Electron Diffraction Investigations on the Molecular Structures of sec-Butyl Chloride and Alcohol

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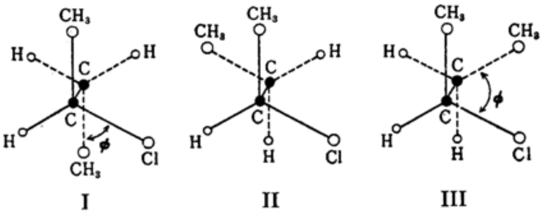
The molecular structures of propane[1], butane[2] and their chlorine derivatives, such as *n*- and isopropyl chloride[3,4], 1, 2-dichloropropane[5] and *tert*-butyl chloride[6,7] have already been studied by electron diffraction, using the visual method or the sector-microphotometer method. It appears that only a few studies have been done on the molecular structures of alcohols[4,8-10].

In this paper the results of electron diffraction investigation about *sec*-butyl chloride and alcohol using the sector-microphotometer method are described and compared with those of the related compounds.

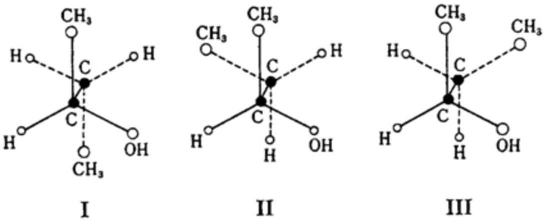
Experimental

sec-Butyl chloride and alcohol were kindly furnished by Dr. T. Miyazawa, the University of Tokyo. They were the same samples which were used in the spectroscopic studies.

The diffraction patterns were taken at room temperature of about 20°C using an apparatus[11] having an r^2-sector which was rotated rapidly during exposure. The exposures of each set were regulated to be about 2 : 1 in order to apply Karle's method[12]. The camera length was 11.82 cm. and the wavelength of electron was about 0.0567 Å, which was determined by measuring the transmission patterns of gold foil.



sec-Butyl chloride



sec-Butyl alcohol

Fig. 1. Rotational isomers of *sec*-butyl chloride and alcohol.

The optical densities of the photographic plates were measured by a microphotometer. The plates were rotated rapidly about their centers during scanning. The optical densities were converted to relative intensities by Karle's procedure[12]. A smooth background line was drawn through the intensity curve multiplied by q and the molecular intensity curve $M(q)$ was obtained using the following formula,

TABLE I. LIST OF MOLECULAR CONSTANTS OF PROPANE, BUTANE AND THIR CHLORINE DERIVATIVES

Molecule	C-C, Å	C-Cl, Å	Angle CCC	Angle CCCl	Reference
Propane	1.54 ±0.02	—	111.5°±3°	—	1
n-Butane	1.539±0.003	—	112°9′ ±9′	—	2
n-Propyl chloride	1.535±0.02	1.775±0.02	109.5°±2.5°	111°±2°	3
Isopropyl chloride	1.55 ±0.02	1.76 ±0.02	109.5°±1.5°	111°±1.5°	4
1, 2-Dichloropropane	1.56 ±0.05	1.79 ±0.035	109.5°(ass.)	108°±4°	5
tert-Butyl chloride	1.54 ±0.01	1.80 ±0.01	111.5°±1°	—	6
tert-Butyl chloride	1.54 ±0.03	1.80 ±0.04	111.5°±1.5°	—	7

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TABLE II. LIST OF MOLECULAR CONSTANTS OF ALCOHOLS

Molecule	C-C, Å	C-O, Å	Reference
Methyl alcohol	—	1.428 ± 0.003	8
Ethyl alcohol	1.54(ass.)	1.48 ± 0.04	9
Ethyl alcohol	1.55 ± 0.02	1.43 ± 0.02	10
Isopropyl alcohol	1.54 ± 0.02	1.45 ± 0.03	4

$$M(q)=(I_T/I_B)-1 \qquad (1)$$

where I_T is the total intensity and I_B is the background intensity.

Analysis

The radial distribution curves were calculated by the following equation,

$$f(r) = \sum_{q=0}^{q=85} qM(q)\exp(-aq^2)\sin(\pi qr/10) \qquad (2)$$

where $M(q)$ is the experimental molecular intensity obtained from Eq. 1. Here the correction for the non-nuclear scatterings was not made. The artificial damping factor a was chosen so that $\exp(-aq^2)=0.1$ at $q=85$, and $q=(40/\lambda)\sin(\theta/2)$, where θ is the angle of scattering and λ is the wavelength of the electron beam.

In the calculation of the radial distribution curve, the intensity curve below $q=15$ was spliced by the theoretical intensity curve with a constant coefficient. The intensity curve in such a region is hardly affected at all by the bond distance changes of the order 0.01 Å, but considerably affected by the internal rotation around the middle C-C bond (Fig. 1). Several steps of successive approximations were taken in order to make the assumed model practically selfconsistent with the final radial distribution curve.

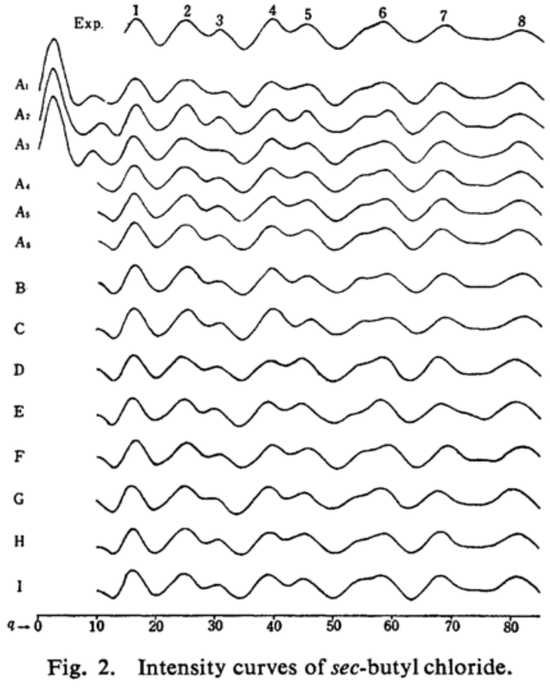

Fig. 2. Intensity curves of *sec*-butyl chloride.

The theoretical intensity curves were calculated using the following equation,

$$qM_c(q)=\sum_{i,j}(Z_iZ_j/r_{ij})\exp(-b_{ij}q^2)\sin(\pi qr_{ij}/10) \qquad (3)$$

where r_{ij} is the interatomic distance between the ith and jth atoms, b_{ij} is its temperature factor which is calculated from the mean amplitude, Z_i is the ith atomic number, except hydrogen, where the effective value 1.25 was used. The mean amplitudes used for the factors b_{ij} are shown in Table III. The theoretical intensity curves of the mixed rotational isomers were considered.

***sec*-Butyl Chloride.**—The radial distribution curve (Fig. 3) has peaks at 1.085, 1.54, 1.80, 2.17, 2.715, 3.23 and 4.15 Å. The first peak is assigned to bonded C-H distances, the second to bonded C-C distances, the third to bonded C-Cl distance with some contributions of nonbonded H···H distances, the fourth to nonbonded C···H distances. The peak of the nonbonded C···H distances, when the fourth peak is resolved into its components, shows that the angles CCH are about 109.5°, if the C–H bond distances are assumed to be 1.09 Å. The fifth peak is mainly resolved into those of nonbonded C···C and C···Cl distances, although it involves some components of the others. If the C-Cl bond distance is assumed to be 1.80 Å, the peak of C···Cl distances shows that the angles CCCl are equal to 109.5°.

TABLE III. MEAN AMPLITUDES USED FOR THE ANALYSIS

Atomic pair	Mean amplitude Å	Atomic pair	Mean amplitude Å
C-C	0.050	O···H	0.114
C-Cl	0.050	H···H	0.135
C-O	0.050	*trans*-C···C	0.070
C-H	0.077	*trans*-C···Cl	0.068
C···C	0.079	*trans*-C···O	0.070
C···Cl	0.073	*gauche*-C···C	0.160
C···O	0.073	*gauche*-C···Cl	0.140
C···H	0.120	*gauche*-C···O	0.140
Cl···H	0.114		

In the same way, the peak of C···C distances, although the height is less than that of C···Cl and its position is somewhat uncertain, shows that the angles CCC are about 110～112°. The peak at about 3.23 Å is characteristic of the gauche C···Cl and shows the existence of I or III or both the forms (Fig. 1). The peak shows also that the azimuthal angle ϕ is about 70°C. The peak at 4.15 Å is characteristic of the trans C···Cl and shows the existence of the form II. The peak of gauche C···C overlaps heavily with the other more predominant peaks and the peak of trans C···C is very low, so these two peaks are not so suitable to estimate the amount of forms I and III. As the area under the peak is approximately proportional to Z_iZ_j/r_{ij}, the amount of each form can be found from the area of the characteristic peak and since the areas of trans C···Cl and gauche C···Cl are

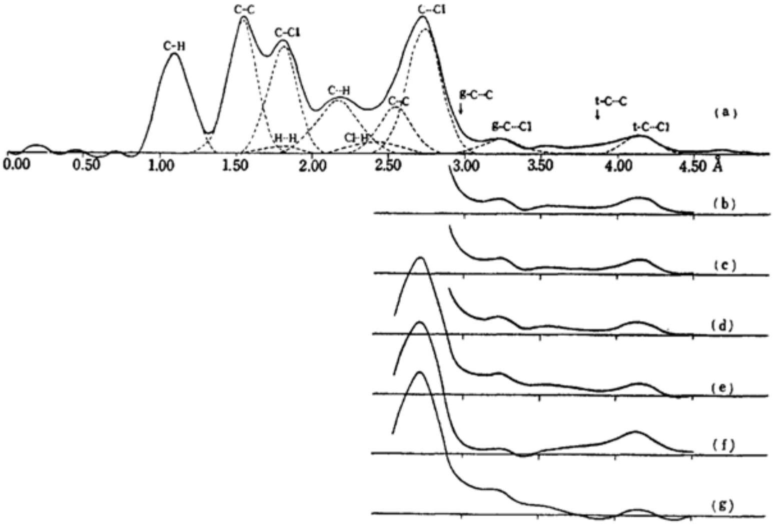

Fig. 3. Radial distribution curves of *sec*-butyl chloride. Spliced theoretical intensity curves below $q=15$ are as follows;

(a) I 50%, II 50%, (b) I 25%, II 50%, III 25%, (c) II 50%, III 50%, (d) I 33%, II 33%, III 33%, (e) I 100%, (f) II 100%, (g) III 100%

affected by the spliced theoretical intensity curves below $q=15$, various ratios of the three forms were tried so that the peaks became almost self consistent with the assumed ratio. The theoretical intensity curves of the forms I and II below $q=15$ are not so different from each other, so the radial distribution curve is not affected very much by the ratio of these two kinds of spliced portions. The ratio of the amounts of the forms I and III could not be obtained unambiguously. Only the ratio of the form II and the sum of the forms I and III was obtained rather definitely.

Its reasonable ratio was about 50% : 50%. The radial distribution curves a, b and c are almost selfconsistent with the assumed amounts of the rotational isomers, but d, e, f and g are not selfconsistent (Fig. 3).

Making reference to the results of the radial distribution curve, the theoretical intensity curves of various models were drawn in order to find the best model. The theoretical intensity curves of the three rotational isomers show some different features respectively at about $q=25\sim50$ and among the three, the forms I and III which have gauche C$\cdots$Cl resemble each other rather than the form II which has trans C$\cdots$Cl. However the theoretical intensity curve of any one rotational isomer does not fit better with the experimental than that of the mixed one, so for one model of assumed bond distances and bond angles, some mixtures of the rotational isomers I, II and III were examined, but for the most part the ratio, form I : form II=50% : 50% was assumed (Table IV). The intensity curves A_5 and A_6 fit with the experimental better than any other (Fig. 2). Next to them B fits well. Both curves C and D in which the C-Cl bond distance is 1.76 and 1.82 Å, respectively, show very different intensities at maxima 4 and 5 compared with the experimental. So the C-Cl bond distance can be determined to be 1.79±0.015 Å.

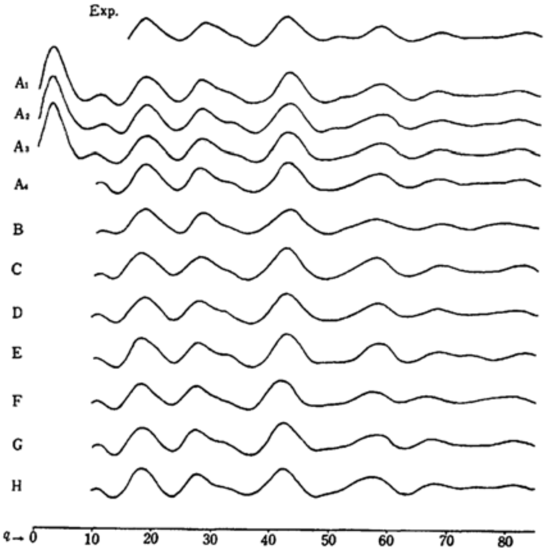

Fig. 4. Intensity curves of *sec*-butyl alcohol.

The intensity curves F and G in which C-C bond distances are 1.52 and 1.56 Å, respectively, have not very different appearances from the experimental, but the $q_{\text{calcd}}/q_{\text{obs}}$ values are not so good as that of 1.54 Å. The C-C bond distances can be considered to be 1.54±0.01 Å. The intensity curves H and I in which C-H bond distances are 1.07 and 1.11 Å, respectively, have different intensity ratios at maxima 4 and 5 compared with the experimental. The C-H bond distances seem to be 1.09±0.015 Å.

***sec*-Butyl Alcohol.**—The radial distribution curve has peaks at 1.06, 1.515, 2.16, 2.485, 2.93 and 3.73 Å (Fig. 5). The first peak is considered to be the resultant of bonded C-H and O-H peaks, the second to be that of bonded C-C and C-O peaks,

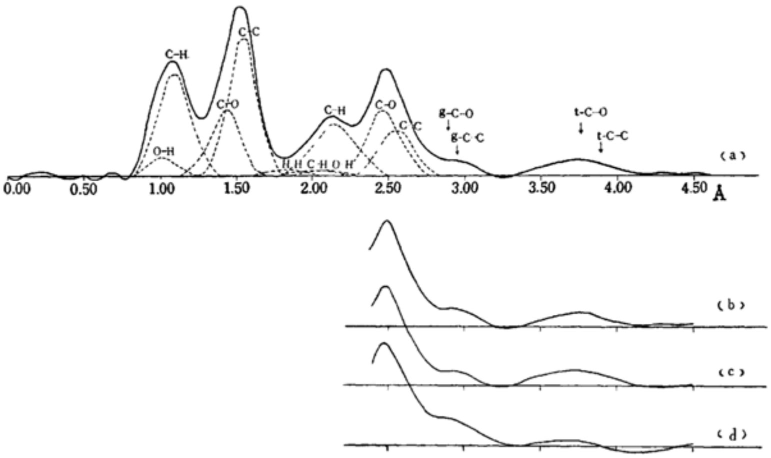

Fig. 5. Radial distribution curves of *sec*-butyl alcohol. Spliced theoretical intensity curves below $q=15$ are as follows;

(a) I 50%, II 50% (b) I 100%, (c) II 100%, (d) III 100%

TABLE IV. MOLECULAR MODELS OF *sec*-BUTYL CHLORIDE AND $q_{\text{calcd}}/q_{\text{obs}}$ VALUES

Model	C-C Å	C-H Å	C-Cl Å	Angle CCC	Angle CCCl	Percent of rotational isomers I	II	III	Mean value of $q_{\text{calcd}}/q_{\text{obs}}$	Average deviation
A_1	1.54	1.09	1.80	109.5°	109.5°	100	0	0	1.004	0.012
A_2	1.54	1.09	1.80	109.5°	109.5°	0	100	0	0.997	0.007
A_3	1.54	1.09	1.80	109.5°	109.5°	0	0	100	—	—
A_4	1.54	1.09	1.80	109.5°	109.5°	33	33	33	0.997	0.006
A_5	1.54	1.09	1.80	109.5°	109.5°	25	50	25	0.999	0.004
A_6	1.54	1.09	1.80	109.5°	109.5°	50	50	0	0.999	0.005
B	1.54	1.09	1.78	109.5°	109.5°	50	50	0	1.006	0.005
C	1.54	1.09	1.76	109.5°	109.5°	50	50	0	—	—
D	1.54	1.09	1.82	109.5°	109.5°	50	50	0	0.991	0.005
E	1.54	1.09	1.80	112°	112°	50	50	0	0.989	0.007
F	1.52	1.09	1.78	109.5°	109.5°	50	50	0	1.014	0.008
G	1.56	1.09	1.80	109.5°	109.5°	50	50	0	0.991	0.008
H	1.54	1.07	1.80	109.5°	109.5°	50	50	0	0.999	0.006
I	1.54	1.11	1.80	109.5°	109.5°	50	50	0	0.997	0.005

TABLE V. MOLECULER MODELS OF *sec*-BUTYL ALCOHOL AND $q_{\text{calcd}}/q_{\text{obs}}$ VALUES

Model	C-C Å	C-H Å	C-O Å	Angle CCC	Angle CCO	Percent of rotational isomers I	II	III	Mean value of $q_{\text{calcd}}/q_{\text{obs}}$	Average deviation
A_1	1.54	1.09	1.43	109.5°	109.5°	100	0	0	1.000	0.009
A_2	1.54	1.09	1.43	109.5°	109.5°	0	100	0	1.005	0.008
A_3	1.54	1.09	1.43	109.5°	109.5°	0	0	100	1.004	0.009
A_4	1.54	1.09	1.43	109.5°	109.5°	50	50	0	1.004	0.013
B	1.54	1.09	1.40	109.5°	109.5°	50	50	0	1.010	0.013
C	1.54	1.09	1.46	109.5°	109.5°	50	50	0	0.996	0.012
D	1.54	1.09	1.43	112°	109.5°	50	50	0	1.001	0.008
E	1.52	1.09	1.43	109.5°	109.5°	50	50	0	1.008	0.006
F	1.56	1.09	1.43	109.5°	109.5°	50	50	0	0.989	0.008
G	1.54	1.07	1.43	109.5°	109.5°	50	50	0	1.004	0.009
H	1.54	1.11	1.43	109.5°	109.5°	50	50	0	1.004	0.008

the third to be that of nonbonded C···cH, C···oH and O···cH peaks, the fourth to be that of nonbonded C···O and C···C peaks. Each of the above peaks consists of two or more components, so it is resolved into its components somewhat arbitrarily. Assuming the mean amplitudes listed in Table III, these peaks were resolved as in Fig. 5. The resolved peaks show that the angles CCH are about 109.5° and the angles CCC and CCO are both slightly greater than 109.5°.

The fifth peak at about 2.93 Å is characteristic of gauche C···O or C···C and the sixth peak at about 3.73 Å is characteristic of trans C···O or C···C. From both the peaks the amount of the rotational isomers are to be obtained. But these peaks are almost entirely controlled by the spliced intensity curves below $q=15$. They can be seen from the fact that the theoretical intensity curves of the rotational isomers above $q=15$ are not very different from each other. Moreover each peak may be constructed respectively from two adjacent components, C···O and C···C, and the resolution into its components is somewhat arbitrary. So it is difficult to determine the amounts of the rotational isomers unambiguously at the present step. It seems, however, that all the three rotational isomers may be present and the form II is predominant among them.

The theoretical intensity curves of various models listed in Table V are drawn in Fig. 4. As the intensity curves of models A, E and F do not show a greatly different appearance compared with the experimental, the C-C bond distances were estimated by the $q_{\text{calcd}}/q_{\text{obs}}$ values as 1.54±0.015 Å (Table V). The intensity curves B and C have slightly different appearances from the experimental at the vicinity $q=50$ and unappropriate $q_{\text{calcd}}/q_{\text{obs}}$ values, so the C-O bond distance is considered to be 1.43±0.02 Å. The intensity curves G and H have not greatly different features and $q_{\text{calcd}}/q_{\text{obs}}$ values compared with A, that the C-H bond distances cannot be determined within small limits of uncertainty. They seem to be 1.09±0.03 Å.

Summary and Discussion

The molecular structures of *sec*-butyl chloride and alcohol have been investigated by the sector and microphotometer method of electron diffraction. The structural information was derived from the radial distribution curves and correlation with the theoretical intensity curves. The results were as follows:

sec-Butyl chloride; C-C=1.54±0.01 Å, C-Cl=1.79±0.015 Å, angles CCC=111±1.5°, angles CCH≈10.95°, angle CCCl≈109.5°, the abundance ratio of the rotational isomer in which C···Cl is trans and that in which C···Cl are gauche is about 50%:50%.

sec-Butyl alcohol; C-C=1.54±0.015 Å, C-O=1.43±0.02 Å, C-H=1.09±0.03 Å, angles CCC and CCO are slightly greater than 109.5°, angles CCH≈109.5°. The abundance ratio of the rotational isomers could not be determined unambiguously at present.

When the above results are compared with Tables I and II, the C-C bond distances, the angles CCC and CCCl coincide with each other, although the accuracies are somewhat different. The C-Cl bond distance of *sec*-butyl chloride coincides with the results on *n*-propyl chloride³⁾, 1,2-dichloropropane⁵⁾ and *tert*-butyl chloride⁶,⁷⁾, but it is about 0.03 Å longer than that of isopropyl chloride⁴⁾.

The C-O bond distance of *sec*-butyl alcohol coincides with most cases of alcohols.

As for the rotational isomers, the abundance ratio was obtained to some extent about *sec*-butyl chloride, but not obtained unambiguously about *sec*-butyl alcohol at the present step.

By the measurement of specific rotation of *D*-*sec*-butyl alcohol, Bernstein and Pedersen¹³⁾ have found the amounts of the three rotational isomers to be 42% (form I), 42% (form II), 15.3% (form III), assuming that forms I and II have the same energy and that the form III is less stable (Fig. 1).

The amounts of rotational isomers will be obtained more accurately by the use of a long camera-length of electron diffraction apparatus.

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13) H. Bernstein and E. E. Pedersen, ibid., 17, 885 (1949).