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Compensation effect in the thermodynamics of conformational equilibria

A. I. FISHMAN* and A. A. STOLOV

Kazan State University, Lenin Street 18, Kazan 420008, U.S.S.R.

and

A. B. REMIZOV

Kazan Chemistry Technology Institute, Karl Marx Street 68, Kazan 420015, U.S.S.R.

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Abstract—The solvent dependence of thermodynamic parameters of conformational equilibria in *trans*-1,2-dichlorocyclohexane and *trans*-1,2-bromochlorocyclohexane was investigated by infrared absorption spectra. The results obtained show the existence of a compensation effect in the thermodynamics of conformational equilibria: the enthalpy (ΔH_0) and entropy (ΔS_0) differences change in the same direction when going from one solvent to another. A semi-quantitative estimation of the effect is given on the basis of the equations of statistical thermodynamics. It is shown that the temperature dependence of the ΔS_0 value must be taken into account when determining the enthalpy difference of the conformers. This yields the equality of the true and observed ΔH_0 values.

INTRODUCTION

THE SOLVENT and temperature dependence of the parameters of conformational equilibria are nowadays the subject of intense studies [1, 2]. In many studies devoted to this problem, the solvent dependences of the values ΔH_0 or ΔG_0 (enthalpy and free enthalpy differences of the conformers) are analysed. However, there is little data concerning the entropy difference of the conformers, ΔS_0 , and its variation with a solvent. The latter fact is probably due to experimental difficulties in determining the ΔS_0 values. The lack of experimental data seems to be responsible for the following assumptions having different forms:

- (1) $\Delta S_0 = 0$ or $\Delta S_0 = R \ln \gamma$, where γ is the statistical weight ratio of the conformers [3];
- (2) $\Delta S_0 \neq 0$, but is independent of solvent [1, 4];
- (3) $\Delta S_0 \neq 0$, but is independent of temperature [1].

It is perfectly clear that, in the common case, the entropy difference of the conformers depends on the solvent and temperature. Therefore, it becomes important to find out if those dependences are sufficient or not, i.e. to evaluate the experimental errors appearing due to the usage of assumptions (1)–(3). To answer this question, it is necessary to determine ΔS_0 values for several model compounds under different experimental conditions. In this paper, the values ΔH_0 , ΔG_0 , ΔS_0 and also ΔH^* and ΔS^* are obtained for two di-substituted halocyclohexanes in polar and non-polar solvents. The modification of the i.r. spectroscopic method proposed earlier [5], was used. On the basis of the data obtained, an attempt is made to answer the above questions.

MATERIALS

Trans-1,2-dichlorocyclohexane (I) and *trans*-1,2-bromochlorocyclohexane (II) were used as models. In the liquid and solution these compounds exist in the form of a mixture of diaxial (A) and diequatorial (B) conformations [6, 7]. The molecule I is one of the basics in analysing the general principles of conformational analysis: thermodynamic parameters of conformational equilibria in I dissolved in different liquids have been determined previously by different methods [1]. The conformational equilibria in II have not been studied quantitatively.

* Author to whom correspondence should be addressed.