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DYNAMIC NMR STUDY OF RATES OF IONIC DISSOCIATION OF 2-CHLOROACETOXY-4,4,5,5-TETRAMETHYL-1,3-DIOXOLANE[1)]

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Ionic dissociation of a carboxylate ester has been detected by the dynamic NMR technique for the first time. The title compound in toluene-d_8 exhibits $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ of 4.1 ± 0.9 kcal/mol and -40 ± 3 e. u., respectively.

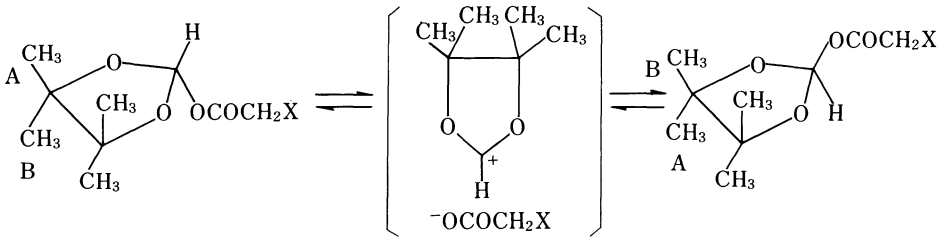
In previous papers from this laboratory,[2)] we have reported that dynamic NMR spectroscopy can be successfully applied to the study of ionic dissociation of organic halides and have demonstrated that we look at the initial stages of S_N1 reactions in general by this method. Since S_N1 reactions are found not only in halides but also in various esters such as sulfonates and carboxylates,[3)] the expansion of the scope of the method into the latter group of compounds will be of value.

A compound which is suitable for the dynamic NMR study must show its dynamic behavior, the rate of which is 10^0-10^3 s^{-1}, in addition to fulfillment of the conditions such as the presence of a pair of diastereotopic protons and the occurrence of the site exchange of the protons due to dissociation. The required rate of dissociation is much larger than that suitable for the classical kinetic work, 10^{-2}-10^{-7} s^{-1}, and hence little has been known about the structural features of a compound which gives rise to a rate constant in the suitable range for the dynamic NMR work.

In recent years, a number of dialkoxymethyl carboxylates and related compounds has been submitted to the study of rates of hydrolysis because of the interest in the tetrahedral intermediates which carry three oxygens on a carbon.[4-6)] Literature search revealed that there was a paper which reports that, whereas 2-acetoxy-4,4,5,5-tetramethyl-1,3-dioxolane (1a) gives two kinds of proton signals due to the four methyl groups in its ^1H NMR in $CDCl_3$, the corresponding 2-chloroacetoxy compound (1b) shows only an apparent singlet in the same solvent.[7)] Although the original authors did not discuss the origin of the difference in the NMR signals, the rationale for the observed phenomena may be given in the following way.

Since chloroacetic acid is a stronger acid than acetic acid[8)] and a strong

acid is generally considered to produce an anion of high leaving ability,[9] compound 1b will be better ionizable than compound 1a. Therefore, it may be assumed that the results are derived from the fact that topomerization shown below is taking place fast in compound 1b whereas it is slow in 1a on the NMR time scale under the conditions. Should the postulate be valid, lowering the temperature of a solution of 1b in $CDCl_3$ should cause decoalescence of the signal due to the four-methyl protons.



1a : X=H
1b : X=Cl

We carried out a preliminary dynamic NMR work on 1b in $CDCl_3$ and found that decoalescence of the signal due to the two kinds of methyls indeed took place at -15.1 °C. From the coalescence temperature and the chemical shift difference (4.95 Hz at 60 MHz) due to the two kinds of methyls, the free energy of activation for the topomerization is obtained as 13.8 kcal/mol at the temperature.

Chloroform-d is not the best solvent in this work since its melting point is -63.5 °C and anisotropic tumbling of molecular species is not assured at the low temperatures in the slow exchange limit. Then we shifted the solvent to toluene-d_8, which enables us to study the change in line shapes in a wide range of temperature and gives large chemical shift differences for the two methyl signals. The results are shown in Fig. 1 together with computed line shapes. The calculation of the spectra was carried out with the use of the modified Binsch program.[10] The agreement between the observed and the calculated spectra was excellent. The coalescence temperature was 43.9 °C, whereas $\Delta\nu_{AB}$ was 11.6 Hz. From the calculated spectra, the following kinetic parameters were obtained: $\Delta H^{\ddagger}$ 4.1 ± 0.9 kcal/mol, $\Delta S^{\ddagger}$ -40 ± 3 e. u., $\Delta G^{\ddagger}_{273}$ 14.9 kcal/mol. From the coalescence temperature and the chemical shift difference, the free energy of activation for topomerization at 43.9 °C was obtained as 14.5 kcal/mol, which agrees quite well with that calculated by the activation parameters obtained by the total line shape analysis.

Comparison of the data for 1b in $CDCl_3$ and that in toluene-d_8 reveals that the topomerization is slow in toluene-d_8 relative to that in $CDCl_3$. This is reasonable because $CDCl_3$ is more polar than toluene-d_8 and the higher polarity of the solvent should facilitate the ionic dissociation of the solute than the lower. A feature of the kinetic parameters for the dissociation of 1b is the large negative entropy of activation. The same trend has been observed in the dissociation of organic halides into ion-pairs,[2,11] and is attributed to the

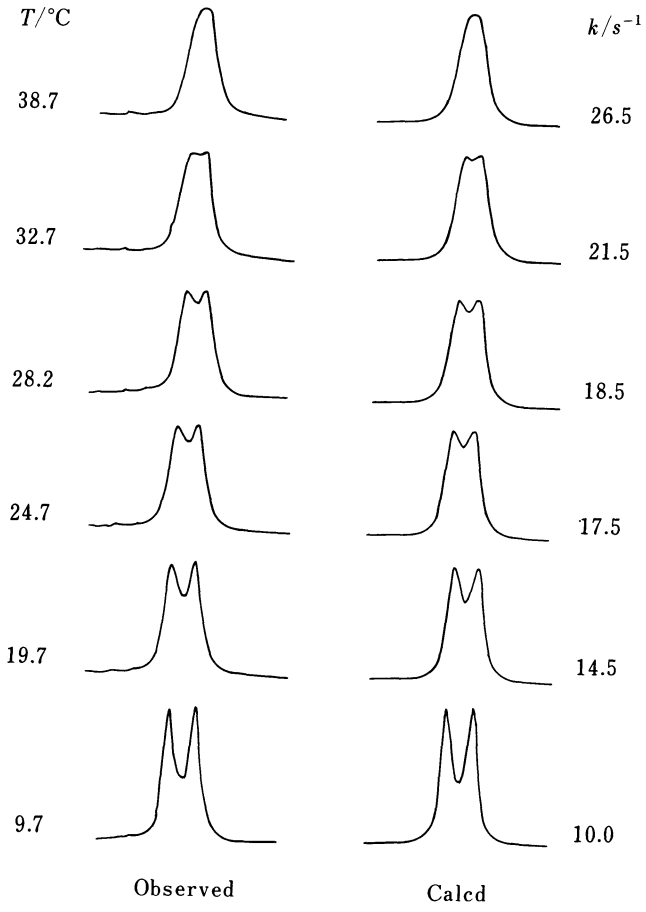


Fig. 1. The observed and calculated spectra for the methyl protons of 2-chloroacetoxy-4,4,5,5-tetramethyl-1,3-dioxolane (1b) in toluene-d_8.

reduction of freedom of motion of solvent molecules due to the development of the electric charges. It seems that the ionic dissociation of organic molecules is commonly accompanied by a large, negative entropy of activation.

Having successfully found the dynamic process in 1b by the dynamic NMR technique, we turned our attention to the dynamic behavior of 1a. Although a solution of 1a in $CDCl_3$ was heated to 56.0 °C, no change in line shapes in ^1H NMR spectra was detected. Thus the free energy of activation for the topomerization in this compound is in excess of 17.6 kcal/mol. Since the topomerization is accompanied by a large, negative entropy of activation, it may not be fair to compare the free energies of activation at different temperatures. An only clear conclusion is that the acetate (1a) dissociates more sluggishly than the chloroacetate (1b) in $CDCl_3$.

In a hope that a polar solvent should reduce the barrier to the topomerization, the solvent was shifted from $CDCl_3$ to a polar one. Acetonitrile-d_3 failed to show any change in line shapes of 1a even at 79.1 °C, whereas preliminary results with nitrobenzene solutions showed that the signals coalesced at 142 °C, the free energy of activation being 22.3 kcal/mol at the temperature. If one considers the solvent

effect on the ionic dissociation, the ionization behavior of the acetate (1a) may be concluded that it is tremendously different from that of the chloroacetate (2b). Further work is needed to shed light on this problem.

The compounds which are described in this paper are vulnerable to the attack of moisture and are thermally labile as well. As a consequence, the compounds tend to be contaminated by impurities during the measurements of the spectra. In both hydrolytic and thermolytic reactions, an acid is formed, which is derived from the acyloxyl group of the compound. The acid acts as a catalyst for the topomerization. Thus in one case, we have found that the coalescence temperature of compound 1b in toluene-d_8 was 6.2 °C, when the purity of the substrate was ca. 90%, as judged from the ^{1}H NMR spectra. Since decomposition of compound 1a at 142 °C is unavoidable, the true coalescence temperature of the signals due to this compound in nitrobenzene can well be higher than that mentioned above. Thus the barrier to topomerization shown here must be taken as a minimum value.

In conclusion, we were able to show that the dynamic NMR technique can be applied to the ionic dissociation of carboxylate esters which carry two oxygens on the carbon atom which is attached to the carboxy-oxygen. The entropy of activation is very large, negative. The results will open up another area which can be studied by the dynamic NMR method.

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References

1) Part VI: Dynamic NMR as a Nondestructive Method for the Determination of Rates of Dissociation. For Part V, see M. Ōki, M. Ohira, Y. Yoshioka, T. Morita, H. Kihara, and N. Nakamura, Bull. Chem. Soc. Jpn., submitted.
2) A. Shimizu, Y. Sakamaki, K. Azuma, H. Kihara, N. Nakamura, and M. Ōki, Bull. Chem. Soc. Jpn., 54, 2774 (1981) and papers cited therein.
3) A. Streitwieser, Jr., Chem. Rev., 56, 571 (1956).
4) B. Capon, A. K. Ghosh, and D. McL. A. Grieve, Acc. Chem. Res., 14, 306 (1981).
5) P. Deslongchamps, "Stereoelectronic Effects in Organic Chemistry," Pergamon Press, Oxford (1983), Chap. 3.
6) R. A. McClelland and L. J. Santry, Acc. Chem. Res., 16, 394 (1983).
7) B. Capon and D. McL. A. Grieve, J. Chem. Soc., Perkin Trans. 2, 1980, 300.
8) E. P. Serjeant and B. Dempsey, "Ionisation Constants of Organic Acids in Aqueous Solution," Pergamon Press, Oxford (1979).
9) C. K. Ingold, "Structure and Mechanisms in Organic Chemistry," Cornell University Press, Ithaca, New York (1953), pp. 338-345.
10) G. Binsch, Top. Stereochem., 3, 97 (1968).
11) C.-Y. Kim, Taehan Hwahakhoe Chi, 24, 44 (1980): Chem. Abstr., 94, 64735s (1981).

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