40. *Electrolytic Dissociation Processes. Part VI. The Dielectric Polarisation of Iodine Cyanide and the Ionisation of the Cyanogen Halides.*

By Fred Fairbrother.

Iodine cyanide undergoes a polarisation in an electron-donor solvent, similar to that shown by molecular iodine. Measurements have been made of its dielectric polarisation in carbon tetrachloride, benzene, di*iso*butylene, and dioxan, and of the ultra-violet light absorption in carbon tetrachloride, di*iso*butylene, and dioxan. The behaviour of the cyanohalogens as halides or as cyanides is due, not to differences in type of bonding, but to differences in solvent–solute interaction in a basic solvent and to the energy relationships involved in ionisation and in the particular reactions.

The observation that the homopolar valency bond in molecular iodine becomes polarised on dissolution of the iodine in a medium which possesses some basic or electron-donor character, even though of low dielectric constant, such as dioxan, benzene, *p*-xylene, or an olefin (Fairbrother, this series, Part V, *J.*, 1948, 1051) suggested that a similar phenomenon might be observed with iodine cyanide, especially if the structure implied by this name, *i.e.*, I^+CN^- made a substantial contribution to the structure of the molecule. The chemical reactions of an aqueous solution of this compound give support to this possibility. Even the usual method of preparation from molecular iodine and an alkali cyanide, *viz.*, $I_2 + CN^- \rightleftharpoons ICN + I^-$, a reaction which is reversed in acid solution, suggests that it is formed in the first place by the union of a cyanide ion with a positive univalent iodine cation stabilised in alkaline solution by the electron-donor hydroxyl ions.

The dielectric polarisation of ICN has now been measured in carbon tetrachloride, benzene, di*iso*butylene, and dioxan, in which, if we assume an electronic polarisation of 19·0 c.c. and neglect the unknown atomic polarisation, the dipole moments are respectively 3·64, 3·76, 4·01, and 4·40 D. In none of these solvents did ICN exhibit appreciable conductivity.

The experimental data are recorded in the following tables, in which w_2 is the weight fraction of solute, f_2 the mol.-fraction of solute, ε the dielectric constant, d_4^{25} the density, and P_2 the molar solute polarisation.

ICN in carbon tetrachloride.

$w_2 \times 10^6$.	f_2.	ε.	d_4^{25}.	P_2 (c.c.).
0	0·000	2·2268	1·5847	—
1469	0·001477	2·2510	1·5851	288
1549	0·001558	2·2526	1·5854	289
2071	0·002090	2·2619	1·5856	292
2698	0·002713	2·2727	1·5860	292
3226	0·003235	2·2828	1·5863	297
			Average	292

$P_0 = 273 \pm 2$ c.c.; $\mu = 3{\cdot}64$ D.

ICN in benzene.

$w_2 \times 10^6$.	f_2.	ε.	d_4^{25}.	P_2 (c.c.).
0	0·000	2·2727	0·8732	—
8,222	0·004216	2·3577	0·8780	308
12,852	0·006605	2·4082	0·8804	311
14,056	0·007228	2·4219	0·8813	311
24,462	0·01264	2·5423	0·8874	312
24,584	0·01271	2·5454	0·8877	313
			Average	311

$P_0 = 292 \pm 1$ c.c.; $\mu = 3{\cdot}76$ D.

ICN in di*iso*butylene.

0	0·000	2·0891	0·7134	—
3589	0·002635	2·1206	0·7151	353
3723	0·002733	2·1218	0·7153	350
4393	0·003227	2·1276	0·7156	351
5334	0·003919	2·1364	0·7162	352
			Average	351·5

$P_0 = 332{\cdot}5 \pm 1$ c.c.; $\mu = 4{\cdot}01$ D.

ICN in dioxan.

0	0·000	2·2124	1·0275	—
11,934	0·006910	2·4062	1·0351	404
13,275	0·007690	2·4250	1·0358	398
16,355	0·009487	2·4784	1·0378	398
20,558	0·01195	2·5458	1·0404	391
21,572	0·01254	2·5639	1·0411	391
28,664	0·01671	2·6970	1·0457	379
30,563	0·01780	2·7097	1·0469	377

${}_{\infty}P_2 = 420$ c.c.; ${}_{\infty}P_0 = 401$ c.c.; $\mu = 4{\cdot}40$ D.

The polarisations and moments have been calculated by the usual Clausius–Mosotti–Debye method. Only in dioxan was there any noticeable change of polarisation with concentration, and in this the molar solute polarisations were extrapolated to infinite dilution against the weight fraction w_2; in the remaining solvents the polarisations were averaged. The extrapolation to infinite dilution of the dielectric constants and densities of the solutions, with a view to using the respective intercepts as solvent parameters (cf. Halverstadt and Kumler, *J. Amer. Chem. Soc.*, 1942, **64**, 2988), gave results which were not significantly different from measurements on the pure solvents, which were therefore used in the calculations. A single large sample (2—3 l.) of each solvent was used for all measurements and kept throughout with its vapour in contact with anhydrous magnesium perchlorate (Fairbrother, *J.*, 1945, 503). Cryoscopic measurements in benzene by Zappi (*Bull. Soc. chim.*, 1930, **47**, 453) and distribution measurements between water and carbon tetrachloride by Yost and Stone (*J. Amer. Chem. Soc.* 1933, **55**, 1889) indicate a normal molecular weight for ICN in these solvents; we may presume the like for the remaining two.

There do not appear to be any recorded measurements of the dielectric polarisations of ICN in the vapour state. Zwartsenberg and Ketelaar (*Rec. Trav. chim.*, 1942, **61**, 877) have measured the dipole moment in benzene solution, which solvent they state " was chosen because solutions in other solvents showed a considerable electrical conductivity." They obtained a value of $\mu = 3{\cdot}82$ D. by the usual Debye method, neglecting atomic polarisation, or $\mu = 3{\cdot}77$ D. assuming an atomic polarisation of 8·3 c.c., which was derived as the mean of the atomic polarisation in molecular iodine and in molecular cyanogen. This method of averaging P_A however, implies an additive character which is not strictly justifiable, and in the absence of direct evidence, the atomic polarisation of ICN must be regarded as an unknown quantity.

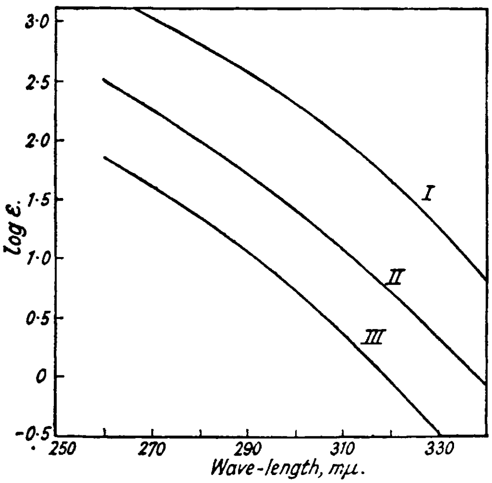
For comparison, therefore, the dipole moments in the several solvents have been calculated with the neglect of atomic polarisation, inclusion of which may reduce the moments given by something under 0·05 Debye unit. The electronic polarisation (Na_D) has been taken as 19·0 c.c. On the one hand, the sum of the partial refractivities of covalently bonded iodine (Eisenlohr, *Z. physikal. Chem.*, 1911, **75**, 585) and of CN derived from the molar refractivity of HCN (Watson and Ramaswamy, *Proc. Roy. Soc.*, 1936, *A*, **156**, 144) is (13·90 + 5·16) = 19·06 c.c., whilst direct determinations of the refractivity, for Na_D, give 19·00 ± 0·05 c.c. in benzene (Zwartsenberg and Ketelaar, *loc. cit.*) and a mean of 19·10 c.c. in alcohol and chloroform (Zappi, *Bull. Soc. chim.*, 1930, **47**, 537).

It may be observed that dissolution of ICN in the electron-donor solvents causes a significant increase in dielectric polarisation; in dioxan it is over 40% greater than in carbon tetrachloride. ICN is very freely soluble in dioxan but only about 0·5 g. dissolves in 100 g. of carbon tetrachloride. It may also be observed that, as with molecular iodine, the π electrons of the ethylenic bond in di*iso*butylene are more effective in bringing about the polarisation than the aromatic electrons of benzene.

Further evidence of solvent–solute interaction is provided by the ultra-violet light absorption of ICN in these solvents. In the case of molecular iodine the shift in the absorption on dissolution in a donor solvent is apparent to the unaided eye; iodine cyanide absorbs only in the ultra-violet.

The ultra-violet light absorption of ICN and BrCN in ethanol and chloroform was studied by Gillam (*Trans. Faraday Soc.*, 1933, **29**, 1132), who found that the absorption curve of ICN, which discloses no maximum down to 240 mμ, is displaced towards the shorter wave-lengths in ethanol as compared with chloroform. There was no evidence of a similar shift in BrCN.

The ultra-violet light absorption of solutions of ICN in carbon tetrachloride, di*iso*butylene, and dioxan has now been measured by a Beckman photoelectric spectrophotometer. The absorption curves (see figure) show a marked displacement towards the shorter wave-lengths in the electron-donor solvents.



I. *Carbon tetrachloride.*
II. *Di*iso*butylene.*
III. 1 : 4-*Dioxan.*

Since the bond moment of –CN in the alkyl cyanides is >3 D., the carbon being positive to the nitrogen, whilst the bond moment of –I in the alkyl iodides is ∼1·5 D., the carbon being positive to the iodine, the magnitude of the moment of ICN suggests that in this molecule the iodine atom is the positive end of the dipole. In ICN, therefore, unless the –CN moment is greatly increased, the iodine is much more positive (or less negative) towards the carbon than in the alkyl iodides and co-ordination with donor solvent molecules would be expected to increase the dielectric polarisation, which in fact does occur.

This is further supported by a consideration of the interatomic distances in ICN. These have recently been measured very accurately by Smith, Ring, Smith, and Gordy (*Physical Rev.*, 1948, **74**, 370) by a micro-wave technique. They find the C–I internuclear separation to be 1·995 A., which is considerably shorter than the separation in methyl iodide, 2·139 A. (Gordy, Simmons, and Smith, *ibid.*, p. 243). This they attribute "largely to resonance between the electronic structures $\overset{+}{X}=C=\overset{-}{N}$ and $X-C\equiv N$ which gives the X–C bond some double character."

It is probable that in all the so-called cyanogen halides, the halogen atom is the positive end of the dipole of the gaseous molecule, with a decrease in moment ICN > BrCN > ClCN. There is experimental evidence of the smaller dipole moment of the bromide in benzene solution, 3·13 D. as compared with 3·82 D. (Zwartsenberg, *Rec. Trav. chim.*, 1943, **62**, 148).

The nature of the valency bonds in iodine cyanide and other cyanohalogens has given rise to much discussion (cf. Gmelin, " Handb. anorg. Chem.," 8th Edn., Berlin, 1933, No. 8, p. 457), chiefly based upon their chemical reactions, which have been studied by a number of workers and have led to conflicting theories.

Iodine cyanide is essentially an oxidising agent in aqueous solution, being unaffected by other oxidising agents and giving, when reduced, either free iodine or iodide ion according to the strength and excess of the reducing agent, *e.g.*, $2ICN + H_2SO_3 + H_2O = 2HCN + H_2SO_4 + 2HI$ (Chattaway and Wadmore, *J.*, 1902, **81**, 191) and $ICN + AsO_3^{3-} + 2OH^- = CN^- + AsO_4^{3-} + I^- + H_2O$ (Gutman, *Z. anal. Chem.*, 1924, **65**, 246), iodine being liberated in each case if the ICN is in excess.

If a solution of ICN in carbon tetrachloride or benzene is shaken with an aqueous solution of ferrous sulphate, the organic solvent slowly takes on the characteristic colour of free iodine. An aqueous solution is apparently unaffected by dilute sulphuric acid, but if it is made slightly alkaline and allowed to stand a few moments, on acidification free iodine is separated. Similarly, if pyridine is added to an aqueous solution, a yellow colour quickly develops and again iodine is precipitated on acidification. These latter reactions are presumably due to the formation of iodide and iodate from the unstable IOH or PyIOH respectively, and the subsequent oxidation of the iodide ion by the iodate on acidification. It is to such formation of iodide that the few reactions reported in which ICN behaves as an iodide are doubtless due. Thus, Normand and Cumming (*J.*, 1912, **101**, 1852) report that an aqueous solution of silver acetate very slowly gave a precipitate which was a mixture of silver cyanide, iodide, and iodate and that, when potassium hydroxide was added to the original solution, a copious precipitate of silver iodide appeared.

The reactions of ICN are essentially those of a cyanide of positive iodine : ClCN in contrast behaves as a chloride of cyanogen.

Zappi (*loc. cit.*, p. 453) has pointed out a number of differences between the reactions of ICN and ClCN : that silver nitrate does not react, or reacts very feebly, with ICN dissolved in water, alcohol, ether, or chloroform, but that ClCN slowly reacts, all the chlorine being ultimately precipitated after the lapse of 2—3 hours; that ICN is completely dissociated in (halogen)-acid solution, $ICN + HI = I_2 + HCN$, and (on gentle warming) $ICN + HCl = HCN + ICl$; that ICN gives iodate with potassium hydroxide (as observed by Nef, *Annalen*, 1895, **287**, 316) and a quantitative yield of iodine with potassium iodide, the cyanogen in both cases appearing as potassium cyanide, but that ClCN does not give chlorate or cyanide with potassium hydroxide, or chlorine with HCl; that whilst a ferrous–ferric mixture gives an abundant cyanide reaction with ICN, it gives a completely negative result with ClCN. (It may be noted that the Prussian-blue test is not given on addition of a solution of ICN to one containing ferrous and ferric salts unless it is first made alkaline and subsequently acidified.) Zappi concluded that such facts seem to indicate a difference in constitution between the two compounds.

Striking as these differences in reaction are, they do not, however, form conclusive evidence that there is any fundamental difference *in kind* between the valency bonds in ClCN and in ICN. Indeed, the physical evidence indicates otherwise. Badger and Woo (*J. Amer. Chem. Soc.*, 1931, **53**, 2573) found that the ultra-violet absorption was of the same type for ClCN, BrCN, and ICN, and West and Farnsworth (*J. Chem. Physics*, 1933, **1**, 402) showed that the Raman spectrum of all three compounds is similar.

The manner in which a given molecule will ionise is not a unique function of the structure of the molecule itself, but also of its environment; this behaviour is familiar as amphoteric reaction in acid–base systems.

Consider the alternative modes of ionisation of ClCN and ICN in a pure solvent. The energies involved in the ionisation and subsequent electrolytic dissociation may be divided into the following steps :

(A) Formation of halide anions and cyanogen cations :

$$e.g.,\ ICN \xrightarrow{a} I_g + CN_g \xrightarrow{b} I_g^- + CN_g^+ \xrightarrow{c} I_s^- + CN_s^+$$

(*a*) Energy of dissociation of dissolved ICN to $I_g + CN_g$.
(*b*) Ionisation potential of $CN_g \longrightarrow CN_g^+$ — electron affinity of $I_g \longrightarrow I_g^-$.
(*c*) Sum of solvation energies of CN_g^+ and I_g^-.

(B) Formation of halide cations and cyanogen anions :

$$e.g.,\ ICN \xrightarrow{a'} I_g + CH_g \xrightarrow{b'} I_g^+ + CN_g^- \xrightarrow{c'} I_s^+ + CN_s^-$$

(*a'*) Energy of dissociation of dissolved ICN to $I_g + CN_g$.
(*b'*) Ionisation potential of $I_g \longrightarrow I_g^+$ — electron affinity of $CN_g \longrightarrow CN_g^-$.
(*c'*) Sum of solvation energies of I_g^+ and CN_g^-.

Since *a* and *a'* are the same, the course of the ionisation is determined by whether $(c - b)$ or $(c' - b')$ is the greater. In NaCN and KCN, which have a rock-salt structure at room temperature, the CN^- ion is believed to achieve spherical symmetry by rotation. The edge of the unit cell in KCN is closely similar to that in KBr, so that the rotating CN^- ion must have an effective radius which is close to that of the Br^- ion (cf. Verweel and Bijvoet, *Z. Krist.*, 1938, **100,** 201 ; and W. G. Palmer, "Valency," Cambridge, 1944, p. 54). It seems probable, therefore, that the ionisation potential and electron affinity of the cyanogen radical may also be similar to those of the bromine atom. The chlorine atom, however, is very much smaller than the iodine atom, its ionisation potential is 2·35 volts greater and its electron affinity 0·53 volt greater than those of iodine.

Consequently, whilst the ionisation of ClCN into Cl^+ and CN^- may be much more endothermic than into$^-$ Cl and CN^+, the ionisation of ICN into I^+ and CN^- may be less difficult than into I^- and CN^+. The differences in heats of solvation of the ions in the respective alternatives would be insufficient to overcome the difference in endothermicity in the case of ClCN. It follows, therefore, that there should be few if any reactions in which ClCN behaves as a cyanide, but a number in which the energies of solvation or reaction of the resulting ions will be sufficient to bring about the ionisation and reaction of ICN as a cyanide.

In computing the energies of solvation of the cations, it is necessary to take into account not only the electrostatic energy of solvation in a chemically indifferent medium, but also the possibility of bond formation between solvent and solute molecules. This will be especially significant in basic, or electron-donor solvents, which are able to form a co-ordinate bond with a halogen cation.

It would appear that water in itself is not sufficiently basic to bring about the appreciable ionisation of ICN, as shown by the lack of reaction with silver nitrate. This, however, may occur in a much more basic solvent or in aqueous solution in the presence of a strongly electron-donor solute species such as hydroxyl ion.

Clark and Streight (*Trans. Roy. Soc. Canada*, 1928, **22**, [3], 323) report that electrolysis of 0·1M-solutions of ICN in a number of carefully dried organic solvents, acetamide, benzene, acetonitrile, nitrobenzene, methanol, ethanol, nitromethane, aniline, and quinoline, gave iodine at the *anode* and cyanide or cyanogen or paracyanogen at the cathode, but that solutions in pyridine gave iodine at the *cathode* and cyanide at the anode, and that on addition of water iodine again appeared at the anode. It is probable, however, that the last observation was due to the secondary decomposition into iodide and iodate as described above.

The electrical conductivity of iodine cyanide in pyridine was studied carefully by Audrieth and Birr (*J. Amer. Chem. Soc.*, 1933, **55**, 668), who found that it increases with time to give maximum values. The experimental evidence indicated that the reaction between solvent and solute resulted in the primary formation of a non-conducting addition compound which in time changes over into a true quaternary pyridinium salt, 1-iodopyridinium cyanide. A similar mechanism the formation of 1-iodopyridinium iodide would account for the conductivity of molecular iodine in pyridine.

This reaction of pyridine and its stabilising effect on the positive iodine is paralleled by its behaviour in stabilising the univalent iodine cation in the salts prepared by Carlsohn (*Angew. Chem.*, 1932, **45**, 580; 1933, **46**, 747) and by the abnormal positive heat of solution of iodine in pyridine. Heats of solution of iodine in a variety of solvents have recently been measured accurately by Hartley and Skinner (to be published); they find that whereas in hydrocarbons and a number of oxygen-containing solvents, the heat of solution of iodine is negative, yet in pyridine it is positive. A simple test-tube experiment shows that the heat of dissolution of ICN in pyridine is also positive.

BrCN, which occupies an intermediate position, is stated to be un-ionised in water, neutral to litmus, and to give no precipitate with silver nitrate solution. It is soluble in cold concentrated sulphuric, hydrochloric, or nitric acid without decomposition, but is instantly hydrolysed by aqueous alkali hydroxides or carbonates into cyanide, bromide, and bromate; bicarbonates have no action (Williams, "Cyanogen Compounds," London, 1948, 9). Its ultra-violet light absorption (Gillam, *loc. cit.*) shows that there is much less solvent–solute interaction in ethanol than in the case of ICN. Clark and Streight (*loc. cit.*), using Sampey's method (*J. Amer. Chem. Soc.*, 1927, **49**, 2849) for the quantitative determination of positive halogen by titration with stannous chloride, report that BrCN repeatedly titrated as if it contained 89·2% of positive bromine, whilst iodocyanogen gave results corresponding to 99% of positive iodine.

It is to be concluded, therefore, that the positive iodine cation does not pre-exist in the free

ICN molecule, but is formed as it is in molecular iodine, either by a solvolytic ionisation alone in a very basic solvent like pyridine, or in other solvents by the action of some strongly electron-donor species in solution such as the hydroxyl ion in its alkaline hydrolysis, and that the contrasting behaviour of ClCN is not due to any great difference in the electronic structures of the free molecules, but to differences of solvent–solute interaction and of the energies involved in the particular reactions.

EXPERIMENTAL.

Materials.—Iodine cyanide was prepared in the usual manner by the slow addition of iodine to concentrated aqueous potassium cyanide, followed by cooling in a refrigerator, filtration, washing and drying of the crystals. The crude product was purified by sublimation in a current of dry nitrogen, and samples were freshly re-sublimed at a comparatively low temperature immediately before each determination. The final product was snow-white.

Solvents.—Benzene (b. p. 80·1° ± 0·1°/762 mm.), dioxan (b. p. 100·2—100·6°/774 mm.), and di*iso*butylene (b. p. 101·0—102·5°/757 mm.) were purified as described in Part V (*J.*, 1948, 1051). (The di*iso*butylene boiled over a wider range and differed in both dielectric constant and density from that used in Part V, which was from a different source.) Carbon tetrachloride, "for medicinal purposes" (Allbright and Wilson), was dried by long contact with phosphoric oxide and fractionated through an efficient column in a stream of dry nitrogen; b. p. 76·4° ± 0·2°/762 mm.

Measurements.—Dielectric constants and densities were measured at 25·00° as previously described (Part IV, *J.*, 1945, 503).

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