

# Thermodynamics of Complexation between Haloalcohols and Tetrahydrofuran: An Indirect Approach to Assess Intramolecular H-bonding in Haloalcohols by IR

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**Summary:** The proton donor-acceptor complexes formed by 2-haloethanols with tetrahydrofuran in carbon tetrachloride solution have been studied. The area of the OH-stretching band corresponding to the intermolecularly H-bonded complexes was plotted against concentration of the THF. From the shape of the curves the relative strength of the intramolecular H-bonds in 2-haloethanols appears to vary in the order  $F > Br > Cl > I$ . The anomaly in the relative strength of chloro and bromoethanol was checked from the results of complexes formed by 2-Cl and 2-Br-ethanol with triethylamine under similar conditions. The order obtained is in agreement to that in the case of THF.

The equilibrium constants for the 1:1 complexes between alcohols and THF at ambient temperature are in the order,  $F < Cl < Br < I$ . The thermodynamic data ( $\Delta H^\circ$ ,  $\Delta S^\circ$ ,  $\Delta G^\circ$ ) for complexes are reported for temperature range 303-328K. The linear plots of  $\Delta H^\circ$  vs.  $\Delta \nu$ ,  $\Delta H^\circ$  vs.  $\Delta S^\circ$  and  $\Delta G^\circ$  vs.  $\Delta S^\circ$  show that Badger-Bauer's rule is obeyed by the system with the exception of 2-F-ethanol complexes.

## Introduction

Although H-bonding in haloalcohols has been the subject of study for different workers during the last two decades, but the frequency of publication on this subject remained very low. M. Kuhen *et al* [1] showed that 2-haloethanols exist only in two conformers (*trans* & *gauch*) in  $CCl_4$  solution. In a number of studies [1-4] it has been mentioned that it is a difficult task to measure the exact strength of intramolecular H-bonded species (*gauch* conformers) due to overlapping with free species (*trans* conformers).

This problem may be solved to some extent by measuring the tendency of haloalcohols to form complexes with different bases. Although some studies [5-4] on the complex formation between different bases and haloalcohols are available in the literature but they are restricted to fluoroalcohols only.

These studies do not provide the information, how the tendencies of haloalcohols vary with the nature of halogens. Thus the aim of the present work is to find out the extent of intramolecular bonding in halo-ethanols from their intermolecular association behaviour with a base (tetrahydrofuran).

## Experimental

### Chemicals

All the alcohols (2-haloethanols) used in this work were of spectroscopic grade (98-99% pure) from Merck & Aldrich. They were dried over an activated molecular sieve (4A) before use.  $CCl_4$  (98% pure) from Merck was stored over an activated molecular sieve (4A). Triethylamine (TEA) 99% pure from Merck was dried over an activated molecular sieve (4A) before use.

*Tetrahydrofuran (THF)*

Commercial THF (Merck) was first dried over preheated molecular sieve (4A) for 2-3 days. Then it was transferred to a flask containing sodium wire and benzophenone used as an indicator. The appearance of light blue colour showed that THF was close to dryness. Then it was refluxed for 2-4 hours, till the contents of the flask obtained a deep purple colour. At this stage the liquid was distilled at 68°C under nitrogen (dried over silica gel column) pressure.

The presence of the moisture if any was tested by collecting the distilled liquid into a container having a deep purple colour solution of sod. metal, benzophenone and THF. No change in colour of the solution indicated the complete dryness of the THF being distilled. It was collected in a predried ampoules which were sealed at the spot and they were stored in a dry box. Ampoules should not be stored for a very long period.

This method [15], applied for drying the THF was considered more easier and reliable than the one reported by Boss *et al.* [16] for two reasons;

(a) Change of deep purple colour to blue colour was observed if it was exposed to atmosphere even for a fraction of a second, where in ref [16] blue colour has been considered as a test for dryness.

(b) The method used by Boss *et al.* [16] is laborious and time consuming and they used Na-K alloy as colour indicator which is rarely available.

In order to avoid moisture contamination from atmosphere, preparation of sol. and filling of cells were carried out in dry-box. For this study the dil sol. (0.02M) of 2-haloethanols were prepared in CCl<sub>4</sub>, where self-association is negligible. The amount of THF was varied in the alcohol solutions by making successive addition of 0.2 M.

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

For temperature variation study 0.02M solutions of alcohols in CCl<sub>4</sub> containing 0.4M THF were prepared. IR spectra for each compound were recorded over the temperature (303-328K<sup>o</sup>). The temperature of heated cell with AgCl windows was controlled with a variable temperature unit SPECAC having  $\pm 1.0$  K<sup>o</sup> accuracy.

*Treatment of Data*

Free and intra bands were resolved by graphical separation method. OH stretching frequency of unbonded OH group was determined in CCl<sub>4</sub> solution. Frequency shifts ( $\Delta\nu = \nu$  unbonded in CCl<sub>4</sub> sol. -  $\nu$  bonded with THF) are reported in Table-1.

Table-1: Spectroscopic properties of 2-haloethanols and their complexes with base in carbon tetrachloride at ambient temperature. (A = 0.02 mol.dm<sup>-3</sup>)

	2F.ethanol	2Cl.ethanol	2.Br.ethanol	2I.ethanol	Ref
Free OH-band					
$\nu \pm 6$ cm <sup>-1</sup>	3630	3620	3620	3620	+
$\nu$ cm <sup>-1</sup>	3639	3634	3631	3629	2
$\nu \pm 2.5$ cm <sup>-1</sup>	3635	3630	3630	3630	3
Intramolecularly H.bonded OH-band					
$\nu \pm 6$ cm <sup>-1</sup>	3618	3580	3575	3575	+
$\nu$ cm <sup>-1</sup>	3624	3601	3593	3582	2
$\nu \pm 2.5$ cm <sup>-1</sup>	3618	3600	3590	3580	3
$\Delta\nu \pm 6$ cm <sup>-1</sup>	12	40	45	45	+
$\Delta\nu$ cm <sup>-1</sup>	15.5	33	38	47	2
$\Delta\nu \pm 2.5$ cm <sup>-1</sup>	17	30	40	48	3
Complexed OH-band (Tetrahydrofuran)					
$\nu \pm 6$ cm <sup>-1</sup>	3410	3390	3400	3390	+
$\Delta\nu \pm 6$ cm <sup>-1</sup>	220	230	220	230	+
$\nu^{1/2} \pm 6$ cm <sup>-1</sup>	140	125	145	145	+
$T^* 10^{-4}$ dm <sup>3</sup> .mol <sup>-1</sup>	4.11	3.12	3.99	3.24	+
Complexed OH-band (Triethylamine)					
$\nu \pm 6$ cm <sup>-1</sup>	-	3135	3125	-	+
$\Delta\nu \pm 6$ cm <sup>-1</sup>	-	490	490	-	+
$\nu^{1/2} \pm 6$ cm <sup>-1</sup>	-	290	322	-	+
$T^* \text{ dm}^3 \cdot \text{mol}^{-1}$	-	5.6586	6.789	-	+

\*C<sub>base</sub> = 0.1 mol.dm<sup>-3</sup> + this work

Band area (A) due to complexes were calculated from equation (1) [17]

$$A = 2.303 \times \pi \times D \times \nu^{1/2} \quad (1)$$

where D and  $\nu^{1/2}$  are absorbance and apparent half-band width of the band due to complex. True integrated intensities (T) were calculated from equation (2)

$$T = K / Cl \log (I_0/I)_{\max} \nu^{1/2} \quad (2)$$

where K is correction factor for instrumental effect on the band shape. The value of K tabulated by Ramsey [17] for various values of  $\log (I_0/I)_{\max}$

and  $S/\nu^{1/2}$  were used.  $S$  is the effective slit-width of spectrometer ( $5.6 \text{ cm}^{-1}$  in the present case) and  $l$  is the path length of the cell.

The equilibrium constants ( $K_{11}$ ) for complexation of alcohol (A) with base (B) tetrahydrofuran,



was calculated (Table 1) from expression

$$K_{11} = \frac{C_{\text{complex}}}{C_A C_B} \quad (3)$$

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

$$\text{Complex} = A/Tx1 \quad (4)$$

The curve between area (due to bonded band) and the concentration of the base added was plotted for all the alcohols (Fig. 1).

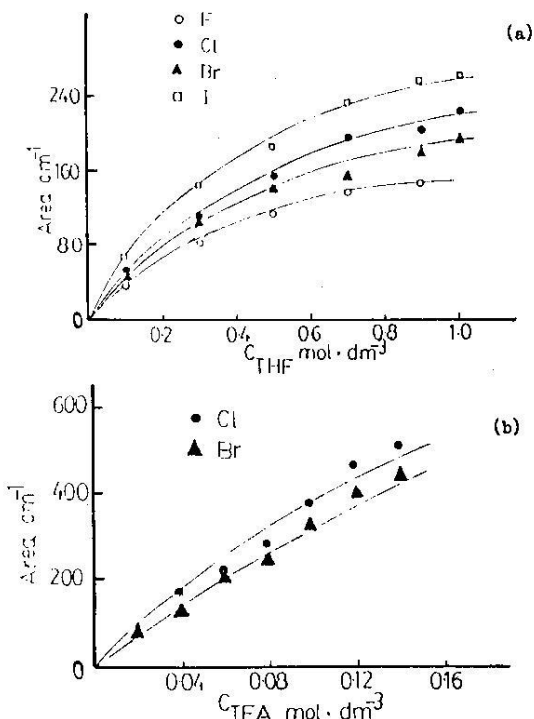


Fig.1: Area vs. concentration (base) curves for H-bonded complexes in 2-haloethanols (a) Tetrahydrofuran (b) Triethylamine

To find the relative strength of intermolecularly H-bonded complexes, change in base concentration  $\Delta C_{\text{Base}}$  needed to raise the specific area, from  $A_1 = 40$  to  $A_2 = 120 \text{ cm}^{-1}$  and the slopes from plots of area (due to bonded band) vs  $C_{\text{base}}$  were measured.

Thermodynamic quantities were obtained from the standard equation (5)

$$\Delta G^\circ = -RT \ln K_{11} = \Delta H^\circ - T\Delta S^\circ \quad (5)$$

Relationship between  $\log K_{11}$  VS.  $1/T$ ,  $\Delta H^\circ$  VS.  $\Delta S^\circ$ ,  $\Delta H^\circ$  VS.  $\Delta \nu$  and  $\Delta G^\circ$  VS.  $\Delta S^\circ$  (Fig. 1-3) were used to explain the stability and strength of the complex formed [18].

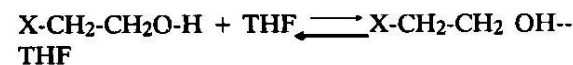
### Discussion

IR spectra show that intensities of free and intramolecular OH- bands at  $3610\text{-}3615$ ,  $3560\text{-}3580 \text{ cm}^{-1}$  respectively for 2-haloethanols diminishes gradually with the addition of the base and at the same time a broad band appears at  $3410$  to  $3415 \text{ cm}^{-1}$ . Gradual increase in area of the complex band indicates the formation of intermolecularly associated species.

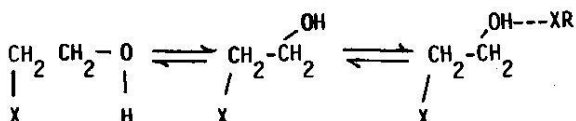
Area versus concentration curves (Fig. 1) show the relative amount of the complexes formed and thus provides a clue about the extent of intramolecular H-bond in the system.

In their study on o-haloephenols Bourassa et al [19] have drawn the curves between integrated intensities of the complexes' bands and the concentration of the ether added. From these curves they concluded that strength of the intramolecular H-bond for o-halophenols is in the order  $I < Br < Cl < F$  having a very small slope for the o-chlorophenol-ether complexes.

In this investigation the slopes of curves (Fig. 1) (a) indicate that complexation of 2-I-ethanol with THF is more rapid as compared to other alcohols while very slow rising of curve in the case of F.alcohol show that the equilibrium is much less in favour of intermolecular association in the reaction,



It indicates the presence of strong intramolecular H-bonding in the molecule. A similar trend has been noted by P.J. Kruger and his associates [2] in a competitive study on inter and intramolecular OH--X bonding. They calculated the  $K_{intra} = 2.08, 0.13$  and  $K_{inter} = 0.28, 1.5$  for F and I in the reaction



from [complex] / [gauch] ratio (1.5, 0.02) for RF-ICH<sub>2</sub>-CH<sub>2</sub>OH and RI-FCH<sub>2</sub>-CH<sub>2</sub>OH system and from experimental curves they concluded that equilibrium is more towards the intermolecular bonding between RF and ICH<sub>2</sub>-CH<sub>2</sub>OH as compared to FCH<sub>2</sub>-CH<sub>2</sub>OH and RI.

This is due to electronegativity of the halogen atoms (F & I) or their ability to work as proton acceptors.

The deviation from natural order for Cl and Br noted in this investigation is not clearly understood. However, the results (Table 1) obtained for Cl and Br-ethanol--TEA complexes also indicate similar trend as observed for haloalcohol--THF system. The slopes of the curves (Fig. 2) and  $\Delta C_{Base}$  and  $\Delta \nu$  values (Table-1) show that complexation with TEA is about 4. times stronger than that with THF. The high values of slope for chloro than bromoethanol advocate the order concluded in the case of THF.

The anomalous behaviour of chloro-and bromo-alcohols towards the proton acceptors (THF and TEA) could be understood to some ex-

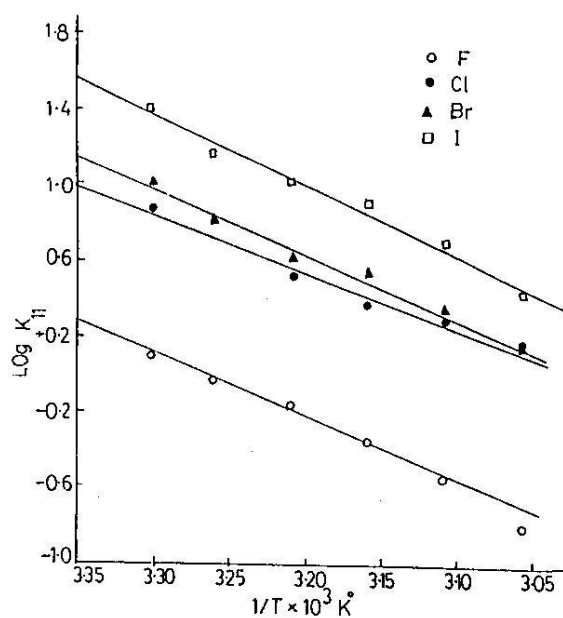
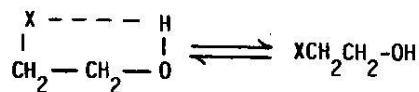


Fig.2: Log K<sub>11</sub> vs.1/T plots for 1:1 complexes of 2-haloethanol with THF in CCl<sub>4</sub>.

tent by considering the electrostatic repulsion factor. On the basis of electronegativity values (Cl = 3.0, O=3.5, Br=2.8) one would expect greater repulsion between X = Cl and oxygen atom as compared to that between X = Br and oxygen



and as a result more free form of Cl-ethanol molecule would be available to form complexes with the proton acceptors.

The Figure 1 also illustrates that formation of the complexes is continued upto a certain limit of

Table-2: Complex formation constant ( $K_{11} \text{ dm}^3 \cdot \text{mol}^{-1}$ ) for 2-haloethanol ( $C = 0.02 \text{ mol} \cdot \text{dm}^{-3}$ ) with tetrahydrofuran at ambient temperature.

CRHF mol.dm <sup>-3</sup>	2-Fluoro- ethanol	K <sub>11</sub> (Mean)	2-chloro- ethanol	K <sub>11</sub> (Mean)	2-Bromo- ethanol	K <sub>11</sub> (Mean)	2-Indo- ethanol	K <sub>11</sub> (Mean)
0.1	1.694		2.959		2.078		4.283	
0.3	1.725		2.884		2.199		4.683	
0.5	1.706		2.973		2.160		4.397	
0.7	1.726	1.714	2.814	2.886	2.330	2.186	4.316	4.366
0.9	1.721		2.848		2.201		4.296	
1.0	-		2.837		2.152		4.220	
St.dev.	± 0.015		± 0.006		± 0.083		± 0.0166	

the base concentration and then it becomes constant i.e. further complexation is not possible beyond this concentration.

Another method [19] of finding the relative strength of H-bonding in the system is the measurement of the change in base concentration,  $\Delta C_B$  needed to raise the area from  $A_1 = 40$  to  $A_2 = 120 \text{ cm}^{-1}$  for all the haloalcohols. The values obtained from the curves are as follows:

Alcohols	$\Delta C_{Base}$	(Mol. $\text{dm}^{-3}$ )
	THF	TEA
2 F.ethanol	0.350	-
2 Cl.ethanol	0.238	0.1390
2 Br.ethanol	0.303	0.1400
2 I.ethanol	0.171	-

The order in these values is the same, as one can conclude from a simple consideration of the order from the curves (Fig. 1).

#### Frequency shift ( $\Delta\nu$ )

The IR stretching frequency of the unbonded OH-group in carbon tetrachloride for 2-haloethanols was compared with that of OH-bonded with tetrahydrofuran. From Table 1 it can be seen that  $\Delta\nu$  varies in the order  $F < Cl < Br < I$ . Although this difference can not be considered as a direct measurement of the energy of the resultant bond, W.J. Middleton and his co-workers [13] have shown that there is a correlation between  $\Delta\nu$  and the relative strength of the hydrogen bond formed between F-alcohols and tetrahydrofuran. They concluded that larger the difference, the stronger is the bond.

In this study small  $\Delta\nu$  value for 2-fluoroethanol manifests a small probability to form complexes which may be due to strong intramolecular H-bonding between highly polarized atoms of the *gauch* conformers. P. J. Kruger and his associates [2] and Shrida *et al* [3] have reported a decrease in the intramolecular H-bonding from F to I with an increased  $\Delta\nu$  values for 2 haloethanols in  $\text{CCl}_4$ , which is in agreement with the observation made in this study (Table-1).

#### Complex Formation Constant ( $K_{11}$ )

The heteroassociation of F-alcohols and phenols with various bases have been extensively

Table-3: Thermodynamic Data on complexation of 2-haloethanol ( $C = 0.02 \text{ mol. dm}^{-3}$ ) with Tetrahydrofuran ( $C = 0.4 \text{ mol. dm}^{-3}$ )

	2-Fluoro-ethanol	2-chloro-ethanol	2-bromo-ethanol	2-Iodo-ethanol
$\Delta H^\circ \text{ KJ.mol}^{-1}$	29.538	21.940	30.269	33.033
$\Delta G^\circ \text{ KJ.mol}^{-1}$	28.515	19.526	27.177	28.962
$\Delta S^\circ \text{ J.mol}^{-1} \text{ degrec}^{-1}$	96.244	65.621	91.306	97.290

studied [14] W.J. Middleton *et al* [13] have reported that THF forms distillable 1:1 complexes with various fluoroalcohols that can boil at constant temperature. The values of complex formation constant calculated in this study remain fairly constant Table-2 over a wide range of concentration for all the alcohols. The constancy of this parameter is an evidence of the formation of 1:1 complexes of 2-haloethanols with THF.

IR spectra due to complexes of 2-haloethanol showed gradual decrease in the absorbances with an increase in temperature, but no prominent variation was noted in the intensity of free OH bands. This may be due to change in the densities of the solution towards higher temperature [20,21,22].

The slopes of the plots of  $\log K_{11}$  versus  $T^{-1}$  (Fig. 2) provide an information about the relative stabilities of complexes.

Very high  $\Delta H^\circ$  and  $\Delta S^\circ$  values (Table- 3) for 2-F-ethanol---THF complexes indicate that very stable complexes are formed in the case of fluoroethanol as compared to the other alcohols. The difference in behaviour may be attributed to strong OH-F interaction due to high electronegativity and small size of the atom. While a gradual increase in  $\Delta H^\circ$  and  $\Delta S^\circ$  from Cl to I-ethanol---THF complexes is an evidence of increased stability along Cl to I-ethanol---THF. A similar conclusion may be drawn from Fig. 3 which illustrates the linear relationship between different sets of thermodynamics parameters. These observations also show that Badger-Bauer's rule [18] is obeyed by the system under investigation with the exception of F-ethanol--THF complexes.

Hence on the basis of the thermodynamic data (Table-3) obtained in this study, one can advance two conclusions

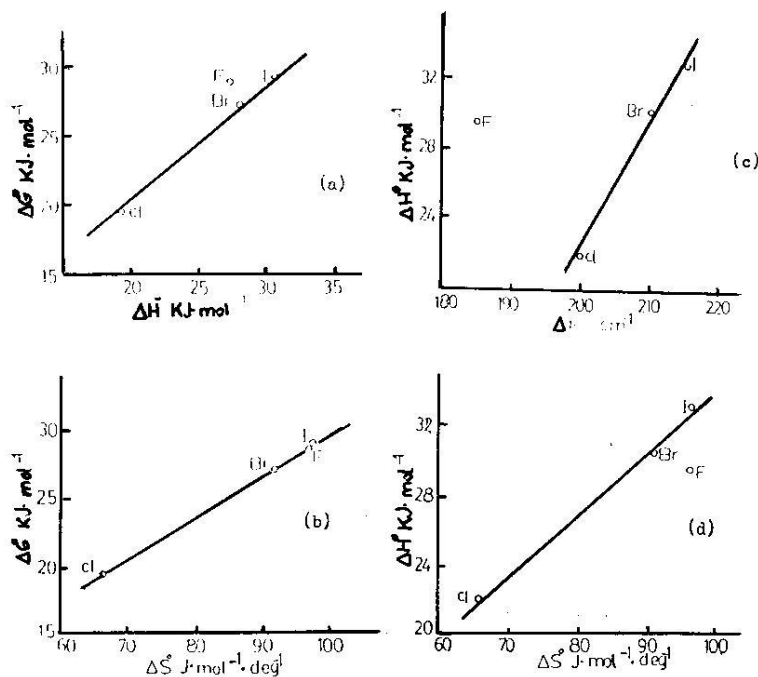


Fig.3: Plots of (a)  $\Delta G^\circ$  vs.  $\Delta H^\circ$  (b)  $\Delta G^\circ$  vs.  $\Delta S^\circ$  (c)  $\Delta H^\circ$  vs.  $\Delta \nu$  and (d)  $\Delta H^\circ$  vs.  $\Delta S^\circ$  for the 2-haloethanol.. THF complexes.

i. The relative ability of the haloethanols to form complexes with a proton acceptor (THF), depends on relative intramolecular associations in alcohols.

ii. The stability of complexes would depend on the nature of the halogen (electronegativity, size etc.) for a given base.

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