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The determination of the parameters of conformational equilibria by infrared absorption spectra

A. I. FISHMAN,* A. A. STOLOV* and A. B. REMIZOV†

*Kazan State University, Lenin Street 18, Kazan 420008, U.S.S.R. and †Kazan Chemistry Technology Institute, Karl Marx Street 68, Kazan 420015, U.S.S.R.

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Abstract—New methods of determining the entropy difference of two conformations, the activation energy of the conformational transitions, of free enthalpy difference and the ratio of integral absorption coefficients of two conformations by i.r. absorption spectra are proposed. The basis of the method of ΔS_0 determination is the study of the i.r. spectra of compounds both in the temperature range where there are conformational transitions and at the temperatures where they do not occur. For the determination of E^\ddagger , ΔG_0 and α_A/α_B it is proposed to investigate the kinetics of the conformational transitions in liquid solutions. The methods have been applied to chloro-, bromo- and *trans*-dichlorocyclohexanes.

1. INTRODUCTION

If there is a dynamic equilibrium of two conformations A and B, the ratio of their concentrations C_A and C_B is defined by the equilibrium constant:

$$K = C_A/C_B = \exp(-\Delta G_0/RT) \\ = \exp(-\Delta H_0/RT + \Delta S_0/R), \quad (1)$$

where ΔG_0 is the difference of free enthalpies of the conformations, ΔH_0 and ΔS_0 are the differences of their enthalpies and entropies, respectively.

Infrared spectroscopy is widely used both for the qualitative analysis of conformationally unhomogeneous compounds and for the quantitative definition of the parameters of conformational equilibria.

(1. i) The method of determination of ΔH_0

It is the difference of the enthalpies of conformations that is most frequently determined by i.r. absorption spectra [1]. Since the intensity of the vibrational band is proportional to the concentration of the molecules of a definite kind, then by choosing a pair of bands belonging to different conformations one may determine ΔH_0 . The intensities of the absorption bands of the conformers may be written down in the form:

$$I_A = \alpha_A C_A l, \quad I_B = \alpha_B C_B l, \quad (2)$$

where I_A and I_B are the observable integral intensities of the absorption bands of the conformers A and B, α_A and α_B are the integral absorption coefficients and l the thickness of the absorbing layer. Then from (1) and (2):

$$\ln \frac{I_A}{I_B} = \ln \frac{\alpha_A}{\alpha_B} + \frac{\Delta S_0}{R} - \frac{\Delta H_0}{RT}. \quad (3)$$

Measuring the intensities at different temperatures, one can determine ΔH_0 by the slope of the linear dependence of $\ln(I_A/I_B)$ upon $1/T$. This method assumes that ΔH_0 , ΔS_0 and the value of α_A/α_B do not depend on temperature.

Possible changes of the ratio α_A/α_B with temperature may lead to errors when determining ΔH_0 . Therefore it is of definite interest to attempt to take these changes into account.

(1. ii) The methods of determination of ΔS_0

In the literature are described ways of determining ΔS_0 by i.r. absorption spectroscopy [2, 3, 4].

In [2] in order to determine ΔS_0 it is proposed to use the changes of the intensities of the absorption bands of conformers in different solvents. This method assumes that the absorption coefficients α_A and α_B do not depend on the solvent, and that the change of the intensities is caused only by the shift of the equilibrium. Furthermore, for the correct use of this method it is necessary to observe a large enough solvent dependence of the intensities. This considerably limits the possibilities of using this method.

In [3] it is proposed to measure the integral intensities of one conformer at different temperatures. The authors of the paper obtained a relation which makes it possible to determine ΔS_0 by the dependence of the intensity of the absorption band of a more stable conformer upon temperature assuming that α does not depend on T .

In [4] to determine ΔS_0 it is proposed first to find the ratio α_A/α_B . If C is the general concentration, then at any temperature $C = C_A + C_B$. From (2) it follows that

$$I_A = \alpha_A l C - \frac{\alpha_A}{\alpha_B} I_B. \quad (4)$$

If α_A and α_B do not depend on temperature then by the slope of the linear dependence of I_A upon I_B one may obtain the value of α_A/α_B . Knowing this relation, from (3) one may determine ΔS_0 . It is seen that to diminish the error of the determination of ΔS_0 it is necessary to carry out the investigation over a large temperature range. However, it is well known [5, 6] that for liquids and solutions the integral absorption coefficients of i.r. bands decrease as a rule with increase in temperature. With an increase in temperature of a liquid or a solution by 100 K the coefficient α may