BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 50 (3), 608—613 (1977) [Vol. 50, No. 3

Reaction of Pyridine Bases with Carboxylic Acids in Benzene

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(Received August 20, 1976)

The reaction of pyridine bases with aliphatic monocarboxylic acids has been studied by means of the partition method. Partition was carried out at 25 °C between benzene and 0.10 mol dm^{-3} (Na, H) ClO_4 aqueous solution, the total concentration of pyridine base and that of carboxylic acid being less than 2×10^{-2} mol dm^{-3} and 1.0 mol dm^{-3}, respectively. Both (1: 1) and (1: 2) complexes (base to acid ratio) are formed in benzene, (1: 3) complex being additionally formed only for 2,4,6-trimethylpyridine. A linear free energy relationship is observed between the formation of the (1: 1) and (1: 2) complexes and the protonation in water of the corresponding bases except for sterically crowded 2,6-dimethyl derivatives of pyridine. The structure of the (1: 2) and (1: 3) complexes is discussed.

The reaction of bases with carboxylic acids in nonpolar solvents is important for understanding the nature of the acid-base reaction, since a carboxylic acid undergoes association in nonpolar solvents.[1] Several interesting features of the acid-base reaction, such as, the formation of higher hydrogen-bonded complexes and the proton transfer complex have been reported.[2] It was revealed that the hydrogen bond strength is parallel to the acidity and basicity of components.[3]

The system involving pyridine bases and carboxylic acids in organic solvents was initially studied by Barrow with use of IR spectroscopy. He revealed the stoichiometry of reaction products and discussed the extent of the proton transfer in relation to the acid strength of a carboxylic acid.[4] Since then, various physical methods, such as IR, visible, NMR, NQR, thermodynamic method and dipole moment measurement, have been applied to the reaction of the pyridine bases with carboxylic acids in solution or in solid state.[5–10] In the present paper, we describe the reaction of carboxylic acid with pyridines in reference to the effect of substituents. The structure of the (1: 2) and (1: 3) species (base to acid ratio) is discussed.

Experimental

Reagent. All the pyridine bases, *i.e.* pyridine, 3-bromopyridine, 2-methylpyridine, 4-methylpyridine, 2,6-dimethylpyridine and 2,4,6-trimethylpyridine were of G. R. grade. Carboxylic acids, *i.e.* butyric acid, valeric acid and hexanoic acid, were of G. R. grade, while decanoic acid was of chemical pure grade. The purification of pyridine bases, carboxylic acids and benzene (G. R.) as a solvent has been described elsewhere.[11,12]

Procedure. The partition was carried out in an incubator thermostated at (25±0.1) °C. Equilibrium is reached within 1 h. Concentrations were 0.1—1.0 mol dm^{-3} for the carboxylic acids and 2×10^{-3}—2×10^{-2} mol dm^{-3} for the pyridine bases. The ionic strength in the aqueous phase was maintained at 0.10 mol dm^{-3} with sodium perchlorate. Hydrogen ion concentration was measured with a Orion Ionalyzer Model 801 and a Beckman Research pH meter. A 1.00×10^{-2} mol dm^{-3} perchloric acid solution containing 0.09 mol dm^{-3} sodium perchlorate was employed as a standard of hydrogen ion concentration. Hydrogen ion concentration was estimated by correcting for a liquid-junction potential.[13] The total concentration of pyridine base in the aqueous phase was determined by colorimetry for 3-bromopyridine; for the other pyridine bases the total concentration in the organic phase was determined by acid-base titration in glacial acetic acid with Crystal Violet as an indicator.

Results

When a pyridine base, B, is extracted with a carboxylic acid, HA, in benzene, the extraction equilibrium between the organic and aqueous phases is written as

$$mB_w + n(HA)_o \rightleftarrows (B_m(HA)_n)_o \qquad (1)$$

where $B_m(HA)_n$ denotes an extracted species which involves m molecules of pyridine base and n molecules of carboxylic acid, and subscripts w and o refer to the aqueous and organic phases, respectively. Since the activity coefficient of each species in both phases is assumed to be kept constant,[14,15] the concentration equilibrium constant, $K_{ex(mn)}$, for Eq. 1 is kept constant.

$$K_{ex(mn)} = [B_m(HA)_n]_o[B]_w^{-m}[HA]_o^{-n} \qquad (2)$$

The association between a pyridine base and a carboxylic acid is negligible in the aqueous phase.

When a pyridine base is extracted with a carboxylic acid in benzene, the total concentration of the pyridine base in the organic phase, $C_{B,o}$, is given by

$$C_{B,o} = \sum_{m=1}\sum_{n=0} m[B_m(HA)_n]_o \qquad (3)$$

Substituting this relation into Eq. 2, we have

$$C_{B,o} = \sum_{m=1}\sum_{n=0} mK_{ex(mn)}[B]_w^m[HA]_o^n \qquad (4)$$

If only species involving m molecules of pyridine base are present in the organic phase, the total concentration of the pyridine base in the organic phase can be written as

$$C_{B,o} = [B]_w^m\{\sum_{n=0} mK_{ex(mn)}[HA]_o^n\} \qquad (5)$$

or

$$\log(C_{B,o}/\text{mol dm}^{-3}) = m\log([B]_w/\text{mol dm}^{-3}) + \log\{\sum_{n=0} mK_{ex(mn)}[HA]_o^n/\text{mol}^{1-m}\,\text{dm}^{3m-3}\} \qquad (5')$$

$\log(C_{B,o}/\text{mol dm}^{-3})$ is linearly related with $\log([B]_w/\text{mol dm}^{-3})$ for a given concentration of monomeric carboxylic acid in the organic phase. From the slope of this linear relationship we find the number of the pyridine base involved in the extracted species. The plots of $\log([B]_w/\text{mol dm}^{-3})$ *vs.* $\log(C_{B,o}/\text{mol dm}^{-3})$ for the extraction of the six pyridine bases with decanoic acid are shown in Fig. 1. They give rise to straight lines

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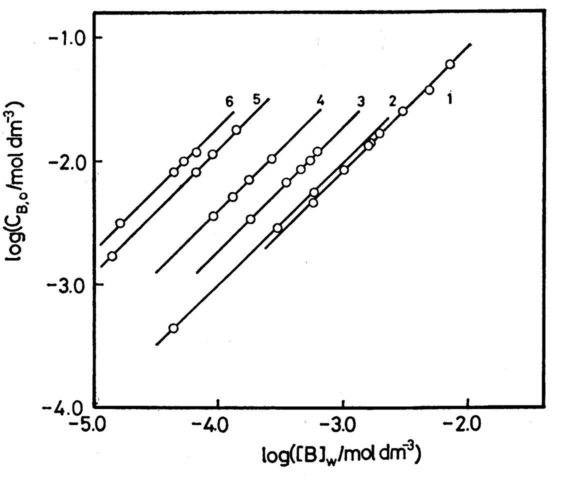


Fig. 1. Determination of the number of pyridine base involved in extracted species.
1: Decanoic acid–pyridine, 2: decanoic acid–3-bromopyridine, 3: decanoic acid–2-methylpyridine, 4: decanoic acid–4-methylpyridine, 5:decanoic acid–2,6-dimethylpyridine, 6: decanoic acid–2,4,6-trimethylpyridine.

with a slope of unity. We thus have extracted species involving only one molecule of pyridine base in benzene.

From Eq. 5 we obtain

$$C_{B,o}[B]_w^{-1} = \sum_{n=0} K_{ex(1n)}[HA]_o^n \tag{6}$$

By use of the distribution ratio, D, and the formation constant of pyridinium in the aqueous solution, K_{HB}, Eq. 6 is rewritten as

$$D \cdot \alpha_B = \sum_{n=0} K_{ex(1n)}[HA]_o^n \tag{7}$$

where α_B is the side reaction coefficient taking into account the protonation of the base:

$$\alpha_B = 1 + K_{HB}[H^+] \tag{8}$$

The $K_{ex(10)}$ in Eq. 7 is identical with the partition constant, $K_{D,B}$, of the pyridine base between benzene and aqueous solution in the absence of a carboxylic acid. In order to determine the number of carboxylic acid involved in the extracted species, $D \cdot \alpha_B$ was plotted against the concentration of the monomeric carboxylic acid in benzene. The latter was calculated from the partition constant and the dimerization constant in benzene[12]:

Acid	Partition constant*	Dimerization constant*
Butyric acid	0.11	182
Valeric acid	0.54	229
Hexanoic acid	1.9_1	251
Decanoic acid	500	260

* Hydration not corrected.

The results for the extraction of 4-methylpyridine with four carboxylic acids are shown in Fig. 2. Non-linearity of the plots indicates the presence of the extracted species involving more than one molecule of the carboxylic acid. Similar results were obtained for the other pyridine bases. Equation 7 can be rewritten as follows:

$$(D \cdot \alpha_B - K_{D,B})[HA]_o^{-1} = K_{ex(11)} + K_{ex(12)}[HA]_o + \cdots \tag{9}$$

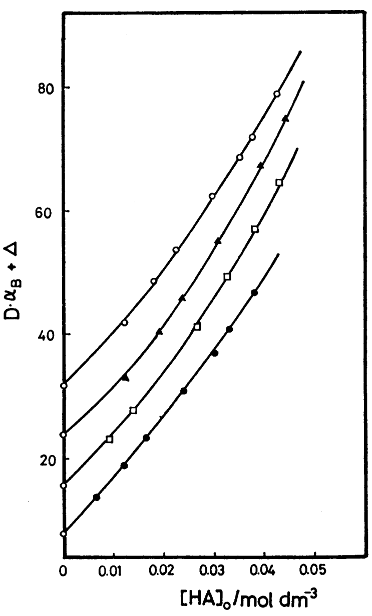


Fig. 2. Determination of the number of carboxylic acid involved in extracted species for 4-methylpyridine. The solid lines represent calculated values.
○: Decanoic acid (Δ=24), ▲: hexanoic acid (Δ=16), □: valeric acid (Δ=8), ●: butyric acid (Δ=0).

If only the first two terms on the right side are important, $(D \cdot \alpha_B - K_{D,B})[HA]_0^{-1}$ should be linearly related to the concentration of monomeric carboxylic acid in the organic phase. The plots of $[HA]_o$ *vs.* $(D \cdot \alpha_B - K_{D,B})$-$[HA]^{-1}$ for the extraction of 4-methylpyridine with the four carboxylic acids are shown in Fig. 3, in which we utilized the partition constants of the pyridine bases determined previously.[16] Straight lines with non-zero intercept (Fig. 3) indicate the presence of 1: 1 and 1: 2 complexes in the organic phase. The extraction constants of 1: 1 and 1: 2 complexes can be obtained from the intercept and the slope, respectively. Similar results were obtained for pyridine and its derivatives except for 2,4,6-trimethylpyridine. The formation of complexes

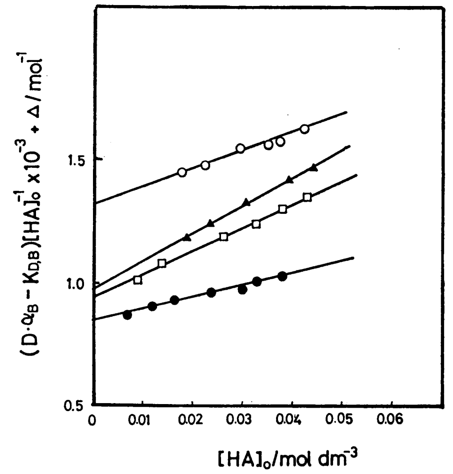


Fig. 3. Determination of the number of carboxylic acid involved in extracted species for 4-methylpyridine.
○: Decanoic acid (Δ=0.6), ▲: hexanoic acid (Δ=0.4), □: valeric acid (Δ=0.2), ●: butyric acid (Δ=0).

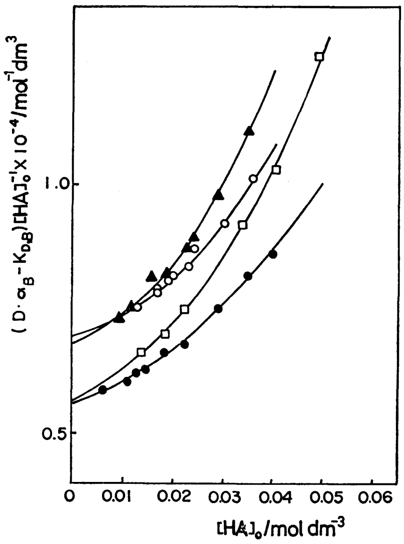


Fig. 4. Determination of the number of carboxylic acid involved in extracted species for 2,4,6-trimethylpyridine. The solid line represent the calculated values. ○: Decanoic acid, ▲: hexanoic acid, □: valeric acid, ●: butyric acid.

with the same compositions in nonpolar solvents such as carbon tetrachloride has been confirmed by IR study for the reaction of pyridine with several carboxylic acids.[4,6,8]

For 2,4,6-trimethylpyridine, the plot of $[HA]_o$ *vs.* $(D\cdot\alpha_B - K_{D,B})[HA]_o^{-1}$ is not linear (Fig. 4). This indicates the presence of higher complexes. Rearranging Eq. 9, we have

$$\{(D\cdot\alpha_B - K_{D,B})[HA]_o^{-1} - K_{ex(11)}\}[HA]_o^{-1}$$
$$= K_{ex(12)} + K_{ex(13)}[HA]_o + \cdots \quad (10)$$

By plotting the values of the left side of Eq. 10 against $[HA]_o$ for 2,4,6-trimethylpyridine we obtain straight lines (Fig. 5). It is obvious that three species, *i.e.* 1: 1, 1: 2, and 1: 3 complexes are present in benzene for 2,4,6-trimethylpyridine. The extraction constants are summarized in Table 1.

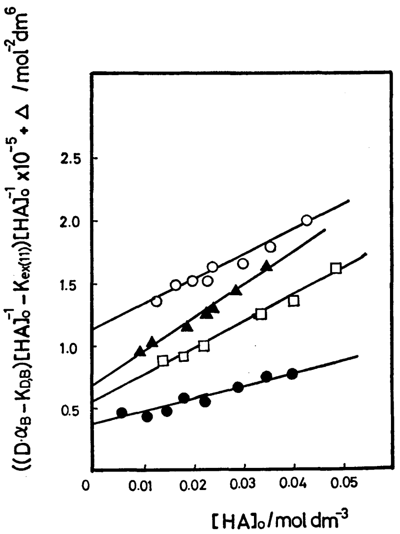


Fig. 5. Determination of the number of carboxylic acid involved in extracted species for 2,4,6-trimethylpyridine. The extraction constants of the 1: 2 and 1: 3 complexes were obtained from the intercept and slope, respectively. ○: Decanoic acid ($\Delta=0.9$), △: hexanoic acid ($\Delta=0.4$), □: valeric acid ($\Delta=0.2$), ●: butyric acid ($\Delta=0$).

TABLE 1. LOGARITHMIC EXTRACTION CONSTANTS OF (B·HA), (B·(HA)$_2$) AND (B·(HA)$_3$) COMPLEXES BETWEEN BENZENE AND AQUEOUS SOLUTION

Base	Acid	log ($K_{ex(11)}$/ mol^{-1} dm^3)	log ($K_{ex(12)}$/ mol^{-2} dm^6)	log ($K_{ex(13)}$/ mol^{-3} dm^9)
3-Bromopyridine	Butyric acid	2.97	3.5_8	
	Valeric acid	3.02	3.8_5	
	Hexanoic acid	2.99	3.9_7	
	Decanoic acid	3.02	3.6_7	
Pyridine	Butyric acid	2.24	3.2_1	
	Valeric acid	2.31	3.2_3	
	Hexanoic acid	2.20	3.3_7	
	Decanoic acid	2.31	3.1_9	
2-Methylpyridine	Butyric acid	2.80	3.7_1	
	Valeric acid	2.70	3.8_6	
	Hexanoic acid	2.77	3.8_3	
	Decanoic acid	2.76	3.7_7	
4-Methylpyridine	Butyric acid	2.93	3.6_9	
	Valeric acid	2.87	3.9_7	
	Hexanoic acid	2.83	4.0_3	
	Decanoic acid	2.91	3.8_7	
2,6-Dimethylpyridine	Butyric acid	3.09	4.1_3	
	Valeric acid	3.12	4.1_9	
	Hexanoic acid	3.15	4.2_9	
	Decanoic acid	3.18	4.0_3	
2,4,6-Trimethylpyridine	Butyric acid	3.75	4.5_1	6.1
	Valeric acid	3.76	4.5_6	6.3
	Hexanoic acid	3.83	4.4_5	6.4
	Decanoic acid	3.84	4.3_8	6.3

$\log(K_{ex(11)}/\text{mol}^{-1}\,\text{dm}^3)$, $\log(K_{ex(12)}/\text{mol}^{-2}\,\text{dm}^6)$, and $\log(K_{ex(13)}/\text{mol}^{-3}\,\text{dm}^9)$ values are estimated to be accurate to ±0.05, ±0.10, and ±0.2, respectively.

From the results, the equilibria of the pyridine bases with the carboxylic acids in benzene are formulated as follows:

$$B_o + (HA)_o \rightleftharpoons (B\cdot HA)_o \qquad K_{11} \quad (11)$$

$$B_o + (HA)_{2,o} \rightleftharpoons (B\cdot(HA)_2)_o \qquad K_{12} \qquad (12)$$

$$(B\cdot(HA)_2)_o + (HA)_o \rightleftharpoons (B\cdot(HA)_3)_o \qquad K_{13} \qquad (13)$$

In addition, the dimerization of a carboxylic acid occurs in benzene:

$$2(HA)_o \rightleftharpoons (HA)_{2,o}$$

The formation constant of complexes in benzene can be evaluated from the corresponding extraction constant by use of the partition constant of the pyridine base and the dimerization constant of the carboxylic acid.

Table 2. Logarithmic formation constants of (B·HA), (B·(HA)$_2$), and (B·(HA)$_3$) complexes in benzene

Base	Acid	log (K_{11}/mol^{-1} dm^3)	log (K_{12}/mol^{-2} dm^6)	log (K_{13}/mol^{-3} dm^9)
3-Bromopyridine	Butyric acid	1.34	−0.4	
	Valeric acid	1.38	−0.2	
	Hexanoic acid	1.34	−0.1	
	Decanoic acid	1.35	−0.5	
Pyridine	Butyric acid	1.97	0.5_9	
	Valeric acid	2.03	0.5_1	
	Hexanoic acid	1.91	0.6_2	
	Decanoic acid	1.99	0.4_2	
2-Methylpyridine	Butyric acid	2.14	0.7_0	
	Valeric acid	2.04	0.7_4	
	Hexanoic acid	2.10	0.6_9	
	Decanoic acid	2.07	0.6_1	
4-Methylpyridine	Butyric acid	2.18	0.6_0	
	Valeric acid	2.12	0.7_8	
	Hexanoic acid	2.06	0.8_0	
	Decanoic acid	2.12	0.6_2	
2,6-Dimethylpyridine	Butyric acid	1.94	0.6_3	
	Valeric acid	1.96	0.5_9	
	Hexanoic acid	1.98	0.6_6	
	Decanoic acid	1.99	0.3_8	
2,4,6-Trimethylpyridine	Butyric acid	2.20	0.6_1	$1._7$
	Valeric acid	2.20	0.5_6	$1._9$
	Hexanoic acid	2.26	0.4_2	$2._1$
	Decanoic acid	2.25	0.3_3	$2._0$

log(K_{11}/mol^{-1} dm^3), log(K_{12}/mol^{-2} dm^6), and log(K_{13}/mol^{-3} dm^9) values are estimated to be accurate to ±0.05, ±0.10, and ±0.2, respectively.

Polar solutes, *i.e.* carboxylic acids and amines, form hydrates in a nonpolar solvent equilibrated with water.[17] Thus correction for hydration of pyridine base and carboxylic acid should be made in order to evaluate the true formation constant of complexes. We have information on the hydration of pyridine bases and carboxylic acids in benzene.[11,12] The formation constants corrected for the hydration of acids and bases are summarized in Table 2.

Discussion

It has been suggested that the extent of formation of hydrogen-bonded complex between a series of bases and phenols or alcohols is a function of basicity of these bases.[18,19] We have observed the linear free energy relationship between the hydration of pyridine bases in benzene and the formation of the corresponding pyridiniums in aqueous solution,[11] a similar relationship being observed for the hydration of carboxylic acids.[12] The formation constants of 1: 1, 1: 2, and 1: 3 complexes for a given pyridine base remain constant for the carboxylic acids studied (Table 2). This seems reasonable since the acidity of the four carboxylic acids does not differ appreciably from each other.

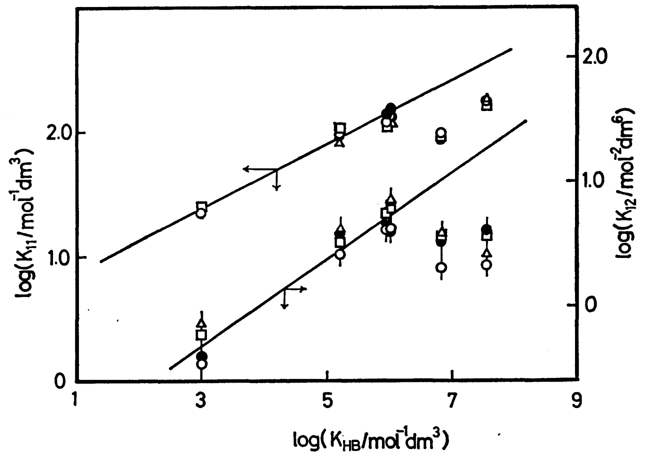


Fig. 6. Correlation between the logarithmic formation constants of the 1:1 and 1:2 complexes and the logarithmic formation constants of pyridinium in aqueous solution. Data of log K_{HB}'s were taken from Ref. 16.

Let us examine the correlation between the formation of 1: 1 complex and the formation of the corresponding pyridinium. The plot of the logarithmic formation constant of 1: 1 complex against log(K_{HB}/mol^{-1} dm^3) is shown in Fig. 6. A linear correlation was obtained between log(K_{11}/mol^{-1} dm^3) and log(K_{HB}/mol^{-1} dm^3) except for sterically crowded 2,6-dimethyl derivatives of pyridine. The relationship is written as follows (dimensions are hereafter omitted for the sake of simplicity):

$$\log K_{11} = 0.25 \log K_{HB} + 0.62 \qquad (15)$$

A similar relationship has been obtained for the formation of the monohydrate of pyridines[11]:

$$\log \beta_{11}(\text{hydrate}) = 0.09 \log K_{HB} - 0.37 \qquad (15')$$

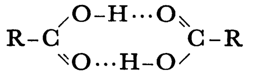
The coefficient of $\log K_{\mathrm{HB}}$ in Eq. 15 is appreciably larger than that in Eq. 15′. In view of the fact that acidity of the carboxylic acid is much higher than that of water, it is reasonable that the extent of the complex formation of the pyridine bases with the carboxylic acids is greater than that of the hydration. The $\log K_{11}$ values for the sterically crowded 2,6-dimethyl derivatives of pyridine are smaller than that expected from $\log K_{\mathrm{HB}}$.

We shall examine the correlation between the reaction of the pyridine base with the dimeric carboxylic acid and the formation of pyridinium. In Fig. 6 the logarithmic formation constant of the 1:2 complex for carboxylic acids is plotted against $\log K_{\mathrm{HB}}$ of corresponding pyridiniums. The correlation is obviously good except for 2,6-dimethyl derivatives of pyridine. This relationship is expressed by

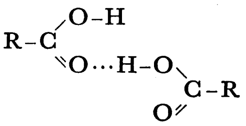
$$\log K_{12} = 0.35 \log K_{\mathrm{HB}} - 1.44 \qquad (16)$$

We see that the formation of the 1:2 complex would occur to a negligible extent for the pyridine bases less basic than 3-brompyridine. A comparison of coefficients of $\log K_{\mathrm{HB}}$ in Eqs. 15 and 16 suggests that the dimeric carboxylic acid is somewhat more acidic than monomeric carboxylic acid.

Let us consider the structure of the 1:2 complex. We have two possible structures of dimeric carboxylic acids:



cyclic dimer, c-$(HA)_2$



open dimer, o-$(HA)_2$

The following equilibrium might take place.

$$\text{o-}(HA)_2 \rightleftarrows \text{c-}(HA)_2 \qquad K_{\mathrm{o-c}} \qquad (17)$$

Pyridine bases are assumed to react only with the open dimer:

$$\text{o-}(HA)_2 + B \rightleftarrows (B\cdot\text{o-}(HA)_2) \qquad K_{\mathrm{OB}} \qquad (18)$$

Then the formation constant of the 1:2 complex can be written as:

$$\begin{aligned} K_{12} &= [B\cdot\text{o-}(HA)_2][B]^{-1}([\text{o-}(HA)_2] + [\text{c-}(HA)_2])^{-1} \\ &= K_{\mathrm{OB}}(1+K_{\mathrm{o-c}})^{-1} \qquad (19) \end{aligned}$$

If K_{OB} is approximated as K_{11}, we have

$$K_{\mathrm{o-c}} = K_{11}K_{12}^{-1} - 1 \qquad (20)$$

Thus the value of $K_{\mathrm{O-C}}$ can be calculated from values of K_{11} and K_{12} given in Table 2. Average values of $K_{\mathrm{O-C}}$ for the four carboxylic acids are as follows: butyric, 31; valeric, 28; hexanoic, 26; decanoic, 44. The proportion of the open dimer is roughly estimated to be *ca.* 3% of acid dimer. IR spectroscopic study and the slopes of the LFER given in Fig. 6 suggest strongly that the acidity of the open dimer should exceed the acidity of the monomeric carboxylic acid, *i.e.*

$$K_{\mathrm{OB}} > K_{11}$$

Then the proportion of the open dimer should be less than 3%.

Combining Eqs. 16 and 19, we have

$$\log K_{\mathrm{OB}} = 0.35 \log K_{\mathrm{HB}} - 1.44 + \log(1+K_{\mathrm{o-c}}) \qquad (21)$$

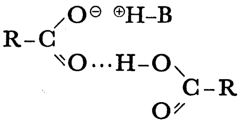
K_{OB} should be greater than K_{11} for all bases including a base of which K_{HB} is equal to 1. Then from Eqs. 15 and 21 we obtain

$$-1.44 + \log(1+K_{\mathrm{o-c}}) > 0.62$$

or

$$K_{\mathrm{o-c}} > 119$$

The fraction of the open dimer in the total dimer concentration seems to be a little less than 1%. Since the estimations are consistent with the previous findings,[20] we can conclude that the open dimer of a carboxylic acid reacts with a pyridine base to form a 1:2 complex:



(22)

2,4,6-Trimethylpyridine forms the 1:3 complex with the four carboxylic acids in benzene. The formation of 1:3 complex in organic solvents has been found in several systems involving more acidic carboxylic acids or more basic amines.[21–24] The stronger the base, the the more extensive the polarization of –OH group in the 1:2 complex (formula 22) and the more basic the terminal –C=O becomes. Thus we have the 1:3 complex for the stronger bases, the situation being similar for stronger acids.

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