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The I–I Bond in Diphenyliodonium Iodide

BY WILLIAM V. MEDLIN

In iodonium compounds iodine apparently forms three bonds, two to carbon atoms and a third to a negative atom such as halogen or oxygen. Some properties of the substance indicate that the third bond is not covalent, but ionic; however, these indications are not conclusive. By x-ray investigation using a radial distribution method, I have verified the ionic structure for crystalline diphenyliodonium iodide; the iodide was chosen for investigation because diffraction produced by the interference of iodine atoms should be much greater than the effect of other atoms in the substance, in view of the relatively great atomic number of iodine. A powder photograph was taken of a sample, mounted with collodion on the outside of a fine tube of low absorbing glass, using copper K radiation filtered through nickel. The intensities of the fifty-one measurable lines, with reflections out to $\sin\Theta = 0.587$, were estimated visually and corrected by means of the Lorentz and polarization factors in the usual manner.

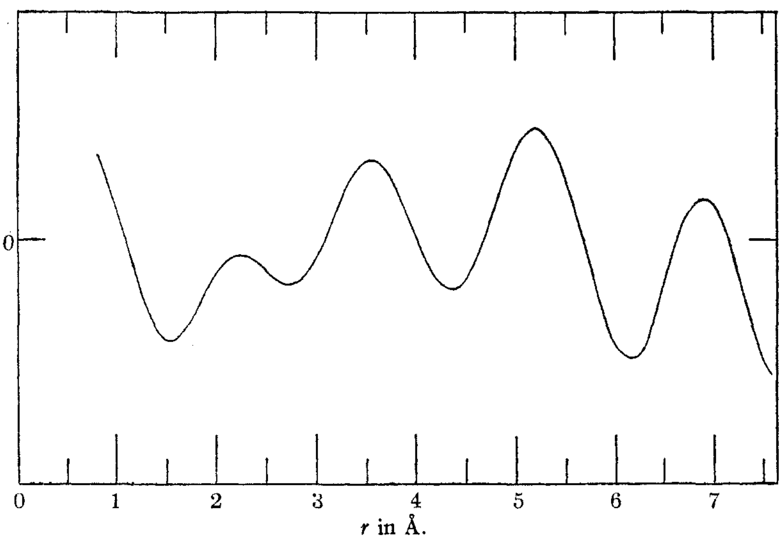

Fig. 1.

The method of analysis used was that introduced by Gingrich and Warren.[1] They showed that for a substance in which all the atoms are identical the average density of atoms about any given atom is given by

$$4\pi r^2\rho(r) = 4\pi r^2\rho_0 + \frac{2r}{\pi}\int_0^\infty s\left(\frac{I(s)}{N\psi(s)} - 1\right)\sin sr\,ds$$

where $s = (4\pi\sin\Theta)/\lambda$ and ρ_0 is the average density of the sample in atoms per cubic centimeter. $I(s)$ is the intensity of reflection, $\psi(s)$ is the intensity of independent unmodified scattering, and N is the number of atoms effectively in the sample. This formula is equally applicable to substances in which the atoms are different from each other, the resulting density function being a superposition of functions each with a different atom as center, and weighted with the scattering power of the central atom. In the case of a crystalline powder radiation is reflected at discrete values of s, so we may replace the integral with a summation

$$4\pi r^2\rho(r) = 4\pi r^2\rho_0 + \frac{2r}{\pi}\sum_{i=1}^{\infty} s_i k_i \sin s_i r$$

where

$$k_i = \int_{\text{line}} \frac{I(s) - N\psi(s)}{N\psi(s)}\,ds$$

k_i is thus closely related to the integrated intensity of the line.

In the present case the series was used, with the corrected estimated intensities in place of k_i. This substitution will give essentially a distribution function of scattering power rather than of atom centers. Because of the increased importance of the lines at large scattering angles, and in view of the low accuracy in the measurements of the corresponding low intensities, a small factor $e^{-B\sin^2\Theta}$ was introduced in order to decrease somewhat the effective intensity of these lines, thus ensuring greater reliability in the result and avoiding a sudden breaking off of the series. The positions of peaks in the resulting curve were found to be independent of the value of this factor; indeed, even omission of the Lorentz factor caused no change in the essential features of the curve.

Figure 1 shows the resulting radial distribution function, with the constant term, $4\pi r^2\rho_0$, subtracted. A small peak is observed at approxi-

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[1] Gingrich and Warren, *Phys. Rev.*, **46**, 368 (1934).

mately 2.24 Å., an important one at 3.55 Å., a third at 5.18 Å. and a fourth at 6.9 Å. The first peak may be attributed to the unresolved C–I and C–C distances, both of which should appear to a smaller extent than I–I distances. Thus it appears that the shortest distance between iodine atoms is 3.55 Å. The electronic structure of the covalent molecule would be similar to that of the triiodide ion, in that both require ten electrons to be assigned to an iodine atom. The I–I distance in ammonium triiodide is 2.8 Å.,[2] and the sum of the covalent radii of the atoms is 2.7 Å.;[3] we would hence expect to find the iodine–iodine distance in diphenyliodonium iodide to be 2.7–2.8 Å. if the bond were covalent. Thus we see that the covalent structure cannot be the correct one. On the other hand, the experimental value of 3.55 Å. is compatible with an ionic structure; the shortest distance between iodine atoms in different molecules in crystalline I_2, with each atom forming one covalent bond, is 3.54 Å., and we would expect a similar distance between an iodonium ion with two covalent bonds and an iodide ion with no covalent bonds.

I am indebted to Mr. E. R. Kennedy for preparing the sample, and to Professor Linus Pauling, who has contributed many suggestions.

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[2] Mooney, *Phys. Rev.*, **45**, 755 (1934).

[3] Pauling and Huggins, *Z. Krist.*, [A] **87**, 205 (1934).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

The Photosynthesis of Hydrogen Chloride

BY J. C. POTTS AND G. K. ROLLEFSON

The photochemical reaction between hydrogen and chlorine has been the subject of numerous investigations in which a wide variety of results has been obtained. The early work was complicated by a failure to work with pure hydrogen and pure chlorine, but even the two most recent investigations show a marked disagreement.[1] The rate laws which have been given are

$$\frac{d(\mathrm{HCl})}{dt} = kI_{\mathrm{abs.}}\,(\mathrm{H_2}) \qquad \text{(Bodenstein and Unger)}$$

$$\frac{d(\mathrm{HCl})}{dt} = \frac{kI^{0.6}_{\mathrm{abs.}}\,({}_2\mathrm{H})}{1 + k'\,(\mathrm{HCl})/(\mathrm{Cl_2})} \qquad \text{(Derived from a formula for } \gamma \text{ given by Norrish and Ritchie)}$$

The effect of extreme drying reported by Coehn and Jung[2] has been shown to be non-existent.[3]

In this paper we are reporting the results of a series of experiments designed to test these rate laws. Most of our results are essentially in agreement with Bodenstein and Unger but we have also succeeded in finding conditions under which the $I^{1/2}_{\mathrm{abs.}}$ law is obeyed.

Experiments have been performed at various temperatures from 140 to 300°K. The apparatus shown in Fig. 1 was used in the lowest part of this temperature range. The reaction vessel (A) was enclosed in the lead radiation shield (B). A stream of cold air, prepared by bubbling dry air through liquid air contained in the space (C) between the bottom of the lead block and the Dewar (D), flowed along the sides of the block (B) and kept it from warming up. A tube (E) provided a means of directing a jet of liquid air directly on the lead block for rapid cooling and a second tube (F) permitted the introduction of liquid air directly into (C). Several sections of copper wire, each 61 meters long (not shown in the figure) wound around the block and the reaction vessel were used both as resistance thermometers and as heating coils. G was a Pyrex window fitted into the lead block. By careful manipulation of this apparatus the temperature could easily be kept constant to better than 0.1°.

In the experiments with this apparatus solid or liquid chlorine was always present, so the reaction could be followed by observing the pressure change; in a few experiments the chlorine and hydrogen chloride were frozen out and the residual hydrogen measured.

For temperatures from 200 to 273°K. the reaction vessel was immersed in a bath of cold methyl alcohol contained in a transparent Dewar flask. At 273°K. and above, water was used instead of methyl alcohol. In these experiments the reaction was followed by removing the water or alcohol

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[1] Bodenstein and Unger, *Z. physik. Chem.*, **B11**, 253 (1930); Norrish and Ritchie, *Proc. Roy. Soc.* (London), **A140**, 112 (1933).

[2] Coehn and Jung, *Z. physik. Chem.*, **110**, 705 (1924).

[3] Allmand and Craggs, *Nature*, **130**, 927 (1932); Rollefson and Potts, THIS JOURNAL, **55**, 860 (1933); Bernreuther and Bodenstein, *Sitzungsber. preuss. Akad.*, 6 (1933); Rodebush and Klingelhoefer, *Proc. Nat. Acad. Sci.*, **18**, 531 (1932).