X-Ray Diffraction by Gaseous Benzene Derivatives

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(Received October 23, 1933)

The Debye method for the determination of interatomic distances in single molecules is applied to ortho and para-dichlorbenzene. Results with monochlorbenzene are used to correct the scattering curves so as to isolate the Cl—Cl scattering. The resulting Cl—Cl curves show good agreement with theoretical curves constructed for distances of 3.0 and 6.25A, respectively. The measurements indicate a plane hexagonal benzene molecule with the chlorine atoms lying in or near the plane.

I T has previously been shown[1] that the positions of peaks in the x-ray scattering curves for ortho and para-dichlorbenzene agree with those in theoretical curves constructed according to Debye's theory.[2] Work of a more quantitative nature has since been in progress and the results may now be reported.

EXPERIMENTAL

A diagram of the scattering camera is shown in Fig. 1. The substance under investigation is heated in the vaporizer B to a temperature somewhat below its boiling point and the vapor carried into the scattering chamber C by a slow current of dry hydrogen. This permits vaporization at a temperature below the softening point of solder (170°) and minimizes decomposition of high boiling samples. The scattering chamber is heated about 15° above the temperature in B. X-rays passing through the slits $S_1 S_2$ enter the scattering chamber at the front window and scattered rays pass through the upper window to the film.

Both windows are sealed by thin nickel foil soldered to the brass container. That over the upper window is bent in a semicircle in order to avoid angular variation of absorption and it serves in
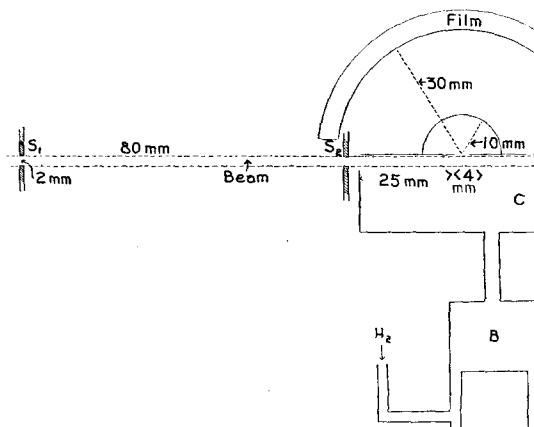
FIG. 1. Gas scattering apparatus.

addition as a filter for the copper radiation used. (It is essential that the filter lie between the scatterer and the film because the fluorescence of the scattering atoms would otherwise obscure interference phenomena.) The thin nickel foil is
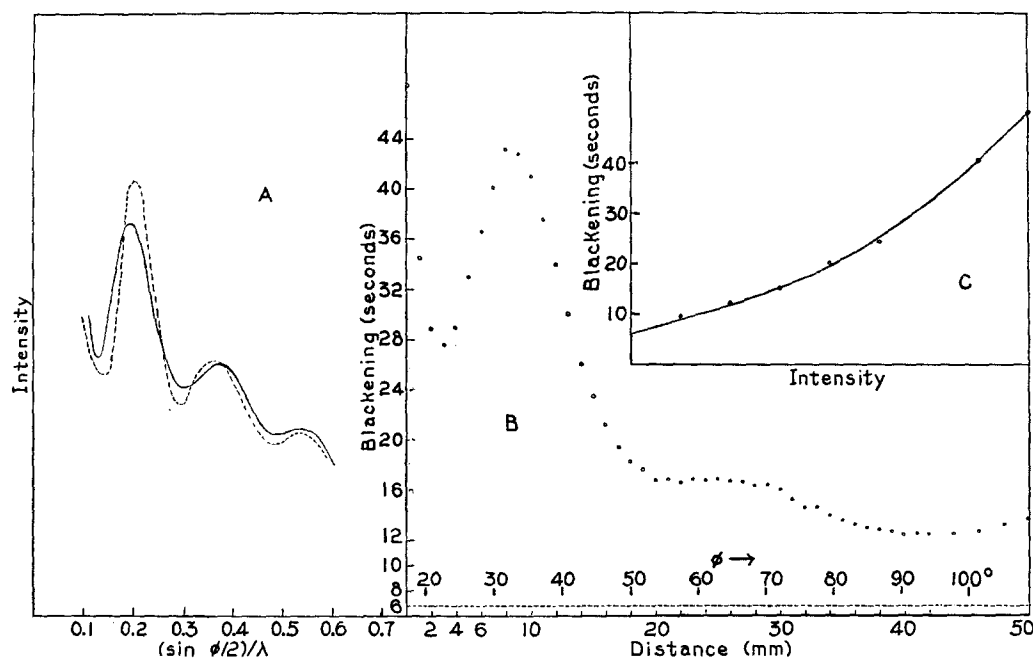
[1] Pierce, Phys. Rev. **43**, 145 (1933).

[2] For a complete discussion of the theory and experimental methods see Bewilogua, Phys. Zeits. **32**, 265 (1931).

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FIG. 2. A, corrected scattering of CCl₄. (Solid curve, experimental; dotted curve, Bewilogua.) B, photometer readings for a typical film. C, intensity-blackening curve for film of 2B.

prepared by electrolysis of a buffered nickel sulfate solution with a molybdenum cathode.[3]

A copper target demountable tube is used as the source of radiation. At 30 kv and 25 m.a. an exposure time of two to six hours is sufficient. The effect of general radiation is only slightly greater at this voltage than at 20 kv and the higher voltage is used because of the great gain in intensity. The relation between photographic blackening and intensity of radiation is determined separately for each film by test spots. These are made by a series of accurately timed exposures for a piece of the same film as the experiment. The two parts of the film are developed simultaneously in a tank. Radiation scattered at 90° from a copper block was used for making the test spots.

Blackening is determined by a photoelectric microphotometer, available through the courtesy of Dr. Elmer Dershem of the Department of Physics, University of Chicago. Experimental film and test spots are measured under identical conditions and a curve of blackening vs. intensity is constructed for the test spots. Blackening

values for the experiment are then read off as intensity values from this curve. Results for a portion of a film for carbon tetrachloride are shown in Fig. 2. B gives the original photometer readings in seconds for 1 mm intervals along the film and C is the test spot curve. A shows the intensity, corrected for polarization by dividing values at each angle by $(1 + \cos^2 \phi)/2$, as a function of $(\sin \phi/2)/\lambda$. Bewilogua's[2] values are shown for comparison as the dotted curve. The general agreement in the position of the inflection points is good, but the intensity values are not so good as those found by Bewilogua. Considerable time was spent in attempting to improve the precision of the intensity measurements. Results were very reproducible in a given blackening range, but perfect agreement could not be obtained for films of widely different photographic blackening and the source of error was not located. This however does not greatly affect the results of the present experiments because no maxima are introduced into the scattering curve by the error. It does render the results in the vicinity of $\phi = 90°$ somewhat uncertain because in making the correction for polarization the factor changes most rapidly there and slight errors in

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[3] Kersten, Rev. Sci. Inst. **2**, 649 (1931).

the intensity curve are magnified. Absence of stray scattering from the camera was proven by an experiment with hydrogen gas. At double the normal exposure time very little blackening was obtained.

Average intensity-angle curves are shown in Fig. 3 for carbon tetrachloride, monochlorbenzene, ortho and para-dichlorbenzene. All are drawn to the same scale but the zero positions are displaced as indicated.

TREATMENT OF RESULTS

The coherent scattering of single molecules may be calculated by the Debye equation

$$I_\varphi \alpha \frac{1+\cos^2 \phi}{2} \sum_1^N \sum_1^N F_i F_j \sin x_{ij}/x_{ij},$$

where $x_{ij} = (4\pi\, d_{ij}\, \sin\, \phi/2)/\lambda$, d_{ij} is the distance from the i-th to the j-th atom, F is the atomic form factor or structure factor, and $(1+\cos^2 \phi)/2$ is the polarization factor. The general method for determining distances d_{ij} is to compare experimental intensity curves with theoretical curves drawn by use of the above equation but this method does not afford a simple and unique solution for such complex molecules as the dichlorbenzenes because of the large number of factors
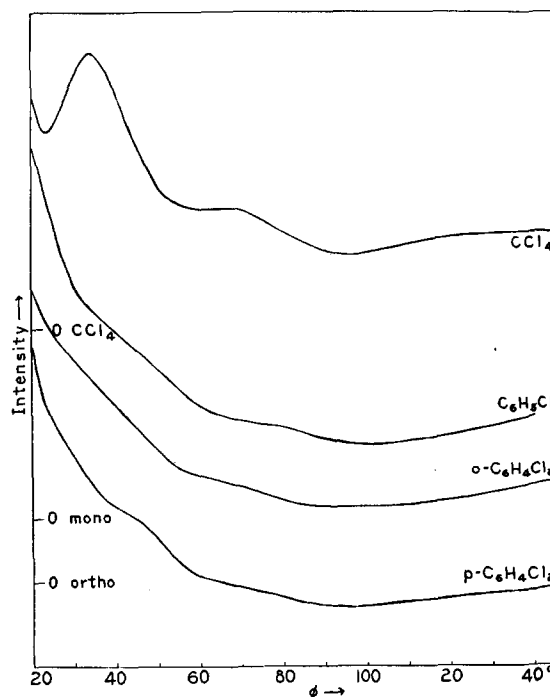

FIG. 3. Experimental intensity curves.

involved. This is shown in Fig. 4 which gives the theoretical intensity curve for each of the components of para-dichlorbenzene. The various scattering curves for the coherent scattering are calculated from the equations:

$$I_{C-C} = 6F_C{}^2 \left[1 + 2\, \frac{\sin x_0}{x_0} + 2\sin \frac{1.73x_0}{1.73x_0} + \frac{\sin 2x_0}{2x_0} \right]; \quad d_0 = d_{C-C} = 1.4\text{A},$$

$$I_{C-Cl} = 4F_C F_{Cl} \left[\frac{\sin x_1}{x_1} + 2\sin \frac{1.54x_1}{1.54x_1} + 2\sin \frac{2.27x_1}{2.27x_1} + \frac{\sin 2.55x_1}{2.55x_1} \right]; \quad d_1 = d_{C-Cl} = 1.8\text{A},$$

$$I_{Cl-Cl} = 2F^2{}_{Cl}[1 + (\sin x_2)/x_2]; \quad d_2 = d_{Cl-Cl} = 6.0\text{A}.$$

F and $(\sin x)/x$ values were obtained respectively from James and Brindley's[4] and Bauer's[5] tables. The incoherent scattering is mainly due to that of the benzene and may be calculated by the method of Heisenberg-Bewilogua.[6] The curve of Fig. 4 is the one given by Bewilogua for benzene.

[4] James and Brindley, Phil. Mag. 12, 81 (1931).

[5] Bauer, J. Opt. Soc. Am. 22, 537 (1932).

[6] Heisenberg, Phys. Zeits. 32, 737 (1931). Bewilogua, Phys. Zeits. 32, 740 (1931).

Inspection of Fig. 4 shows that the scattering is largely determined by the Cl−Cl curve but it is somewhat modified by the C−C and less by the C−Cl curves. This suggests a simple method for isolating the Cl−Cl curve by subtracting from the total the C−C, C−Cl and incoherent scattering. A combined subtraction curve containing the effects of all three may be made either from the theoretical curves of Fig. 4 or experimentally from the scattering of monochlorbenzene. The latter method was thought best because fewer as-
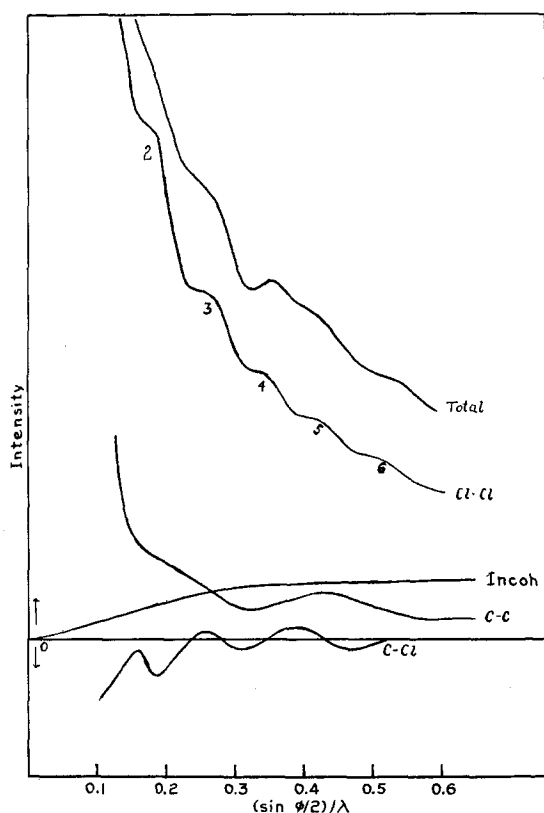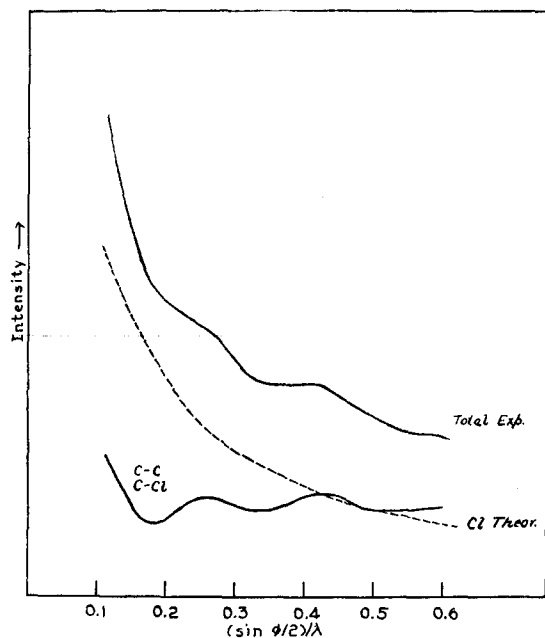
FIG. 4. Theoretical scattering of p-dichlorbenzene.

sumptions are involved and the correction curve was constructed as shown in Fig. 5. Experimental scattering was determined for monochlorbenzene and the values arbitrarily equated at one point to a theoretical scattering curve similar to the one of Fig. 4. Subtraction of James and Brindley's F^2_{Cl} values from this curve leaves a correction curve containing the $C-C$, $C-Cl$ and incoherent scattering. The $C-Cl$ term occurs only one-half as much in this as in the dichlorbenzenes, but the influence of this term is so small that the discrepancy may be neglected.

$Cl-Cl$ curves for ortho and para-dichlorbenzene are obtained by subtracting the correction curve from the respective total scattering curves. These are arbitrarily set at intensity values corresponding to the values of Fig. 4 for the theoretical para-dichlorbenzene curves. The derived $Cl-Cl$ curves are shown as the lower curves of Fig. 6. Corresponding theoretical curves for appropriate distances are shown in the upper curves. Comparison of the two give $Cl-Cl$ distances of 3.0 and 6.25A, respectively. Identification may be made at the first and second theoretical maxima for ortho and the second and third
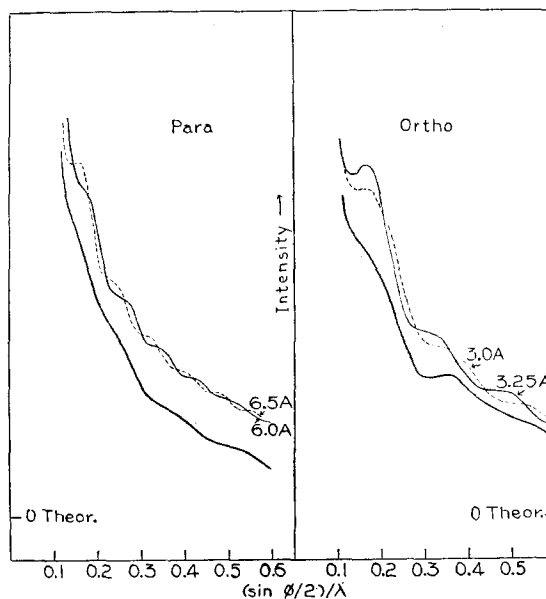

FIG. 5. Construction of correction curve from the scattering of monochlorbenzene.

FIG. 6. Corrected $Cl-Cl$ scattering of ortho and para-dichlorbenzene (lower curves). Theoretical $Cl-Cl$ scattering (upper curves).

for para. The first para peak could not be experimentally determined with radiation of the wavelength used. As previously mentioned no significance can be attached to small fluctuations in the intensity curves at large angle values but the major peaks at which the comparisons are made may be recognized even in the original photometer curves before any corrections are made.

The Cl — Cl distances thus measured do not depend on any assumptions regarding the structure of the benzene molecule except that the C — C and C — Cl scattering is the same in mono- and dichlorbenzene. It is therefore only necessary to seek for a structure for benzene that will permit the Cl atoms to lie 3.0 and 6.25A apart. If C — C and C — Cl distances of 1.4 and 1.8A are assumed the measured Cl — Cl distances are best accounted for by a plane hexagonal benzene molecule with the Cl atoms lying on valence lines in or near the plane of the ring. This model gives calculated values of 3.2 and 6.4A which agree within experimental error with the values found. The result for para-dichlorbenzene is in agreement with the crystallographic measurements of Hendricks.[7] He finds that the intramolecular Cl — Cl distance in the solid compound is 6.20A.

Hendricks, Maxwell, Mosley and Jefferson[8] have recently reported measurements with electron diffraction from the di-iodobenzenes. Their results are in line with the present ones except for ortho-di-iodobenzene. They find that the ortho-iodine atoms mutually repel one another to positions about 10° from the valence angles. The precision of the present work is not as high as that obtained for the iodine compounds and it is possible that an effect of this sort might escape detection. However, since the measured value is smaller rather than larger than the calculated one it seems doubtful if this mutual repulsion exists in the chlorine compounds. The smaller value might be accounted for by a slight displacement of the Cl atoms from the plane of the ring. The general agreement in the two methods imparts confidence in the results and in their interpretations.

[7] Hendricks, Zeits. f. Krist. **84**, 85 (1932).

[8] Hendricks, Maxwell, Mosley and Jefferson, J. Chem. Phys. **1**, 549 (1933).