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RATES OF DISSOCIATION OF N,N-DIBENZYLANILINIUM IONS IN APROTIC SOLVENTS[1)]

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Rates of dissociation of N,N-dibenzylanilinium ions into N,N-dibenzylaniline and proton which is captured by chloride anion have been determined by the dynamic NMR technique. The method supplies information about proton affinities of amine and anion in aprotic solvents.

In the preceding paper of this series, we have demonstrated that the dynamic NMR technique can conveniently be used for determination of rates of ionic dissociation of an organic halide and have predicted that the method should be applicable to the dissociation of other species including ammonium ions.[1)] We now wish to report that the prediction is verified, using N,N-dibenzylanilinium chloride. This compound has been selected for the following reasons: 1) it possesses diastereotopic protons and is soluble in nonpolar solvents to some degree, and

$$(C_6H_5CH_2)_2\overset{+}{N}HC_6H_5 \underset{\bigcirc}{\rightleftharpoons} [(C_6H_5CH_2)_2NC_6H_5 + H^+] \overset{\bigcirc}{\rightleftharpoons} (C_6H_5CH_2)_2\overset{+}{N}HC_6H_5$$

2) the diastereotopicity of the benzylic protons is lost on dissociation of the anilinium ion to free amine and proton followed by inversion of nitrogen and then reprotonation. The process is observed as the change in line shapes of the ^1H NMR spectra. The rates of dissociation of this species were found to be conveniently measured by the NMR technique.

N,N-Dibenzylaniline was prepared according to a published method[2)] and was converted to its hydrochloride. Solvents were dried carefully with Molecular Sieves 4A but it was not possible to remove all the water in the solvents. The solvents were either chloroform-d or acetonitrile-d_3. The concentrations of the solute were varied to see the effect of concentration on the rates of dissociation. ^1H NMR spectra were obtained with a JEOL FX-60 spectrometer which was equipped with a temperature variation accessory. Usually data were collected for 500 times and, when exact parameters were obtained at low temperatures, the region was scanned 1,000 times. The spectra were analyzed as the AB part of an ABX spin system. The difference in chemical shifts did not change over the range of -30 ∿ -50°C where the exchange was slow. Thus the chemical shift difference was assumed to be constant in the temperature range where the line shapes drastically changed. The spectra were simulated with the use of the modified Binsch program.[3)] T_2 was obtained from the line width due to the methylene protons at the slow limit of the exchange and modified by taking the line width of TMS at the temperature observed into consideration. T_2's of the observed spectra seemed to be different for the A and B protons. The difference is included in the calculated spectra. The feature of the spectra was the coalescence of a quartet to a singlet rather than to a doublet. This is because the anilinium ion dissociates4) and the line shape had to be treated by including the coupling constant as a variant. The results are shown in Fig. 1. The rate constants were put into the Eyring equation to obtain activation parameters. The results are shown in Table 1.

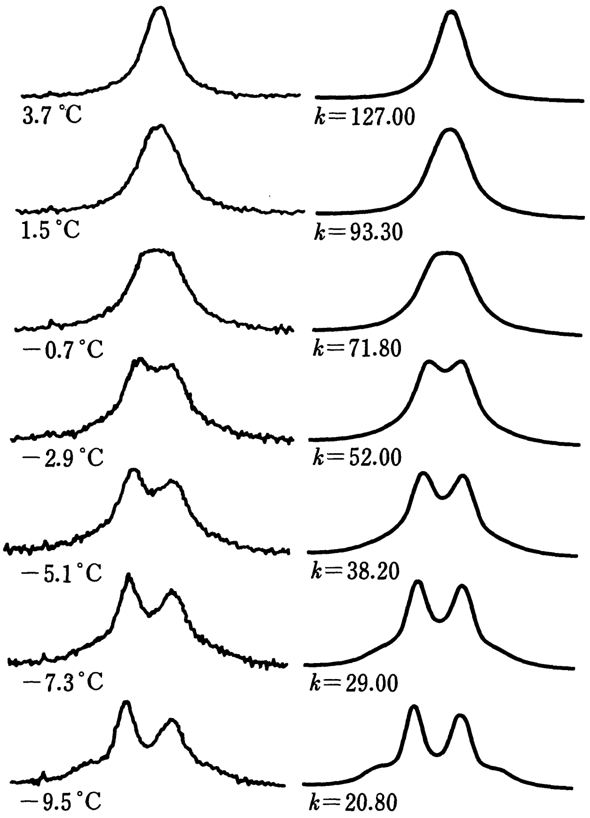

Fig. 1 Observed (left) and calculated (right) spectra of the methylene part of N,N-dibenzylanilinium chloride in $CDCl_3$ (run 1)

Table 1 Conditions of Measurements and Kinetic Parameters for the Dissociation of N,N-Dibenzylanilinium Ion a) (as Chloride) in Chloroform-d

	Run 1	Run 2	Run 3	Run 4	Run 5
Concentration of Solute (mmol L^{-1})	61.5	62.0	62.5	121.6	31.0
Concentration of H_2O b) (mmol L^{-1})	0.9	5.4	14.9	2.1	3.3
$\Delta H^{\ddagger}$ (kcal mol^{-1})	18.5	19.0	18.1	20.3	17.7
$\Delta S^{\ddagger}$ (e. u.)	18	20	17	23	15
$\Delta G^{\ddagger}_{273}$ (kcal mol^{-1})	13.6	13.6	13.6	14.0	13.3
Correlation Coefficient	0.9991	0.9993	0.9926	0.9999	0.9999

a) NMR data were $\Delta\delta_{AB}$ 25.9 Hz, J_{AB} 12.6 Hz, J_{AX} 2.1 Hz, and J_{BX} 7.1 Hz.

b) The amount was estimated by comparing the peak area of H_2O with those of the solute.

The first point which has to be discussed is the nature of the exchange process which can be any of the following three. The proton of the anilinium ion is given 1) to the chloride ion, 2) to free amine which is formed by dissociation, or 3) to water which is present in a minute amount. The nitrogen inversion follows any process of the above and then comes reprotonation. The data in Table 1 indicate that the rates of dissociation are not a function of concentration of the anilinium salt. Therefore the possibility of the free amine intervention may be ruled out. Since water is known to be a good proton acceptor and it has not been removed completely from the system, the possibility of the third case must be carefully examined. Two points were examined. Firstly the NH^+ proton resonance at δ ca. 14 remained intact at the coalescence temperature to indicate that the exchange of this proton was slow. Since, at this temperature, the exchange of the AB protons is fairly fast on the NMR time scale, the result is an indication that it is not water that accepts proton. Secondly, we intentionally added water to the system (run 3). As are seen in Table 1, adding 15 mmol L^{-1} of water caused an inferior linearity than others to indicate that another mechanism might be intervening at this concentration to a limited extent. However, the kinetic parameters were still in good agreement with those obtained with the samples of less water content. From these two lines of results, we conclude that the third is not the case. Then chloride ion as a closely-located counterion must be the proton-accepting species.

Another interesting feature of the data in Table 1 is that the $\Delta S^{\ddagger}$ term is positive and large in contrast to the fact that the ionic dissociation of an organic halide gave a very large, negative value. This contrasting behavior may be attributed to that the dissociation of the anilinium ion takes place from the ionic to the covalent species whereas the reverse occurs in the ionization of the halide. Probably the solvent molecule intervening the ion pair aquire more freedom in the transition state of the proton exchange. In this connection, it will be interesting to see the solvent effect on the rates of dissociation of the anilinium ion. We examined the rates of ionization of N,N-dibenzylanilinium ions in acetonitrile-d_3 to find $\Delta H^{\ddagger}$ 20.9 kcal mol^{-1}, $\Delta S^{\ddagger}$ 28 e. u., and $\Delta G^{\ddagger}_{273}$ 13.6 kcal mol^{-1}. The results are almost the same with those obtained with chloroform-d solutions. Solvent polarity does not seem to affect the dissociation of the anilinium ion in contrast to the case of ionization of the organic halide. The contrasting behavior is again attributed to dissociation of the ionic species to the covalent species.

Exchange of protons between ammonium salts and solvents have been variously treated. In aqueous solution, line shape dependence on pH has been used to measure the rates.5) In a polar aprotic solvent, nitrogen inversion was observed to see the exchange.6) At any rate, however, these authors used excess of acid. Therefore, our method is unique in that no other foreign materials, which might affect the rates, are used and that we can use nonpolar aprotic solvents.

Basicity of amines has been an old yet a new problem. Unmonotonous trend of basic strength in mono-, di-, and trialkylamines aroused interests of many investigators and is now explained by hydration energies in aqueous solutions.7) An MO calculation supported the idea.8) In recent years, proton affinities in the gas phase have been investigated and the results agree with the prediction9) and hydration energies are related to the base strengths.10) However, basicity in nonpolar solvents remains to be solved. We hope our method provides useful data in this field which bridges the gaseous state and the solution in a polar or a protic solvent.

Dissociation of coordinated compounds has been treated by dynamic NMR by looking at the disappearance of the coupling between the nuclei concerned.4) Our method contrasts with this method in that it does not require coupling interaction between the nuclei dissociating. Therefore these two methods may be complementary in studying the rates of dissociation of molecular species.

A work to compare proton affinities of amines and various anions is in progress.

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