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Abstract

Full Text

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On the Kinetics of the Reaction of Rotational Isomerization

(Presented by Academician A. N. Frumkin, 4 XII 1956)

The potential barrier for the mutual transformation of rotational isomers (trans and gauche) of molecules of the 1,2-dichloroethane type, $CXY_2—CXY_2$, may be represented in the form (1)

$$-V|\varphi| = \frac{1}{6}\left[V_0 + 2V_1 + 2V_2 - (2V_0 - 2V_1 + 2V_2)\cos\varphi - (-2V_0 + 2V_1 + 2V_2)\cos 2\varphi - (V_0 + 2V_1 - 2V_2)\cos 3\varphi\right]. \qquad (1)$$

Figure 1 shows the form of this function (curve I) for the transformation in the gas phase. For a complete determination of the potential function it is necessary to know three parameters, V_0, V_1, V_2. Knowledge of these parameters is necessary not only for a general understanding of the nature of the phenomenon of hindered internal rotation and rotational isomerism of molecules, but also for the statistical calculation of their thermodynamic functions.

Fig. 1. Form of the potential function for molecules of the 1,2-dichloroethane type

There are no direct methods for determining the constants V_0, V_1 of the hindering potential. In general, for molecules of the 1,2-dichloroethane type only a certain effective value of the hindering potential has been determined from comparison, for example, of the entropy value found from the third law of thermodynamics with the value calculated under the assumption of free internal rotation, or else under simplified assumptions about the shape of the barrier ($V_2 = 0, V_1 = V_0$). Of the three parameters indicated above, one (V_2—the energy difference of the rotational isomers) can be determined exactly experimentally from the temperature dependence of the relative intensities of bands (lines) of

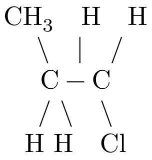
Fig. 2. Curve of the decrease in intensity of the 1310 cm^-1 band of propyl chloride with time and temperature

Figure 2: Fig. 2. Curve of the decrease in intensity of the 1310 cm^-1 band of propyl chloride with time and temperature

the infrared spectrum (the combination-scattering spectrum), using the known expression for the equilibrium constant of a mixture of rotational isomers.

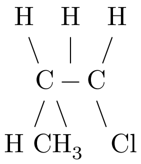
Let us try to show that in some cases it is possible independently and experimentally to determine the second parameter V_1 in the expression for the potential function by studying the kinetics of isomerization of rotational isomers. We previously found a simplification of the infrared spectrum of propyl chloride in the crystalline state as compared with the spectrum of the liquid (^{2}). It was established that the propyl chloride molecule occurs in two spectroscopically distinguishable rotational-isomeric forms:

C_s—trans configuration



$$\begin{array}{ccc} CH_3 & H & H \\ \backslash & | & / \\ & C - C & \\ / \backslash & & \backslash \\ H\ H & & Cl \end{array}$$

and C_1—gauche configuration



$$\begin{array}{ccc} H & H & H \\ \backslash & | & / \\ & C - C & \\ / \backslash & & \backslash \\ H\ CH_3 & & Cl \end{array}$$

In the solid phase, at a certain temperature, a transition is observed from the equilibrium present in a rapidly frozen vapor (both isomers) to the equilibrium of the crystalline state, when practically only the trans isomer of this substance remains (^{2}). In the present work we have succeeded in following with time the disappearance of a number of frequencies in the spectrum of crystalline propyl chloride over a definite temperature interval.

Fig. 2. Curve of the decrease in intensity of the 1310 cm^{-1} band of propyl chloride with time and temperature

Figure 2 presents a time record of the decrease in the intensity of the band with frequency 1310 cm^{-1}, which we assign to the out-of-plane deformation vibrations of the CH_2 group of the gauche isomer of propyl chloride. The process of disappearance of a series of bands may evidently be regarded as the result of the rotational-isomerization reaction

$$N_{\text{gauche}} \longrightarrow N_{\text{trans}}.$$

This reaction is described by the kinetic equation of a monomolecular reaction, which in our case has the form

$$N_1 = N_{01} e^{-K(t-t_0)}, \tag{2}$$

where N_0 is the number of moles of the gauche isomer at t_0; N_1 is the number of moles of the gauche isomer remaining by time t; K is the rate constant of the reaction.

To determine the reaction rate constant, it is necessary to know the ratio N_1/N_{01}, which can be readily found. Indeed, $I_{01} = i_{01}N_{01}$, $I_1 = i_{01}N_1$, where i_{01} is the molar intensity of the rotated isomer, whence $N_1/N_{01} = I_1/I_{01}$. The ratio I_1/I_{01} is obtained from experiment (Fig. 2).

Having thus determined the reaction rate constants for different temperatures of that temperature interval in which this reaction proceeds (Fig. 2), using the Arrhenius—van' t Hoff equation

$$\ln K = H - \frac{A_{\text{tv}}}{kT}$$

we calculated the activation energy A_{tv} for the isomeric transformation under consideration in the solid phase and obtained the value 4800 ± 500 cal/mole, which, at least as to order of magnitude, is quite reasonable. It can be shown that the desired value $V_{1\text{gas}}$ can be found with a high degree of accuracy in the form

$$V_{1\text{gas}} = V_{2\text{gas}} + A_{\text{tv}},$$

where A_{tv} is the activation energy of the reaction of transformation of the isomers in the solid phase. In fact, in Fig. 1, curve *II* shown by the dashed line represents the potential curve of internal rotation of molecules about the middle C–C bond in the solid phase. As is seen from curves *I* and *II* (Fig. 1), there is the following relation between the quantities pertaining to the gas and solid phases:

$$V_{1\text{gas}} = V_{2\text{gas}} + A_{\text{gas}}, \quad V_{1\text{tv}} = V_{2\text{tv}} + A_{\text{tv}},$$

$$V_{1\text{gas}} = V_{1\text{tv}} + L_1 - L, \quad V_{2\text{gas}} = V_{2\text{tv}} + L_2 - L,$$

where L_1, L_2, L are the internal energies of evaporation at $T = 0$ of the pure eclipsed, rotated, and trans forms, respectively.

From these relations we obtain

$$A_{\text{gas}} = V_{1\text{tv}} - V_{2\text{tv}} + L_1 - L_2,$$

$$V_{1\text{gas}} = V_{2\text{gas}} + V_{1\text{tv}} - V_{2\text{tv}} + L_1 - L_2.$$

Since each of the quantities L_1 and L_2 is of the same order as $V_{1\text{tv}} - V_{2\text{tv}}$ (several kcal/mole), then

$$L_1 - L_2 \ll V_{1\text{tv}} - V_{2\text{tv}},$$

and therefore

$$V_{1\text{gas}} \simeq V_{2\text{gas}} + V_{1\text{tv}} - V_{2\text{tv}}.$$

Thus, the value $V_{1\text{gas}}$ can be measured rather accurately in studying the isomerization process in the solid phase. Knowledge of the quantities V_1 and V_2 apparently also makes it possible to determine the third parameter of the potential curve, V_0, if from a comparison of the experimental value of the entropy and the value calculated statistically under the assumption of free internal rotation one obtains the magnitude of the effective barrier.

Thus, the method presented here for studying the kinetics of the reaction of rotational isomerization opens up new and interesting prospects for investigating the phenomena of hindered internal rotation and rotational isomerism.

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Note: Figure translations are in progress. See original paper for figures.

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