MOLECULAR COMPLEXES OF CHLOROFORM WITH METHYL-SUBSTITUTED 1,3-DIOXANES

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The $^1$H NMR method was used to study the relative electron donor capacity of a number of methyl-substituted 1,3-dioxanes in complex formation with chloroform. The spectral and thermodynamic parameters of 1:1 H-complexes were determined. The values of the chemical shifts from the hydrogen bond in the complexes vary in correlation with the charges on the oxygen atoms of the investigated bases, calculated by the CNDO/2 method.

In studies of acid-catalyzed conversions of 1,3-dioxacycloalkanes it is suggested that the reactivity is largely determined by the basicity of the acetal [1, 2]. A study of the spectral and thermodynamic characteristics of hydrogen bonds with H-acids permits an estimation of the donor properties of the compounds and a characterization of the influence of the electronic and geometrical structure of the molecules on these properties [3, 4]. Earlier the relative basicity of 1,3-dioxane and some of its derivatives was determined in the reaction of complex formation with iodine [5], deuteromethanol [6], and phenol [7, 8] by the method of IR spectroscopy.

In this work the electron donor properties of 1,3-dioxane and its derivatives were investigated by the $^1$H NMR method as a function of the number and position of the methyl substituents in the ring. Chloroform was used as the standard CH acid. The selection was due to the weakness of the autoassociates of chloroform [9] and its rather high ability to form molecular complexes with various bases [10-18].

When chloroform is diluted with an inert solvent, cyclohexane, the signal of the chloroform proton is shifted by 0.13 ppm in the strong-field direction, which is explained by the presence of weak autoassociates in the solutions [9]. In the region of chloroform concentrations below 0.10 mole fraction, the chemical shift (CS) of the proton ($\delta^M = 7.06$ ppm) is unchanged. This is evidence of the absence of association of the molecules in CHCl$_3$ at high dilutions. In solutions of compounds I-XIII the signal of the proton of chloroform is shifted in the weak-field direction with increasing concentration of the base (Fig. 1), which is an indication of the formation of intermolecular associates through a hydrogen bond. In the series of 1,3-dioxanes studied (Table 1), the least changes in the CS of the CHCl$_3$ proton due...
to complex formation are observed in the system chloroform—5,5-dimethyl-1,3-dioxane ($\Delta_\alpha = 0.52$ ppm) and the greatest in the system chloroform—2,2-dimethyl-1,3-dioxane ($\Delta_\alpha = 0.77$ ppm).

The most important characteristic of the hydrogen bond is its energy [19]. Generalization of a large number of experimental data on the thermodynamics of hydrogen bonds and their spectral manifestations in NMR has made it possible to establish [20–24] that for complex formation of the type

$$A_iH + Bj \rightarrow A_iH \cdots B_j \pm \Delta H_{ij}$$

in most cases a correlation between the chemical shift ($\Delta_c = \delta_C - \delta_M$) and the energies of the H-bond in the complexes (in an approximation that does not consider the anisotropy of the base $B_j$), of the following type, is fulfilled:

$$-\Delta H [\text{cal/mole}] = k \cdot \Delta_c [\text{ppm}],$$

where $k$ is a coefficient of proportionality, the accuracy of the finding of which is determined by the accuracy of the finding of $\delta_M$. For weak molecular complexes of $\alpha$-acetylenes and mercaptans, $k = 1.15$ [24, 26]. According to the data of [24], this ratio is also rather well fulfilled for complexes of phenols, alcohols, hydroperoxides, chloroform, and acids with various bases. When there is no precise values of $\Delta_c$ available, in a first approximation we can use the value of $\Delta_\alpha$ obtained by extrapolation of the CS of the proton participating in the formation of a hydrogen bond to infinite dilution in a solution of the given base [25].

To determine the equilibrium constants of the complex formation of chloroform with bases we used the graphical method of Lin et al. [18] for binary complexes. The method suggests that for the equilibrium of binary association, the constant expressed in mole fractions is set by the equation:

$$K = \frac{X_{AH \cdots B}}{X_{AH} \cdot X_B} = \frac{N_{AH \cdots B} (N_{AH0} + N_{B0} - N_{AH \cdots B})}{(N_{AH0} - N_{AH \cdots B}) (N_{B0} - N_{AH \cdots B})},$$

where $X$ represents the mole fractions of the complex $A-H \cdots B$, the acid $A-H$, and the base $B$; $N_0$ is the initial number of moles; $N_{AH \cdots B}$ is the number of moles of the complex at equilibrium.