Electron Diffraction Studies of Tertiary Butyl Chloride and Tertiary Butyl Fluoride

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The structures of derivatives of methane are of considerable interest. Because of their simplicity they allow a relatively accurate determination of parameter values and permit a study of the relationships between them and various substituents. The result of a joint electron diffraction-microwave investigation on tertiary butyl fluoride has already been published [1]. In the present paper we shall give a brief description of the electron diffraction studies of as well the tertiary butyl chloride as the tertiary butyl fluoride.

The upper curve of Fig. 1 is a $\frac{\sigma(r)}{r}$ -curve of tertiary butyl chloride, the lower curve that of the fluoride. We have calculated two $\frac{\sigma(r)}{r}$ -curves for the chloride and three for the fluoride. The first curves of both compounds were based upon intensity curves ranging from $s = 3$ to $s = 26$ Å^{-1}. The best molecular models obtained from these curves were used to calculate theoretical intensity curves, from which the data from $s = 0$ to $s = 3$ were taken and together with the experimental data were used to calculate the second $\frac{\sigma(r)}{r}$ -curves. The third $\frac{\sigma(r)}{r}$ -curve for the fluoride was based upon a better calculated intensity curve for $0 < s < 3$. Since the third curve was only slightly different from the second one, we felt it unnecessary to continue the calculation.

The first peak of the $\frac{\sigma(r)}{r}$ -curves corresponds to the C-H bond distance. The average value of the position of this maximum for all the calculated $\frac{\sigma(r)}{r}$ -curves is 1.10 Å, with a mean deviation of somewhat less than 0.02 Å. For
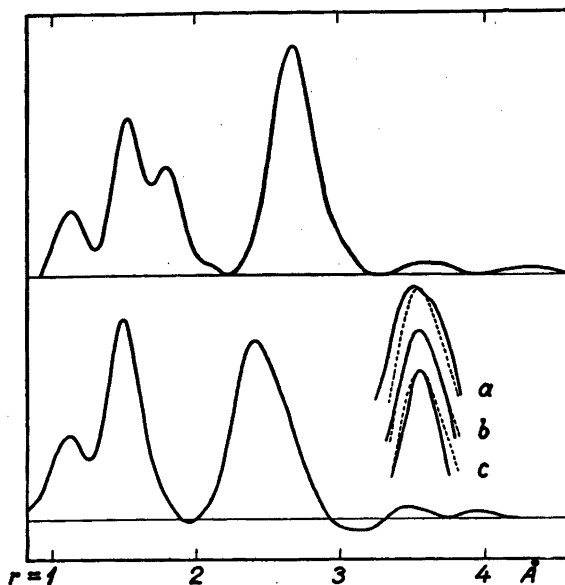
Fig. 1. $\dfrac{\sigma\,(r)}{r}$ *curves of tertiary butyl chloride (upper-curve) and tertiary butyl fluoride (lower curve). The curves are calculated from intensity functions multiplied with the modification factor* $e^{-0.007s^2}$.

the chloride the C-C and the C-Cl distances give rise to two separate maxima in the $\dfrac{\sigma\,(r)}{r}$ -curve. The position of the C—C bond distance peak is 1.54 Å for both the calculated $\dfrac{\sigma\,(r)}{r}$ -curves of the chloride. From the curve of Fig. 1 the C—Cl bond distance is found to be 1.80 Å. The error of these values is estimated to be approximately 0.01 Å, probably somewhat less for the C—C distance.

By an analysis of the peak at $r = 2.69$ Å of the upper curve of Fig. 1 we can find the C—C—Cl angle. The position of the peak is mainly determined by the C ... Cl distance. Normal curves were used to calculate theoretical $\dfrac{\sigma\,(r)}{r}$ -curves. This procedure led to a C—C—Cl angle of $107.0° \pm 1°$ corresponding to a C—C—C angle of $111.8° \pm 1°$. This is in good agreement with the results of Beach and Stevenson [2], who from a visual electron diffraction investigation found the following parameters for the molecule: C—C (assumed) 1.54 Å, C—Cl $= 1.78 \pm 0.03$ Å, and $< $ C—C—C $= 111.5° \pm 2°$.

Since for the tertiary butyl fluoride the contribution from the C—C and C—F bond distances results in one unresolved peak, the C—F distance cannot be determined directly. If we calculate the C—F bond distance simply from the maximum position by giving the distances their usual weight factors $\left(\frac{Z_iZ_j}{r_{ij}}n_{ij}\right)$ and assume the C—C distance equal to 1.54 Å, we find a C—F distance of 1.38—1.40 Å. A more satisfactory approach to the problem of finding the C—F bond distance is based upon the assumption that the contributions of the C—H terms and of the C—C terms are the same for the two compounds. If this assumption is correct we should end up with the same form of the $\frac{\sigma\ (r)}{r}$ curve in the range 1—2 Å, when the C-halogen bond contributions are subtracted. The contribution of the C—Cl bond can easily be allowed for since the value of this distance is known. The normal curve of the C—Cl bond distance is subtracted from the $\frac{\sigma\ (r)}{r}$ -curve of the tertiary chloride. The result is given as the upper curve of Fig. 2. This curve is now subtracted in turn from the inner part of the $\frac{\sigma\ (r)}{r}$ -curve of the fluoride. The resulting curve consists of a peak at 1.38 Å as indicated in the lower curve of Fig. 2. This must correspond to the C—F bond.

There is some uncertainty in the form of the normal curves. The form of the C—Cl normal curve used in this case does not, however, influence the position of the maximum of the C—F peak, but it will to a certain extent influence the shape of the curve in the neighbourhood of the peak. The minimum at the outer side of the C—F peak might well be the results of the use of a somewhat inaccurate normal curve. However, as this does not affect the determination of the C—F bond distance we have made no particular effort to obtain the best normal curve.

To subtract the upper curve of Fig. 2 from the $\frac{\sigma\ (r)}{r}$ -curve of the fluoride we have to introduce a proper normalization factor which introduces uncertainties. We have varied this normalization factor through a reasonable interval and thus obtained peaks with maxima varying from 1.375 to 1.396 Å. Our conclusion, then, based on the above information and upon consideration of calculated intensity curves is that the C—F bond distance is equal to 1.38 ± 0.02 Å.

The deviation of the carbon bond angles from the tetrahedral value in the fluorine compound cannot be determined with great accuracy from the bond distances and the position of the peak at 2.415 Å. The position of this

Fig. 2. Difference $\dfrac{\sigma\,(r)}{r}$ *curves for the determination of the* $C-F$ *bond distance of tertiary butyl fluoride.*
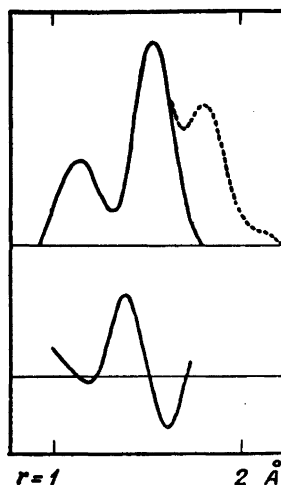
peak is very little influenced by variation of the angles. The deviation from the tetrahedral symmetry will obviously not destroy the trigonal symmetry about the C—F axis. Thus, an increase in the C—C—C angle will result in a decrease of the C—C—F angle. Now, since the contribution from the long

C ... C distance to the $\dfrac{\sigma\,(r)}{r}$ -curve is approximately the same as the contribution

of the long C ... F distance, the position of the maximum of the resulting peak will vary very little with the angle. On the other hand, the *shape* of the peak under discussion is rather sensitive to variation of the angles. To illustrate this fact three pairs of curves (a, b and c) are drawn in Fig. 1. The broken curve is the same in all three cases, namely, the experimental peak. The solid curve are theoretical peaks claculated from a C—C—F angle of a) 107°, b) 108.4° and c) 109.5°. Since the curve pair b) no doubt exhibits better agreement than the other pairs, we believe that the C—C—F angle is somewhat smaller than the tetrahedral angle. These considerations and others (the relative weights of the terms contributing to this peak were also examined) lead us to the value 108 ± 1.5° for <C—C—F, corresponding to a C—C—C angle of 111° ± 1.5°. Although the tetrahedral value 109.5° lies just at the edge of our limit of error, we feel that our electron diffraction result is strongly suggestive of a small deviation in the same direction as for the other tertiary butyl halogenides studied [2,3].

The conclusion drawn from the joint electron diffraction microwave investigation leading to a C—F bond distance of 1.37 ± 0.01 Å is based upon the tacit assumption that the two different methods in principle give

identical values for corresponding bond distances in the same molecule. A microwave distance determination leads to a bond distance value for the molecule in a definite quantum state (here the ground state), while an electron diffraction study gives the average bond distance at the temperature in the diffraction point. One might, therefore, expect that a distance determined by the microwave method should be somewhat smaller than the distance determined by the electron diffraction method. However, the deviation is probably within the limit of the errors of the two methods, though future improvements of the methods might perhaps reveal measureable differences in the results from the two methods.

A detailed discussion of the microwave investigation of the tertiary butyl fluoride is given in the preceding paper by F. Andersen, B. Bak, and J. Rastrup-Andersen [4].

SUMMARY

Electron diffraction studies of tertiary butyl chloride and tertiary butyl fluoride leads to the following molecular parameters of the two compounds: Tertiary butyl chloride: $C-H = 1.10 \pm 0.02$ Å, $C-C = 1.54 \pm 0.01$ Å, $C-Cl = 1.80 \pm 0.01$ Å and $-C-C-Cl = 107 \pm 1°$. Tertiary butyl fluoride: $C-F = 1.38 \pm 0.02$ Å and $C-C-F = 108 \pm 1.5°$.

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