

INFRA RED STUDY ON INTERMOLECULAR ASSOCIATION OF 2-CHLORO, 2,2-DICHLORO AND 2,2,2-TRICHLOROETHANOLS WITH DIFFERENT BASES

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The proton donor-acceptor complexes formed by mono, di and trichloroethanols with THF and TEA in CCl_4 solution have been investigated by IR spectroscopy. From the area VS. concentration curves it is concluded that complexation tendency for trichloroethanol is greater than that of its mono and di-derivatives. The frequency shift ($\Delta\nu$) and equilibrium constant (K_{11}) measured for 1:1 complexes between alcohols and bases (THE and TEA) at ambient temperature indicate that the association between alcohols and TEA are about 3-times stronger than those between alcohols and THF.

Key words: Intermolecular association, Mono, di and tri chloroethanole, Different bases.

INTRODUCTION

In our previous work [1] we reported that 2-halooethanols make 1:1 complexes with tetrahydrofuran in CCl_4 solution. The curves between area of the OH stretching band corresponding to the intermolecularly H-bonded complexes and concentration of the base (THF) were considered as an indirect approach for measuring the strength of the intramolecular H-bonding. The interaction varied in the order:

$\text{F} > \text{Br} > \text{Cl} > \text{I}$. Frequency shift ($\Delta\nu = \nu_{\text{unbonded in } \text{CCl}_4} - \nu_{\text{bonded in base sol.}}$) also varied in the same order while the enthalpy difference (ΔH°) values showed increase in the order $\text{Cl} < \text{F} < \text{Br} < \text{I}$. Anomaly in the position of F was not clear. The ΔH° VS. $\Delta\nu$ plot was linear and showed that BadgerBauer's rule [2] was obeyed by the system with the exception of the 2-Fluoroethanol complexes.

The previous study [1] has been extended to 2,2-di and 2,2,2-trichloroethanols to examine their relative intermolecular associative tendency with THF and TEA in CCl_4 . On the basis of the results, described in the previous paper [1] it was expected that the molecules showing strong acidic properties would be completely intramolecularly bonded and as a result a small amount of the complexes would be obtained.

P.J. Krueger [3] *et al.* concluded that most of the trihaloethanols would be completely intramolecularly bonded. It has also been reported that intramolecular hydrogen bonds in $\text{Cl}_2\text{CHCH}_2\text{OH}$ are stronger than those in $\text{ClCH}_2\text{CH}_2\text{OH}$.

In the present work, the shape of the curve and frequency shift ($\Delta\nu$) values were used for a qualitative estimation of the energies involved in the intramolecular OH . . . X bonding. K_{11} values (at ambient temperature)

were considered as a measurement of the relative tendency for making the complexes of mono, di and trichloroethanols with the bases in carbontetra-chloride solution.

EXPERIMENTAL

The alcohols used were of spectroscopic grade (98-99 % pure) from Merck and Aldrich. All the alcohols and CCl_4 (98 % pure from Merck) were dried over an activated Molecular Sieve (4A) before use. Commercial tetrahydrofuran (THF) was purified by an effective method described elsewhere [4].

Triethylamine (TEA) used as a proton acceptor was dried over an activated molecular sieve (4A) before use.

In order to avoid moisture contamination from atmosphere, preparation of solution & filling of cells were carried out in drybox under N_2 pressure. 0.02 M solutions of the alcohols were prepared in CCl_4 , where self association is negligible. The amount of THF ($0.00\text{-}1.10 \text{ mol.dm}^{-3}$) and TEA ($0.00\text{-}0.40 \text{ mol.dm}^{-3}$) was varied in the alcohol solutions by making successive addition of 0.2 and 0.02 mol.dm^{-3} respectively.

10-15 minutes were allowed for the solution to equilibrate at room temperature in the case of THF while spectra were recorded immediately after preparing the solution of TEA to avoid the possible interference due to reaction of the amine with CCl_4 .

Spectra were recorded on a Pye-Unicam SP3-100 IR spectrophotometer using KBr windows. The path length of the cell was 0.29 cm and scan time was 3.0 minutes for each spectrum. The concentration of the base in the sample and reference cells was kept the same.

Treatment of data. The measurements were carried out at such a dilution (0.02 mol.dm^{-3}) where the self associa-

tion of alcohols could be neglected. Free and intra bands were resolved by graphical separation method (Figs. 1,2). OH stretching frequency of unbonded OH group was determined in CCl_4 solution. Frequency shift ($\Delta\nu = \nu_{\text{unbonded}}$ in $\text{CCl}_4 - \nu_{\text{bonded}}$ with base) are reported in Table 1.

Band area due to complexes were calculated from equation (1).

$$\text{Area} = 2.303 \times \pi/2 \times A \times \nu_{1/2}^a \dots \dots \dots (1)$$

where A and $\nu_{1/2}^a$ are the absorbance and half band width. True integrated intensities (T) were calculated from equation (2)

$$T = K/C.1 \text{ Log } (I/I_0)_{\text{max}} \times \nu_{1/2}^a \dots \dots \dots (2)$$

where K is correction factor for instrumental effect on the band shape. The values of the K tabulated by Ramsey [5] for various values of $\text{Log}(I/I_0)_{\text{max}}$ and $S/\nu_{1/2}^a$ were used. S is selective slit width of spectrophotometer (5.6 cm^{-1} in the present case).

The equilibrium constant (K_{11}) for 1:1 complexation of alcohol (A) with base (B); tetrahydrofuran,



was calculated from expression (4)

$$K_{11} = \frac{C_{\text{Complex}}}{C_{\text{Alcohol}} \times C_{\text{Base}}} \dots \dots \dots (4)$$

where the concentrations are molar concentration at equilibrium and the activity coefficients have been neglected for dilute solutions. Concentrations of alcohol and base used were the known initial concentrations while the concentration of complex was calculated as follows :

$$C_{\text{Complex}} = \frac{\text{Area}}{T.1} \dots \dots \dots (5)$$

where 1 is the path length of the cell used.

Table 1. Data on H-bonding between haloalcohols and bases ($C_{\text{alcohol}} = 0.02 \text{ mol.dm}^{-3}$, $C_{\text{TEA}} = 0.04 \text{ mol.dm}^{-3}$, $C_{\text{THF}} = 0.10 \text{ mol.dm}^{-3}$).

Proton acceptor	Proton donor	$\nu_{\text{OH}}(\text{free})$ cm^{-1}	$\nu_{\text{OH}}(\text{bonded})$ cm^{-1}	$\Delta\nu$ cm^{-1}	$\nu_{1/2}^a$ cm^{-1}	ΔC_{Base} mol.dm^{-3}
THF	$\text{ClCH}_2\text{CH}_2\text{OH}$	3620	3395	225	125	0.245
"	$\text{Cl}_2\text{CHCH}_2\text{OH}$	3600	3360	240	165	0.125
"	$\text{Cl}_3\text{CCH}_2\text{OH}$	3600	3325	275	180	0.080
TEA	$\text{ClCH}_2\text{CH}_2\text{OH}$	3620	3130	490	—	0.122
"	$\text{Cl}_2\text{CHCH}_2\text{OH}$	3590	3070	520	—	0.040
"	$\text{Cl}_3\text{CCH}_2\text{OH}$	3600	3070	530	—	0.026

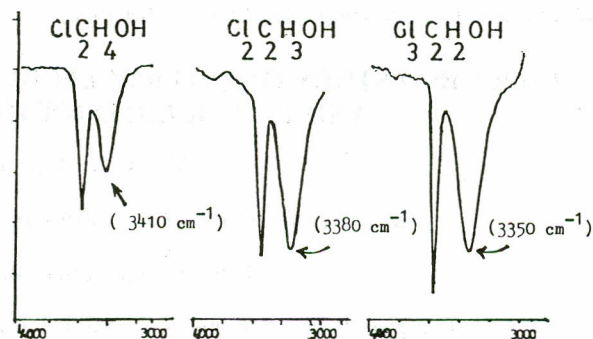


Fig. 1. Illustration of the complexation tendency of mono, di and trichloroethanols with tetrahydrofuran in CCl_4 solution. The increased number of halogen has pronounced effect on the IR band shape and position of bonded OH group. ($C_{\text{Alcohol}} = 0.02 \text{ mol.dm}^{-3}$, $C_{\text{THF}} = 0.1 \text{ mol.dm}^{-3}$).

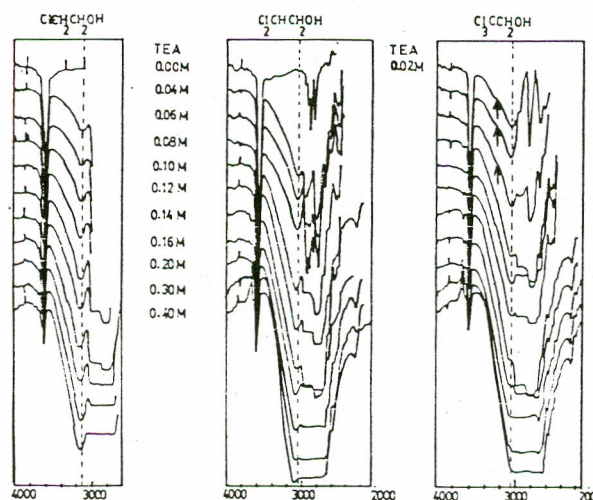


Fig. 2. IR spectra of the complexes formed between alcohol and TEA in carbon tetrachloride solution. Broken line (---) indicates the position of 1:1 complex bands, which gradually overlaps the CH-band with increase in TEA concentration. The arrow indicates the position of 2:1 complexes between alcohols and TEA. ($C_{\text{Alcohol}} = 0.02 \text{ mol.dm}^{-3}$).

The curves between area (due to banded bands) and the concentration of the base added were plotted for all the alcohols (Fig. 3).

For the system containing TEA as a base the values of K_{11} association constant for 1:1 complexes was calculated with the help of expression (6)

$$K_{11} = \frac{1 - A/A_0}{A/A_0 (C_B^0 - C_A^0(1-A/A_0))} \dots\dots\dots (6)$$

where C_A^0 and C_B^0 are the molar concentrations of an alcohol and base and A_0 and A are the absorbances at the frequency of the stretching vibration of the free OH group before and after complex formation respectively. The

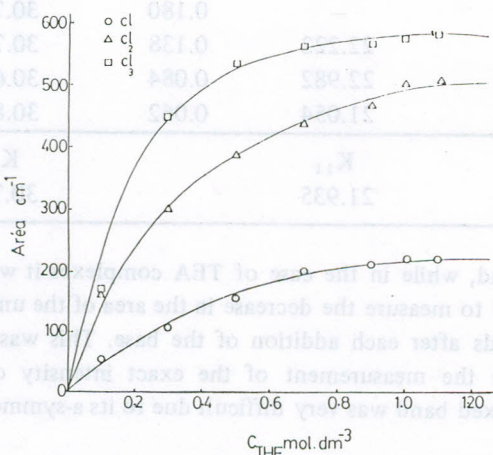


Fig. 3. Area VS. concentration curves for the H-bonded complexes of alcohols with THF in CCl_4 solution ($C_{Alcohol} = 0.02 \text{ mol.dm}^{-3}$).

Table 2. Complex formation constant (K_{11}) for alcohols . . . THF complexes at ambient temperature ($C_{alcohol} = 0.02 \text{ mol.dm}^{-3}$).

C_{THF} mol.dm ⁻³	2-Chloroethanol		2,2-Dichloroethanol		2,2,2-Trichloroethanol	
	$C_{complex}$ x10 ² mol.dm ⁻³	K_{11} dm ⁻³ .mol ⁻¹	$C_{complex}$ x10 ² mol.dm ⁻³	K_{11} dm ³ .mol ⁻¹	$C_{complex}$ x10 ² mol.dm ⁻³	K_{11} dm ³ .mol ⁻¹
0.10	0.591	2.955	2.299	11.498	2.049	10.245
0.30	1.730	2.884	6.924	11.541	—	—
0.50	2.973	2.973	11.385	11.385	14.116	14.116
0.70	3.940	2.814	16.224	11.589	26.088	18.634
0.90	5.120	2.848	21.009	11.672	32.893	18.274
1.00	5.675	2.837	24.560	12.281	37.196	18.598
1.10	6.042	2.747	25.570	11.623	40.974	18.625
		K_{11} 2.886		K_{11} 11.548		K_{11} 18.533

curves between area of the unbanded band and the concentration of the base (TEA) were plotted (Fig. 4). Spectroscopic data (OH. Stretching frequencies of the free and bonded species, half bandwidth and frequency shifts) and equilibrium constant K_{11} are collected in Table 1-3.

In order to find the relative strength of the intermolecularly H-bonded complexes, change in base concentration ΔC_{Base} ; needed to raise the specific area, from $A_1 = 40$ to $A_2 = 120 \text{ cm}^{-1}$ for alcohol . . . THF complexes while in the case of TEA . . . alcohol complexes, ΔC_{Base} ; required to bring a decrease in the specific area (from $A_1=40$ to $A_2=80 \text{ cm}^{-1}$) was measured for all the alcohols (Table 1).

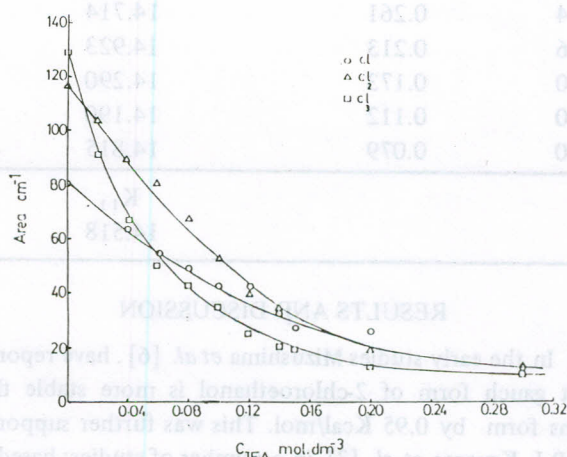


Fig. 4. Area VS. Concentration Curves for the H-bonded complexes of alcohols with TEA in CCl_4 solution. In this case relative decrease in the area of the unbanded bands is plotted. ($C_{Alcohol} = 0.02 \text{ mol.dm}^{-3}$).

Table 3. Complex formation constant (K_{11}) for alcohol . . . TEA complexes at ambient temperature. ($C_{\text{alcohol}} = 0.02 \text{ mol.dm}^{-3}$)

C_{TEA} mol.dm^{-3}	2-Chloroethanol		2,2-Dichloroethanol		2,2,2-Trichloroethanol	
	$A_{\text{OH}}(\text{free})$ cm^{-1}	K_{11} $\text{dm}^3.\text{mol}^{-1}$	$A_{\text{OH}}(\text{free})$ cm^{-1}	K_{11} $\text{dm}^3.\text{mol}^{-1}$	$A_{\text{OH}}(\text{free})$ cm^{-1}	K_{11} $\text{dm}^3.\text{mol}^{-1}$
0.00	0.445	—	0.720	—	0.720	—
0.04	0.434	52.140	0.58	61.867	0.462	78.068
0.06	0.402	27.679	0.462	32.035	0.502	66.619
0.08	0.391	18.969	0.538	22.305	0.328	36.611
0.10	0.351	15.847	0.413	21.793	0.282	31.915
0.12	0.314	14.137	0.325	22.158	0.325	30,642
0.14	0.261	14.714	0.272	22.064	0.195	30.770
0.16	0.213	14.923	—	—	0.180	30.769
0.20	0.173	14.290	0.180	22.222	0.138	30.770
0.30	0.112	14.190	0.117	22.982	0.084	30.613
0.40	0.079	14.815	0.090	21.054	0.062	30.815
		K_{11} 14.518		K_{11} 21.935		K_{11} 30.727

RESULTS AND DISCUSSION

In the early studies Mizushima *et al.* [6] have reported that gauche form of 2-chloroethanol is more stable than trans form by 0.95 Kcal/mol. This was further supported by P.J. Krueger *et al.* [3] in a number of studies; based on conformational analysis that the OH band for $\text{Cl}_3\text{CCH}_2\text{OH}$ was symmetrical at low temperature but exhibited slight asymmetry on the high frequency side at 45° . On the other hand they investigated that $\text{Cl}_2\text{CHCH}_2\text{OH}$ shows small but significant asymmetry on the high frequency side over the entire temperature range. Almost similar behaviour has been observed from this work.

In the present work IR spectra (Figs. 1,2) recorded for the ternary solutions indicate that there is a gradual decrease in the intensity of the free and intra OH bands with the successive addition of the base and at the same time a broad band appears at $3350\text{--}3410 \text{ cm}^{-1}$ for alcohol . . . THF complexes while an asymmetrical broad band for TEA . . . alcohol complexes appear below 3000 cm^{-1} . Estimation of the frequency of the OH-stretching band (complexed) seems difficult due to the overlapping of the OH band with the CH-stretching band. So the system containing TEA as a base was treated in a different way and required special attention as compared to that of THF.

Area vs. concentration curves. Fig. 3,4 illustrate that trichloroethanol has a greater tendency for association with THF & TEA as compared to the others. In alcohol . . . THF complexes, we noticed the increase in the area of the com-

plexband, while in the case of TEA complexes it was advisable to measure the decrease in the area of the unbonded bands after each addition of the base. This was done because the measurement of the exact intensity of the complexed band was very difficult due to its a-symmetrical nature.

ΔC_{Base} values (Table 1) calculated for both the systems appear in decreasing order for mono, di- and trichloroethanol. ΔC_{Base} values for THF . . . alcohol complexes are about 3 time greater than those of TEA . . . alcohol system.

An abrupt change (either decrease or increase) in ΔC_{Base} value for trichloroethanol is an evidence of strong intermolecular association as compared to the molecule having one or two chlorine atoms. P.J. Krueger *et al.* [3] have reported that trichloroethanols are mostly intramolecularly bonded in a solution phase. So on the basis of this study one can understand that molecules showing strong acidic nature, must have strong intramolecular hydrogen bonding. And when it comes in contact with the strong proton acceptor (i.e. base molecule) large amount of the intermolecularly bonded complexes would be formed.



Frequency shift ($\Delta\nu$). The frequency shift ($\Delta\nu$) obtained in this study are reported in Table 1. From data obtained in this work it can be seen that $\Delta\nu$ values for trichloro-

ethanol . . . base complexes are higher than that of di- and monochloroethanols. Similar trend has been reported elsewhere [7] for complex formation of fluoroethanol, difluoroethanol and trifluoroethanol with dimethyl ether.

$\Delta\nu$ values for TEA complexes are about twice of the THF complexes. This shows that TEA has greater ability to form complexes with the alcohols. Although this difference can not be considered as a direct measurement of the energy of resultant bond, W.J. Middleton [8] and his coworkers have shown that there is a correlation between $\Delta\nu$ and the relative strength of the hydrogen bond formed between fluoroalcohols and THF. They concluded that larger the difference, the stronger is the bond.

Complex formation constant (K_{11}). The values of the complex formation constant (K_{11}) (Table 2) calculated for THF . . . alcohol complexes remain fairly constant over a wide range of concentration of base. The constancy of this parameter is an evidence of the formation of 1:1 complexes in the system under investigation. It is necessary to mention that method used for the system containing THF is not applicable for the alcohol . . . TEA complexes.

IR spectra (Fig. 2) for the system containing mono, di and trichloroethanol, triethylamine and CCl_4 show that OH absorption bands are broad having a shoulder on high frequency side, which is not visible at higher base concentration. It means that at low concentration of base the formation of complexes other than 1:1 type are possible. Formation of 2:1 complexes have been observed by Antti Kivinen *et al.* [9-11] in the system containing considerably low concentration of the base than that of an alcohol.

Our results (Table 3) for the case of TEA complexes show gradual decrease in K_{11} values at low concentration of the base (i.e. upto 0.08 mol.dm^{-3}) and then become constant. This indicates the presence of more than one kind of complexes at such a low concentration of TEA. Since main objective of the work was to study the 1:1 complexes only so no effort was made to calculate the K_{21} values. For obtaining the better K_{11} values for TEA . . . alcohol complexes initial readings showing variation have been ignored.

The comparison of the K_{11} values for mono, di and trichloroethanols shows that trichloroethanol has a greater tendency for intermolecular association with the electron donating molecules. A similar order for complexation of mono, di and trichloroacetic acids with a number of oxygen containing bases in CCl_4 solution has been found by Hadzi and Rajnvajn [12].

On comparison of the data obtained in this study it is clear that values for all parameters are significantly higher

in case of TEA as compared to those of THF. Higher values of K_{11} for TEA . . . alcohol complexes advocate for the higher tendency of TEA to form the complexes with the alcohols as compared to THF. This may be due to strong basic character ($\text{PK}_a = 10.778$) of TEA than of THF ($\text{PK}_a = 1.970$). This is further supported by their dipole moments (0.87D and 1.75D for TEA and THF respectively) [13].

Almost similar conclusions have been drawn from the studies on the complexation of trifluoroethanol and hexafluoropropanol with triethylamine and tetrahydrofuran in CCl_4 solution.

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