

An Electron Diffraction Investigation of Hexachloroacetone

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The molecular structure of hexachloroacetone has been determined by the gas electron diffraction method at 65°C and 300°C. The following bond distances and angles have been found at 65°C: C—O: 1.184(13) Å; C—C: 1.574(9) Å; C—Cl: 1.764(4); \angle OCC: 118.9°(0.7°); \angle OCCCl: 16.2°(1.4°) and 36.1°(1.8°); the angle between the three-fold axes of the CCl₃ group and C—Cl: 70.5°(0.3°). The three-fold axis is tilted 3.7° towards the carbonyl group. A structure having a C₂ symmetry could be determined by assuming a small amount of another conformer to be present. To see if this was probable, the structure determination was repeated at 300°C but no change in the ratio of the possible two conformers could be seen.

In an attempt to verify the structure of the CCl₃ free radical¹⁻³ hexachloroacetone was used as a source of the radicals through thermal decomposition. The decomposition took place within a quartz nozzle which could be heated to about 1000°C over a region of a few mm of the nozzle 1–2 mm from the point of scattering.³ In the earlier experiment^{1,2} the decomposition took place in front of the nozzle about 12 mm from the point of scattering. In both cases the reaction products were studied in a mass spectrometer by letting the gas in through the same nozzle as is used in the electron diffraction unit. The analysis of the radial distribution (RD) curve made it necessary to determine the structure of the parent molecule, (CCl₃)₂C=O. This structure has not been determined earlier although acetone itself and hexafluoroacetone have been studied^{2,4-6} in the gas phase by many groups using the microwave or the electron diffraction methods. From the most recent electron diffraction investigation by Bauer and coworkers⁴ it is concluded that both molecules have a C₂ symmetry and that the dihedral angles are (OCCH)=32° and

(OCCF)=36.6°. In hexachloroacetone where both the non-bonded Cl...Cl and Cl...O distances could be expected to be fairly short, one should probably expect a similar staggering of the two CCl₃ groups as in the fluoro compound.

EXPERIMENTAL

The hexachloroacetone was obtained from Fluka AG, Switzerland, and was further purified in a gas chromatograph. The electron diffraction photographs were taken in the usual way. One set of data was obtained from the Balzers apparatus at two nozzle-plate distances of 250 mm and 500 mm, and 60 kV electrons; the nozzle temperature was 65°C. The second set was obtained from the Oslo apparatus at 200 mm and 480 mm nozzle-plate distances, 35 kV electrons, and a nozzle temperature of 300°C. The first set covers an *s* range of 1.25–18.625 Å⁻¹ and 2.75–35.25 Å⁻¹, and the second set an *s* range of 1.375–18.625 Å⁻¹ and 7.25–42.75 Å⁻¹.

The resulting modified molecular intensity values over the range from 1.25 Å⁻¹ to 30.0 Å⁻¹ for the first set and from 1.375 Å⁻¹ to 38.0 Å⁻¹ for the second set are shown in Fig. 1.

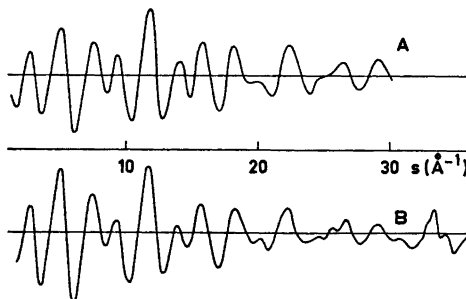


Fig. 1. Hexachloroacetone. Experimental molecular intensity curves. A: nozzle temperature 65°C. B: nozzle temperature 300°C.

The data were analysed in the usual way using the radial distribution curve to determine an approximate structure and then refining the molecular parameters by a least-squares fitting of the intensity data. The computer programs available in Oslo⁶ were used throughout this investigation.

STRUCTURE ANALYSIS

The radial distribution curve obtained by Fourier transformation of the experimental molecular intensity curve of the low temperature experiment is shown in Fig. 2. The structure

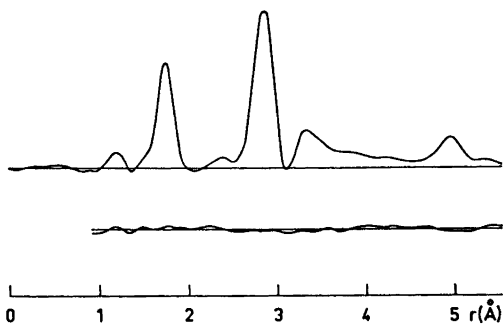


Fig. 2. Hexachloroacetone. Experimental radial distribution curve. The lower curve shows the difference between the experimental and the calculated values. Nozzle temperature 65°C. Artificial damping constant $k = 0.0023 \text{ \AA}$.

was initially analysed assuming the molecule to possess a C_2 symmetry. Approximate values for the C=O, C-C, and C-Cl bond lengths could be determined from the two first peaks on the RD curve at about 2.9 Å and 1.75 Å. The CCC angle, the ClCCl angle, and the twist angle of the CCl_3 groups could be estimated from the maxima at about 2.9 Å, 3.3 Å, and 5.0 Å. Attempts to reproduce the experimental RD curve in the region of 2–5 Å assuming the approximate values of bond lengths and angles was unsuccessful and so were least-squares refinements. Two possibilities were taken into account at this stage, one which assumed that the molecule did not have a C_2 symmetry and one which assumed that two conformations were present both having a C_2 symmetry. Refinements assuming that the molecule did not have a two-fold axis gave a fairly good agreement in the 3–5 Å region with approximately 36° and 16° twist angles

of the two CCl_3 groups. In order to improve the agreement between the calculated and the experimental RD curve a new parameter, the angle between the three-fold axis of the CCl_3 group and the C-C bond direction (Fig. 3),

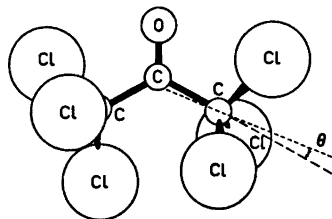


Fig. 3. Hexachloroacetone. θ is the angle between the three-fold axis of the CCl_3 group (---) and the continuation of the C-C bond (- - -).

was introduced. Further refinements showed that the best agreement was obtained when the CCl_3 groups were tilted 3.7° towards the carbonyl group.

The result of these refinements was unexpected since one could not see why the two sides of the molecule should behave differently as far as the twist angles of the CCl_3 groups were concerned. The possibility of two conformations being present was then taken into account. The two conformations were assumed to have a C_2 symmetry and the two determined twist angles were used as starting parameters for a least-squares refinement. A good agreement was obtained for a predominant contribution of a conformation having approximately 35° twist angle and a small contribution of a conformation having a small twist angle. In order to decide whether one or two conformations could be present the experiment was repeated with a nozzle temperature of 300°C where the contribution of the higher energy conformation could be expected to increase.

The analysis of the RD and molecular intensity curves from the high temperature experiment was carried out in the same way as on the 65°C curves. The RD and the difference curve between the high and low temperature curves are reproduced in Fig. 4. The analysis of the high temperature structure did not result in any significant changes in the molecular parameters except for the thermal vibrations as can be seen from Table 1. If the presence of a small contribution of another conformation

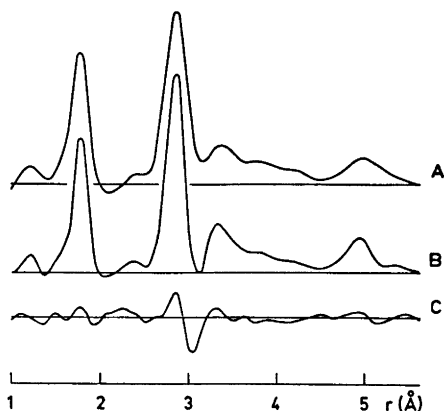


Fig. 4. Hexachloroacetone. Experimental radial distribution curves. A: nozzle temperature 300°C. B: nozzle temperature 65°C. C: the difference between the high and low temperature curves. Artificial damping constant $k=0.0023 \text{ \AA}$.

was assumed, this ratio between the two conformations was not changed by increasing the temperature from 65°C to 300°C. This indicates that only one conformation is present.

Attempts to calculate the energy difference between the conformations did not give results which could justify the conclusion that the molecule should have a C_1 symmetry. Harmonic shrinkage corrections^{8,9} on the best conformation having a C_2 symmetry were calculated. But the value of these calculations is doubtful since the force constants for hexachloroacetone were not known and had to be estimated from the values known for similar molecules.^{10,11} The shrinkage corrections improved somewhat the agreement with the experimental curve, but did not indicate in a conclusive way that the molecule could have a C_2 symmetry.

DISCUSSION

The C—O bond length (Table 1) of 1.184 Å differs somewhat from the values determined for acetone and hexafluoroacetone⁴ which are 1.210 Å and 1.246 Å, respectively. The resolved peak corresponding to this distance on the RD curve is probably well determined for this molecule. The increase in the C—C bond length from 1.507 Å in acetone to 1.549 Å in hexafluoroacetone and 1.574 Å in this work could be expected. Some of the non-bonded Cl...Cl

and Cl...O distances (Table 2) are much shorter than should be expected from the size of the van der Waals radii. No change in bond angles or twist angles would increase all these distances appreciably and the lengthening is not unexpected. The C—Cl bond length of 1.764 Å is reasonable and so are the CCC angle of 122.2° and the ClCCl angle of 109.4°. The shortest Cl...Cl distance between the two CCl_3 groups are about 3.24 Å and 3.31 Å and the shortest Cl...O distances on the other side of the molecule are 2.73 Å and 2.84 Å. These four distances are all shorter than could be assumed from the van der Waals radii of the chlorine and oxygen atoms. It is obviously preferred to tilt the three-fold axis of the CCl_3 groups towards the oxygen atom instead of increasing the CCC angle to approximately 130° which is the angle between the two three-fold axes.

The dihedral angle Cl(5)—C(3)...C(4)—Cl(8) (Fig. 3) is 66° so that the two CCl_3 groups are staggered. This is in good agreement with what was found for hexafluoroacetone. However,

Table 1. Structure parameters for hexachloroacetone obtained by least squares refinement on the intensity data. Distances (r_a -values) and mean amplitudes of vibration (u -values) are given in Å, angles in degrees. The standard deviations given in parentheses have been corrected to take into account data correlation. The uncertainty arising from error in the electron wave length is included. (For numbering system of the atoms see Fig. 5.).

| | Low temperature (65°C) | | High temperature (300°) | |
|---------------------|---------------------------|----------|----------------------------|----------|
| Distances r | u | r | u | |
| C=O | 1.184(13) | 0.037 | 1.200(14) | 0.038 |
| C—C | 1.574(9) | 0.050 | 1.595(9) | 0.054 |
| C—Cl | 1.764(4) | 0.043(4) | 1.766(4) | 0.052(4) |
| Angles | deg. | | deg. | |
| $\angle \text{OCC}$ | 118.9(0.7) | | 118.3(0.9) | |
| α^a | 70.5(0.3) | | 70.8(0.3) | |
| θ^b | 3.7(0.8) | | 2.7(1.0) | |
| τ_1^c | 16.2(1.4) | | 16.9(1.4) | |
| τ_2^c | 36.1(1.8) | | 39.5(1.8) | |

^a α is the angle between the C—Cl bond and the three-fold axis of the CCl_3 group. ^b θ is the angle between the three-fold axis of the CCl_3 group and the continuation of the C—C bond. ^c τ_1 and τ_2 are the twist angles of the CCl_3 groups about the C—C bonds.

Table 2. Hexachloroacetone. Non-bonded Cl...O and Cl...Cl distances in Å. Nozzle temperature 65°C. (For numbering system of the atoms see Fig. 5.)

| Distances | <i>r</i> |
|----------------|----------|
| Cl(5)...O(1) | 2.727 |
| Cl(6)...O(1) | 3.749 |
| Cl(7)...O(1) | 3.488 |
| Cl(8)...O(1) | 2.843 |
| Cl(9)...O(1) | 3.290 |
| Cl(10)...O(1) | 3.847 |
| Cl(5)...Cl(8) | 5.280 |
| Cl(5)...Cl(9) | 4.900 |
| Cl(5)...Cl(10) | 4.910 |
| Cl(6)...Cl(8) | 4.991 |
| Cl(6)...Cl(9) | 3.643 |
| Cl(6)...Cl(10) | 3.241 |
| Cl(7)...Cl(8) | 4.553 |
| Cl(7)...Cl(9) | 4.985 |
| Cl(7)...Cl(10) | 3.309 |

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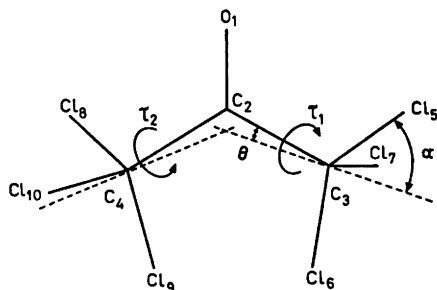


Fig. 5. Hexachloroacetone. The symbols and numbering system.

we have no good explanation for why the two twist angles Cl(5)-C(3)-C(2)-O and Cl(8)-C(4)-C(2)-O of the CCl₃ groups should be 16.2° and 36.1° and not equal.

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