyclo*Hexene.* A commercial product, after a preliminary fractionation, was refluxed for 12 hours over sodium, and fractionated from fresh sodium in a stream of dry nitrogen; b. p. 82·2° ± 0·2°/758 mm.

1 : 4-*Dioxan.* A commercial product was refluxed with ~ 10% of its volume of N-hydrochloric acid in a stream of nitrogen to decompose the acetal and remove the acetaldehyde (cf. Eigenberger, *J. pr. Chem.*, 1931, **130**, 75). It was then treated with potassium hydroxide pellets until no further water separated on standing and the pellets did not adhere, refluxed over sodium for two hours and fractionated in a stream of nitrogen, and finally refluxed for 6 hours over potassium and again fractionated from potassium in a stream of dry nitrogen; b. p. 100·3° ± 0·1°/750 mm.

*Di*iso*butylene.* A sample kindly presented by Messrs. Imperial Chemical Industries Ltd. (Billingham) and consisting originally of about 80% of 2 : 2 : 4-trimethylpent-4-ene and about 20% of the Δ^3-isomer was given an initial drying over anhydrous sodium sulphate, refluxed over sodium for two hours, and over potassium for six hours, and finally distilled from potassium in a stream of dry nitrogen; b. p. 101·5° ± 0·1°/748 mm.

Iodine. " AnalaR " Iodine was resublimed in a current of dry nitrogen.

All solvents were stored over anhydrous magnesium perchlorate in vessels of the form previously described (Part IV, *J.*, 1945, 503).

Measurements.—Dielectric constants and densities were measured as previously described (Part IV, *loc. cit.*). Refractive indices were measured by a Pulfrich refractometer in which the usual silvered immersion heater was replaced by a glass heater (Fairbrother, *J.*, 1932, 43) to prevent chemical action by the iodine solutions.

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