Hydrogen Bonding between Chloroform and Hexamethylphosphoramide. 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 hexamethylphosphoramide 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.[1] Recently it has become evident that some of the so-called inert solvents may interact appreciably with the system under investigation.[2] 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 hexamethylphosphoramide 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.[3]

Experimental. Cyclohexane, chloroform, and dichloromethane (Merck, Uvasol grade) were chromatographed through basic aluminium oxide and dried over molecular sieves. Hexamethylphosphoramide (HMPA) was distilled under reduced pressure in N_2-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 $\pm 0.5°C$. Chemical shifts were measured with a precision of ± 0.2 Hz.

Results and dicussion. Fig. 1 shows the ^{1}H 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
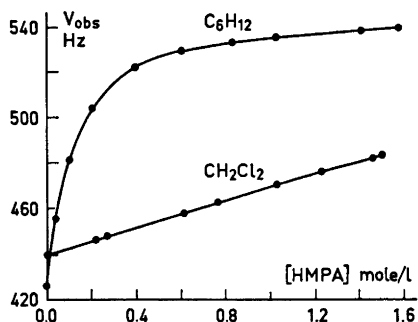
Fig. 1. [1]H chemical shift of the chloroform proton *vs.* [HMPA] in the solvent cyclohexane and dichloromethane at 20°C. [$CHCl_3$]=0.10 mole/l.

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.[4] The values of K and ΔV are listed in Table 1. The associa-

Table 1. Hydrogen bonding parameters for HMPA-$CHCl_3$ at 20°C. Chemical shift measured downfield from TMS.

Solvent	K (l/mole)	V_{free} (Hz)	ΔV (Hz)
C_6H_{12}	13.4	425.5	121.2
CH_2Cl_2	0.07	438.8	448.8

V_{free}: 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-$CHCl_3$-CH_2Cl_2 were

examined with the view that there may be association between HMPA and CH_2Cl_2 and also between $CHCl_3$ and CH_2Cl_2. For the measurements of the association between HMPA and CH_2Cl_2, the concentration of dichloromethane was kept about 0.06 mole/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 $CHCl_3$ 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 $CHCl_3$ and CH_2Cl_2, 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.[5] The association constant and spectral parameters are listed in Table 2.

Table 2. Hydrogen bonding parameters at 20°C. Solvent cyclohexane.

Complex	K (l/mole)	V_{free} (Hz)	ΔV (Hz)
HMPA-$CHCl_3$	13.4	425.5	121.2
HMPA-CH_2Cl_2	1.4	306.7	57.0
CH_2Cl_2-$CHCl_3$	0.07	425.5	26.5

From these experiments, it can be concluded that equilibria exist between $CHCl_3$ and CH_2Cl_2 and between CH_2Cl_2 and HMPA. Consequently, the simple 1:1 model is invalid for describing the system HMPA-$CHCl_3$-CH_2Cl_2 and the K and ΔV 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-$CHCl_3$-CH_2Cl_2 was calculated at various HMPA concentrations. The results are shown in Fig. 2. The good

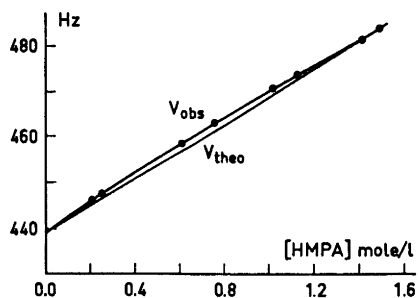*Fig. 2.* Observed and calculated ^{1}H chemical shift of the chloroform proton vs. [HMPA] in the solvent dichloromethane at 20°C.

fit between observed and calculated chemical shifts indicates that the real association constant between HMPA and $CHCl_3$ 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 as shown from the calculations be due to competitive equilibria between solvent and solutes.

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