# Hydrogen-bonded Species of the Complex of 4-Methylpyridine with Dichloroacetic Acid in Toluene at 35°

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The average molecular weights and n.m.r. chemical shifts of the hydrogen-bonded proton of the 4-methylpyridine–dichloroacetic acid complex have been measured in toluene at 35°. The observed chemical shift can be quantitatively explained by assuming the following equilibria: $2B + 2HA \rightleftharpoons 2(BHA) \rightleftharpoons (BHA)_2$. The structure of $(BHA)_2$ is discussed.

THE reaction of protic acids (HA) with bases (B) in low dielectric solvents leads, for acids and bases of sufficient strength, to formation of a hydrogen-bonded ion pair complex ($A^- \cdots HB^+$).[1] Depending upon the nature of the complex and its concentration, and the nature of the organic solvent employed, the hydrogen-bonded ion pairs may either dissociate or associate into higher aggregates (oligomers). In solvents with poor solvating ability the dissociation can be practically negligible ($C > 0{\cdot}01$M).[2a] Molecular association of the ion pairs into dimer and oligomers in nonpolar solvents is a common phenomenon in complexes of alkylamines with acids.[2-5] A similar ability to form dimers has been observed in complexes of oxo-bases such as heterocyclic *N*-oxides with halogenoacetic acids.[6]

Complexes of nitrogen bases such as pyridine and its derivatives with halogenoacetic acids have been investigated by i.r. spectroscopy,[7-9] dipole moments,[10] and conductivity.[11] The results, however, were discussed in terms of an equilibrium of a simple hydrogen-bonded complex ($AH \cdots B$) and a hydrogen ion pair ($A^- \cdots HB^+$). We believe that dimers and perhaps oligomers are also important and have sought evidence for the existence of dimers in the present study of the complex of 4-methylpyridine with dichloroacetic acid.

## EXPERIMENTAL

The crystalline complex of 4-methylpyridine with dichloroacetic acid was prepared by dissolving 4-methylpyridine in a small volume of chloroform followed by adding dichloroacetic acid in a small volume of carbon tetrachloride. The *complex* was recrystallized from toluene, m.p. 74° (Found: C, 43·05; H, 4·05; N, 6·15. $C_8H_9Cl_2NO_2$ requires C, 43·25; H, 4·1; N, 6·3%).

The measurements of molecular weight were done at 35° in toluene on a Hewlett–Packard model 302 vapour pressure osmometer (v.p.o.) using techniques recommended by the manufacturer. The molecular weight standard was benzil. The output microvoltages quoted are averages of 10 readings usually on three separate and freshly prepared solutions; reproducibility was ±2%. Toluene and benzil were purified as before.[6c]

All n.m.r. spectra were measured at 80 MHz on a Tesla BS 487 A spectrometer in toluene at 35 ± 1°. Spectra were calibrated with respect to internal tetramethylsilane. Chemical shifts quoted are averages of at least six determinations, usually on three separate and freshly prepared solutions. The complex shows a single 'average' resonance at a very low field; the reproducibility of the chemical shifts was ±10 Hz.

I.r. absorption spectra were recorded on a UR-10 Zeiss-Jena spectrometer. The complex was examined as Nujol and hexachlorobutadiene mulls, and in solution in toluene (0·3M in 0·1 mm NaCl cells).

## RESULTS AND DISCUSSION

The procedure for determining the calibration constant ($K$) and solute molecular weight ($M$) was the same as previously.[6c,d] Equations (1) and (2) were used where

$$V/C = K/M \qquad (1)$$

$$K = MV/C = M(A_1 + A_2C) \qquad (2)$$

$V$ is the measured resistance difference (μV), $C$ is the concentration of the solute (g kg$^{-1}$), and $A_1$ and $A_2$ are constants obtained by use of a least-squares procedure.

The Table collects the data for the complex. The values obtained for molecular weights have a marked concentration dependence. For all cases the values are higher than the value expected for a 1 : 1 complex ($M - M_1 > 0$). This strongly supports the formation of a dimer (2 : 2 complex) or even oligomers. In order

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to estimate the extent of association the degree of aggregation ($\bar{n}$)[4] was calculated (Table). Values of $\bar{n}$ for the investigated complex are much lower than those of complexes of alkylamines.[4] The low $\bar{n}$ values suggest that the complex is a dimer.

The Figure shows the characteristic shape of the $\delta = f(x)$ plot, which is very similar to those obtained earlier for complexes of 4-R-quinoline[6b,d-f,h] and 4-methylpyridine[6g] *N*-oxides. This behaviour is that expected from a system in which proton is present in various molecular species which are in a rapid equilibrium.

Summary of v.p.o. results and calculated hydrogen bond chemical shifts for the 4-methylpyridine complex with dichloroacetic acid in toluene at 35° (for benzil $V/C = 51{\cdot}524 - 0{\cdot}092C$)

| $x$/mol kg$^{-1}$ | $C$/g kg$^{-1}$ | $V$/μV | $M$ | $M - M_1$ | $\bar{n}$ | $m$/mol kg$^{-1}$ | $K_{21}$ | $\delta_{\text{calc.}}$*/Hz |
|---|---|---|---|---|---|---|---|---|
| 0·0117 | 2·59 | 110·7 | 252·08 | 30·01 | 1·13 | 0·0089 | 190 | 1007 |
| 0·0233 | 5·17 | 207·0 | 267·75 | 45·68 | 1·21 | 0·0153 | 178 | 1071 |
| 0·0349 | 7·74 | 298·3 | 277·16 | 55·09 | 1·25 | 0·0210 | 172 | 1106 |
| 0·0466 | 10·34 | 384·8 | 285·79 | 63·72 | 1·29 | 0·0258 | 168 | 1135 |
| 0·0698 | 15·51 | 559·1 | 292·05 | 69·98 | 1·32 | 0·0363 | 139 | 1156 |
| 0·0930 | 20·66 | 718·8 | 299·85 | 77·78 | 1·35 | 0·0448 | 131 | 1180 |
| 0·1162 | 25·81 | 869·0 | 306·87 | 84·80 | 1·38 | 0·0520 | 130 | 1201 |
| 0·1395 | 30·99 | 1014 | 312·62 | 90·55 | 1·41 | 0·0586 | 129 | 1218 |
| 0·1623 | 36·05 | 1116 | 314·63 | 92·56 | 1·42 | 0·0668 | 117 | 1223 |
| 0·1858 | 41·27 | 1307 | 316·91 | 94·84 | 1·43 | 0·0745 | 110 | 1230 |
| 0·2087 | 46·35 | 1431 | 321·83 | 99·76 | 1·45 | 0·0793 | 113 | 1243 |
| 0·2329 | 51·73 | 1567 | 324·56 | 102·49 | 1·46 | 0·0858 | 110 | 1250 |
| 0·2893 | 64·25 | 1853 | 332·48 | 110·41 | 1·50 | 0·0971 | 113 | 1270 |
| 0·3481 | 77·32 | 2156 | 334·86 | 112·79 | 1·51 | 0·1136 | 101 | 1276 |
| 0·4063 | 90·23 | 2444 | 335·41 | 113·34 | 1·51 | 0·1317 | 88 | 1277 |

* From equation (6) with $\delta_{1:1} = 859$ and $\delta_{2:2} = 1478$ Hz.

Assuming an activity coefficient equal to unity, and neglecting the possibility of the occurrence of such species as monomeric acid and base or oligomers, the equilibrium between the 1 : 1 and 2 : 2 complexes can be written as (3) with $K_{21}$ [given by equation (4)] the

$$2(\text{BHA}) \rightleftharpoons (\text{BHA})_2 \qquad (3)$$

$$K_{21} = \frac{x_{M_2}}{(x_{M_1})^2} = \frac{(x - m)(2s + x + m)}{4m^2} \qquad (4)$$

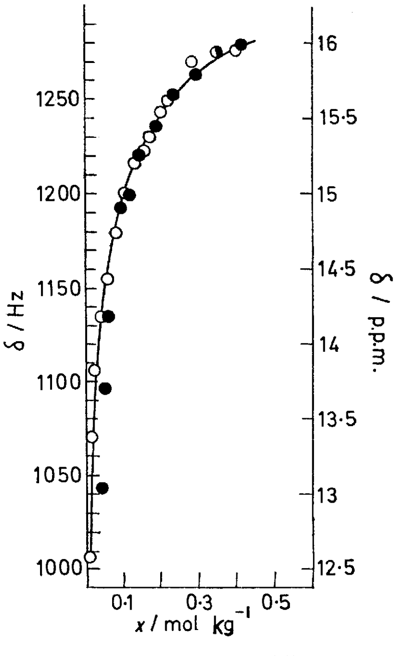
equilibrium constant for the formation of the 2 : 2 complex.[6c,d] $x_{M_1}$ and $x_{M_2}$ are mole fractions of 1 : 1 and 2 : 2 complexes, respectively, $x$ is the total number of moles of all complexes, $s$ is the number of moles of solvent, and $m$ is the number of moles of 1 : 1 complex. Knowledge of the values of $M$ affords $m$[6c] at a given concentration [equation (5)]. Values for $m$ and $K_{21}$ are given in the Table.

$$m = 2M_1x/M - x \qquad (5)$$

In the case where two complexes, 1 : 1 and 2 : 2, are in equilibrium, the observed chemical shift of hydrogen-bonded protons is given by expression (6)[6d]

$$\delta = m\delta_{1:1}/x + (x - m)\delta_{2:2}/x \qquad (6)$$

where $\delta_{1:1}$ and $\delta_{2:2}$ are the chemical shifts for 1 : 1 and 2 : 2 complexes, respectively, $m$ is the number of moles of complex in the 1 : 1 form and $x$ is the total number of moles of all complexes. Since $m$ is known from v.p.o. data, it can be substituted into equation (6) along with the measured $\delta$ for that solution. The unknown quantities $\delta_{1:1}$ and $\delta_{2:2}$ can then be obtained simultaneously by solving any such equations for two different solutions of the complex. Since, there are some differences in the concentrations used in v.p.o. and n.m.r. measurements, $m$ values were obtained from equation (4). The average values of $\delta_{1:1}$ and $\delta_{2:2}$ are 859 and 1478 Hz, respectively. Next the average values of $\delta_{1:1}$ and $\delta_{2:2}$ and equation (6) were used to calculate $\delta$ values for each solution used in v.p.o. measurements. The results are in the Table. In the Figure the observed and calculated values of $\delta$ are compared. The agreement is very satisfactory, except for the lowest concentrations. The calculated values of $\delta$ for dilute solutions



Hydrogen bond shift in 4-methylpyridine–$HO_2CCHCl_2$ as a function of concentration: ● observed; ○ calculated

($x \leqslant 0{\cdot}07$ mol kg$^{-1}$) are higher than the observed values. These differences suggest some contribution of monomeric (' free ') acid and base in solution.

It is widely accepted that the position of a proton resonance signal is shifted toward lower fields when a hydrogen bond is weakened.[12] The magnitude of the shift can be taken as a qualitative measure of hydrogen bond strength.[12] Accordingly, we found that the formation of dimer increases the strength of hydrogen bonding. The reverse effect has been observed in complexes of alkylamines.[13]

In contrast to the n.m.r. spectra, the i.r. spectrum of the complex is practically independent of concentration (0·1—0·6M). The absence of a marked effect of higher aggregate formation on spectral features has also been observed in other complexes.[3,4,6a,g,8,13]

The other point we discuss concerns the structure of the 2 : 2 complex. Although it has long been assumed that alkylammonium complexes in nonpolar solvents form oligomers, little if anything is known about the structure of these oligomers. In the case of the complexes of oxo-bases (*e.g.* 4-R-quinoline [6a] and 4-methylpyridine [6g] *N*-oxides), with halogenoacetic acids, structures of the type $(BHB)^+(AHA)^-$ have been proposed. This structure is based on i.r. spectra which are essentially the sum of the absorptions of heterocyclic *N*-oxide hemihydrobromides $(BHB)^+Br^-$ and the acid salts of halogenoacetic acids $(AHA)^-K^+$.

The solid state spectrum of the 4-methylpyridine–dichloroacetic acid complex shows $\nu_{CO_2^-}$ bands at 1640 and 1385 cm$^{-1}$, two $\nu_{N^+H}$ bands near 2460 and 2110 cm$^{-1}$, and no broad absorption below 1200 cm$^{-1}$. This leads directly to the conclusion that a proton transfer has occurred and we are here dealing with an ion pair species. The solution spectrum shows significant differences. Instead of the $\nu_{CO_2^-}$ bands, a typical $\nu_{C=O}$ band at 1745 cm$^{-1}$ is observed. A very broad and strong absorption appears in the region below 1300 cm$^{-1}$ whose structure is markedly different from that in the spectrum of $Bu_4N^+(AHA)^-$ where A is $CHCl_2CO_2$. The difference indicates the absence of anion $(AHA)^-$, and rules out structures of the type $(BHB)^+(AHA)^-$. Further support of this conclusion can be adduced from i.r. absorptions above 1800 cm$^{-1}$. The complex shows two weak and broad bands at about 2450 and 1870 cm$^{-1}$. Cations $(BHB)^+$, where B is a heterocyclic base, have a well defined absorption near 2500 and 2100 cm$^{-1}$.[14,15] To summarise, it seems that the i.r. spectrum of the complex of 4-methylpyridine reflects a hydrogen bonding interaction in the monomeric complex (BHA). Although 4-methylpyridine, as do oxo-bases, forms a 2 : 2 complex, the structure of the complex is different. It is supposed that the 2 : 2 complex of 4-methylpyridine with dichloroacetic acid has a quadrupole type structure. Further work is needed to establish this.

*Conclusions.*—The results of molecular weight measurements support the existence of a 4-methylpyridine–dichloroacetic acid complex in toluene. Variation of the n.m.r. shift with concentration can be interpreted in terms of equilibria $2B + 2HA \rightleftharpoons 2(BHA) \rightleftharpoons (BHA)_2$. The i.r. spectrum reflects a hydrogen bonding interaction in the monomeric complex (BHA). The extent of association of complexes between carboxylic acids and bases is independent of the p$K_a$ value of the base, *e.g.* alkylamines p$K_a$ *ca.* 10·5,[2-5,16] 4-methylpyridine p$K_a$ 6·02,[16] heterocyclic *N*-oxides p$K_a$ 0·47—1·62.[6f]

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