Kinetic Studies of Proton Transfer between 2,6-Di-t-butylpyridine and its Conjugate Acid in [$^2H_2$]Dichloromethane and in Methanol

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Proton transfer from the 2,6-di-t-butylpyridinium ion (as the chloride or bromide) to 2,6-di-t-butylpyridine has been investigated by ^1H n.m.r. line-shape analysis of solutions in a non-polar medium (CD_2Cl_2) and in a polar medium (MeOH). The mechanism in the former solvent depends on dissociation of the contact ion pair. In the presence of water the mechanism involves proton jump *via* an intervening water molecule rather than an acid dissociation step, although at high water concentrations this latter process becomes important. In methanol as solvent the acid dissociation step is the dominant one.

2,6-Di-t-butylpyridine (DBP) has attracted considerable attention over the years because of the pronounced steric hindrance to approach at the nitrogen atom. Only the proton is sufficiently small to have access to the nitrogen site and for this reason DBP has been used to distinguish between protic and Lewis acid behaviour.[1] This basicity, without accompanying nucleophilicity, has led to the use of DBP in the synthesis of unstable carbanions.[2–4] The precision tailoring of certain polymers, by preventing proton-initiated side reactions, has also been accomplished with the aid of this amine.[5]

DBP represents a unique example of basicity behaviour. For pyridines this is enhanced when the ring is alkylated, but for DBP the pK_a of the conjugate acid falls to 2.78 from 3.65 in C_5H_5N (in 30:70 H_2O–EtOH).[6] Gas-phase basicities however show DBP to be more basic than unsubstituted pyridine.[7] Hydration studies by Arnett and Chawla on substituted pyridines also show it to be a special case, and they deduced that it is the inhibiting of hydrogen bonding between the nitrogen and water molecules that is responsible.[8]

The inability of DBP to form hydrogen bonds is shown by the ν_{NH} mode of its salts, DBP·HX. For a variety of these, the ν_{NH} band is sharp and above 3 275 cm^{-1},[8] whereas for the corresponding pyridinium salts this band shows the expected broadness and falls below 2 880 cm^{-1}; both observations are indicative of hydrogen bonding.[9] Thus strong association between DBP and $DBPH^+$, as occurs with other amine bases and the corresponding ammonium cations,[10] is not possible.

Proton transfer between DBP and H_3O^+ has been studied by temperature-jump methods and is 60—70 times slower than for C_5H_5N and $C_5H_5NH^+$.[4] The system was studied in 20:80 dioxane–water since DBP itself is of low solubility in water. In a preliminary communication[11] we reported a study of the proton transfer in dichloromethane using n.m.r. line-shape analysis. Solubility is no problem, and in the present paper we extend this investigation to include the effect of added water in this solvent. We also report on the likely mechanism which is adopted in a very different solvent, methanol.

Experimental

DBP (97%; Aldrich) was purified by distillation under a reduced pressure of N_2, and the fraction of b.p. 100—101 °C at 23 mmHg was used. HCl gas (BOC) was dried by passage through pure H_2SO_4. HBr was generated from KBr (AnalaR) and pure H_2SO_4 and dried by passage through a pair of traps cooled at 195 K (CO_2–Me_2CO) to remove H_2O and Br_2. DCl (Merck, Sharp and Dohme) was used without further purification. CD_2Cl_2 and CD_3OD (Aldrich) were of the highest purity and D content available, and were stored under N_2 and over 4 Å molecular sieves. Spectroscopic-grade methanol (99.9%; Aldrich) was used without further purification and was stored under N_2 and over 4 Å molecular sieves. Solutions were prepared by the addition of a measured weight or volume of HCl or HBr to a solution of DBP in CD_2Cl_2 or MeOH on a vacuum line.

The ^1H n.m.r. spectra were recorded with a Bruker WM250 Fourier transform spectrometer operating at a field strength of 5.875 T (proton resonance 250.13 MHz). Spectra were run in the Fourier transform mode, with 16 K data points (Aspect 2000 computer). Line-shape analysis was carried out using the program LSHAPE, details of which have been reported.[12,13]

For the proton-exchange reaction (1) the exchange rates may

$$\mathrm{BH^+ + B} \underset{k_\mathrm{B}}{\overset{k_\mathrm{BH}}{\rightleftharpoons}} \mathrm{B + HB^+} \qquad (1)$$

be determined by measuring the line-broadening of the acid (BH^+) and conjugate acid (B) signals, provided these are clearly differentiated in the n.m.r. spectrum.[14] The ^1H n.m.r. signals of the t-butyl groups are ideal for this purpose, being clearly differentiated for DBP and $DBPH^+$ at 250 K for the chloride system and even at 290 K for the bromide, as illustrated in our previous note.[11]

The exchange rates, k_{BH} for the acid site, k_B for the base, are equal to $\pi\Delta W_{BH}$ and $\pi\Delta W_B$, respectively, where ΔW is the broadening of the signal with respect to the line-width in the absence of exchange. The determination of these natural line-widths has been described.[13]

Results

The rate constants and populations (*p*) are defined for the system according to equation (2). In the Tables the values of k_{BH}

$$\mathrm{DBPH^+ + DBP} \underset{k_\mathrm{B}}{\overset{k_\mathrm{BH}}{\rightleftharpoons}} \mathrm{DBP + DBPH^+} \qquad (2)$$

$$P_{PH} = \frac{[\mathrm{BH}]}{[\mathrm{B}] + [\mathrm{BH}]} \quad P_B = \frac{[\mathrm{B}]}{[\mathrm{B}] + [\mathrm{BH}]} \quad \text{where B = DBP}$$

and k_B are those obtained from Arrhenius plots (ln k *vs.* $1/T$), an example of which was given earlier.[11]

Table 1 gives the k_{BH} and k_B values for runs in which P_B was kept constant and the concentrations were varied by a factor of *ca.* 10^2. Table 2 shows the effects on the rate constants when P_B is varied from 0.181 to 0.784. A plot of k_{BH} and k_B was given in the earlier communication[11] showing how the former remains the same as [BH]/[B] changes, while the latter rate constant varies linearly with the ratio of the concentration of salt to that of amine. Table 3 reports results of the same experiments as Table 2 but for the bromide salt.

The isotope effect on k_{BH} was studied on two samples in which values of x_D ([DBP•DCl]/[DBP•DCl] + [DBP•HCl]) were 0.881 and 0.900. The observed k_{BH} values were 134 ± 10 and 138 ± 10 s^{-1}, respectively. From these, values of k_{BD} were calculated from $k_{BH}(\text{obs}) = k_{BD}x_D + k_{BH}(1 - x_D)$ as 102 ± 13 and 110 ± 12 s^{-1}, respectively. The ratios k_{BH}/k_{BD} are thus 3.7 ± 0.6 and 3.6 ± 0.5, respectively.

To a sample of DBP•HBr (0.0048M) and DBP (0.0054M) in CD_2Cl_2, water was added, and k_B was measured as [H_2O] was varied from 0.008 to 0.274M. Figure 1 shows the dependence of k_B on [H_2O] at 280 K. Even when there was a large excess of H_2O, separate signals were observed for the water and the two kinds of t-butyl group.

In another sequence of reactions the amount of DBP was varied relative to [DBP•HBr] (0.0141M) and [H_2O] (0.010M). Rate constants were obtained between 240 and 260 K since at these temperatures only the reaction with water is significant. The results are given in Table 4 and Figure 2, which shows that k_{BH} is directly proportional to [DBP]; k_B remains fairly constant.

Table 5 shows the pseudo-first-order rate constants for DBP and DBP•HCl in MeOH. The effect of temperature on the proton resonances of the t-butyl groups is shown in Figure 3(a); Figure 3(b) shows the aromatic proton signals, clearly revealing

Table 1. Values of k_{BH} and k_B for DBP and DBP•HCl in CD_2Cl_2 with p_B constant

[DBP]/M		0.1185	0.0235	0.0089	1.30×10^{-3}
[DBP•HCl]/M		0.1142	0.0275	0.0104	1.39×10^{-3}
p_B		0.5091	0.4606	0.4618	0.382 3
T/K					
240	k_{BH}/s^{-1}	2.01	1.82	2.01	2.01
	k_B/s^{-1}	1.94	2.13	2.34	2.16
250	k_{BH}/s^{-1}	12.8	11.9	12.2	13.5
	k_B/s^{-1}	12.4	14.0	14.2	14.5
260	k_{BH}/s^{-1}	65.4	65.4	65.4	70.1
	k_B/s^{-1}	63.0	76.6	76.2	75.3
270	k_{BH}/s^{-1}	337	337	365	365
	k_B/s^{-1}	324	395	425	392
280	k_{BH}/s^{-1}	1 408	1 480	1 604	1 556
	k_B/s^{-1}	1 358	1 733	1 869	1 670
290	k_{BH}/s^{-1}	5 271	5 825	6 063	6 003
	k_B/s^{-1}	5 083	6 822	7 066	6 444

Arrhenius plot gives $E_a = 93 \pm 6$ kJ mol^{-1}; $\Delta S = +140 \pm 25$ J K^{-1} mol^{-1}.

Table 2. Values of k_{BH} and k_B for DBP and DBP•HCl in CD_2Cl_2 with p_B varied.

[DBP]/M		7.8×10^{-3}	4.12×10^{-2}	1.48×10^{-1}	3.35×10^{-2}
[DBP•HCl]/M		35.4×10^{-3}	8.68×10^{-2}	0.789×10^{-1}	0.92×10^{-2}
p_B		0.1806	0.3222	0.6525	0.7838
T/K					
240	k_{HB}/s^{-1}	3.25	3.25	2.18	2.00
	k_B/s^{-1}	14.8	6.85	1.16	0.55
250	k_{HB}/s^{-1}	17.1	17.3	14.4	13.6
	k_B/s^{-1}	77.7	36.4	7.69	3.75
260	k_{HB}/s^{-1}	75.2	75.2	73.7	74.4
	k_B/s^{-1}	341	158	39.3	20.5
270	k_{HB}/s^{-1}	340	337	338	403
	k_B/s^{-1}	1 543	709	208	111
280	k_{HB}/s^{-1}	1 236	1 249	1 604	1 772
	k_B/s^{-1}	5 609	2 628	854	489
290	k_{HB}/s^{-1}		4 024	6 003	6 768
	k_B/s^{-1}		8 469	3 197	1 867

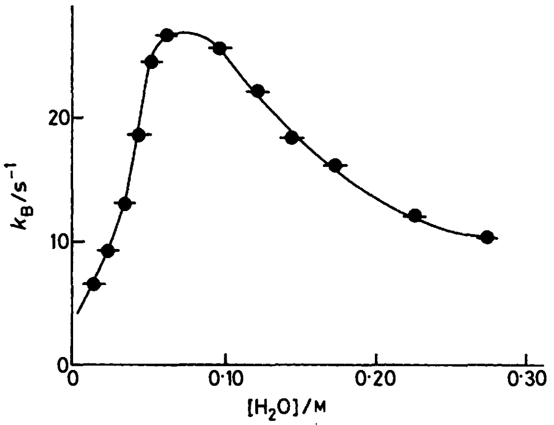


Figure 1. Plot of k_B against [H_2O] for DBP–DBP•HBr in dichloromethane at 280 K

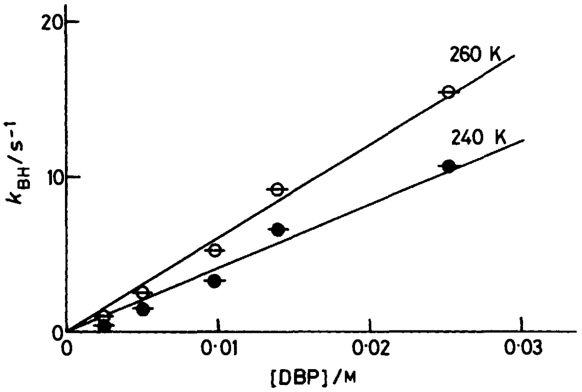


Figure 2. Plot of k_B against [DBP] for DBP–DBP•HBr in dichloromethane at 280 K

Table 3. Values of k_{BH} and k_B for DBP and DBP•KBr in CD_2Cl_2

[DBP]/M		2.30×10^{-3}	4.90×10^{-3}	9.72×10^{-3}	1.35×10^{-2}	2.518×10^{-2}	3.917×10^{-2}
[DBP•HBr]/M		0.0141	0.0141	0.0141	0.0141	0.0141	0.0141
p_B		0.1404	0.2966	0.4079	0.4907	0.6420	0.7347
[$DBPH^+$]/[DBP]		6.13	2.88	1.45	1.04	0.56	0.36
T/K							
280	k_{BH}/s^{-1}	3.46	3.88	2.42	1.92	3.60	2.89
	k_B/s^{-1}	21.2	11.2	3.52	2.00	2.00	1.04
290	k_{BH}/s^{-1}	14.5	14.7	13.5	13.6	15.7	15.2
	k_B/s^{-1}	88.9	42.4	19.6	14.1	8.75	5.50
300	k_{BH}/s^{-1}	43.1	53.5	56.2	58.8	59.3	62.3
	k_B/s^{-1}	264	154	81.7	61.2	33.0	22.5

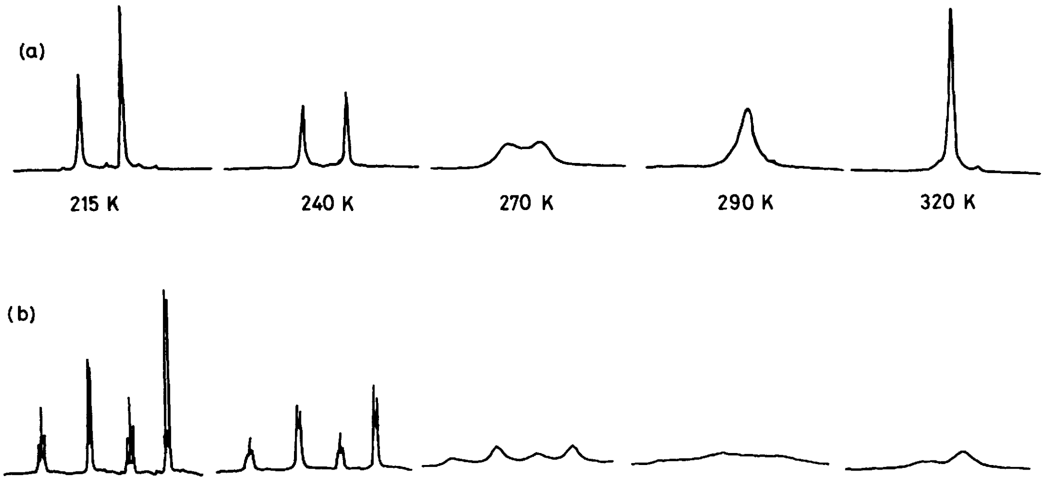


Figure 3. ^{1}H N.m.r. signals of (a) t-butyl groups and (b) aromatic protons of DBP–DBP•HCl in methanol at various temperatures

Table 4. Values of k_{BH} and k_B for DBP•HBr in CD_2Cl_2 with H_2O; [DBP•HBr] = 0.0141M; [H_2O] = 0.100M

[DBP]/M		0.0023	0.0049	0.0097	0.0136	0.0253
p_B		0.1404	0.2966	0.4079	0.4907	0.6420
240 K	k_{BH}/s^{-1}	0.50	1.67	3.42	6.23	10.6
	k_B/s^{-1}	3.06	3.96	4.96	6.47	5.91
250 K	k_{BH}/s^{-1}	0.62	2.00	4.31	8.17	13.4
	k_B/s^{-1}	3.80	4.74	6.26	8.48	7.47
260 K	k_{BH}/s^{-1}	0.83	2.31	5.36	8.84	15.3
	k_B/s^{-1}	5.08	5.48	7.78	9.18	8.53

Table 5. Values of k_{BH} and k_B for DBP and DBP•HCl in MeOH

[DBP]/M		0.2178	0.0627	0.0666
[DBP•HCl]/M		0.0677	0.0214	0.0523
p_B		0.7629	0.7456	0.566
T/K				
230	k_{BH}/s^{-1}	9.03	7.85	6.17
	k_B/s^{-1}	2.81	2.68	4.85
240	k_{BH}/s^{-1}	20.1	18.5	14.9
	k_B/s^{-1}	6.24	6.31	11.7
250	k_{BH}/s^{-1}	44.7	42.5	34.1
	k_B/s^{-1}	13.9	14.5	26.8
260	k_{BH}/s^{-1}	89.1	88.2	72.2
	k_B/s^{-1}	27.7	30.1	56.7
270	k_{BH}/s^{-1}	176	181	147
	k_B/s^{-1}	54.7	61.8	116
280	k_{BH}/s^{-1}	321	337	276
	k_B/s^{-1}	99.9	115	217
290	k_{BH}/s^{-1}	545	602	493
	k_B/s^{-1}	169	205	387
300	k_{BH}/s^{-1}	934	1 075	880
	k_B/s^{-1}	290	367	691
E_a/kJ mol^{-1}		38	40	40

the two triplets for the *para*-hydrogen atom and the doublets for the *meta*-hydrogen atoms. This ability to resolve the signals for the two species, the base and the conjugate acid, again demonstrates the uniqueness of this system. Measurements made in CD_3OD are given in Table 6 in which [DBP] was varied by a factor of twenty. The ratio k_{BH}/k_{BD} (obtained by using average $k_{BH,D}$ values) is *ca.* 4.

When DBP•HBr was used in place of DBP•HCl the results were similar (Table 7).

Table 6. Values of k_{BD} and k_B for DBP and DBP•DCl in CD_3OD

[DBP]/M		0.2290	0.1022	0.0572	0.0114
[DBP•DCl]/M		0.0662	0.0299	0.0163	0.0033
p_B		0.7758	0.7735	0.7786	0.7755
T/K					
240	k_{BD}/s^{-1}	6.36	6.49	6.17	4.71
	k_B/s^{-1}	1.84	1.90	1.75	1.36
260	k_{BD}/s^{-1}	25.3	25.3	24.8	20.5
	k_B/s^{-1}	7.31	7.40	7.05	5.93
280	k_{BD}/s^{-1}	83.9	83.9	82.3	73.7
	k_B/s^{-1}	24.3	24.6	23.4	21.3
300	k_{BD}/s^{-1}	238	237	240	219
	k_B/s^{-1}	68.6	69.4	68.2	63.4

Table 7. Values of k_{BH} and k_B for DBP and DBP•HBr in MeOH

[DBP]/M		0.2688	0.0819
[DBP•HBr]/M		0.2575	0.0808
p_B		0.5108	0.5036
T/K			
240	k_{BH}/s^{-1}	11.4	10.8
	k_B/s^{-1}	10.9	10.6
260	k_{BH}/s^{-1}	51.4	50.4
	k_B/s^{-1}	49.2	49.7
280	k_{BH}/s^{-1}	192	198
	k_B/s^{-1}	184	196
300	k_{BH}/s^{-1}	602	659
	k_B/s^{-1}	577	650

Discussion

A substantial amount of work has gone into studying proton transfer between amines in protic solvents.[15,16] Three mechanisms are possible. The first [equation (3)] is simple bimolecular transfer of H^+ from the ammonium ion to the amine. The second involves solvent participation [equation

$$\mathrm{BH^+ + B \longrightarrow B + HB^+} \tag{3}$$

$$\mathrm{BH^+ + \underset{\substack{|\\ R}}{OH} + B \longrightarrow B + \underset{\substack{|\\ R}}{HO} + HB^+} \tag{4}$$

$$\mathrm{BH^+ + ROH \longrightarrow B + ROH_2{}^+} \tag{5}$$

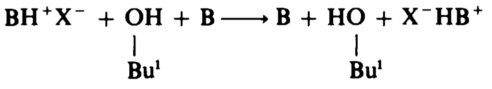
Table 8. Values of k_{BH} for proton exchange of substituted pyridinium ions in methanol at 298 K

	k_{BH}/s^{-1}	$pK_a{}^a$	E_a/kJ mol^{-1}	Ref.
4-Methylpyridine	10 600	5.98	41	21
2-Methylpyridine	9 080	5.97	38	21
2,4-Dimethylpyridine	1 320	6.76	40	21
2,6-Dimethylpyridine	1 150	6.72	40	21
2,6-Di-t-butylpyridine	880	4.91	39	This work

^{a} In H_2O.

(4)], in which a termolecular reaction takes place. The number of solvent molecules involved in this reaction has been found to exceed one.[17,18] The third reaction [equation (5)] is acid dissociation followed by transfer from the protonated solvent to another amine.

In t-butyl alcohol, a solvent of low relative permittivity (ε = 12.5), there is anion association, and while the mechanism is analogous to (4) the process is much slower [equation (6)].[19]



$$\mathrm{BH^+X^- + \underset{\displaystyle Bu^t}{OH} + B \longrightarrow B + \underset{\displaystyle Bu^t}{HO} + X^-HB^+} \qquad (6)$$

Glacial acetic acid (ε = 6.2) systems have also been studied over a wide range of temperatures for a variety of amines, and again ion pairs are involved.[20] In this case the first step is proton transfer within the ion pair itself [equation (7)], followed by

$$\mathrm{BH^+\cdot{}^-OAc \longrightarrow B\cdot HOAc} \qquad (7)$$

exchange of acetic acid with the solvent shell and bulk solvent. In previous studies the concentration of free base has been undetectable and measurements were made by line-shape analysis of NH or a closely associated methyl group. For this work we have chosen to study an extremely hindered amine in a system in which it is present in significant amounts both as free base and as conjugate acid. In addition we have used two solvents, one of low polarity (CH_2Cl_2; ε = 8.9) and the other the most polar of the alcohols (CH_3OH; ε = 32.7). In both systems the exchange of proton between amine and ammonium sites is sufficiently slow on the n.m.r. timescale to permit separate signals for both species to be observed. The protons of their t-butyl groups resonate at well separated frequencies, and this allowed good line-shape analysis to be carried out.

Dichloromethane as Solvent.—Table 1 shows the results for the exchange between DBP and its hydrochloride salt $DBPH^+Cl^-$. It can be seen that k_{BH} and k_B [equation (2)] are independent of concentration, while P_B remains constant at *ca.* 0.5. This being so then (3) cannot be the mechanism of proton transfer, nor is this direct exchange expected since the bulky t-butyl groups will prevent close approach and formation of the necessary NHN hydrogen bond.

Since by definition $k_{BH}/k_B = P_B/P_{BH}$, then by varying the population of each species (Table 1) it can be shown that while k_{BH} remains constant k_B is directly proportional to [BH]/[B]. The mechanism of proton transfer in this solvent is therefore different from any one of those already discussed and involves steps (8) and (9), although clearly (8) will involve a proton-transfer step like that of (7). The value of ΔS also indicates unimolecular dissociation.

$$\mathrm{DBPH^+X^-} \xrightarrow{k_d} \mathrm{DBP + HX} \qquad (8)$$

$$\mathrm{DBP + HX} \xrightarrow{k_a} \mathrm{DBPH^+X^-} \qquad (9)$$

Support for this mechanism was obtained by changing the counter-anion from chloride to bromide (Table 3). This resulted in a ratio $k_{BH}(Cl)/k_{BH}$ (Br) of 400, very much in keeping with there being a stronger NHCl hydrogen bond in the $DBPH^+Cl^-$ contact ion pair than in $DBPH^+Br^-$. The effect of raising the temperature on the proton resonance was to cause coalescence of the t-butyl signals above 305 K for the bromide system, whereas for the chloride this occurred at 270 K.[11]

The exchange rate at coalescence is thus greater for the chloride system than for the bromide, even though this rate is related only to the difference in the frequencies of the two proton sites, *i.e.* DBP and $DBPH^+$, which remain the same in both cases. This shows clearly that the anion is involved in the proton transfer and that Cl^- facilitates this more than Br^-.

If the mechanism is consistent with (8), it will involve proton transfer along the vector of a hydrogen bond as in (10) in which

$$\mathrm{R_2N{-}H \cdots X^- \longrightarrow R_2N \cdots H{-}X} \qquad (10)$$

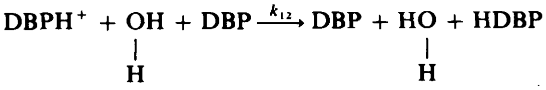
case the closer approach of Cl^- will help the jump from one potential energy well of the hydrogen bond to the other.

Alternatively there is the possibility of proton tunnelling to achieve this step. Moreover this will be favoured in dichloromethane the low polarity of which encourages closer ion pairing and a stronger hydrogen bond. If tunnelling is occurring this will be disrupted in the deuteriated system since D, with double the mass and lower zero-point energy, is prevented from tunnelling. This would show in a high value of k_{BH}/k_{BD}. The results (Table 4) show $k_{BH}/k_{BD} = 3.6$, which is inconsistent with a tunnelling mechanism for H.

Dichloromethane invariably is contaminated with traces of water; the solutions studied were found to have *ca.* 150 p.p.m. H_2O. The effect of this was investigated in a series of reactions in which k_B was determined for different amounts of added H_2O (Figure 1). After an initial increase a maximum is reached and thereafter the rate decreases, indicating that the equilibrium (11) is responsible for the increase in [DBP] that explains the decrease in k_B.

$$\mathrm{DBPH^+ + H_2O} \xrightarrow{k_{11}} \mathrm{DBP + H_3O^+} \qquad (11)$$

The presence of water could have an effect on the proton-transfer mechanism either by the acid dissociation (11) which corresponds to the third kind of process (5), or by a termolecular reaction of type (4) in which a water molecule acts as the agent for proton transfer, *i.e.* equation (12). That (12) is



$$\mathrm{DBPH^+ + \underset{\displaystyle H}{OH} + DBP} \xrightarrow{k_{12}} \mathrm{DBP + \underset{\displaystyle H}{HO} + HDBP^+} \qquad (12)$$

the principal mechanism was deduced as follows. The chemical flux of protons out of $DBPH^+$ is given by equation (13), where

$$\varphi = k_{BH}[BH^+] = k_{11}[BH^+][H_2O] + k_{12}[H_2O][B][BH^+] \qquad (13)$$

B is used to represent DBP. Equation (14) follows. Under the

$$k_{BH} = k_{11}[H_2O] + k_{12}[H_2O][B] \qquad (14)$$

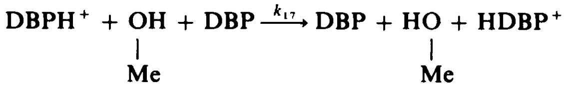
experimental conditions in which only [DBP] is varied this becomes (15).

$$k_{BH} = k_{11}' + k_{12}'[B] \; (k' = k[H_2O]) \qquad (15)$$

Figure 2 shows the linear dependence of k_{BH} on [DBP], and since the plot goes through the origin it indicates that k_{10} is insignificant and that (11) plays little or no part in the proton-transfer process. Hence $k_{BH} = k_{12}[H_2O][B]$, and since $k_B = (P_{HB}/P_B)k_{BH}$ then $k_B = k_{12}[H_2O][BH]$, which shows that since H_2O and $DBPH^+$ remained constant then so would k_B. This is borne out in Table 4. The value of k_{12} calculated from the results at 240 K is 4.1×10^4 l^2 mol^{-2} s^{-1}.

Methanol as Solvent.—In addition to the three mechanisms (3)—(5) postulated, a fourth involving MeO^- may also be imagined. Thus the corresponding equilibria (16)—(19) for

$$DBPH^+ + DBP \xrightarrow{k_{16}} DBP + DBPH^+ \qquad (16)$$



$$DBPH^+ + \underset{\displaystyle Me}{\underset{|}{O}}H + DBP \xrightarrow{k_{17}} DBP + H\underset{\displaystyle Me}{\underset{|}{O}} + HDBP^+ \qquad (17)$$

$$DBPH^+ + MeOH \xrightarrow{k_{18}} DBP + MeOH_2^+ \qquad (18)$$

$$DBPH^+ + MeO^- \xrightarrow{k_{19}} DBP + MeOH \qquad (19)$$

DBP and $DBPH^+$ in this solvent give rise to a chemical flux out of $DBPH^+$ as in equation (20), which simplifies to (21). Since

$$\varphi = k_{BH}[BH^+] = k_{16}[B][BH^+] + k_{17}[BH^+][MeOH][B] + k_{18}[BH^+][MeOH] + k_{19}[BH^+][MeO^-] \qquad (20)$$

$$k_{BH} = k_{16}[B] + k_{17}[MeOH][B] + k_{18}[MeOH] + k_{19}[MeO^-] \qquad (21)$$

the first-order rate constant is unaffected by dilution by a factor of twenty (Table 6) the contributions to k_{BH} from (16) and (17) must be negligible and the equation for k_{BH} reduces to (22).

$$k_{BH} = k_{18}[MeOH] + k_{19}[MeO^-] \qquad (22)$$

Moreover, since $k_{19}[MeO^-] = k_{-19}[B][MeOH]/[BH]$ and there is no change in k_{BH} when p_B changes, this term can also be ignored. Consequently we are left with only (18) as the proton-transfer mechanism, *i.e.* $k_{BH} = k_{18}[MeOH]$, which explains the constancy of k_{BH} in this medium.

The mechanism of proton transfer in dichloromethane involves dissociation of the ion pair and, as observed, depends on the nature of the counter-ion. In methanol there is no difference between the results for DBP·HCl and those for DBP·HBr, and this therefore rules out (8) and (9) as mechanisms for the process in this solvent.

The values of k_{18} calculated from Table 7 are: 0.96 (Cl^-) and 0.94 (Br^-) at 240 K; 4.25 and 4.24 at 260 K; 15.3 and 15.8 at 280 K; and 44.5 and 49.7 l^2 mol^{-2} s^{-1} at 300 K.

In CD_3OD k_{BH}/k_{BD} was *ca.* 4, the same as in CD_2Cl_2, again ruling out a proton-tunnelling stage in the transfer.

Our results for DBP in methanol extend those on methyl-substituted pyridines obtained by Cocivera.[21] Table 8 gives the values of k_{HB} and pK_a thought to be responsible for the differences in behaviour. On this basis the rate for DBP should be significantly greater than experimentally observed. We thus conclude that steric factors are important not only in DBP but also in the 2-methyl- and 2,6-dimethyl-substituted pyridines.

Acknowledgements

We thank the S.E.R.C. for a grant (for R. A. L.).

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Received 17*th April* 1986; *Paper* 6/742