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Dynamic NMR as a Nondestructive Method for the Determination of Rates of Dissociation. VIII. Proton Affinities of Anions Derived from Strong Acids in Chloroform[1]

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Synopsis. Dynamic NMR study of topomerization by dissociation of *N*,*N*-dibenzylanilinium salt was applied to the determination of proton affinities of anions derived from strong acids in chloroform-*d*. The total line shape analysis of the benzylic proton signals gave the following order of proton affinity:

$$Cl^- > p\text{-}CH_3C_6H_4SO_3^- > CH_3SO_3^- > Br^-.$$

In a previous paper, we reported that the rates of proton exchange between *p*-substituted *N*,*N*-dibenzylanilinium and chloride ions could be determined by the dynamic NMR technique.[2] That paper was concerned about the proton affinity of amines affected by substituents. However, it is expected that we can determine the proton affinity of anions, if we fix the *N*,*N*-dibenzylanilinium ion and vary the anion which forms an ion pair with the former, because the anion in the ion pair is the proton acceptor in the exchange reaction. In turn, the proton affinity of anions affords information about the acidity of the conjugate acids. Although it is possible to titrate acids in nonaqueous solutions against indicators, the knowledge of "intrinsic acidity", that means the acidity without foreign materials, will be of value, especially because acids very often act as catalysts in organic reactions. To contribute to this area, we have compared proton affinity of chloride, bromide, methanesulfonate, and *p*-toluenesulfonate anions. This paper is to report the results.

The kinetic parameters for the proton exchange between *N*,*N*-dibenzylanilinium ion and some anions are summarized in Table 1. Although iodide salt was also prepared, it discolored easily. The data are not included in Table 1 because of the low reliability, but broadening of lines was observed at temperatures close to the boiling point of chloroform. The coalescence temperature was estimated to be 70—80 °C.

The results indicated that the bromide ion has less proton affinity than the chloride anion and probably the iodide ion has the least proton affinity among the anions examined. This result is in conformity with the acidity data in water.[3]

Comparison of the proton affinity of sulfonate anions and halide anions in water has some difficulty. Although Bessière calculated pK_a's of various inorganic acids and sulfonic acids from the data in trifluoroacetic acid,[4] the pKa's are not in conformity with other standard values. One point which is certain from the report by Bessière is that methanesulfonic acid and *p*-toluenesulfonic acid have comparable acidity. Our data confirm this point and establish that the acidity of the sulfonic acids can be placed between hydrochloric acid and hydrobromic acid in chloroform. The order of acidity, $HBr > CH_3SO_3H > HCl$, obtained by titration in chloroform,[5] agrees with the present results as well.

The interesting point in the kinetic data is that, whereas the anilinium halides give large positive entropy of activation, the sulfonates give small negative entropy of activation. We have shown that an ammonium perchlorate gives negative entropy of activation on dissociation of the C–N bond in it and have developed a hypothesis that the origin of the negative entropy of activation is the loss of freedom of motion of the perchlorate ion in the transition state.[1] The data shown in Table 1 suggest that the negative entropy of activation is common when the anion carries more than two negatively charged, equivalent oxygens. The reason for this must be, as suggested in the previous paper, the loss of freedom of motion of the anion in the transition state by forming a partial O–H bond, whereas the anion is rotating in the ground state due to the presence of three or four negatively charged oxygen atoms. We may now conclude that the entropy of activation for the dissociation of the N–H or N–C bond in ammonium salts is large positive when the anion is halide, while it is small negaitve if the anion is sulfonate or perchlorate.

So far, we have discussed the proton exchange of *N*,*N*-dibenzylanilinium ions and anions. The data are confined to strong acids. This has a special meaning because it is difficult to obtain exact p*K*a values of strong acids in water. A book which compiles acidities of organic substances cites the p*K*a of methanesulfonic acid (−1∼−2) as uncertain.[6] This technique is expected to provide a method of approach to acidities of very strong acids.

TABLE 1. KINETIC PARAMETERS AND RELATED DATA FOR THE PROTON EXCHANGE BETWEEN *N*,*N*-DIBENZYLANILINIUM ION AND ANIONS DERIVED FROM STRONG ACIDS IN CHLOROFORM-*d*

Anions	Cl^{-} [b]	Br^-	$CH_3SO_3^-$	$p\text{-}CH_3C_6H_4SO_3^-$
T_c/°C	−0.7	47.8	12.3	10.6
Correlatior Coeff.	0.999	0.998	0.999	0.999
$\Delta H^{\neq}$/kcal mol^{-1} [a]	18.5±0.7	21.1±1.1	14.1±0.3	11.6±0.5
$\Delta S^{\neq}$/e.u.	18.0±2.6	15.5±3.3	−0.2±1.2	−8.9±1.7
$\Delta G^{\neq}_{273}$/kcal mol^{-1}	13.6	16.9	14.2	14.0

a) 1 cal=4.184 J. b) The data were obtained in the previous paper.[2]

However, this technique should not be limited to the anilinium salt. If a more basic amine, which fulfil the following conditions, is used, the proton affinity of anions, of which conjugate acid is less acidic than those described here, should be obtained. The necessary conditions are, 1) possession of diastereotopic nuclei which are NMR-active, and 2) exchange of their sites by dissociation followed by inversion. Thus this technique is potentially useful for determining acidity of various acids in aprotic solvents.

Experimental

N,N-Dibenzylaniline was commercially available from Tokyo Kasei Co. and was used as received. Preparation and acquisition of kinetic data of hydrochloride were described in the previous paper.[2]

Hydrobromide was prepared by mixing 1 g of *N,N*-dibenzylaniline in 50 mL of carbon tetrachloride with 2 mL of 47% hydrobromic acid followed by recrystallization of the precipitate from tetrahydrofurane–hexane, colorless crystals. ^{1}H NMR ($CDCl_3$, δ): 4.72 and 5.03 (4H, m), 7.1—7.7 (15H, m).

Hydriodide was prepared similarly from 57% hydriodic acid. It discolored easily under normal protections against oxygen and light. Removal of the brown color was difficult, brown crystals. ^{1}H NMR ($CDCl_3$, δ): 4.79—5.11 (4H, m), 7.0—7.8 (15H, m).

p-Toluenesulfonate was prepared by mixing an ethanolic solution of *N,N*-dibenzylaniline with *p*-toluenesulfonic acid in ethanol. The salt was recrystallized from chloroform–hexane, colorless crystals which discolor easily. ^{1}H NMR ($CDCl_3$, δ): 2.36 (3H, s), 4.88 (4H, br s), 7.0—8.0 (19H, m).

Methanesulfonate was prepared similarly, colorless oil. ^{1}H NMR ($CDCl_3$, δ): 2.97 (3H, s), 4.83 (4H, br s), 7.0—7.4 (15H, m).

Dynamic NMR measurement was performed as reported previously with chloroform-*d* solutions.[2] The following chemical shift differences ($\Delta\nu_{AB}$) and coupling constants (J_{AB}) were used throughout the total line shape analyses because they did not change at several temperatures where the exchange of protons was negligibly slow. J_{AX} and J_{BX} of which low temperature values are shown below, were treated as reciprocally variable with temperature.

HBr salt: $\Delta\nu_{AB}$ 25.9 Hz, J_{AB} −12.7 Hz, J_{AX} 3.2 Hz, J_{BX} 7.0 Hz.

CH_3SO_3H salt: $\Delta\nu_{AB}$ 34.0 Hz, J_{AB} −12.5 Hz, J_{AX} 2.4 Hz, J_{BX} 7.3 Hz.

p-$CH_3C_6H_4SO_3H$ salt: $\Delta\nu_{AB}$ 33.0 Hz, J_{AB} -12.5 Hz, J_{AX} 2.4 Hz, J_{BX} 7.3 Hz.

The following rate constants (s^{-1}) were obtained (temperature in °C in parentheses).

HBr salt: 28.0 (40.5), 39.0 (42.9), 49.0 (45.5), 63.0 (47.8), 81.0 (50.2), 107.0 (52.7)

CH_3SO_3H salt: 24.0 (-0.7), 37.0 (3.6), 40.0 (4.5), 49.0 (6.7), 57.0 (8.4), 72.0 (11.0), 82.0 (12.3), 103.0 (14.5)

p-$CH_3C_6H_4SO_3H$ salt: 30.0 (-2.4), 40.0 (1.0), 54.0 (4.9), 65.0 (6.7), 77.0 (9.7), 85.0 (10.6), 106.0 (13.6)

The kinetic parameters were obtained by the usual manner with the use of these rate constants and temperatures.

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