Reports of the Academy of Sciences of the USSR

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1958

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR

1958. Volume 118, No. 1

PHYSICAL CHEMISTRY

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ELECTRON-DIFFRACTION STUDY OF THE STRUCTURE OF THE CHLOROPRENE MOLECULE

(Presented by Academician N. N. Semenov, 3 I 1957)

The structure of butadiene and its derivatives, which form the basis of natural and synthetic rubbers, is of great interest for the theory of the structure of organic compounds and is widely discussed in the literature. The principal questions under discussion are the state of the single C—C bond located between two double bonds and rotational isomerism about this bond. The widespread idea of a planar configuration of molecules with a system of conjugated double bonds is confirmed only in some of the simplest compounds; in the general case, in molecules of dienes and their derivatives, the existence of rotated isomers with a nonplanar system of conjugated double bonds is possible. The rotational isomerism of compounds containing conjugated double bonds, as well as the question of the form of the potential barrier hindering rotation about the central C—C bond, have been little studied. Establishing the structure, the concentration ratios, and the heats of transition of various isomers is necessary for understanding the mechanism of chemical transformations, and also for calculating the thermodynamic functions of these compounds. Such data can be obtained by using, along with chemical methods, various physical and physicochemical methods of investigation.

The purpose of the present work was to determine the spatial configuration and geometrical parameters of the chloroprene molecule by the method of diffraction of fast electrons in a vapor jet of the substance under investigation*. The electron-diffraction photographs were taken with an apparatus described earlier (1). Seven series of electron-diffraction patterns were obtained (3 photographs per series) at electron wavelengths from 0.0520 to 0.0540 Å and at a distance from the evaporator nozzle to the plate of 117 mm. On the electron-diffraction patterns, 8 maxima and 7 minima were measured, with visual estimation of their intensities. On the basis of the experimental data obtained, given in Table

1, a radial distribution curve (Fig. 1) was constructed by the Walter and Beach method (^{2}).

A calculation carried out with variation of the values of the intensities of the extrema confirmed the reliability of the radial distribution curve. We made the following assignment of the peaks of the radial distribution curve to interatomic distances in the chloroprene molecule** (see Fig. 2):

1) 1.34 Å —composite, includes 5 r (C—H), 2 r (C=C) and r (C—C);
2) 1.71 Å —r (C—Cl);
3) 2.02 Å —very small, composite: 5 r ($C_2 \cdots H_1$) and r ($C_2 \cdots H_3$);
4) 2.67 Å —very large, composite: r ($C_1 \cdots C_3$), r ($C_2 \cdots C_4$), r ($Cl \cdots C_3$), r ($Cl \cdots C_1$);

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* Chloroprene is a colorless mobile liquid (b.p. 59°) with a sharp odor; it polymerizes readily even in the absence of light. To inhibit polymerization, hydroquinone was added to the ampoule with chloroprene.

** In the notation of interatomic distances, a dash is used for atoms forming a chemical bond, and a dotted line for atoms not directly bonded.

Table 1

Results of processing electron diffraction patterns of chloroprene vapor

Maxima	Minima	$f(s)$	s_{exp}	s_{theor}/s_{exp} (model 4)	s_{theor}/s_{exp} (model 5)
1		+1	2.91	—	—
	1	−12	4.07	—	—
2		+10	5.05	(1.034)	(1.034)
	2	−7	6.54	0.998	0.998
3		+5	7.33	—	—
	3	−3	9.11	(1.026)	(1.026)
4		+4	10.44	0.991	0.994
	4	−4	11.47	0.994	0.994
5		+4.5	12.46	1.002	1.004
	5	−5	13.75	0.989	0.985
6		+5	14.78	1.008	1.007
	6	−0.5	15.99	1.010	1.010
7		+0.5	16.86	1.005	1.002
	7	−0.6	18.03	0.993	0.992
8		+6	19.19	0.999	0.998
		Mean value		0.999	0.998

Figure 1 and Figure 2

Figure 1: Figure 1 and Figure 2

Maxima	Minima	$f(s)$	s_{exp}	$s_{\text{theor}}/s_{\text{exp}}$(model 4)	$s_{\text{theor}}/s_{\text{exp}}$(model 5)
		Mean deviation		±0.006	±0.006

5) 3.06 Å—$r(\text{Cl} \ldots \text{C}_4)$ and 6) 3.70 Å—$r(\text{C}_1 \ldots \text{C}_4)$ for the trans configuration of the double bonds;

6) 4.02 Å—a small peak, which may correspond to $r(\text{Cl} \ldots \text{C}_4)$ for the cis configuration. Taking into account that on the radial distribution curve constructed from the data taken from theoretical curve 5, corresponding to the rotated trans isomer (see below), a peak at 4.02 Å also appears, one should refrain from assigning this peak to the cis isomer.

Fig. 1. Radial distribution curve according to the equation of Walter and Beach (2) for the chloroprene molecule

Fig. 2. Skeleton of the chloroprene molecule

Then, for several models whose structural parameters are given in Table 2, theoretical intensity curves were calculated by the method of successive approximations (3), and these were compared with the intensity curve constructed from the experimental values (Fig. 3). In this case

Table 2

Values of the structural parameters of various models of the chloroprene molecule

Model	r (C=C)	r (C–C)	r (C–Cl)	$\angle$ $\text{C}_1\text{C}_2\text{Cl}$ = $\angle$ $\text{C}_1\text{C}_2\text{C}_3$	$\angle$ $\text{C}_2\text{C}_3\text{C}_4$	α*
1 planar trans	1.36	1.46	1.70	122°	122°	0°
2 planar cis	1.36	1.46	1.70	122°	122°	180°
3 rotated	1.36	1.46	1.70	122°	122°	90°

Fig. 3. Theoretical intensity curves for models 1-8 of the chloroprene molecule and the experimental curve

Figure 2: Fig. 3. Theoretical intensity curves for models 1-8 of the chloroprene molecule and the experimental curve

Model	r (C=C)	r (C–C)	r (C–Cl)	$\angle C_1C_2Cl = \angle C_1C_2C_3$	$\angle C_2C_3C_4$	α*
4 planar trans	1.36	1.46	1.70	122°	127°	0°
5 rotated	1.36	1.46	1.70	122°	122°	32°
6 ”	1.36	1.50	1.70	122°	122°	32°
7 ”	1.36	1.46	1.70	122°	122°	42°
8 ”	1.36	1.46	1.70	122°	122°	22°

* α is the angle between the planes of the vinyl groups.

The distances C–H, C=C, and C_2–C_3, not resolved separately on the radial-distribution curve, were taken equal to the corresponding distances in butadiene (4); the distance C–Cl, in accordance with the radial-distribution curve, was taken as 1.70 Å; the hydrogen atoms were taken into account by the method described in (5).

The theoretical intensity curves 1, 2, and 3 do not agree with the experimental intensity curve of the scattered electrons. Curve 1 (planar trans isomer) does not reproduce the sharp asymmetry of maximum 3 and greatly underestimates the intensities of maxima 5 and 4. Curve 2 (planar cis isomer) does not reproduce the sharp asymmetry of maximum 3 or the shape of maximum 5 and has no maximum 7. Curve 3 (rotated isomer with rotation of the vinyl groups about the C_2–C_3 bond by 90°) does not show the asymmetry for maximum 3 and has minima 4 that are too small and maximum 5. The best agreement with the experimental curve is shown by theoretical curves 4 and 5. Curve 4 corresponds to a planar model of the chloroprene molecule with a trans arrangement of the double bonds and with angles $C_1C_2C_3$ and $C_2C_3C_4$ differing by 5°. Curve 5 corresponds to a nonplanar model of the molecule with rotation of the vinyl groups about the single C_2–C_3 bond by an angle of 32° from the trans position and with equal angles $C_1C_2C_3$ and $C_2C_3C_4$.

Fig. 3. Theoretical intensity curves for models 1-8 of the chloroprene molecule and the experimental curve

The principal parameters of models 4 and 5 agree quite satisfactorily with the values of the internuclear distances obtained from the radial-distribution curve. Curves 6, 7, and 8 were calculated in order to determine the possible limits of variation of the $C_2{-}C_3$ bond length and the $Cl \cdots C_4$ distance, which proved to be, respectively, ±0.04 Å and ±0.06 Å. Thus, the experimental data obtained by us in the electron-diffraction study of the geometrical structure of the chloroprene molecule correspond to two most probable structures:

1) a planar chloroprene molecule with a trans arrangement of the double bonds and with the following values of the interatomic distances and valence angles:

$$r(\mathrm{C=C}) = 1.36\ \text{Å (adopted)};\quad r(\mathrm{C{-}C}) = 1.46{\pm}0.04\ \text{Å};\quad r(\mathrm{C{-}Cl}) = 1.70{\pm}0.02\ \text{Å};$$

$$\angle \mathrm{C_1C_2Cl} = \angle \mathrm{C_1C_2C_3} = 122^\circ\ \text{(adopted)} \quad \text{and} \quad \angle \mathrm{C_2C_3C_4} = 127^\circ \pm 3^\circ.$$

2) a nonplanar chloroprene molecule with an angle of rotation of the vinyl groups about the single $C_2 - C_3$ bond by $30^\circ \pm 10^\circ$ from the trans position and with the following values of the interatomic distances and valence angles:

$$r(\mathrm{C=C}) = 1.36\ \text{Å (adopted)};\quad r(\mathrm{C{-}C}) = 1.46{\pm}0.04\ \text{Å};\quad r(\mathrm{C{-}Cl}) = 1.70{\pm}0.02\ \text{Å};$$

$$\angle \mathrm{C_1C_2Cl} = \angle \mathrm{C_1C_2C_3} = 122^\circ\ \text{(adopted)}.$$

The ambiguity in the interpretation of the experimental data is associated with the insufficient sensitivity of the theoretical intensity curves to changes in the distance $C_4 \ldots C_1$ and $C_4 \ldots C_2$ in different models of the chloroprene molecule.

The results of the present investigation show that the carbon-carbon double bonds in the chloroprene molecule have a trans, or nearly trans, configuration, which agrees with previously obtained data from studies of the infrared and ultraviolet spectra of chloroprene ($^{6-8}$). Confirmation of the trans configuration of the chloroprene molecule is also provided by the structure of its polymer—neoprene, consisting of repeating groups of atoms with a trans arrangement of methylene groups relative to the $C - C$ bonds (^{9}). It is interesting to note that the trans configuration of double bonds is characteristic of the majority of the simple compounds studied that contain a system of two conjugated double bonds (for example, butadiene, glyoxal, dimethylglyoxal, acrolein, etc.). In considering the results of the study of the geometry of the chloroprene molecule, attention is drawn to the distance $Cl \ldots C_4 = 3.05$ Å, which is greatly decreased in comparison with the sum of the intermolecular radii of the CH_2 group and the chlorine atom, equal to 3.70 Å. This cannot be explained by invoking the idea of an induction interaction between the chlorine atom and the CH_2 group, since in the allyl chloride molecule ([10,11]) the corresponding distance is unchanged and is equal to 3.70 Å.

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Received
29 XII 1956

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