

## Complexation Tendency of 1,3-disubstituted Halopropane-2-ols with Different Bases. An IR Study

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(Received 29th September, 1991, revised 5th February, 1992)

**Summary:** The proton donor-acceptor complexes formed by 1,3-disubstituted halopropane 2-ols with tetrahydrofuran (THF) and triethylamine (TEA) 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 THF to determine the relative strength of H-bonding. The equilibrium constant and the frequency shifts were calculated. The equilibrium constants for the 1:1 complexes between alcohols and the base are in the order;  $\text{Br} < \text{Cl} < \text{F}$ .

### Introduction

A few studies on the complex formation between haloalcohols and different bases are available [1-5], but they are restricted to fluoroalcohols, especially to fluorophenols [3-5]. In our previous work, we reported hydrogen bonding tendency of haloethanols with different bases [6]. Now we have selected a series of 1,3-disubstituted halopropane-2-ols to investigate the relative ability of these alcohols to form complexes with proton acceptors. This series is selected to see the effect of branching on hydrogen bonding ability of the alcohols.

### Results and Discussion

The infrared spectra of the three 1,3-disubstituted halopropane-2-ols were measured in  $\text{CCl}_4$  containing variable amounts of bases (TEA and THF). From the relative intensities of the band at  $(3600\text{-}3560\text{ cm}^{-1})$ , Fig. 1, we concluded that the strength of intramolecular hydrogen bond increases in the order  $\text{F} < \text{Cl} < \text{Br}$ . However, S.M. Chitale [8] found that the amount of intramolecularly H-bonded species in 3-halopropanols decreases with increase in size of halogen. This discrepancy may be due to the steric repulsion. In contrast to 3-fluoropropanols [8], the greater amount of free (OH) species observed in 1,3-difluoro-2-propanol may be attributed to a five membered ring (1) formed in this molecule, whereas in 3-fluoropropanols a six membered ring would be formed easily (2).

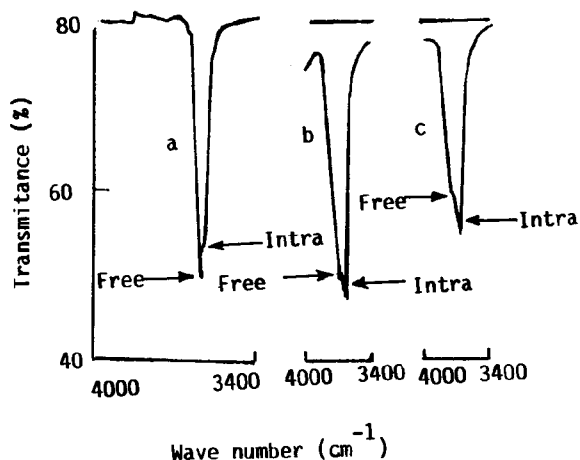
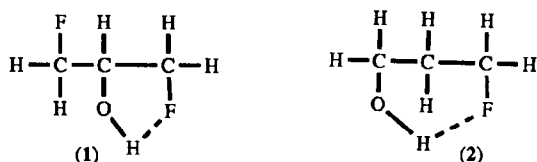


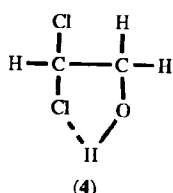
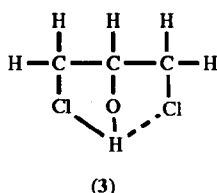
Fig. 1: IR spectra of (a) DiFip, (b) DiClip, (c) DiBrip 0.01M solution in  $\text{CCl}_4$ , Path length 0.29 cm

The six-membered ring would be more stable as compared to the five membered ring [9]. Another reason for more free OH in 1,3-difluoro-2-propanol may be due to the free rotation of "H" about C—O—H bond. In case of Cl and Br through the electronegativity is small but due to their large size, the amount of intra bonded species is increased.

Since 1,3-difluoro-2-propanol molecules have greater number of free OH, the possibility of complex formation with bases may also be enhanced in this case. On the basis of  $K_f$  values (Table 1,2) we can say that the order of complex formation by 1,3-disubstituted halo-2-propanols is as follows  $\text{F} > \text{Cl} > \text{Br}$ .

The amount of intramolecularly bonded species is greater in haloethanols as compared to halopropanols. It was observed by S.M. Chitale [8] that the  $K_{IF}$  values in the 3-halo-propanol increased from F to I as in the case of 2-halo-ethanols; but the amount of intramolecularly hydrogen bonded species was low as compared to that in haloethanols. It means that there would be more free halopropanols to form complexes with bases.

It has been observed that 2,2-dichloro-ethanol forms stronger complexes ( $K_{THF} = 11.548$ ,  $K_{TEA} = 21.935$ ) than 1,3-dichloro-2-propanol ( $K_{THF} = 2.520$ ,  $K_{TEA} = 9.117$ ) though the later have free as well as intra-bonded OH. The weak complexation by 1,3-dichloro-2-propanol (3) as compared to 2,2-dichloro-ethanol (4) may be due to the hindrance of bulky groups on either side of OH, whereas in the dichloro-ethanols the bulky Cl atoms are on one side of OH group and hence there is no hindrance for the THF to form complex with this molecule.



From the comparison of spectroscopic data (Tables 1,2), it can be seen that  $K_f$  values for TEA complexes are higher than THF, which means that TEA has higher tendency to form complexes with alcohols as compared to THF. This may be due to the stronger basic character of TEA ( $PK_a = 10.778$ ) than that of THF ( $PK_a = 1.970$ ).

The frequency shift,  $\Delta\nu$   $\text{cm}^{-1}$  for 1,3-disubstituted 2-propanols.... base complexes obtained in this study are increasing in the order Table 3  $\text{Br} < \text{Cl} > \text{F}$ .

The frequency shift values for TEA complexes are about twice those of THF complexes, which further support the idea that TEA has greater ability to form complexes with alcohols.

#### Area vs conc. curves

From the area vs conc. curves (Fig. 2), we can measure the complexation tendency of halo-al-

Table 1: Complex formation constant ( $K_{11} \text{ dm}^3 \text{ mol}^{-1}$ ) for halo propanol ( $C_A = 0.01 \text{ mol. dm}^{-3}$ ) with THF at ambient temperature

$C_{THF}$ $\text{mol. dm}^{-3}$	1,3-di- fluoro- 2-pro- panol	$K_{11}$ mean	1,3-di- chloro- 2-pro- panol.	$K_{11}$ mean	1,3-di- bromo- 2-pro- panol	$K_{11}$ mean
0.1	3.465		2.377		2.231	
0.3	3.673		2.464		2.315	
0.5	3.738	3.710	2.656	2.520	2.521	2.351
0.7	3.763		2.540		2.587	
0.9	3.911		2.580		2.256	
1.0	-		2.507		7.2198	

Table 2: Complex formation constant ( $K_{11} \text{ dm}^3 \text{ mol}^{-1}$ ) for the halopropanols with TEA at ambient temperature

$C_{TEA}$ $\text{mol. dm}^{-3}$	1,3-difluoro- 2-propanol	$K_{11}$ mean	1,3-dichloro 2-propanol	$K_{11}$ mean
0.10	13.732		9.268	
0.12	11.807		9.071	
0.14	11.879	11.643	8.648	9.117
0.16	11.506		9.190	
0.18	11.369		-	
0.20	11.696		9.239	
0.30	11.599		9.288	

Table 3: Spectroscopic properties of halo-propanols and their complexes with base in carbonatetra-chloride at ambient temperature ( $C_A = 0.01 \text{ mol dm}^{-3}$ )

1,3-difluoro- 2-propanol	1,3-dichloro- 2-propanol	1,3-dibromo- 2-propanol
$\nu \pm 6 \text{ cm}^{-1}$ 3620	Free OH-band 3590	3675
$\nu \pm 6 \text{ cm}^{-1}$ 3600	Intra molecularly-H-bonded OH-band 3575	3560
$\delta\nu \pm 6 \text{ cm}^{-1}$ 20	15	15
$\nu \pm 6 \text{ cm}^{-1}$ 3385	Complexed OH-band (THF) 3380	3375
$\Delta\nu \pm 6 \text{ cm}^{-1}$ 235	210	200
$\nu \pm 6 \text{ cm}^{-1}$ 3070	Complexed OH-band (TEA) 3070	
$\Delta\nu \pm 6 \text{ cm}^{-1}$ 550	520	

-  $C_{base} = 0.1 \text{ mol. dm}^{-3}$

cohols with different bases. The slopes of the curves indicate that the complexation of 1,3-difluoro-2-propanol is more rapid as compared to other alcohols. It indicates that the intramolecular H-bonding is very weak in this alcohol, which is also obvious from the equilibrium constant values. The slow rising of curve in the case of Br-alcohol indicates that the intramolecular association is much stronger than the F-alcohols and that is why the complexation is slow.

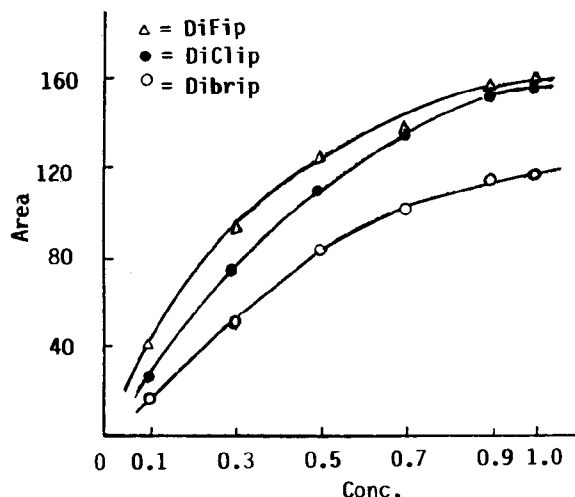


Fig.2: Area vs concentration (base) curves for H-bonded complexes of halo-propanols

The relative strength of H-bonding is also measured by the change in base concentration ( $\Delta C_B$ ) needed to raise the area from  $A_1 = 15$  to  $A_2 = 157 \text{ cm}^{-1}$  for the F, Cl and Br alcohols. The values obtained from the curves are as follows:

S.No.	Alcohols	$\Delta C_{\text{base}}$ (THF)
1.	1,3-difluoro-2-propanol	0.166
2.	1,3-dichloro-2-propanol	0.205
3.	1,3-dibromo-2-propanol	0.285

These values indicate that for the same area, the concentration of base increases as we go from F to Br. It means that the complexation becomes difficult from F to Br.

The plot of the area vs concentration of the base (TEA) is difficult to construct, because free (OH) band overlaps with the intra-bonded OH band.

### Experimental

#### Materials

The alcohols, 1,3-difluoro-2-propanol, 1,3-dichloro-2-propanol and 1,3-dibromo-2-propanol used in this work were of spectroscopic grade from Merck and Aldrich. Before use they were dried over 4 A molecular sieve. The solvent  $\text{CCl}_4$  from BDH was distilled over sodium hydroxide. THF was distilled by the method given elsewhere [6].

TEA from Fluka (98% pure) was stored over 4 A molecular sieve.

The preparation of solutions and filling of cells were carried out in a dry box, in order to avoid the moisture contamination. For this study the dilute solution (0.01M) of haloalcohols were prepared in  $\text{CCl}_4$ , where self association is negligible. The amount of base was varied in the alcohol solution by making successive additions of 0.2M THF and 0.02M TEA. 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.

#### Treatment of data

The stretching frequency of free OH group was measured from the spectrum in  $\text{CCl}_4$  solution.

Frequency shift ( $\Delta\nu = \nu_{\text{unbonded in } \text{CCl}_4} - \nu_{\text{bonded with base}}$ ) are reported in Table 3. The band areas (A) due to complexes [7] were calculated from eq. (1)

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

where D is absorbance and  $\nu^a 1/2$  is apparent half band width due to complex band.

The equilibrium constants ( $K_f$ ) for complexation of alcohol with base was calculated [4] from expression (2)

$$K_f = \frac{[A_o] - [A]}{[A]([B_o] - [C])} \quad (2)$$

where  $[A_o]$  = initial concentration of proton-donor

$[C]$  = concentration of H-bonded complex.

$[B_o]$  = initial concentration of base

$[A]$  = equilibrium concentration of free donor (alcohol)

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