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Abstract

Full Text

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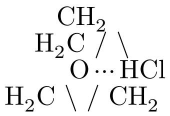
INTERMOLECULAR INTERACTION OF TETRAHYDROFURAN WITH HYDROGEN CHLORIDE

Using Raman spectra and vapor-pressure methods it was shown earlier that a hydrogen bond is formed between dimethyl ether and HCl, with an enthalpy of formation $\Delta H = -7.4$ kcal/mole and an entropy $\Delta S = -28$ e.u. (^{1}).

In the present work the Raman and infrared absorption spectra of the tetrahydrofuran–HCl system were studied at various temperatures and concentrations. Of the known ethers, tetrahydrofuran has the largest dipole moment ($\mu = 1.71$ D) (^{2}); therefore the formation of a strong hydrogen bond may be expected. The Raman spectra were studied on an ISP-51 spectrograph with photoelectric recording. The scheme of the apparatus for saturating tetrahydrofuran with gaseous HCl and the optically thermostated cuvette are shown in Fig. 1. The concentration of HCl in the solution was determined by weighing the apparatus before and after saturation. After this the solution was forced into the optical cuvette. The infrared absorption was studied on a UR-10 spectrometer. In this case the HCl concentration was determined by direct titration.

Fig. 1. General view of the apparatus for saturating tetrahydrofuran with hydrogen chloride and of the temperature cuvette. 1 —vessel for saturation, 2 —cuvette with the liquid under study, 3 —Dewar jacket, 4 —inlet and outlet for gaseous nitrogen, 5 —guide tube reducing the temperature gradient.

Experiments showed that the symmetric and antisymmetric valence vibrations of the group C<$^{\mathrm{O}}$>C are the most sensitive to intermolecular interaction; their frequencies are located at about 914 and 1070 cm^{-1}, respectively (^{3}). Upon saturation of tetrahydrofuran with hydrogen chloride, the Raman spectrum of the latter shows a decrease in the intensity of the line with frequency 914 cm^{-1} and the appearance of a new broad line near 870 cm^{-1} (Fig. 2). The new line should be assigned to the symmetric valence vibration of the group $C{<}^{O}{>}C$, perturbed as a result of the formation of the molecular compound



The dependence of the integral intensity of the line with $\Delta\nu = 914$ cm^{-1} on the concentration of HCl is shown in Fig. 3. Along the ordinate axis is plotted the value of the ratio—

of the integral intensities of the lines $I_{914\ \mathrm{cm}^{-1}}/I_{1030\ \mathrm{cm}^{-1}}$. This made it possible to compare the results obtained at several different values of the spectral slit width of the spectrograph. The line with $\Delta\nu = 1030$ cm^{-1} was chosen as an "intramolecular standard," since its intensity and frequency are little sensitive to the interaction of tetrahydrofuran with HCl (see Fig. 2). The dependence of the intensity of the line with $\Delta\nu = 914$ cm^{-1} on temperature is shown in Fig. 3, from which it is seen that in the tetrahydrofuran—HCl system the temperature behavior is different from that of individual tetrahydrofuran. This is apparently explained by a shift of the equilibrium toward formation of complexes as the temperature is lowered.

Upon saturation of tetrahydrofuran with hydrogen chloride, two new bands appear in the infrared absorption spectrum, at about 882 and 1052 cm^{-1}, attributable to the symmetric and antisymmetric stretching vibrations of the group

$$C-O-C$$

perturbed as a result of hydrogen-bond formation (Fig. 4). Increasing the concentration of HCl in a solution of tetrahydrofuran (using n-hexane and CCl_4 as solvents) causes an increase in the intensity of the low-frequency components and a decrease in that of the high-frequency components. Raising the temperature from 0 to 50° leads to the opposite effect. All this shows that the new bands correspond to vibrations of the group

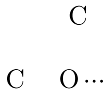


Fig. 2. Combination scattering spectrum of tetrahydrofuran

Figure 2: Fig. 2. Combination scattering spectrum of tetrahydrofuran

The spectrum also contains an absorption band with frequency ~ 2360 cm^{-1} and width $\Delta\nu_{1/2} \approx 300$ cm^{-1}, which corresponds to vibrations of HCl molecules participating in the formation of the molecular compound.

Fig. 2. Combination scattering spectrum of tetrahydrofuran

From the temperature dependence of the integral intensity of the band with $\nu = 914$ cm^{-1}, the changes in enthalpy (ΔH), entropy (ΔS), and free energy (ΔF) upon formation of the molecular compound of tetrahydrofuran with HCl were estimated. They were found to be, respectively: $\Delta H = -11.5 \pm 2.5$ kcal/mol, $\Delta S = -32 \pm 6$ e.u., $\Delta F \approx -2$ kcal/mol. It is interesting to compare the results obtained in the present work with some known literature data.

It is seen from Table 1 that tetrahydrofuran forms the strongest hydrogen bond with HCl. In general, ethers form stronger hydrogen bonds than ketones. This conclusion follows from the fact that, in the case of ethers, the change in enthalpy is larger and the shift of the frequency of the stretching vibrations $\nu_{\text{X-H}}$ toward lower frequencies is larger. We note that the strength of the hydrogen bond is estimated from the enthalpy value. As for the change in free energy, it is another characteristic determining the equilibrium constant, which depends not only on the enthalpy but also on the entropy. The fact that, with the same molecules, ethers form stronger hydrogen bonds than ketones cannot be explained by a difference in dipole-dipole interaction (since $\mu_{\text{ether}} < \mu_{\text{ket}}$).

Table 1

Systems	ΔH, kcal/mole	$\Delta\nu_{\text{X-H}}$, cm^{-1}	μ, D	I, eV
Acetone + chloroform (4)	−4.2		2.7	9.69
+ chloroform (5)	−2.5			
+ chloroform (6)	−3.3			
+ chloroform (7)	−2.7			
+ deutero-chloroform (11)		$\nu_1 - \nu_{\text{C,D}} = 0$		

Systems	ΔH, kcal/mole	$\Delta\nu_{X-H}$, cm^{-1}	μ, D	I, eV
+ pyrrole (9)		$\nu_0 - \nu_{NH} = -140$		
+ phenol (9)		$\nu_0 - \nu_{OH} = -200$		
Acetyl chloride + HCl (10)		$\nu_0 - \nu_{HCl} = -80$	2.40	
Diphenylcyclopropenone + HCl (11)	−6.0	$\nu_0 - \nu_{HCl} = -106$	5.08	
Tetrahydrofuran + HCl	−11.5	$\nu_0 - \nu_{HCl} = -526$	1.71	
Dimethyl ether + HCl (1)	−7.4	$\nu_0 - \nu_{HCl} = -486$	1.29	10
Diethyl ether + HCl (12)		$\nu_0 - \nu_{HCl} = -435$	1.16	9.53
+ pyrrole (5)		$\nu_0 - \nu_{NH} = -178$		
+ phenol (9)		$\nu_0 - \nu_{OH} = -310$		
+ chloroform (13)	−6.02			
+ chloroform (14)	−6.0			
+ chloroform (15)	−(6-7)			
+ deutero-chloroform (8)		$\nu_1 - \nu_{C,D} = -10$		

Note. ν_0 is the vibration frequency in the gas, ν_1 in the individual substance, ν in solution.

Our experiments show that the reaction

$$\text{THF} + \text{diphenylcyclopropenone} \cdots \text{HCl} \rightleftharpoons \text{THF} \cdots \text{HCl} + \text{diphenylcyclopropenone}$$

proceeds from left to right. This clearly shows that formation of a hydrogen

Fig. 3

Figure 3: Fig. 3

Fig. 4. IR absorption spectrum

Figure 4: Fig. 4. IR absorption spectrum

bond with an ether having a moment of 1.71 D is preferable to formation of a hydrogen bond with a ketone whose moment is 5.08 D ([11]). We note that

Fig. 3. Dependence of the ratio of the integral intensities I^{913}/I^{1028} of the Raman lines of tetrahydrofuran on the concentration (in mole fractions) of hydrogen chloride (1) and on temperature (2). I—individual tetrahydrofuran, II —tetrahydrofuran + HCl, $C_{\mathrm{HCl}} = 0.37$, III–$C_{\mathrm{HCl}} = 0.38$, IV–$C_{\mathrm{HCl}} = 0.44$

although in this reaction the entropy decreases, it is nevertheless strongly shifted to the right, evidently owing to a decrease in enthalpy. The ionization potentials, which to some extent reflect donor properties, are very close for ethers and ketones; for example, acetone has 9.69 eV, and dimethyl ether 10 eV ([16]). The explanation of the difference should evidently be sought in the quantum nature of the hydrogen bond.

Many works have been devoted to the theory of the hydrogen bond. The quantum-chemical treatment of this question is due to Coulson and Danielsson ([17]). Along with the usual covalent bond (ψ_1), the ionic component (ψ_2)

the oxonium structure (ψ_3) is taken into account,

$$\begin{array}{llll} \mathrm{Cl-H} & \mathrm{O<} & \psi_1 & \\ \overline{\mathrm{Cl}} & \overset{+}{\mathrm{H}} & \mathrm{O<} & \psi_2 \\ \overline{\mathrm{Cl}} & \mathrm{H-}\overset{+}{\mathrm{O}}\mathrm{<} & \psi_3 & \end{array}$$

so that the complete wave function has the form $\psi = C_1\psi_1 + C_2\psi_2 + C_3\psi_3$. With an ordinary long hydrogen bond, when the hydrogen is far removed from the oxygen, the weight of the structure ψ_3 is small. It amounts to only a few percent. Thus one obtains the result that is the most natural: an ordinary hydrogen bond is mainly due to van der Waals interaction. Coulson and Danielson showed that, in the case of tetrahedral sp^3-orbitals, the weight of the oxonium state is greater than when pure p-orbitals are used. This is explained by the larger value of the overlap integral.

We believe that the difference between ethers and ketones is associated with the weight of the oxonium structure, which is considered as the covalent component of the hydrogen bond. In the formation of a hydrogen bond, not only polarity but also hybridization of the oxygen atom plays a determining role.

Fig. 4. IR absorption spectrum of tetrahydrofuran in a solution of CCl_4 (1) ($C_{\text{THF}} = 0.77$ mol/l, $t = 25°$) and the IR absorption spectrum of the system tetrahydrofuran + HCl (2) ($C_{\text{THF}} = 0.77$ mol/l, $C_{\text{HCl}} = 0.54$ mol/l, $t = 25°$)

However, in the case of compounds of the same type, molecules with a larger dipole moment give stronger hydrogen bonds, as is seen from a comparison of tetrahydrofuran ($\mu = 1.71$ D, $\Delta H = -11.5$ kcal/mol) and dimethyl ether ($\mu = 1.29$ D, $\Delta H = -7.4$ kcal/mol). The authors of some theoretical works come to the conclusion that carbonyl oxygen should form stronger hydrogen bonds than ether oxygen (^{18}). But this conclusion contradicts experiment.

In conclusion, we note that, in order to explain the difference in the strength of hydrogen bonds formed by ketones and ethers, it would be interesting to know the energy of their affinity for the proton.

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