CHEMISTRY LETTERS, pp. 607-610, 1980.

DYNAMIC NMR AS A NONDESTRUCTIVE METHOD FOR THE DETERMINATION OF RATES OF DISSOCIATION. SCOPE OF THE METHOD AS APPLIED TO THE IONIC DISSOCIATION OF α-CHLORODIBENZYL SULFIDE

Michinori ŌKI,* Atsushi SHIMIZU, Hiroshi KIHARA, and Nobuo NAKAMURA
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

Dynamic NMR technique was applied to the determination of the rates of ionic dissociation of α-chlorodibenzyl sulfide in chloroform-d. Total line shape analysis afforded $\Delta H^{\ddagger}$ 28 kJ mol^{-1} and $\Delta S^{\ddagger}$ -120 J K^{-1} mol^{-1} which were not dependent on the concentration of the substrate. The results imply that the initial steps of S_N1 reactions can be studied by the method. Scope of the method is discussed.

The ionization process of α-chloro sulfides have been observed by the dynamic NMR technique as an AB proton exchange and free energies of activation for the ionization have been obtained by the coalescence-temperature technique.[1,2] If we are observing a unimolecular dissociation process, the method may claim great importance since it gives information about the initial steps of S_N1 reactions which are considered to take place via ion pairs as shown by eq. 1.[3]

$$\begin{tikzcd}
RX \arrow[r, harpoon, shift left] & R^+X^- \arrow[l, harpoon, shift left] \arrow[r, harpoon, shift left] \arrow[d] & R^+/\!/X^- \arrow[l, harpoon, shift left] \arrow[r, harpoon, shift left] \arrow[d] & R^+ + X^- \arrow[l, harpoon, shift left] \arrow[d] \\
& \text{products} & \text{products} & \text{products}
\end{tikzcd} \tag{1}$$

The key problem of the technique is the concentration of substrates: while the NMR technique utilizes the concentration of 0.5 mol L^{-1} in general, the classic technique of determining the rates of solvolysis is applied to an order of magnitude dilute solutions. In order for the dynamic NMR technique to be conveniently applied to the investigation of the dissociation of α-chloro sulfides, its measurement with solutions of ordinary concentration is desirable. Thus we have studied the rates of ionization of α-chlorodibenzyl sulfide to settle the following two points: 1) are we observing the unimolecular dissociation process at the concentration of ca. 0.5 mol L^{-1}, and 2) can we obtain kinetic parameters of the ionic dissociation to seek information about the initial steps of S_N1 reactions? This letter reveals for the first time that useful information about the ionization process is provided by the technique.

α-Chlorodibenzyl sulfide was prepared as reported elsewhere.[2] The sampling was carried out under dry nitrogen in a closed system to avoid decomposition of the substrate. Dried chloroform-d (activated Zeolite) was added to make up appropriate concentrations. NMR spectra were obtained with a Hitachi R-20B spectrometer operating at 60 MHz when the solution was rather concentrated and with a JEOL FX-60 spectrometer equipped with the FT facilities and operating also at 60 MHz when the concentration was low. Temperature was calibrated by the chemical shifts of methanol and ethylene glycol if it was not read directly by a thermocouple. The chemical shift differences and the coupling constants of the AB protons should change, in principle, from temperature to temperature because we are observing them as weighted means of various conformers. In the event, however, they were found invariant throughout the temperature range studied. Therefore the same chemical shift difference and coupling constant which were obtained at low temperatures were used for calculation of the spectra. T_2 was obtained from the half-band width of the signal due to the methine proton. The simulation of the spectra was carried out using the modified Binsch program.$^{4)}$ The rate constants obtained by the simulations were put into the Eyring equation and the kinetic parameters were obtained. The results are shown in Table 1 together with some other pertinent data.

Table 1 AB Proton Exchange in α-Chlorodibenzyl Sulfide in $CDCl_3$: NMR Data at 60 MHz and Kinetic Parameters

Concentration/mol L^{-1}	0.267	0.195	0.116	0.0190
T_C/°C	37	32	34	36
$\Delta\delta_{AB}$/Hz	9.49	9.39	8.97	9.26
J_{AB}/Hz	13.80	13.20	13.20	13.66
$\Delta H^{\ddagger}$/kJ mol^{-1}	28.3 ± 4.1	28.5 ± 2.6	28.5 ± 0.5	28.4 ± 2.6
ΔS/J mol^{-1} K^{-1}	-124 ± 14	-121 ± 9	-124 ± 2	-126 ± 9
$\Delta G_C^{\ddagger}$/kJ mol^{-1} a)	64.9	64.0	64.4	64.6
$\Delta G_C^{\ddagger}$/kJ mol^{-1} b)	67	65	67	67
k_{273}/s^{-1} c)	6.95	9.89	6.95	5.58

a) Obtained by coalescence temperature method by putting the available data to $\Delta G_C^{\ddagger}(\text{cal mol}^{-1}) = 47.22\ T_C - 4.576\ T_C \log k_C/T_C$.

b) Obtained by using $\Delta H^{\ddagger}$, $\Delta S^{\ddagger}$ and T_C. c) Calculated from $\Delta G_{273}^{\ddagger}$ (see text).

If the process observed by dynamic NMR were not a first order reaction, k's obtained by the method would contain the concentration term of the substrate. Since the ions themselves are not observed in this technique and the concentration of the ions is minute, the concentration of the substrate can be taken as constant. Then the Eyring plot will produce straight lines with a same slope irrespective of the concentration. However, while the slope, which is $-\Delta H^{\ddagger}/R$, is constant irrespective of the order of the reaction, the apparent entropy of activation may contain a concentration dependent term if the reaction is of the second or higher order. This leads to the conclusion that, if the process obtained by the dynamic NMR technique is the second or high order reaction, the apparent entropy of activation should vary with the concentration. Data in Table 1 reveal that the entropy of activation is constant within the error limit throughout the concentration range studied, although the concentration varied an order of magnitude. Thus we conclude that we are observing a unimolecular process even at a concentration which is convenient for the routine NMR measurement.

Agreement among kinetic data obtained under various conditions is satisfactory.

Although the rate constants, which reflect the reliability most sensitivity, have not been obtained at a common temperature due to the convenience of the measurement, those which are calculated using $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ for 273 K are listed in Table 1. These k's are in conformity with the values obtained by the line shape analysis at near-by temperatures and the agreement is satisfactory. Another check of the kinetic parameters is provided: the free energies of activation at the coalescence temperature are in full agreement with those obtained by the coalescence temperature method.

Since we are dealing with the system in chloroform, we may neglect free ions. Then the mechanism of the proton exchange may be shown by eq. 2. Since

$$RX \rightleftharpoons R^{+}X^{-} \rightleftharpoons R^{+} /\!/ X^{-} \rightleftharpoons X^{-} /\!/ R^{+} \rightleftharpoons X^{-}R^{+} \qquad (2)$$

either R^{+} rotates or X^{-} moves from one side of the cation plane to another enantiotopic side for racemization (AB proton exchange), it will be reasonable to assume that the racemization takes place in the solvent separated ion pairs. Thus, by the dynamic NMR technique, we deal with the initial two steps of S_N1 reactions. Although the results show that large, negative entropies of activation are associated with the process, the phenomenon is often found with nonaqueous solutions.[5] The implication of the data awaits further study.

The main apparent limitation of the method is five fold. Firstly, the molecular species must have the rates of dissociation suitable for the measurement by the dynamic NMR technique, 10^{0}-10^{5} s^{-1}. This will necessarily mean that the molecule is rather labile. The sample must be handled with great care. The second is associated with the lability. A minute amount of the sample may be destroyed during the handling. In the case of α-chlorodibenzyl sulfide, its reaction with atmospheric moisture and/or trace water in solvents produces hydrogen chloride and α,α-bis(benzylthio)-toluene among others. The former acts as a catalyst for ionization and the latter interferes the line shape analysis. Therefore the data in Table 1 may include errors other than those obtained by the least squares method which are given. Thirdly, the rates of racemization do not necessarily mean the rates of ionization because, if the ion pairs collapse before the rotation of R^{+} or the movement of X^{-}, the collapse is not counted as racemization. It will be necessary to use a method such as isotope scrambling to see the ratio of rates of ionization and those of internal return occurring with retention of configuration.[6] Fourthly it may not be applicable to the cases in protic solvents and finally the concentration may not be too high because the high concentration means the change in solvent properties.

If we have the limitations arising from the above mentioned points in mind, the method seems to be widely applicable to the dissociation problem. In principle, conditions necessary for the observation of the exchange of AB protons are that a molecule possesses a diastereotopic methylene or gem-dimethyl group and its diastereotopicity is lost on dissociation. This principle is not, of course, limited to the case of organic halides which lose its chirality by ionization. A complex between a Lewis acid and an amine, which has potential diastereotopic protons, and that between a metal and an olefin, which has potential diastereotopic protons, are two of the examples which span wide variety of molecular species whose methylene or gem-dimethyl group loses diastereotopicity on dissociation. The method may be applied to all of these cases.

Another intriguing feature of this method is that it does not require to observe both covalent and ionic species, as are common in usual dynamic NMR techniques.[7] We do not have to observe products. Therefore the method is nondestructive. The measurement can be carried out in the absence of foreign materials. Although rates of ion-exchange of organic halides have been investigated in the presence of isotope-labeled salts,[2] this method requires a substrate only. Neither it requires optical resolution for the measurement of rates of racemization. The method enables to obtain data of dissociation in nonpolar solvents. This will play some key roles to connect results in solvolytic reactions, which are investigated in protic polar solvents, with those in the gas phase, which are obtained by ion cyclotron resonance or high pressure mass spectroscopy. Application of this technique to areas other than ionization of α-chlorodibenzyl sulfide is in progress.

We gratefully acknowledge the receipt of a Grant in Aid for Scientific Research from the Ministry of Education which supported this work.

References

1) K. Arai and M. Ōki, Bull. Chem. Soc. Jpn., 49, 553 (1976).
2) K. Arai and M. Ōki, Bull. Chem. Soc. Jpn., 50, 175 (1977).
3) D. J. Raber, J. M. Harris, and P. v. R. Schleyer, "Ions and Ion Pairs in Solvolysis Reactions," in "Ions and Ion Pairs in Organic Reactions" ed by M. Szwarc, John Wiley & Sons, New York (1974), Vol. 2, pp. 247-374.
4) G. Binsch, "Topics in Stereochem.," ed by E. L. Eliel and N. L. Allinger, Interscience, New York (1970), Vol. 3, p. 87.
5) A. A. Frost and R. G. Pearson, "Kinetics and Mechanisms," 2nd ed, John Wiley & Sons, New York (1962), pp. 132-142.
6) H. L. Goering and J. F. Levy, Tetrahedron Lett., 1961, 644; H. L. Goering and J. F. Levy, J. Am. Chem. Soc., 84, 3853 (1962).
7) M. Feigel, H. Kessler, and A. Walter, Chem. Ber., 111, 2947 (1978) and earlier papers.

(Received March 12, 1980)