Dynamic NMR as a Nondestructive Method for the Determination of Rates of Dissociation. V. Proton Affinities of *p*-Substituted *N*,*N*-Dibenzylanilines in Aprotic Solvents[1,2)]

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Rates of proton exchange between *p*-substituted *N*,*N*-dibenzylanilinium ion and chloride ion in chloroform-*d* and acetonitrile-d_3 were determined by the dynamic NMR technique. Comparison of the kinetic proton affinity of the anilines in the aprotic solvents with the proton affinity of anilines in the gas phase and the basicity in water revealed that they could be linearly correlated. The feature of the kinetic data was a large positive entropy of activation which can be ascribed to the change from an ionic ground state to a covalent transition state. The entropy of activation was somewhat smaller in acetonitrile-d_3 than in chloroform-*d*. This was attributed to the change in the stage of the transition state for the exchange. A small amount of water which could not be removed easily from the aprotic solvents was proved not to harm the results.

Basicities of amines in water are well documented.3) In recent years, proton affinity of amines in the gas phase was studied by the ion cyclotron resonance technique or high pressure mass spectrometry.4) The results were treated thermodynamically to understand the basicity of amines in aqueous solutions by taking the solvation energy into consideration.5) The correlation between the gas phase proton affinity and the basicity in water could be examined in detail due to the wealth of literatures on the latter. However, basicity data of amines in aprotic solvents are rather few. Therefore, the understanding of basicities in aprotic solvents requires experimental data which can be obtained by variety of methods.

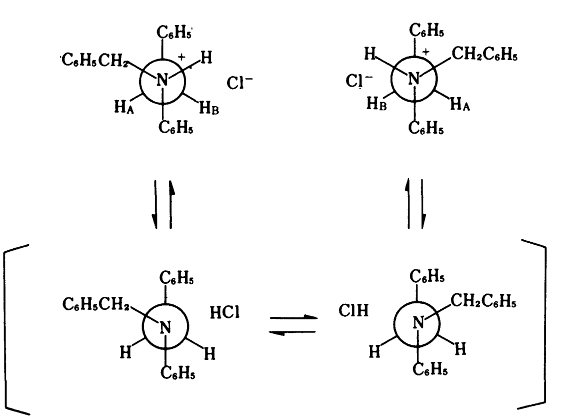
The dynamic NMR technique had been playing some role in measuring the basicity of amines in various solvents. Grunwald, Lowenstein, and Meiboom pioneered in this area by showing that the methyl proton signal of methylamine in strongly acidic media was a quartet due to coupling with -NH_3^+ protons but it coalesced and became a singlet when the pH of the solution was raised.6) Saunders and Yamada followed this work to study the rates of proton exchange and nitrogen inversion in *N*,*N*-dibenzylmethylamine.7) This technique now becomes widely applicable and Delpuech and collaborators have studied the rates of inversion of various amines in acidic aqueous media.8) They further elaborated the study in the area of acidic dimethyl sulfoxide solutions.9) There exist some ambiguities in the exchange in aqueous solutions and strongly polar media: The acceptor of proton can be the free amine, the solvent, and the anion which is derived from the acid, though the free amine is assumed to be the acceptor in these cases. This may be one of the reasons for which the technique has a shortcoming.10)

The rates of proton exchange of ammonium salts with bases in nonaqueous solutions have been reported in some instances other than dimethyl sulfoxide. Reynolds and Schaefer found that *N*,*N*-dibenzylmethylamine in trifluoroacetic acid did not show the disappearance of the coupling between NH^+ and CH.11) This is reasonable because trifluoroacetic acid is a strong acid and trifluoroacetate anion exists as a very dilute solution. As is expected, Delpuech and Gay reported that the proton exchange takes place in a solution of *N*-methylpiperidine derivatives in formic acid.12) Menger *et al.* determined the rates of proton exchange between *N*,*N*-dimethylcyclohexylammonium ion and pyridine in the presence of excess of the latter in chloroform-*d* by the dynamic NMR method.13) Perrin and Wang reexamined the case.14) Determination of the rates of proton transfer in trisubstituted methanes-triethylamine systems15) may be considered another area of application of this technique.

We have demonstrated that topomerization by dissociation could be used for determination of the rates of dissociation. Thus dissociation of some organic halides was studied by this technique.16) This technique is unique in the sense that the rates of dissociation can be determined in the absence of foreign materials, contrasting with the applications cited above which needed excess of either acids or proton accepting bases. Thus it will be possible to see "intrinsic" acidity of an ammonium ion in aprotic solvents by this method.

To observe topomerization by dissociation by dynamic NMR, the compound in question should fulfill the following requirements: 1) The presence of a pair of diastereotopic protons and 2) the site exchange on dissociation. We have found that *N*,*N*-dibenzylaniline hydrochloride satisfies the conditions and the rates of dissociation of the anilinium ion are suitable for the dynamic NMR study.2) The principle of the topomerization processes may be written as in Scheme 1.

The benzylic protons are diastereotopic as far as the anilinium proton sticks to the nitrogen atom. When the proton dissociates, the amine inverts, and reprotonation takes place, the whole process corresponds to topomerization and exchange of the sites takes place. Since the free energy of activation for inversion of *N*,*N*-dibenzylmethylamine is 6.6 kcal/mol (1 cal= 4.184 J),17) that for inversion of *N*,*N*-dibenzylaniline must be smaller than this value. Thus if the dynamic NMR technique affords the free energy of activation for the topomerization much higher than 6 kcal/mol, it will mean that we are looking at the proton exchange rates. It was indeed the case as will be discussed later. Then we obtain proton affinity of *N*,*N*-dibenzylaniline



Scheme 1.

as free energy of activation or other kinetic parameters.

Being driven by the success in determining the kinetics, we extended the work to *p*-substituted *N*,*N*-dibenzylanilines to compare the proton affinity in aprotic solvents with that in the gas phase and the basicity in water. This paper describes the results and discusses the proton affinity of *p*-substituted *N*,*N*-dibenzylanilines in aprotic solvents together with some points which were important for obtaining reliable data.

Experimental

N,*N*-Dibenzylaniline is commercially available from Tokyo Kasei Co. and was used as received. It could be purified by recrystallization from ethanol, if necessary. ^{1}H NMR ($CDCl_3$) δ=4.57 (4H, s), 6.6—7.3 (15H, br s).

N,N-*Dibenzyl*-p-*methoxyaniline.* A mixture of 10.0 g (80 mmol) of *p*-methoxyaniline, 23 mL (200 mmol) of benzyl chloride and 20 g of potassium carbonate were heated at 100 °C for 5 h with stirring. The reaction mixture was poured into water and the organic compounds were extracted with ether. After evaporation of the solvent, the residue was recrystallized from ethanol to give 83.4% of the desired compound, mp 80.7 °C (lit,[18,19] mp 81—82 °C). ^{1}H NMR ($CDCl_3$) δ=3.71 (3H, s), 4.53 (4H, s), 6.70 (4H, s), 7.27 (10H, br s).

N,N-*Dibenzyl*-p-*nitroaniline,* mp 131.9 °C, was similarly prepared by heating *p*-nitroaniline and benzyl chloride at 150 °C for 7 d and was purified by recrystallization from hexane-dichloromethane. Found: C, 75.36; H, 5.72; N, 8.54%. Calcd for $C_{20}H_{18}N_2O_2$: C, 75.45; H, 5.69; N. 8.79%. ^{1}H NMR ($CDCl_3$) δ=4.76 (4H, s), 6.72 and 8.08 (4H, ABq, J= 9.6 Hz), 7.1—7.6 (10H, m).

N,N-*Dibenzyl*-p-*chloroaniline,* mp 104.5 °C, was prepared similarly. Found: C, 78.11; H, 5.80; N, 4.54; Cl, 11.55%. Calcd for $C_{20}H_{18}ClN$: C, 78.03; H, 5.89; N, 4.55; Cl, 11.51%. ^{1}H NMR ($CDCl_3$) δ=4.58 (4H, s), 6.60 and 7.03 (4H, ABq, J= 9.5 Hz), 7.1—7.4 (10H, br s).

N,N-*Dibenzyl*-p-*methylaniline,* mp 55.3 °C, was prepared from 2.1 g of *p*-methylaniline and 4.5 g of benzyl chloride in 20 mL of dioxane and 3 g of potassium carbonate by heating for 4 d. Found: C, 87.89; H, 7.08; N, 5.02%. Calcd for $C_{21}H_{21}N$: C, 87.76; H, 7.36; N, 4.87%. ^{1}H NMR ($CDCl_3$) δ= 2.20 (3H, s), 4.57 (4H, s), 6.63 and 6.93 (4H, ABq, J=10 Hz), 7.1—7.4 (10H, br s).

Hydrochlorides. The *N*,*N*-dibenzylanilines were dissolved in benzene and dry hydrogen chloride was introduced to the solution. The precipitate was collected (it was necessary for the methoxy compound to concentrate the solution) and recrystallized from either hexane-dichloromethane or hexane-tetrahydrofuran. They exhibited the following ^{1}H NMR spectra ($CDCl_3$) δ (only the *p*-substituent given). H, 4.77 (br s), 7.1—7.6 (15H, m); CH_3O, 3.67 (3H, s), 4.64 (4H, br s), 6.7—8.2 (14H, m); Cl, 4.66 (4H, s), 6.8—7.6 (14H, m); CH_3, 2.16 (3H, s), 4.65 (4H, s), 6.8—7.6 (14H, m).

N,*N*-Dibenzyl-*p*-nitroaniline hydrochloride lost hydrogen chloride on drying.

Dynamic NMR Measurement, Analysis, and Kinetic Parameters. Samples were dissolved in appropriate solvents to make up 30—70 mM solutions unless otherwise stated. ^{1}H NMR spectra were recorded on a JEOL FX-60 spectrometer which operated at 60 MHz. Data were accumulated 500—1000 times. Temperatures were directly read by a thermocouple. The total line shape analysis was performed with the use of a modified Binsch program.[20] The chemical shift differences and coupling constants of the AB protons were checked at several temperatures, where the exchange rate was negligibly small, and were found to be constant within the experimental error. The disappearance of coupling between the NH^+ and CH_2 protons were treated by assuming that J_{AX} and J_{BX} were inversely proportional to the rate constant. T_2 was estimated to be 0.1—0.2 s and treated as a variant, taking into account the line width of tetramethylsilane, together with the rate constant. The AB part of ABX (strictly speaking AA'BB'X) showed different line widths for the A and B protons, as are seen in Fig. 1, due to the different magnitude of couplings with the X proton. Typical values for the coupling constants (J_{AB}, J_{AX}, and J_{BX} and the chemical shift differences ($\Delta\nu_{AB}$) are compiled in Table 1. They differ to some extent by concentrations. The calculated and the observed spectra were compared by the visual fitting. The agreement between the two spectra was excellent.

The rate constant (s^{-1}) used for the calculation of activation parameters shown in Table 4 and 5 are as follows (*p*-substituent, solvent, and temperatures in °C in parentheses given).

p-CH_3O($CDCl_3$): 18.0(8.1), 23.4(10.3), 31.8(12.5), 38.0(14.7), 50.0(16.9), 66.6(19.1) 90.6(21.3), 118(23.5)

TABLE 1. CHEMICAL SHIFT DIFFERENCES ($\Delta\nu_{AB}$) AND COUPLING CONSTANTS (J_{AB}, J_{AX}, AND J_{BX}) OF *N*,*N*-DIBENZYLANILINIUM CHLORIDES AT LOW TEMPERATURES

p-Substituent	Solvent	$\Delta\nu_{AB}$/Hz	J_{AB}/Hz	J_{AX}/Hz	J_{BX}/Hz
CH_3O	$CDCl_3$	25.4	−12.6	3.7	7.8
	CD_3CN	22.0	−12.9	3.7	7.8
CH_3	$CDCl_3$	24.0	−13.1	3.2	7.0
	CD_3CN	22.7	−12.9	3.9	7.8
H	$CDCl_3$	25.9	−12.6	3.8	7.5
	CD_3CN	23.3	−12.8	3.7	8.1
Cl[a]	$CDCl_3$	24.8	−12.9	3.4	7.1

a) The coupling constsnts of this entry are those of hydrobromide which were diverted to the hydrochloride because the latter compound showed evidence of exchange, though slow, at the lowest temperature attainable in this solvent.

p-CH$_3$O(CD$_3$CN): 14.0(2.3), 19.0(4.9), 29.0(8.8), 41.9(11.9), 47.0(13.6), 57.0(14.9) 74.0(17.1)
p-CH$_3$(CDCl$_3$): 12.0(−7.0), 17.0(−4.1), 20.0 (−3.5), 27.0(−1.1), 29.0(−0.6), 33.0(0.5), 48.0(3.1), 60.0(5.0), 84.0(7.9), 92.0(8.5), 122(11.0)
p-CH$_3$(CD$_3$CN): 18.0(−5.2), 28.2(−2.0), 38.0 (0.6), 51.0(3.2), 62.0(4.9), 84.0 (7.5)
H(CDCl$_3$): 13.4(−9.5), 25.0(−7.4), 35.4 (−5.1), 47.0(−2.9), 62.5(−0.7), 84.0(1.5), 110(3.7)
H(CD$_3$CN): 32.0(−9.5), 54.0(−5.1), 93.0 (−0.7), 180(3.7)
p-Cl(CDCl$_3$): 13.0(−27.8), 16.0(−25.8) 22.0 (−23.8), 29.0(−22.0), 41.0 (−19.6), 60.0(−17.9).

Results and Discussion

In Fig. 1 are shown temperature dependent spectra of the AB part of ABX signals of *N,N*-dibenzyl-*p*-methoxyaniline hydrochloride in chloroform-*d* together with the calculated. This was chosen because those of *N,N*-dibenzylaniline hydrochloride were given in a preliminary note.[2]

Although we observe the change in line shapes of the benzylic protons, the dynamic process needs proton acceptors. Since the solvents are not basic in the normal sense, we may neglect the possibility that solvent molecules act as proton acceptors. There are three possible acceptors: chloride ion, free amine, and water. Since water in the solvent was found not easily removable, we turned our attention to the effect of water. Two methodologies were used. First we observed the NH$^+$ proton signal at δ *ca.* 14 and followed the line shape at temperatures where the coalescence of the CH$_2$ proton signal took place. No change was observed. If water in the system were the proton acceptor, coalescence of the NH$^+$ signal with that of water would have been observed. Secondly, we examined the rates of topomerization in chloroform-*d*, which was carefully dried and to which water was intentionally added.

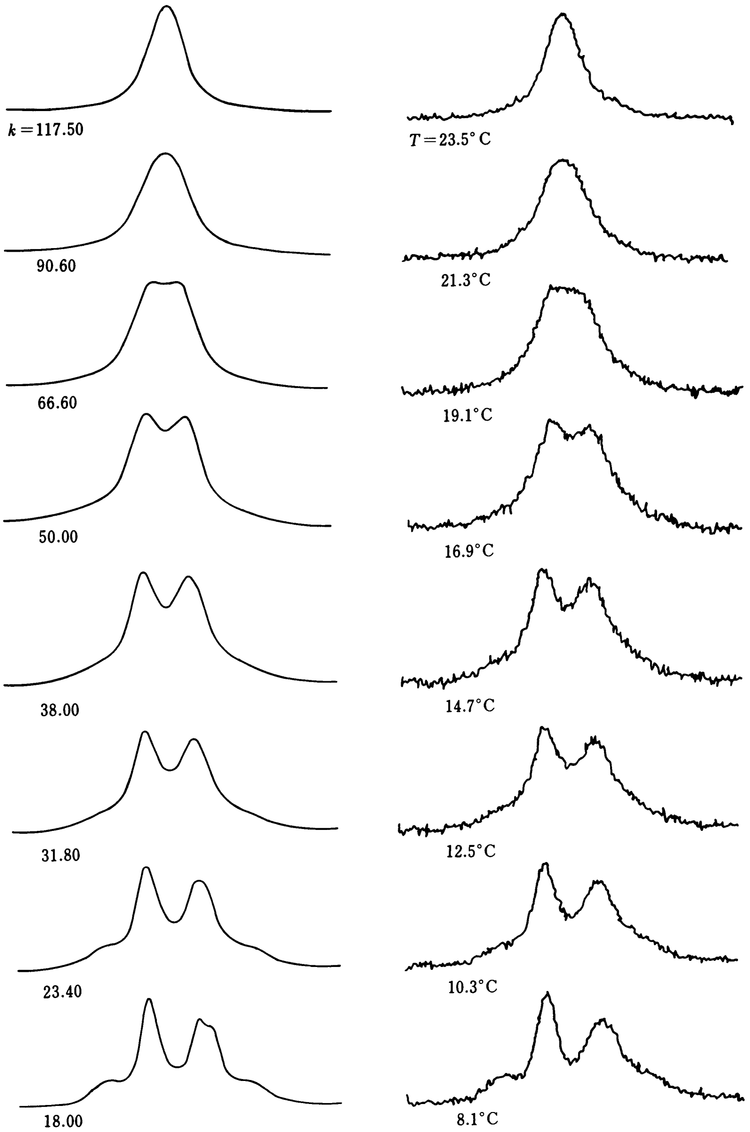


Fig. 1. Calculated and observed spectra of the AB part of ABX signals of *N,N*-dibenzyl-*p*-methoxyaniline hydrochloride in chloroform-*d*.

TABLE 2. EFFECT OF WATER IN THE SYSTEM ON THE KINETIC PARAMETERS OF PROTON-EXCHANGE IN *N*,*N*-DIBENZYLANILINIUM CHLORIDE IN CHLOROFORM-*d*

Run	1	2	3
Concentration of H_2O (mmol/L)	0.9	5.4	14.9
Correlation Coeff.	0.9991	0.9993	0.9926
ΔH^{*}/kcal mol^{-1}	18.5±0.7	19.0±0.6	18.1±2.0
ΔS^{*}/e. u.	18.0±2.6	19.7±2.4	16.5±7.4
ΔG^{*}_{273}/kcal mol^{-1}	13.6	13.6	13.6

TABLE 3. EFFECT OF CONCENTRATION OF SUBSTRATE ON KINETIC PARAMETERS OF PROTON EXCHANGE IN *N*,*N*-DIBENZYLANILINIUM CHLORIDE IN CHLOROFORM-*d*

Run	1	2	3
Concn/mmol L^{-1}	31.0	62.0	121.6
Correlation coeff.	1.0000	0.9993	0.9999
ΔH^{*}/kcal mol^{-1}	20.9±0.0	19.6±0.6	20.3±0.0
ΔS^{*}/e. u.	27.8±0.0	19.7±2.4	23.4±0.1
ΔG^{*}_{273}/kcal mol^{-1}	13.3	13.6	14.0

TABLE 4. SUBSTITUENT EFFECT ON KINETIC PARAMETERS OF PROTON EXCHANGE IN *N*,*N*-DIBENZYLANILINIUM CHLORIDE IN CHLOROFORM-*d*

p-Substituent	CH_3O	CH_3	H	Cl
T_c/°C	19.1	5.0	−0.7	−17.9
Correlation coeff.	0.998	0.999	0.999	0.995
ΔH^{*}/kcal mol^{-1}	19.5±0.9	19.0±0.4	18.5±0.7	18.6±1.8
ΔS^{*}/e. u.	16.6±3.1	17.9±1.4	18.0±2.6	22.8±7.5
ΔG^{*}_{273}/ kcal mol^{-1}	15.0	14.1	13.6	12.4
k_{289}/s^{-1}	1.35×10^2	6.33×10^2	1.48×10^3	1.32×10^4

The results are compared in Table 2, where chloroform-*d* containing 5.4 mmol L^{-1} of water is the commercially available and is used as such. As are seen in Table 2, if water was intentionally added, the correlation coefficient in the Eyring plot became inferior and consequently the errors involved became large. Yet the free energy of activation is reproduced. We ran the similar determination of rates of dissociation in the methoxy compound with various concentrations of water. No effect of the water was observed. Therefore, as far as we use ordinary chloroform-*d*, the data are reliable. These results also rejects the possibility that water is the proton acceptor in the system.

If the free amine which exists in a minute amount in the system accepts proton, we should be able to observe the concentration effects. The data are collected at three concentrations and are summarized in Table 3. It may seem that the free energy of activation increases as the concentration increases. However, we do not believe that the tendency is significant because of the experimental errors which do not appear here. If free amine accepts proton, the rates of exchange of proton must increase as the concentration increases, contrary to the data shown in Table 3. Therefore, we conclude that the amine in the system, if any, is not the proton acceptor.

These two lines of evidence establish that the chloride ion in the system is the proton acceptor. From the concentration effect, we may conclude that the chloride ion, which exists as an ion pair with the anilinium ion, accepts proton in the process which is observed by the present technique.

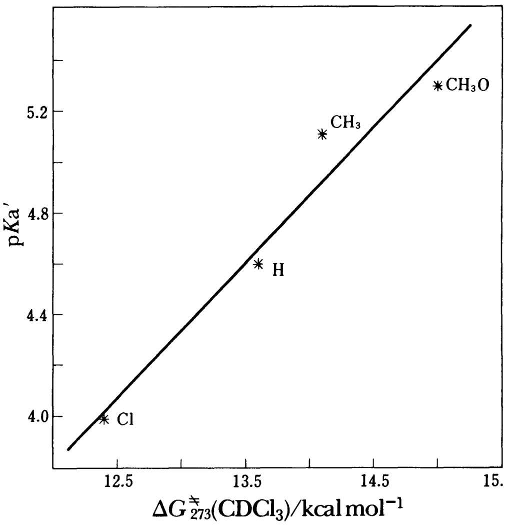


Fig. 2. Correlation between pK_a′ values of *p*-substituted *N*,*N*-dimethylanilines and free energies of activation for the proton exchange of *p*-substituted *N*,*N*-dibenzylanilinium chlorides in chloroform-*d*.

Having established that the kinetic proton affinity of *N*,*N*-dibenzylaniline can be obtained by this technique, we turned our attention to the substituent effects. The study in this area will contribute to the genral understanding of acid-base properties of amines in aprotic solvents which are often important in organic chemistry. The results are compiled in Table 4. The results are in good agreement with the expectation from basicities in water: the *p*-methoxy compound is the strongest base and the chloro compound is the weakest of the four. It is unfortunate that the nitro compound failed to give stable hydrochloride but, if it could, the free energy of activation for the proton exchange of the compound must have been still smaller.

The feature of the data is a very large positive entropy of activation. Since the dissociation of a covalent compound into ionic species is known to be accompanied by a large negative entropy of activation,[21] the reaction studied here, from the ionic to the covalent, can be accompanied by positive entropy of activation. The freedom of motion of solvent molecules is cited to be responsible to the phenomena. The increase in entropy of activation seems to become large when we go from an electron-donating substituent to an electron-withdrawing one. If this trend is significant, that will mean that the transition state for the exchange is less covalent in the electron-rich compound than in the electron-poor one. That is the transition state is earlier in the former than in the latter. The enthalpy of activation varies little but there is a tendency that an electron-rich amine shows a large value.

It should be of interest to compare the proton affinity of the *N*,*N*-dibenzylanilines obtained here with those in water and in the gas phase. Hammett plot yielded a good linear relationship, the correlation coefficient being 0.979 and ρ being 3.59. Fig. 2 illustrates the relationship between the free energy of activation and the pK_a′ values reported for *N*,*N*-dimethylanilines.[22] The correlation coefficient is 0.996. Since the proton

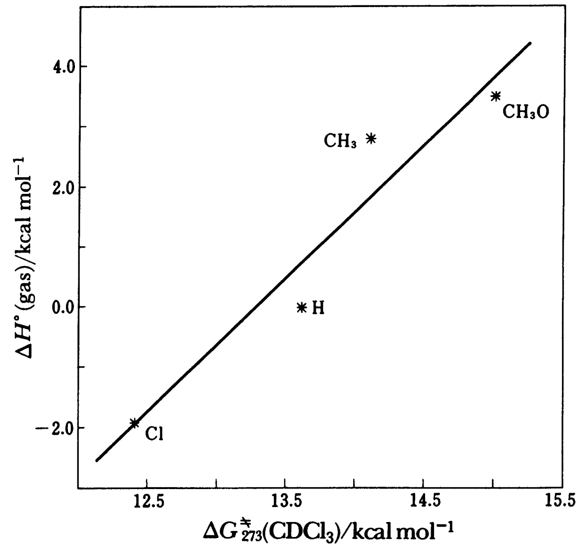


Fig. 3. Enthalpies of isodesmic process, $C_6H_5NH_3^+ + p\text{-}XC_6H_4NH_2 \rightleftharpoons C_6H_5NH_2 + p\text{-}XC_6H_4NH_3^+$ in the gas phase *vs.* free energies of activation for the proton exchange of *p*-substituted *N,N*-dibenzylanilinium chlorides in chloroform-*d*.

affinity of anilines in the gas phase is linearly correlated with the pK_a in water,[23] it will be no wonder to obtain a linear relationship between the proton affinity in the gas phase and that in the aprotic solvent. Figure 3 illustrates the result. The correlation coefficient is 0.958. Although it is known that the gas-phase proton affinity is quite different from the basicity in water when the structures of bases change,[4c] the proton affinity of substituted anilines in chloroform, at least, can be linearly correlated with the basicity in water and the proton affinity in the gas phase.

In order to get into further insight, we have tried to change the solvent. Acetone-d_6 was found to exchange proton with NH$^+$ and tetrahydrofuran was a poor solvent for the anilinium chloride. Acetonitrile-d_3 could afford data of 3 compounds, although the solubility of the chloro compound was too low to be practical in the measurement. The kinetic data are compiled in Table 5. The data have similar trends which are pointed out in the above sections on the behaviors in chloroform-*d* except some points discussed below.

Comparison of the data in acetonitrile-d_3 and those in chloroform-*d* reveals some interesting points. First of all, the solvent effect is not so dramatic as is expected from the change in dielectric constants. One might have expected that dissociation in acetonitrile should be slower than in chloroform because the ionic ground state is stabilized in the former. However, this similarity of the rates of dissociation in the two solvents is a mere coincidence at or near temperatures where coalescence of the signals takes place. When we divide the activation parameters into enthalpy of activation and entropy of activation, difference is clear. This may be one of the examples of enthalpy-entropy compensation effect.[24] Both enthalpy and entropy of activation with the chloroform solutions are larger than those with acetonitrile solutions. Possibly the transition state for the proton exchange in acetonitrile becomes earlier than that in chloroform because the ionic ground state is stabilized and the transition state is like the ground state in the former. The smaller entropy of activation in acetonitrile solutions than that in chloroform supports the idea. Thus we conclude that the transition state for the proton exchange in these aprotic solvents becomes early as the proton afinity of the base and the dielectric constant of the solvent increase. The rationale for the phenomena on the molecular basis undoubtedly includes the polar nature and/or hydrogen-bonding ability of the molecule but there may remain some others which are not clear at the moment.

TABLE 5. SUBSTITUENT EFFECT ON KINETIC PARAMETERS OF PROTON EXCHANGE IN *N,N*-DIBENZYLANILINIUM CHLORIDE IN ACETONITRILE-d_3

p-Substituent	CH$_3$O	CH$_3$	H
T_c/°C	14.9	4.9	—
Correlation coeff.	0.999	0.999	0.999
$\Delta H^{\ddagger}$/kcal mol^{-1}	17.0±0.6	17.4±0.5	17.2±0.8
$\Delta S^{\ddagger}$/e. u.	8.6±2.3	12.3±1.9	13.7±2.8
$\Delta G^{\ddagger}_{273}$/ kcal mol^{-1}	14.7	14.0	13.4
k_{289}/s^{-1}	1.60×10^2	5.58×10^2	1.30×10^3

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References

1) Part IV: M. Ōki and M. Ohira, *Chem. Lett.*, **1982**, 1267.

2) A preliminary note was published: M. Ōki, Y. Yoshioka, H. Kihara, and N. Nakamura, *Chem. Lett.*, **1980**, 1625.

3) For example, see D. D. Perrin, "Dissociation Constants of Organic Bases in Aqueous Solution", Butterworth, London (1965): Supplement, 1972.

4) a) M. S. B. Mansou, *J. Am. Chem. Soc.*, **87**, 2332 (1965); b) J. I. Brauman, J. M. Riveros, and L. K. Blair, *ibid.*, **93**, 3914 (1971); c) J. P. Briggs, R. Yamdagni, and P. Kebarle, *ibid.*, **94**, 5128 (1972).

5) F. M. Jones, III, and E. M. Arnett, *Progr. Phys. Org. Chem.*, **11**, 263 (1974): E. M. Arnett, F. M. Jones, III, M. Taagapera, W. G. Henderson, D. Holtz, J. L. Beauchamp, and R. W. Taft, *J. Am. Chem. Soc.*, **94**, 4724 (1972); R. W. Taft, J. F. Wolf, J. L. Beauchamp, G. Scorrano, and E. M. Arnett, *ibid.*, **100**, 1240 (1978).

6) E. Grunwald, A. Loewenstein, and S. Meiboom, *J. Chem. Phys.*, **27**, 630 (1957).

7) M. Saunders and F. Yamada, *J. Am. Chem. Soc.*, **85**, 1882 (1963).

8) a) J.-J. Delpuech and M.-M. Deschamps, *Nouv. J. Chim.*, **2**, 563 (1978); b) B. Bianchin, J. Chrisment, J.-J. Delpuech, M. N. Deschamps, D. Nicole, and G. Serratrice, *Protons Ions Involved Fast Dyn. Phenom., Proc. Int. Meet. Soc. Chim. Phys., 30th 1977*, 265: *CA*, **90**, 120775m (1979).

9) J.-J. Delpuech and B. Bianchin, *J. Am. Chem. Soc.*, **101**, 383 (1979). See also ref. 8b.

10) W. R. Morgan and D. E. Leyden, *J. Am. Chem. Soc.*, **92**, 4527 (1970).

11) W. F. Reynolds and T. Schaefer, *Can. J. Chem.*, **42**, 2119 (1964).

12) J.-J. Delpuech and C. Gay, *Tetrahedron Lett.*, **1966**, 2603.

13) F. M. Menger, T. D. Singh, and F. L. Bayer, *J. Am. Chem. Soc.*, **98**, 5011 (1976).

14) C. L. Perrin and W.-H. Wang, *J. Am. Chem. Soc.*, **104**, 2325 (1982).

15) V. K. Pogorelyi, T. B. Vishnyakova, and I. P. Gragerov, *Ter. Exsp. Khim.*, **18**, 590 (1982): *CA*, **98**, 34146r (1983).

16) M. Ōki, A. Shimizu, H. Kihara, and N. Nakamura, *Chem. Lett.*, **1980**, 607: A. Shimizu, Y. Sakamaki, K. Azuma, H. Kihara, N. Nakamura, and M. Ōki, *Bull. Chem. Soc. Jpn.*, **54**, 2774 (1981).

17) C. H. Bushweller, J. W. O'Neil, and H. S. Bilofsky, *Tetrahedron*, **28**, 2697 (1972).

18) F. Walls and J. Cabarello, *Bol. Inst. Quim. Univ. Nacl. Auton. Mex.*, **15**, 74 (1963): *CA*, **61**, 8215 (1964).

19) M. Sekiya, M. Tomie, and N. J. Leonard, *J. Org. Chem.*, **33**, 318 (1968).

20) G. Binsch, *Top. Stereochem.*, **3**, 97 (1968).

21) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John-Wiley, New York (1953), p. 127.

22) Y. Ogata and I. Tabushi, *Bull. Chem. Soc. Jpn.*, **31**, 969 (1958).

23) K. D. Summerhays, S. K. Pollack, R. W. Taft, and W. J. Hehre, *J. Am. Chem. Soc.*, **99**, 4585 (1977).

24) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).