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Thermodynamic parameters of conformational equilibrium in 1,2-dichloroethane: influence of medium, benzene and compensation effects

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Abstract

The conformational equilibrium of 1,2-dichloroethane (DCE) in 19 different media (vapour phase, liquid, solutions in *n*-hexane, *n*-heptane, carbon tetrachloride, benzene, toluene, ethyl benzene (EB), carbon disulphide, diethyl ether, bromoform, chloroform, dichloromethane, pyridine, acetone, methanol-*d*₃, acetonitrile, glassy polystyrene (PS) matrix and 1:1 mixture of PS and EB) has been studied by IR absorption spectra. The enthalpy differences (ΔH_0) between *trans* (t) and *gauche* (g) conformers were determined from the dependencies of $\ln(I_t/I_g)$ upon T^{-1} , where I_t and I_g are the integrated intensities of the bands belonging to *trans* and *gauche* conformers, respectively. The values of $RT \ln(I_t/I_g)$ and $(R \ln(I_t/I_g) + \Delta H_0/T)$ obtained at 296 K were used as measures of the free enthalpy (ΔG_0) and entropy (ΔS_0) differences of the conformers respectively, when considering their changes with solvent. Good correlations between ΔG_0 , ΔH_0 and the function of the dielectric permittivity of the medium $(0.5 - (\epsilon - 1)/(2\epsilon + 1))^{1/2}$ were observed for all solvents except methanol-*d*₃ (effect of self-association) and the aromatic solvents (benzene effect). Notwithstanding the similar structures and dielectric permittivities of EB and PS, the former medium behaves as a significantly more polar solvent. The analysis of the ΔH_0 values obtained for DCE in PS and EB enabled confirmation of Eliel and Hofer's concept of the origin of the benzene effect; the effect is assigned to the relatively high anisotropy of the polarizability tensor of aromatic compounds. As a consequence, the electrostatic and dispersion interactions of a solute dipole with a neighbouring aromatic ring is crucial to their mutual orientation. Significantly non-linear (close to quadratic) dependencies $\ln(I_t/I_g) = f(T^{-1})$ were observed for DCE in toluene and EB in the range 180–370 K; the ΔH_0 value increased from $-170 \text{ cal mol}^{-1}$ at 358 K to 820 cal mol^{-1} at 190 K for the toluene solution. These results are considered within the framework of the manifestations of the benzene effect. Significant changes in ΔS_0 with the media have been found; they cover more than $2.0 \text{ cal mol}^{-1} \text{ K}^{-1}$ when going from the vapour phase to polar solvents. Satisfactory correlation between ΔH_0 and ΔS_0 (compensation effect) has been observed, the points corresponding to all the media, including methanol-*d*₄ and the aromatic solvents, being scattered along a straight line. The tangent of the slope $(\Delta\Delta S_0/\Delta\Delta H_0) = (1.4 \pm 0.4) \times 10^{-3} \text{ K}^{-1}$ is close to those determined earlier for 1,2-bromofluoroethane, *trans*-1,2-dichlorocyclohexane and *o*-iodophenol.

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