284. *Reactions of Iodine Monohalides in Different Solvents.*

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The course of the reaction between iodine monochloride and phenols varies with experimental conditions: in the absence of a solvent the main reaction is chlorination; in solution it is iodination. Iodine monobromide always acts as a brominating agent. The relation between such reactions and the physical properties of the solvents and reactants is discussed.

It has been recognised for some time that there is a connection between the dielectric constant of a solvent and the type of reaction that usually occurs in it (Hughes and Ingold, *J.*, 1935, 244; Waters, *J.*, 1942, 153; *idem*, " The Chemistry of Free Radicals," Oxford, 1946). Solvents of high dielectric constant favour heterolytic, those of low dielectric constant homolytic, fission of bonds; gaseous reactions nearly always involve homolytic fission. There is, however, a scarcity of examples of the course of a reaction varying steadily as the dielectric constant of the medium is increased.

The interaction of iodine monochloride and salicylic acid affords such an example. The main reaction between the solid acid and iodine monochloride vapour, which is only 0·4% dissociated at 25°, is one of chlorination; in carbon tetrachloride ($\varepsilon = 2{\cdot}2$) iodination predominates; and in nitrobenzene ($\varepsilon = 36$) iodination takes place exclusively. The course of the reaction between iodine monochloride and phenol varies in a similar way.

The effect of a solvent on the polarity of the I–Cl bond was discussed by Fairbrother (*J.*, 1936, 847), who found the dipole moment of iodine monochloride to be 0·8 D. in the vapour phase and 1·5 D. in carbon tetrachloride. From the first ionisation potential of iodine (10·44 e.v.) and the electron affinity of chlorine (3·75 e.v.) he calculated that dissociation of an ICl molecule into infinitely separated I^+ and Cl^- ions requires 6·69 e.v. (*i.e.*, 155 kcals.mol.$^{-1}$) more energy than dissociation into atoms. When the bond breaks during reaction in the absence of a solvent, atoms rather than ions will thus result, and the observed reaction with phenols is the expected one.

Fairbrother also estimated the magnitude of the difference between the two dissociation energies in various solvents and concluded that in a solvent of dielectric constant greater than 3·9 free ions should be formed; a feeble conductivity in chlorobenzene ($\varepsilon = 5{\cdot}8$) was observed. In carbon tetrachloride, the preponderance of iodination when an electron-donating group (OH) is present in the organic molecule indicates that the main reaction involves heterolytic fission of the I–Cl bond. In acetic acid ($\varepsilon = 7{\cdot}1$) and nitrobenzene iodine monochloride yields conducting solutions (Sandonnini and Borghello, *Atti R. Accad. Lincei*, 1937, **25**, 46; Bruner and Galecki, *Z. physikal. Chem.*, 1913, **84**, 513) and in these solvents, in which free ions are present before reaction, iodination alone occurs. Mr. N. Greenwood has recently shown that iodine monochloride in carbon tetrachloride is a non-conductor.

It was pointed out by Gillam and Morton (*Proc. Roy. Soc.*, 1929, *A*, **124**, 610; 1931, *A*, **132**, 154) that solutions of iodine monochloride in solvents of low dielectric constant are usually brown, whilst those in solvents of higher dielectric constant are yellow. A further illustration of the effect of the solvent has been found in the reaction between iodine monochloride and silver perchlorate: in carbon tetrachloride precipitation of silver chloride is exceedingly slow, whilst in nitrobenzene formation of a precipitate is instantaneous, and after four hours is quantitative.

Although iodine monochloride (usually in acetic acid) is widely used for the iodination of phenols and amines, Militzer (*J. Amer. Chem. Soc.*, 1938, **60**, 256) found that in carbon tetrachloride or acetic acid iodine monobromide functions only as a brominating agent. It has now been found that even in nitrobenzene, in which the bromide forms conducting solutions (Bruner and Galecki, *loc. cit.*), the reaction with phenol or salicylic acid is still one of bromination.

Several factors enter into the explanation of this. The electron affinity of bromine (3·56 e.v.) is less than that of chlorine and formation of ions from gaseous atoms would therefore absorb more energy than the corresponding process for the chloride. The energy of solvation of the bromide ion ($r = 1{\cdot}95$ A.) will be less than that of the chloride ion ($r = 1{\cdot}81$ A.) in the same solvent (Webb, *J. Amer. Chem. Soc.*, 1926, **48**, 2589). Iodine bromide is dissociated into free halogens to a much greater extent than iodine monochloride. Bromination by bromine is a much faster process than iodination by the I^+ ion.

The free-energy changes attending the reactions

$$IBr_{(\text{in } CCl_4)} \rightleftharpoons \tfrac{1}{2}I_{2\,(\text{in } CCl_4)} + \tfrac{1}{2}Br_{2\,(\text{in } CCl_4)} \quad (\Delta G = 1{\cdot}75 \text{ kcals.})$$

and

$$ICl_{(\text{in } CCl_4)} \rightleftharpoons \tfrac{1}{2}I_{2\,(\text{in } CCl_4)} + \tfrac{1}{2}Cl_{2\,(\text{in } CCl_4)} \quad (\Delta G = 4{\cdot}02 \text{ kcals.})$$

have been determined by Yost, Anderson, and Skoog (*ibid.*, 1933, **55**, 552) and Blair and Yost (*ibid.*, p. 4489). Since no change in the number of molecules is involved, the degree of dissociation is independent of the concentration; it is 9·5% for the bromide and 0·25% for the chloride. Thermodynamic data for solutions in other solvents are unfortunately not available, but there is no reason to believe that iodine bromide will not always be dissociated into its elements to a much greater extent than iodine monochloride.

In a solution of a phenol and iodine bromide in nitrobenzene, free bromine and I^+ ions will therefore compete for the phenol. Since the bromination of a phenol by bromine is a very fast reaction, whereas iodination by the iodine cation is relatively slow (see, *e.g.*, Lambourne and Robertson, *J.*, 1947, 1167) the resultant reaction is iodine-catalysed bromination, and iodine may be recovered at the end of the reaction.

EXPERIMENTAL.

Materials.—Iodine monochloride was prepared and purified by the method of Cornog and Karges (*Inorg. Synth.*, Vol. I, p. 165). Iodine bromide was made by warming together the theoretical proportions of the elements. Silver perchlorate, obtained according to Hill (*J. Amer. Chem. Soc.*, 1921, **43**, 254) was analysed by precipitation of the silver as chloride (Found: Ag, 51·7. Calc. for $AgClO_4$: Ag, 52·0%). Carbon tetrachloride was dried by distillation; nitrobenzene was dried ($CaCl_2$) and distilled. The phenol and salicylic acid were free from halogen-containing impurities. Soda-lime used for decomposition of organic materials contained a trace of chloride; this was determined and a small correction for halide thus introduced was made and has been incorporated in the results quoted below.

Interaction of Iodine Monochloride and Salicylic Acid.—Iodine monochloride (11·6 g.) and salicylic acid (5·0 g.) were allowed to react in solution in carbon tetrachloride or nitrobenzene, or in the absence of a solvent. In absence of a solvent a large amount of iodine was rapidly liberated on the surface of the salicylic acid; in carbon tetrachloride a little iodine was liberated, and in nitrobenzene no free iodine was detected even by shaking the reaction mixture with starch solution.

After 24 hours, by which time about half of the original oxidising power had disappeared, the reaction mixture was shaken with sodium hydrogen sulphite solution (to remove iodine or unchanged iodine monochloride) and then with aqueous sodium hydroxide. The aqueous extract was separated from the organic solvent and acidified with hydrochloric acid; salicylic acid (unchanged) and its substitution products were extracted with ether. The ethereal extracts were combined and evaporated to dryness, and the product was kept in a desiccator over silica gel for a week. Since the object of the experiment was to identify the type of substitution, no attempt to separate the mixture of organic acids was made. The mixture was finely powdered and thoroughly mixed, and relatively large samples (*ca.* 1 g.) were decomposed by heating them at a red heat with a measured large excess of soda-lime. The product was dissolved in dilute nitric acid and treated with a known excess of 0·1M-silver nitrate; the silver halides were filtered off and weighed, and the silver remaining in solution was precipitated and weighed as chloride. In addition to this quantitative analysis, qualitative analyses were made on the organic products obtained from both salicylic acid and phenol. Results with phenol and iodine monochloride were qualitatively similar to those obtained with salicylic acid.

The product from interaction in absence of a solvent always contained a considerable quantity of chlorine and less iodine; the silver halide precipitate contained 62·4% of Ag (Calc. for AgCl: Ag, 72·3. Calc. for AgI: Ag, 45·9%). This corresponds to a chlorine : iodine ratio in the products of approximately 2 : 1; chlorination is therefore the main reaction.

From carbon tetrachloride solution the product always contained iodine and a little chlorine; the introduction of the chlorine agreed with the observed slight liberation of iodine. The silver halide precipitate contained 52·7% of silver, corresponding to an approximate chlorine : iodine ratio of 1 : 12.

The product from the reaction in nitrobenzene was free from chlorine; the silver halide precipitate contained 46·4% of silver. In one experiment in glacial acetic acid the result was qualitatively similar to that in nitrobenzene; no iodine was liberated during the reaction between iodine monochloride and salicylic acid.

Interaction of Iodine Monochloride and Silver Perchlorate.—When silver perchlorate, dissolved in a little benzene, was added to iodine monochloride in carbon tetrachloride no precipitate appeared for several minutes. When the mixture was kept, a precipitate of silver chloride was produced. In nitrobenzene the appearance of a precipitate was immediate, and within four hours precipitation was complete and no silver remained in solution. By use of equivalent amounts of iodine monochloride and silver perchlorate, the weight of precipitate obtained after filtration in a Gooch crucible and drying at 120° corresponded to a silver content of 72·6%. The reaction may therefore be represented by the equation: $ICl + AgClO_4 = AgCl + IClO_4$.

Reactions of Iodine Bromide.—Militzer's experiments with iodine bromide (*J. Amer. Chem. Soc.*, 1938, **60**, 256) were repeated with nitrobenzene as solvent and phenol and salicylic acid as substances to be halogenated. The organic products contained no more than a trace of iodine. At the end of the brisk reaction between iodine bromide and phenol a large quantity of iodine was precipitated and thiosulphate titration showed that 54% of the original oxidising power remained.

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