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DYNAMIC NMR STUDY ON RATES OF DISSOCIATION OF AN AMINE LIGAND IN AN ORGANOMETALLIC COMPOUND(1)

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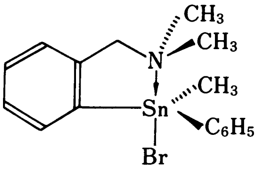
Rates of topomerization of 2-(N,N-diethylaminomethyl)phenyldimethyltin bromide were obtained at various temperatures by simulating the ^{1}H NMR spectra. The data afforded the following activation parameters: $\Delta H^{\ddagger}$ 23.4 ± 1.1 kcal/mol, $\Delta S^{\ddagger}$ 31.0 ± 3.8 e. u., $\Delta G^{\ddagger}_{273}$ 15.0 kcal/mol. Application of this technique to general problems of ligand dissociation in organometallic chemistry is discussed.

Rates of dissociation of an anilinium ion (as chloride) were measured with the use of dynamic NMR technique.(2) If one makes an operation of changing the proton in the anilinium ion to another Lewis acid, such as a metal cation, he notices that the rates of dissociation of a ligand in an organometallic compound should be measured by this technique. Since the ligand dissociation in organometallic compounds is the first step in ligand exchange, if the reaction proceeds in S_N1 fashion,(3) the technique can be valuable in organometallic chemistry as well as in coordination chemistry, as is the case in organic halides.(4)

Literature search revealed that there are a few cases in which the dynamic NMR technique has been applied to the estimation of the rates of dissociation in organometallic chemistry. In earlier days, the change in line shapes due to disappearance of coupling between the nuclei in the ligand and the central cation was used for the estimation of the rates.(5) More recently, van Koten and coworkers found that spin-exchange between diastereotopic methyl protons took place in a tin compound, (1) which has an amine ligand, by dynamic NMR method.(6) They observed slow isomerization of a diastereomer (2) to another at a low temperature to verify the observation by dynamic NMR spectra.(7) Corriu et al. reported that silicon analogs (3) of the tin compound exhibited a similar behavior,(8) although the activation energy for the silicon compounds was lower than that for the tin compound.



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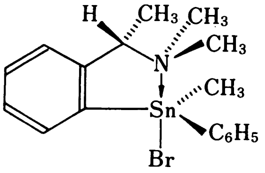
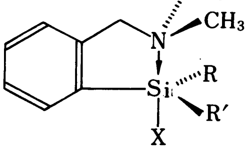
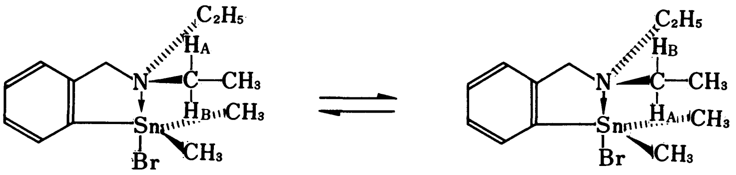


(2)



(3)

These latter investigators utilize the topomerization phenomenon which is possible because the metal (and carbon) center is chiral. The topomerization does not necessarily need a chiral center, however. If one can show that topomerization by dissociation of a ligand can be followed in organometallic compounds in general by designing a proper compound, that will mean that the technique opens up a new field of application of the technique, as predicted before.[1,9] According to the prediction, if a pair of diastereotopic protons is present and the compound topomerizes by dissociation, the NMR line shapes should change in the cases where the rates of dissociation are appropriate. We designed a compound which meets the conditions. Although 2-(diethylaminomethyl)phenyldimethyltin bromide (4) has no chiral center, the methylene protons on the ethyl groups which are attached to the nitrogen are diastereotopic and their diastereotopicity should be lost if the ligand dissoicates, rotates about the $C_{ph}-C_{N}$ bond (without this rotation, inversion of the nitrogen leads to an unfavorable conformation for ligation), and recombines after nitrogen inversion. This paper reports successful observation of the change in line shapes of compound 4 and the results of the investigation.



(4)

The compound in question was prepared by lithiation of N,N-diethylbenzylamine with butyllithium followed by the reaction of the lithium compound with dimethyltin dibromide, in essentially the same manner with the method reported for the preparation of analogous compounds.[10] It melted at 145 - 146°C. A sample of the compound was dissolved in chloroform-d to make up a solution of 121 mM. Dynamic NMR was recorded on a JEOL FX-400 spectrometer which operates at 400 MHz. Temperature was calibrated by the chemical shifts of methanol protons.

The following NMR parameters were obtained with the spectra at the slow exchange limit: $\Delta\delta_{AB} = 27.1$ Hz, $\Delta\delta_{AX} = 680$ Hz, $J_{AB} = -13.9$ Hz, $J_{AX} = J_{BX} = 7.2$ Hz. T_2 was obtained from the line width of benzylic proton signals and was found to be nearly constant at 0.16 s over the temperature range of observation. The observed and calculated spectra are shown in Fig. 1.[11] The agreement between them was excellent.

Putting the rate constants obtained by simulation into the Eyring equation yielded the following activation parameters: $\Delta H^{\ddagger}$ 23.4 ± 1.1 kcal/mol (1 cal = 4.18 J), $\Delta S^{\ddagger}$ 31.0 ± 3.8 e. u. (1 e. u. = 4.18 J K^{-1} mol^{-1}), $\Delta G^{\ddagger}_{273}$ 15.0 kcal/mol. The correlation factor was 0.9987.

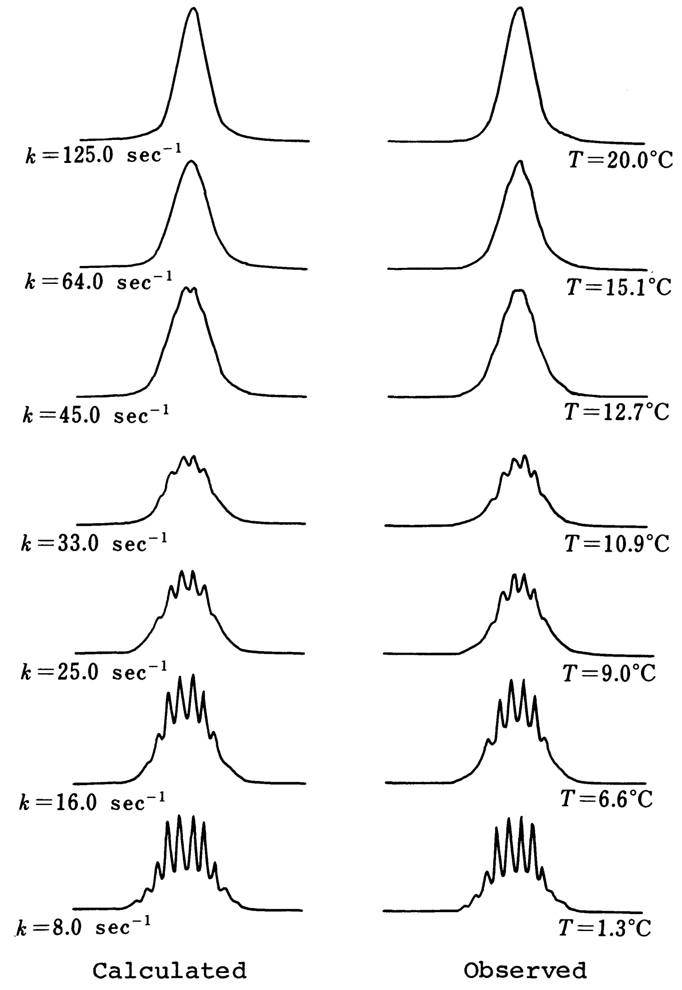


Fig. 1. Calculated and observed spectra of the AB part of ABX_3 in 4.

The feature of the activation parameters is that the entropy of activation is large, positive. This tendency was observed in the dissociation of the dibenzylanilinium ion.[2)] It seems that a large, positive entropy of activation is commonly observed when an ionic species, such as an ammonium ion or a Lewis acid-base complex, dissociates into covalent species. The rationale for the phenomenon must be the increase in freedom of motion of the solvent molecules, due to the decrease in the ionic character of the solute, in the transition state.

Although van Koten et al. did not report the free energy of activation for the dissociation of compound 1, it can be calculated from the available data:[6)] it is 15.4 kcal/mol at 30°C. It seems that compound 4 has a little smaller free energy of activation than compound 1. Dependence of the free energy of activation for dissociation on substituents is still to be explored.

The method is now applied to the dissociation problem of an amine ligand in an organometallic compound and is proved to be applicable to the field of organometallic chemistry. Further application of the method to other areas, such as dissociation of a sulfur ligand in organometallic compounds as well as the extension of the problems of amine ligands, is anticipated.

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11) As can be seen from the difference ($\Delta\delta_{AB}$) in chemical shifts of A and B protons at 400 MHz, the $\Delta\delta_{AB}$ was too small to observe the AB part of an ABX_3 system at either a 60 or a 90 MHz spectrometer. If this is a general trend, the small $\Delta\delta_{AB}$ can be a drawback of the method when applied to systems like this, because spectrometers equipped with a very high magnetic field are not yet available for the routine use.

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