

ferent from 0.78. The comparison of relative probabilities of T for H substitution can be extended through other binary comparisons to CH<sub>4</sub>, CH<sub>3</sub>F, and *n*-C<sub>4</sub>H<sub>10</sub>, giving the ratios shown in Table VI.<sup>4,5,14</sup>

TABLE VI

RELATIVE PROBABILITY OF T-FOR-H SUBSTITUTION REACTION PER C-H BOND IN THE MOLECULE

Target molecule, RH	Ratio for RT alone <sup>a</sup>	vs. cyclo-C <sub>4</sub> H <sub>7</sub> T	—Decomposition product—			Relative probability of reacn.
			Identity	Yield	Ref.	
CH <sub>4</sub>	0.83	4	CH <sub>2</sub> T	0.12 × RT	20	0.93
<i>n</i> -C <sub>4</sub> H <sub>10</sub>	.82	4, 23	C <sub>2</sub> H <sub>4</sub> T(?)	...	...	≥ .82 <sup>b</sup>
CH <sub>3</sub> F	.61	14	?	...	...	≥ .61 <sup>b</sup>
CH <sub>3</sub> Cl	.41	Present work	CH <sub>2</sub> T	This work		.78
Cyclo-C <sub>4</sub> H <sub>8</sub>	.60	4	C <sub>2</sub> H <sub>3</sub> T	0.40	4	1.00

<sup>a</sup> Measured at about 1 atmosphere. <sup>b</sup> Possible decomposition products not included in the absence of experiments in the liquid phase.

The data of Table VI include gas phase comparisons only for the molecules CH<sub>3</sub>F and *n*-C<sub>4</sub>H<sub>10</sub> and are consequently subject to possible increase if some of the originally produced labeled molecules have decomposed at this pressure. No gas pressure-dependent yields were observed with CH<sub>4</sub> or CH<sub>3</sub>F, but labeled radicals have been caught with I<sub>2</sub> scavenger in each case.<sup>10,20</sup> Liquid phase scavenger experiments have not yet been run because of the very high vapor pressures at ambient reactor temperature.<sup>4,14</sup> The yield of *n*-C<sub>4</sub>H<sub>9</sub>T from *n*-C<sub>4</sub>H<sub>10</sub> does show a gas phase pressure dependence,<sup>24</sup> but liquid phase studies indicate that decomposition in the 1-atmosphere gas phase work is not severe.<sup>25</sup>

The relative figures in the final column of Table VI indicate that the variations in T-for-H substitution are much less than the factors of 3 suggested by the per-

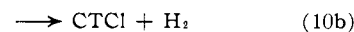
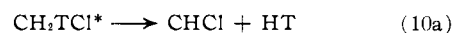
(24) E. K. C. Lee, Ph.D. Thesis, University of Kansas, 1963.

(25) R. Koob and F. S. Rowland, unpublished results.

centage yields of labeled parent molecule measured at 1 atmosphere gas pressure. We conclude that the average ease of substitution of T for H does not change greatly among these molecules, and, as a corollary conclusion, that steric interference with the substitution reaction is not very important for either chlorine atoms or alkyl radicals. If there is a variation in the last column of Table VI, it may be a decrease in the direction CH<sub>4</sub>-CH<sub>3</sub>Cl-CH<sub>3</sub>F and indicates an influence not of atomic size of H, Cl, and F, but probably of increasing electronegativity. Experiments with liquid CH<sub>3</sub>F seen necessary to determine whether any appreciable decomposition of CH<sub>2</sub>TF has taken place if a more accurate estimate of these relative T for H substitution probabilities is described.

**The Abstraction of H by Energetic T Atoms.**—A large fraction of the recoil tritium atoms formed in the presence of CH<sub>3</sub>Cl react by abstracting an H atom to form HT. Comparison of the results in scavenged and unscavenged samples indicates that essentially all of this HT yield is obtained from a hot reaction. The magnitude of this yield has been definitely correlated with the bond strength of the C-H bonds in the target molecule, and results with CH<sub>3</sub>Cl are in reasonable agreement with those obtained for hydrocarbons.<sup>26</sup>

If CH<sub>2</sub>TCl molecules decomposed partially by dehydrohalogenation, a pressure-dependent yield of HT could arise from eq. 10a. The constancy of the HT yield relative to the total gaseous activity indicates no appreciable contribution from such methylenic decompositions.



**Acknowledgment.**—The cooperation of the operating personnel of the Omaha VA Hospital reactor is gratefully acknowledged.

(26) W. Breckenridge, J. W. Root, and F. S. Rowland, *J. Chem. Phys.*, **39**, 2374 (1963).

[CONTRIBUTION NO. 1173 FROM THE CHEMICAL LABORATORIES OF INDIANA UNIVERSITY, BLOOMINGTON, IND.]

## Electron Diffraction Determination of the Molecular Structure of the Butyl Halides. V. The Structure and Conformational Analysis of Isobutyl Chloride

BY G. H. PAULI, F. A. MOMANY, AND R. A. BONHAM<sup>1</sup>

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The structure and conformational analysis of gaseous isobutyl chloride has been carried out by the sector-microphotometer method of electron diffraction. The molecular parameters for the bonded distances were found to be:  $r_{\mu}(\text{C-H})_{\text{av}} = 1.105 \text{ \AA}$ ,  $r_{\mu}(\text{C-C}) = 1.534 \text{ \AA}$ , and  $r_{\mu}(\text{C-Cl}) = 1.804 \text{ \AA}$ ;  $l_m(\text{C-H}) = 0.074 \text{ \AA}$ ,  $l_m(\text{C-C}) = 0.053 \text{ \AA}$ , and  $l_m(\text{C-Cl}) = 0.052 \text{ \AA}$ ; and  $\angle \text{C-C-C} = 111^\circ$ ,  $\angle \text{C-C-Cl} = 112^\circ$ ,  $\angle \text{C-C-H (methyl)} = 110^\circ$ , and  $\angle \text{C-C-H (tertiary hydrogen)} = 108^\circ$ . About 80% of the molecules at room temperature were in the conformer where the chlorine is *gauche* to one methyl group and *trans* to the other. The *gauche* angle for this conformer was found to be  $66^\circ$ . A summary of the data on the available structural parameters for butyl halide molecules is given.

Previous work on the analysis of alkyl halide structures in the gas phase<sup>2,3</sup> has shown that fluorine and chlorine groups stabilize *gauche* conformations if the opposite substituent is a methyl or methylene group.

(1) The authors wish to thank the National Science Foundation and the Petroleum Research Fund of the American Chemical Society for their financial support of this work.

(2) (a) Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **28**, 175 (1958); (b) T. Ukaji and R. A. Bonham, *J. Am. Chem. Soc.*, **84**, 3631 (1962).

(3) E. Hirota, *J. Chem. Phys.*, **37**, 283 (1962).

On the other hand, it appears that methyl and bromine substituents stabilize *trans* conformations<sup>4,5</sup> when the opposite group is methyl or methylene. Isobutyl chloride is thus a very interesting case to investigate as the Cl atom can either be *trans* and *gauche* to methyl groups at the same time or else simultaneously *gauche*

(4) F. A. Momany, R. A. Bonham, and W. H. McCoy, *J. Am. Chem. Soc.*, **85**, 3077 (1963).

(5) R. A. Bonham and L. S. Bartell, *ibid.*, **81**, 3491 (1959).

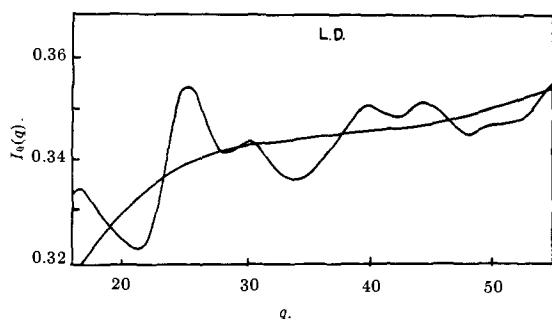


Fig. 1.—Long camera distance data,  $I_0(q)$ , and the background function,  $B(q)$  (smooth curve). The ordinate values refer to an arbitrary relative intensity scale.

to two methyl groups. It is also of interest to compare the C-Cl bond length in isobutyl chloride with that obtained for *t*-butyl chloride in previous investigations.<sup>6,7</sup>

### Experimental

A sample of isobutyl chloride was obtained from the Columbia Chemical Co. and analyzed by gas chromatography. The boiling point and index of refraction were checked and the sample used appeared to be over 99% pure. To avoid possible decomposition, the sample was purified immediately prior to the taking of the diffraction photographs by vacuum distillation. Electron diffraction photographs were obtained with an  $r^3$  sector using the sector electron diffraction camera in Professor L. S. Bartell's laboratory at Iowa State University. Specimen pressures of 20 to 50 mm. with exposure times of 1 to 5 sec. were used at a temperature of 298°K. The beam current was 0.39  $\mu$ a. and the accelerating voltage was 40 kv. Four research grade plates at each of two camera distances were obtained for each molecule. The photographic plates were microphotometered in Professor L. O. Brockway's laboratory at the University of Michigan.

The microphotometer traces of the electron diffraction photographs were read at 0.25-mm. intervals, to four significant figures, with the aid of a Bausch and Lomb 7-power measuring magnifier. The photographic emulsion was calibrated by the procedure of Bartell and Brockway.<sup>8</sup> The index of resolution for the 21.35-cm. camera distance was found to be 0.91 and for the 10.66-cm. distance, 0.92. It was felt that the near unity values of the indices indicated the absence of any serious extraneous scattering effects.

**Structural Analysis.**—The experimental data were analyzed according to schemes outlined elsewhere.<sup>9-11</sup> Bond lengths, vibrational amplitudes, and information on hindered rotation were all obtained by least squares analysis of the radial distribution curve. Corrections for electron-electron scattering, failure of the Born approximation,<sup>12</sup> asymmetry of vibration for bonded distances, and Fourier integral termination errors were all applied. The calculated experimental radial distribution curve made use of experimental data, at integral  $q$ -values, from  $q = 16$  to 100. An artificial convergence factor,  $e^{-dq^2}$ , was employed where  $d$  was chosen so that the experimental value at  $q = 100$  was reduced to a tenth of its value.

In order to make the analysis of the data tractable, it was assumed that all methyl groups were equivalent. An ethane-like barrier was assumed to exist about each carbon-carbon bond so that the molecular structure at room temperature could be described in terms of a mixture of conformers as in the case of *sec*-butyl chloride.<sup>2b</sup> Also, the bonded C-C and C-H distances reported in this investigation are average values of what might be unequivalent distances. Previous work has indicated that C-C distances tend to be constant throughout the molecule to within the experimental error, while C-H distances tend to increase somewhat as the number of methylene groups increase in proportion to the number of methyl groups.<sup>13</sup>

(6) D. R. Lide, Jr., and M. Jen, *J. Chem. Phys.*, **38**, 1504 (1963).

(7) F. A. Momany, R. A. Bonham, and M. L. Druelinger, *J. Am. Chem. Soc.*, **85**, 3075 (1963).

(8) L. S. Bartell and L. O. Brockway, *J. Appl. Phys.*, **24**, 656 (1953).

(9) R. A. Bonham and L. S. Bartell, *J. Chem. Phys.*, **31**, 702 (1959).

(10) R. A. Bonham and F. A. Momany, *J. Phys. Chem.*, **67**, 2474 (1963).

(11) M. Traetteberg and R. A. Bonham, *J. Chem. Phys.*, accepted for publication.

(12) R. A. Bonham and T. Ukaji, *ibid.*, **36**, 72 (1962).

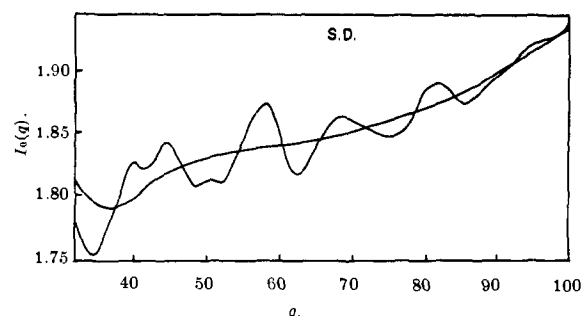


Fig. 2.—Short camera distance intensity data,  $I_0(q)$ , and the background function,  $B(q)$  (smooth curve). The ordinate values refer to an arbitrary intensity scale.

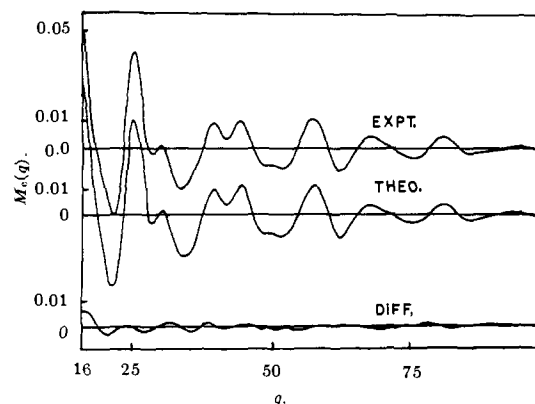


Fig. 3.—Experimental and theoretical reduced molecular intensity function curves and their difference. The ordinate scale refers to the absolute value of  $M_c(q)$ .

In the conformational analysis, *gauche* angles were initially assumed to be 60° but were later adjusted to fit the data. A *trans* angle of 180° was also assumed. The percentage of each conformer present at room temperature was determined by fitting the intensity data and radial distribution curves with a linear combination of the curves for the pure conformeric forms. The curves for the pure forms were computed using all the experimental data obtained in the analysis of the rigid framework parameters from the radial distribution curve and the necessary assumed parameters discussed above.

An independent analysis of the data was also carried out using improved values of the scattering factors for the atoms.<sup>14</sup> In this analysis an entirely new background function was used.

### Results

Figures 1 and 2 show the experimental long and short camera distance intensity curves and the corresponding background functions. In Fig. 3, the experimental and theoretical  $M_c(q)$  curves and their difference are presented. Figure 4 shows the experimental radial distribution curve and the difference between it and the curve for the best theoretical model.

The results of the least squares analysis for the bond distances and root mean square amplitudes of vibration are presented in Table I. The least squares results of the analysis carried out with the newer electron scattering factors are also presented in Table I. The estimated uncertainties were computed using techniques described elsewhere.<sup>9</sup> These estimates do not include possible sources of error due to the use of the simple kinematic scattering theory. A comparison of the results found by this investigation and with previous results for similar molecules is presented in Table II.

(13) R. A. Bonham, L. S. Bartell, and D. A. Kohl, *J. Am. Chem. Soc.*, **81**, 4765 (1959).

(14) T. G. Strand and R. A. Bonham, *J. Chem. Phys.*, accepted for publication.

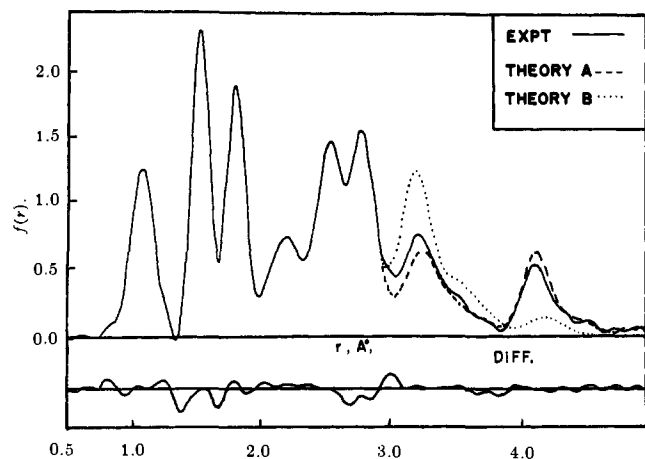


Fig. 4.—Radial distribution curves for isobutyl chloride. The solid line is the experimental  $f(r)$  with theoretical data used for  $q = 1-15$ . The theoretical radial distribution curves for 100% conformer A and for 100% conformer B are shown at distances larger than 3 Å. The difference between the experimental  $f(r)$  and the theoretical  $f(r)$  obtained by combining 80% conformer A and 20% conformer B is shown at the bottom.

The possible conformers for isobutyl chloride are shown in Fig. 5. That part of the radial distribution curve dependent on the conformer percentages is shown in Fig. 4. It should be noted that the peak at 4.11 Å. is a C<sup>4</sup>-Cl nonbonded distance for the form A in Fig. 5. This distance is given as 4.14 Å. by the rigid

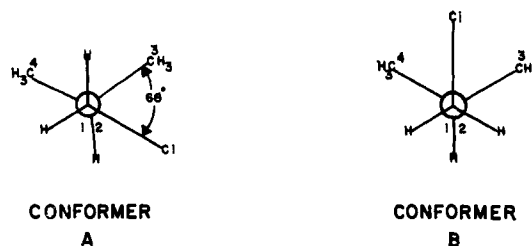
TABLE I  
MOLECULAR PARAMETERS FOR ISOBUTYL CHLORIDE

Peak	Improved scattering factors <sup>a</sup>				Old scattering factors <sup>b</sup>	
	$r_g$	$\delta r_g$	$l_m$	$\delta l_m$	$r_g$	$l_m$
C-H	1.105	0.005	0.074	0.010	1.100	0.078
C-C	1.534	.004	.053	.006	1.534	.056
C-Cl	1.804	.007	.052	.006	1.804	.052
C-C	2.522	.010	.071	.010	2.522	.073
C <sup>2</sup> -Cl	2.771	.010	.078	.010	2.775	.075
Model A C <sup>3</sup> -Cl	3.243	.020	.110	.015	3.243	.110
Model B C <sup>3</sup> -Cl	3.192	.020	.110	.015	3.192	.110
Model A C <sup>4</sup> -Cl	4.109	.015	.086	.015	4.121	.086

<sup>a</sup> See ref. 14. <sup>b</sup> See ref. 9.

framework model. Probably most of this shrinkage is due to a distortion of the *gauche* angle which, reckoned from the adjacent methyl group, may be as large as 66°. The percentage of molecules in form A under the conditions of the experiment ( $T = 300^\circ\text{K.}$ ) was 80%. This leads to a stability of the A conformer over the B conformer of about  $400 \pm 160$  cal./mole. The energy just quoted is a measure of  $\Delta F$  for the reaction  $A \rightleftharpoons B$ . The error limits reflect uncertainties in the least squares fit of the radial distribution curve to determine the conformer percentages as well as in the temperature.

It is extremely interesting that the A form is the more stable. One might conclude by invoking an electrostatic model for methyl-chlorine attractions that the B form with both methyl groups simultaneously *gauche* to the chlorine should be the more stable form.



ISOBUTYL CHLORIDE

Fig. 5.—The possible conformers of isobutyl chloride. The four carbon atoms are labeled with superscripts.

It is possible of course that the B form is severely sterically hindered. The distortion of the *gauche* angle in the direction away from the methyl group may be indicative of such a mechanism. At any rate it would seem that the *trans-gauche* conformer phenomena which have been observed in the butyl chloride

TABLE II  
COMPARISON OF STUDIES OF MOLECULES WITH SIMILAR PARAMETERS

	Isobutyl chloride E.D.	<i>n</i> -Butyl chloride E.D. <sup>a</sup>	<i>sec</i> -Butyl chloride E.D. <sup>a</sup>	<i>t</i> -Butyl chloride— E.D. <sup>b</sup>	M.W. <sup>c</sup>	Iso- butane M.W. <sup>d</sup>
C-H	1.105	1.110	1.109	1.104		1.100
C-C	1.534	1.534	1.534	1.532	1.530	1.525
C-Cl	1.804	1.780	1.781	1.828	1.803	
$l_m$						
C-H	0.074	0.078	0.078	0.075		
C-C	.053	.055	.056	.056		
C-Cl	.052	.059	.059	.050		
$\angle\text{C-C-C}$	111°	112°	111°	112°	111°	111°
$\angle\text{C-C-Cl}$	112°	111°	112°	107°	108°	

<sup>a</sup> T. Ukaji and R. A. Bonham, *J. Am. Chem. Soc.*, **84**, 3627 (1962). <sup>b</sup> See ref. 7. <sup>c</sup> M.W. = microwave, see ref. 6. <sup>d</sup> D. R. Lide, Jr., *J. Chem. Phys.*, **33**, 1519 (1960).

series must involve an interplay between repulsive as well as methyl or methylene-chlorine attractive forces. In Table I the results obtained in this study are summarized. The *t*-butyl parameters seem to be in good agreement with those found in previous studies.<sup>6,7</sup> The C-C-H (tertiary) angle was obtained by assuming that the tertiary hydrogen was on the threefold axis of the carbon framework. Table II presents a summary of results obtained for alkyl halide molecules. The carbon-chlorine bond reported in this work appears to be slightly elongated for a primary chlorine-carbon distance, but it is much less than the 1.828 tertiary value obtained by electron diffraction for *t*-butyl chloride.

**Acknowledgments.**—We wish to thank the Indiana University Research Computing Center for the use of their IBM 709 digital computer and Mrs. Joanne Knight for her help in the preparation of the manuscript. Thanks are also due to Mr. M. L. Druehlinger for his help in reading traces.