

## 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  $\Delta S_0$  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  $E^\ddagger$ ,  $\Delta G_0$  and  $\alpha_A/\alpha_B$  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  $\Delta G_0$  is the difference of free enthalpies of the conformations,  $\Delta H_0$  and  $\Delta S_0$  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 $\Delta H_0$

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  $\Delta H_0$ . 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,  $\alpha_A$  and  $\alpha_B$  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  $\Delta H_0$  by the slope of the linear dependence of  $\ln(I_A/I_B)$  upon  $1/T$ . This method assumes that  $\Delta H_0$ ,  $\Delta S_0$  and the value of  $\alpha_A/\alpha_B$  do not depend on temperature.

Possible changes of the ratio  $\alpha_A/\alpha_B$  with temperature may lead to errors when determining  $\Delta H_0$ . Therefore it is of definite interest to attempt to take these changes into account.

#### (1. ii) The methods of determination of $\Delta S_0$

In the literature are described ways of determining  $\Delta S_0$  by i.r. absorption spectroscopy [2, 3, 4].

In [2] in order to determine  $\Delta S_0$  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  $\alpha_A$  and  $\alpha_B$  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  $\Delta S_0$  by the dependence of the intensity of the absorption band of a more stable conformer upon temperature assuming that  $\alpha$  does not depend on  $T$ .

In [4] to determine  $\Delta S_0$  it is proposed first to find the ratio  $\alpha_A/\alpha_B$ . 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  $\alpha_A$  and  $\alpha_B$  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  $\alpha_A/\alpha_B$ . Knowing this relation, from (3) one may determine  $\Delta S_0$ . It is seen that to diminish the error of the determination of  $\Delta S_0$  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  $\alpha$  may