Hydrogen Bonding between Chloroform and Hexamethylphosphoramid. Solvent Effects
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This paper reports the results of a study, by proton magnetic resonance methods, of hydrogen bonding between chloroform and hexamethylphosphoramid in the solvents cyclohexane and dichloromethane. The apparent association constant is found to be considerably smaller in dichloromethane. This can be explained in terms of competitive equilibria between dichloromethane and hydrogen donor and acceptor.

Although hydrogen bonding has been the subject of extensive studies, little attention has been paid to the effects of solvent. Recently it has become evident that some of the so-called inert solvents may interact appreciably with the system under investigation. Although the association constant between solvent and solute may be small, the large concentration of solvent may nevertheless have a profound effect on the apparent association constant between hydrogen donor and acceptor. For example, the association constant between chloroform and hexamethylphosphoramid is found to be 13.4 l/mole in cyclohexane, 9.9 l/mole in decalin, 3.0 l/mole in carbon tetrachloride, at 20°C.

Experimental. Cyclohexane, chloroform, and dichloromethane (Merck, Uvasol grade) were chromatographed through basic aluminium oxide and dried over molecular sieves. Hexamethylphosphoramid (HMPA) was distilled under reduced pressure in a N₂-atmosphere. These purification procedures were carried out immediately before the samples were used.

The NMR spectra were obtained on a JNM-C-60H (JEOL) spectrometer using TMS as internal reference. During recording, the temperature remained constant to ±0.5°C. Chemical shifts were measured with a precision of ±0.2 Hz.

Results and discussion. Fig. 1 shows the ¹H chemical shift of the chloroform proton as a function of HMPA concentration in the solvents cyclohexane and dichloromethane, respectively. Assuming a simple 1:1 model with no interaction between solvent and solutes, the association constant, K, and the hydrogen bond shift, ΔV, between complexed and free donor were calculated by a method published by Nakano and co-workers. The values of K and ΔV are listed in Table 1. The associa-

Table 1. Hydrogen bonding parameters for HMPA-CHCl₃ at 20°C. Chemical shifts measured downfield from TMS.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>K (l/mole)</th>
<th>V&lt;sub&gt;free&lt;/sub&gt; (Hz)</th>
<th>ΔV (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C₆H₁₂</td>
<td>13.4</td>
<td>425.5</td>
<td>121.2</td>
</tr>
<tr>
<td>CH₂Cl₂</td>
<td>0.07</td>
<td>438.8</td>
<td>448.8</td>
</tr>
</tbody>
</table>

V<sub>free</sub>: Chemical shift of hydrogen donor at infinitive dilution.

tion constant, K, decreases from 13.4 l/ mole in cyclohexane to 0.07 l/mole in dichloromethane, while the increase of the corresponding ΔV is from 121.2 Hz to 448.8 Hz. The calculated chemical shifts agree well with the observed ones in both solvents studied. However, the considerable decrease of K and increase of ΔV on going from cyclohexane to dichloromethane, suggest that additional equilibria are involved in dichloromethane.

Therefore, two other possible equilibria in the system HMPA-CHCl₃-CH₂Cl₂ were

examined with the view that there may be association between HMPA and CH₃Cl, and also between CHCl₃ and CH₃Cl. For the measurements of the association between HMPA and CH₃Cl, the concentration of dichloromethane was kept about 0.06 mol/l. The chemical shift of the dichloromethane protons was measured as the solvent varied gradually from cyclohexane to HMPA. At 20°C, the association constant was determined to be \( K = 1.4 \) l/mole and \( \Delta V = 57.0 \) Hz using the simple 1:1 model. This seems reasonable compared to the value of the association constant for HMPA and CHCl₃ in cyclohexane. Chloroform is expected to be a stronger hydrogen donor than dichloromethane owing to its more electron-deficient carbon atom. For the equilibrium between CHCl₃ and CH₃Cl, the chemical shift of the chloroform proton was measured as the solvent varied from cyclohexane to dichloromethane. The association constant was determined to be \( K = 0.07 \) l/mole and \( \Delta V = 26.5 \) Hz.⁴ The association constant and spectral parameters are listed in Table 2.

<table>
<thead>
<tr>
<th>Complex</th>
<th>( K ) (l/mole)</th>
<th>( V_{\text{free}} ) (Hz)</th>
<th>( \Delta V ) (Hz)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HMPA-CHCl₃</td>
<td>13.4</td>
<td>425.5</td>
<td>121.2</td>
</tr>
<tr>
<td>HMPA-CH₂Cl₂</td>
<td>1.4</td>
<td>306.7</td>
<td>57.0</td>
</tr>
<tr>
<td>CH₂Cl₂-CHCl₃</td>
<td>0.07</td>
<td>425.5</td>
<td>26.5</td>
</tr>
</tbody>
</table>

From these experiments, it can be concluded that equilibria exist between CHCl₃ and CH₂Cl₂ and between CH₂Cl₂ and HMPA. Consequently, the simple 1:1 model is invalid for describing the system HMPA-CHCl₃-CH₂Cl₂, and the \( K \) and \( \Delta V \) listed in Table 1 for the system, are only apparently correct. Therefore, using cyclohexane as reference solvent, and including equilibria listed in Table 2, the chemical shift of the chloroform proton in the system HMPA-CHCl₃-CH₂Cl₂ was calculated at various HMPA concentrations. The results are shown in Fig. 2. The good fit between observed and calculated chemical shifts indicates that the real association constant between HMPA and CHCl₃ is the same in cyclohexane and dichloromethane. The decrease of the apparent association constant on going from cyclohexane (13.4 l/mole) to dichloromethane (0.07 l/mole) can only be explained by the same changes as due to competitive equilibria between solvent and solutes.

Fig. 2. Observed and calculated \( ^1H \) chemical shift of the chloroform proton vs. [HMPA] in the solvent dichloromethane at 20°C.

3. Gramstad, T. and Mundheim, O. To be published.

Received October 9, 1970.