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Applications of dynamic NMR spectroscopy to the dissociation of chemical bonds in organic, organometallic, and coordination compounds

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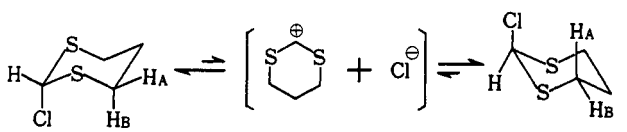
Abstract Dynamic NMR spectroscopy was found to be useful in studying the rates of bond dissociation, if the molecule in question meets certain conditions. The examples are dissociation of organic halides, ammonium salts, and coordination compounds involving amine, thioether, or olefin ligands. The entropy of activation is characteristic depending upon the nature of the transition state: it is large positive if ionic character is reduced, and is large negative if ionic character is increased. The kinetic data obtained by various probes are critically examined to show that those examined in this study give satisfactory agreement.

INTRODUCTION

During the course of study on the anomeric effect in the thiane series, we have come across an interesting line shape change in ^{1}H NMR spectra of 2-chloro-1,3-dithiane (1). Namely, the spetra obtained as solutions in nonpolar solvents showed broad signals for the methylene protons, whereas those in polar solvents did sharp signals which indicated that the two protons were equivalent. The spectrum of carbon disulfide solutions showed, when temperature was lowered, distinct AB patterns for the methylene protons to indicate that a kind of dynamic process was taking place in the compound (ref. 1). The tendency of the spectra described above suggest that the process must be ionic. Thus we concluded that the process was the ionization of the compound followed by internal return of the ion pairs, when the anion combined from the rear of the site where it was originally bound (eq. 1). The results suggest that the topomerization of an organic compound by ionic dissociation of a bond can be followed by the dynamic NMR technique.



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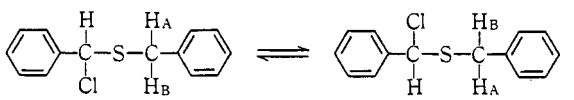
The method was extended and it was found that the racemization of α-chlorodibenzyl sulfide (2) could be followed by this technique (ref. 2) because racemization of the compound means the site exchange of the diastereotopic protons (eq. 2). The results suggest wide applicability of the method in



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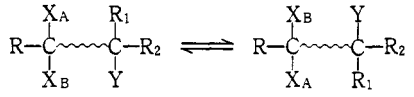
following the bond dissoication. If a molecule meets conditions described below, the bond disociation should be observed as the line shape change in NMR spectroscopy. The conditions are 1) the compound in question should pos-

sess a diastereotopic pair of NMR active nuclei of which sites are exchanged on dissociation of the bond, and 2) the rates of the bond dissociation should be suitable for the NMR investigation. The process can be expressed in the general form by eq. 3.



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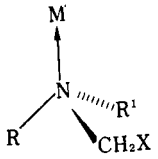
If one considers the conditions for the observation of the line shape changes in the NMR spectroscopy, it becomes clear that this method is applicable not only to dissociation of organic halides but to other types of compounds. If ligation of appropriately substituted amines takes place to a Leiws acid (3) and its rates of dissociation is in the range of NMR-detectable time scale, then the site exchange of diastereotopic protons should be observable by this technique. The same is true for the case of ligation of thioethers (4) and ethers (5), though the oxygen inversion in the latter may be too fast on the NMR time scale, and that of the ligated form of olefins (6). This paper is to describe examples of such applications.



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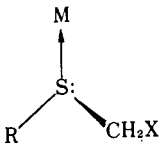

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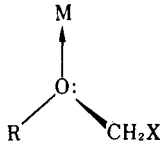

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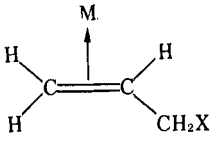

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APPLICATION TO ORGANIC CHEMISTRY

One should notice that the ionic dissociation followed by racemization is observed by the site exchange of the diastereotopic protons in compound 2 (eq. 2). That means one is following the ionic dissociation of an organic halide in nonpolar organic solvents. According to the Winstein theory (ref. 3), an organic halide ionizes first to a contact ion pair which then changes to a solvent-separated ion pair and finally to free ions (eq. 4) in solvolytic reactions. Since we use rather nonpolar solvents, it may be assumed that free ions in these solvents can be neglected. Further it may be reasonably assumed that the racemization does not occur in contact ion pairs. Then one can write the equation of the transformation we observe as shown by eq. 5. Therefore, the investigation of ionization of organic halides in nonpolar aprotic solvents should cast light in understanding the early stages of the S_N1 reactions in general.

$$R{-}X \rightleftharpoons R^+X^- \rightleftharpoons R^+/\!/X^- \rightleftharpoons R^+ + X^- \qquad (4)$$

$$R{-}X \rightleftharpoons R^+X^- \rightleftharpoons R^+/\!/X^- \rightleftharpoons X^-/\!/R^+ \rightleftharpoons X^-R^+ \rightleftharpoons X{-}R \qquad (5)$$

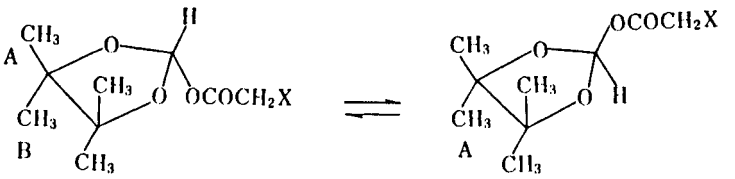
There is one thing which should be confirmed before claiming the important contribution of this technique in organic chemistry, however. That is the concentration of the solutions used: while conentration of the solution which is used in solvolytic works is usually of the order of 10^{-3} mol L^{-1}, that for the NMR work is 10^{-1} for the classical CW type NMR spectrometer and 10^{-2} for the modern FT spectrometer. Clearly confirmation of the negligible effects of concentration on the rates of dissociation is needed. This was accomplished by carrying out the study of the effects of concentrations on the rates of racemization of compound 2 (ref. 4). The results shown in Table 1 clearly indicate that the rates are not affected by the concentration of the substrate. This is because, though the total concentration of the substrate

TABLE 1. Kinetic Data for the Dissociation of Compound 2 at Various Concentrations

Concentration/mol L^{-1}	0.267	0.195	0.116	0.0190
$\Delta H^{\ddagger}$/kcal mol^{-1}	6.8±1.0	6.8±0.6	6.8±0.1	6.8±0.6
$\Delta S^{\ddagger}$/ e. u.	-29.8±3.2	-28.9±2.0	-29.7±0.3	-30.1±2.0
T_c/°C	37	32	34	36
k_c/s^{-1}	78.0	74.8	74.5	77.1

is high, the concentration of the ionized species is so low that they can not be detected by the present technique.

The method was also applied to the dissociation of carboxylates (ref. 5). For example, compound 7 has a necessary diastereotopic pair of methyl groups. When the compound ionizes and the carboxylate anion comes back from the rear of the site where the carboxylate group was originally located, the topomerization completes (eq. 6). The rates of ionization afforded the activation parameters of this process as follows: $\Delta H^{\ddagger}$ 4.1±0.9 kcal mol^{-1}, $\Delta S^{\ddagger}$ -40±3 e. u.



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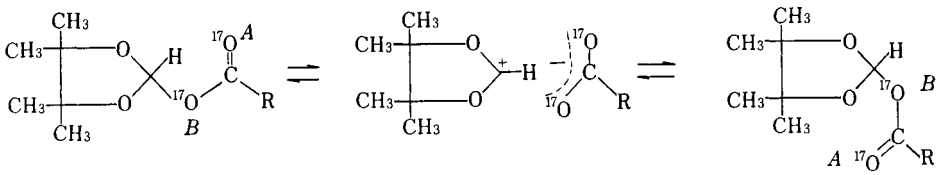
The dissociation of the type of compound 7 was also followed by ^{17}O dynamic NMR spectroscopy (ref. 6). If one uses ^{17}O isotopes for the oxygen atoms in the carboxyl group, it is possible to see the exchange between carbonyl oxygen and ether oxygen (eq. 7). The rates of dissociation thus obtained were in good agreement with those obtained by the ^{1}H NMR spectroscopy.



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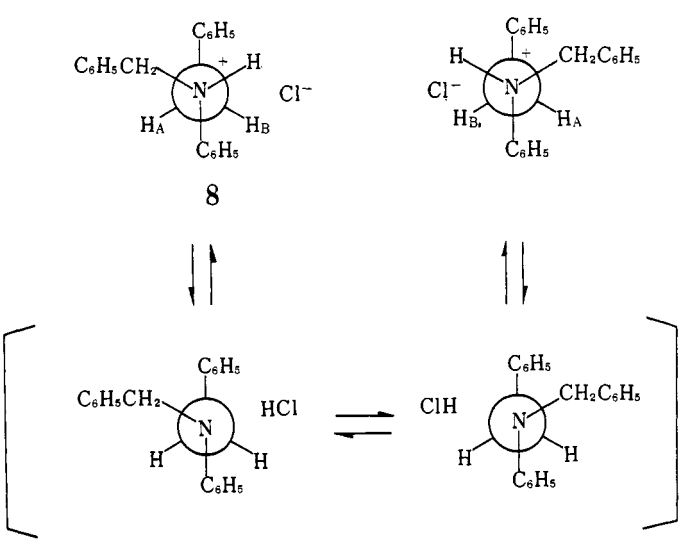
The feature of the kinetic parameters for the ionic dissociation of organic compounds is the very large, negative entropy of activation. This tendency is always observed when a covalent compound dissociates to form ion pairs. It is reasonable to assume that the freedom of motion of the solvent molecules is restricted in the transition state due to the appearance of the electric charge to make the entropy of activation negative.

BASICITIES AND ACIDITIES IN ORGANIC SOLVENTS

An example of amines that meet the conditions described above is N,N-dibenzylaniline. When its hydrochloride (8) is formed, there is a necessary pair of diastereotopic protons. As shown in the following scheme (eq. 8), if the pro-



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(8)

ton which has been originally attached to the amino-nitrogen dissociates and nitrogen inverts before the proton reattached to the nitrogen atom, then the sites of the benzylic protons are exchanged. Therefore, by this method we should be able to observe dissociation of the N-H bond in the ammonium ions derived from tertiary amines. Indeed, we were able to observe the change in line shapes of the NMR spectra of the benzylic methylene protons of N,N-dibenzylaniline hydrochloride (ref. 7).

This process is simple in the sense of organic reactions but is complicated in the sense of NMR, because the line shapes due to the benzylic methylene protons are affected by both the site exchange and the detachment of the proton from the ammonium nitrogen. Since this pair of dynamic processes is not accommodated by available programs of line shape analysis, an appropriate assumption was made (see later section for the validation of this assumption).

Various factors that might affect the rates of proton detachment from the amino-nitrogen have been examined. The concentration of the substrate has negligible effect on the rates as well as the presence of trace water in the solvent. Solvent properties have an effect, though small, on the rates of dissociation of the ammonium ion. The results show that the method is now extended to the detachment of proton from an ammonium moiety. If the rate is small, the basicity of amine must be strong. We thus obtain "kinetic" basicities of amines by this method. Since the method affords data in non-polar aprotic solvents, the data will be more useful in designing organic reactions in such solvents than those obtained as aqueous solutions.

We were first interested in the effects of substituents on the basicities of anilines in aprotic solvents, because they were known both in water (ref. 8) and in the gas phase (ref. 9). The results (ref. 7) are compiled in Table 2 and the relations of the kinetic basicities, as given by the free energies of activation, of substituted N,N-dibenzylanilines with basicities of

TABLE 2. Substituent Effects on the Kinetic Parameters for Proton-Detachment from the Ammonium-Nitrogen in p-Substituted N,N-Dibenzylammonium Chloride in Chloroform-d

Substituent	CH_3O	CH_3	H	Cl
$\Delta H^{\ddagger}$/kcal mol^{-1}	19.5±0.9	19.0±0.4	18.5±0.7	18.6±1.8
$\Delta S^{\ddagger}$/e. u.	16.6±3.1	17.9±1.4	19.7±2.6	22.8±7.5
$k_{298}/\times 10^2$ s^{-1}	1.35	6.33	14.8	132

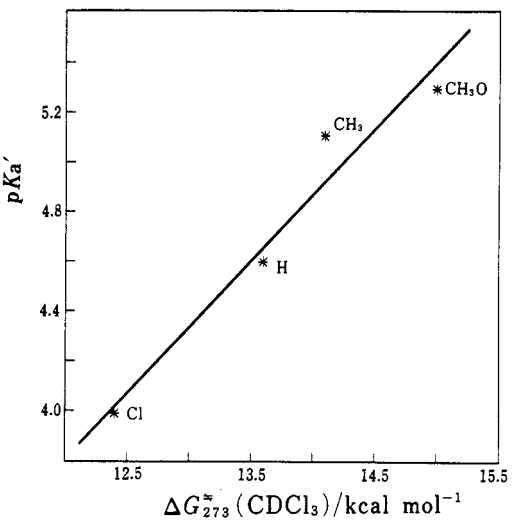


Fig. 1. Correlation between pKa' values of p-substituted N,N-dimethylanilines and $\Delta G^{\ddagger}$ values for the proton exchange in p-substituted N,N-dibenzylanilinium chlorides

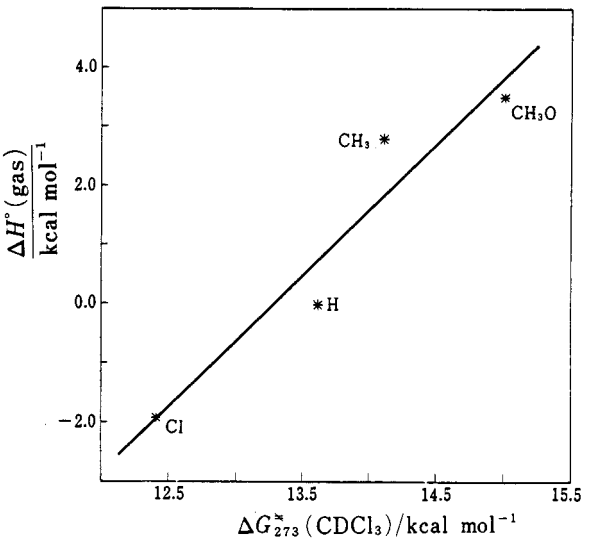
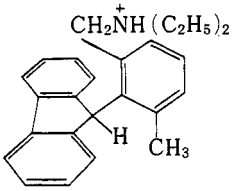


Fig. 2. Correlation between enthalpies for the proton exchange between aniline and p-substituted anilinium ions in the gas phase and $\Delta G^{\ddagger}$ values for the proton exchange in p-substituted N,N-dibenzylanilinium chlorides

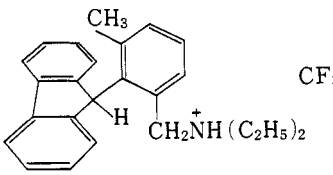
substituted N,N-dimethylanilines in water and proton affinities of substituted anilines in the gas phase shown in Figs. 1 and 2, respectively.

As expected, the electron-donating groups enhance the barriers to proton exchange and the electron-withdrawing substituents facilitate the process. Interestingly, the basicity of the substituted anilines can be linearly correlated with those in the gas phase and in water. This correlation may not hold always, but at least the linear relation holds among the gas phase, aqueous solution, and solutions in nonpolar solvents, when we compare the basicity change by substitution.

One of the applications of this technique to the determination of the basicity of amines in aprotic solvents is shown by the case of rotational isomers of 9-(2-diethylaminomethyl-6-methylphenyl)fluorene trifluoroacetate (**9**) (ref. 10). In chloroform, the ap isomer is known to be more basic than the sp by ca. 1.5 pKa units due to the presence of the NH...π interaction in the ap. Dynamic NMR study of the trifluoroacetates gave the following free energy of activation for the proton transfer between the ammonium ion and the trifluoroacetate anion at 298 K: sp 14.1 kcal mol^{-1}, ap 16.4 kcal mol^{-1}.



CF_3COO^-



CF_3COO^-

ap-**9** *sp*-**9**

The basicity of amines can be determined if one fixes the anion, the chloride anion for the case of N,N-dibenzylaniline hydrochlorides and the trifluoroacetate anion in the case of compound **9**. This is because the proton acceptor in the exchange reaction we are interested in is the anion which is present as an ion pair. This statement is verified by the fact that the rates of proton detachment from the anilinium ion were not affected by water which was present in the system in a minor amount.

This consideration leads to an idea that, if we fix the anilinium ion and change the anion which should accept proton in the exchange reaction, then we should get information about the proton affinity of anions or acidity of acids in organic solvents. Accordingly, the proton exchange process in N,N-dibenzylanilinium salts that contain anions derived from strong acids was investigated by this technique. The results are shown in Table 3 (ref. 11).

TABLE 3. Kinetic Parameters for the Proton Exchange between N,N-Dibenzylanilinium Cation and Anions Derived from Strong Acids in $CDCl_3$

Anion	Cl^-	Br^-	$CH_3SO_3^-$	p-$CH_3C_6H_4SO_3^-$
$\Delta H^{\ddagger}$/kcal mol^{-1}	18.5±0.7	21.1±1.1	14.1±0.3	11.6±0.5
$\Delta S^{\ddagger}$/e. u.	18.0±2.6	15.5±3.3	-0.2±1.2	-8.9±1.7
$\Delta G^{\ddagger}_{273}$/kcal mol^{-1}	13.6	16.9	14.2	14.0

Clearly anions derived from stronger acids in water are more reluctant in accepting proton in the dynamic process. Although the method has some limitations such as the fact that trace water in the system more easily accepts proton than anions derived from super acids, the method will be useful in obtaining information of acidity of strong acids in organic solvents.

The feature of the activation parameters is large, positive entropy of activation except for two cases which involve sulfonate anions. We attribute this phenomenon to the increase of freedom of motion of solvent molecules in the transition state of the proton exchange because the ionic character in the ground state is reduced in the transition state. The small entropy of activation for the sulfonates is attributed to the decrease in the freedom of motion of the anion in the transition state due to the fact that the sulfonates possess three equivalent oxygen atoms which share anionic charge, though the freedom of solvent molecules will increase in the transition state.

If we switch the proton to carbocation in forming the Lewis acid-amine

complexes, then it is the case of quaternary ammonium salts. The quaternary ammonium salts must be fairly unstabale on the laboratory time scale to meet the dynamic NMR conditions and thus the carbocation must be fairly stable. We found that 1-(4,4,5,5-tetramethyl-1,3-dithiolan-2-yl)pyridinium perchlorates (10) were suitable for our purpose (ref. 12). In this case, the four methyl groups serve as probes in the spectroscopy (eq. 9). The results are shown in Table 4. Clearly, the more basic the pyridine derivative, the slower the bond dissociation, indicating that the bond energy is governed by the basicity of the amine.

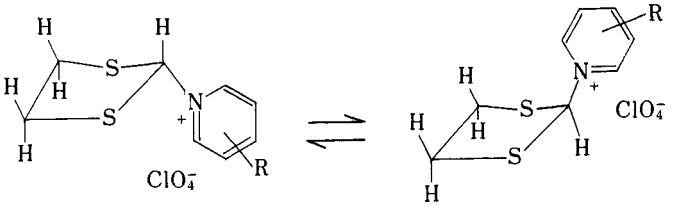


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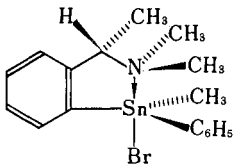
TABLE 4. Kinetic Parameters for Dissociation of the C-N Bond in Compound 10 and pKa Values of the Corresponding Pyridines

Substituent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/e. u.	k_{298}/s^{-1}	pKa
4-CH_3O	19.0±0.8	1.2±2.4	0.142	6.58
4-CH_3	17.8±0.8	0.9±2.3	0.804	6.03
H	15.0±0.7	-5.6±1.7	3.79	5.21
3-CH_3	15.9±0.5	-0.3±1.6	11.2	4.78

APPLICATION TO COORDINATION CHEMISTRY

If an amine, which possesses a diastereotopic pair of protons when the inversion is slow, is ligated to a metal atom or cation, the coordination compound should exhibit the dynamic process as well, provided that the rates of the dissociation of the metal-to-nitrogen bond are appropriate for the NMR spectroscopy. The cases of tin-amine complexes (11) (ref. 13) and silicon-amine complexes (12) (ref. 14) fall into this category. In these cases the metals comprise center of chirality and methyls attached to the nitrogen are diastereotopic.



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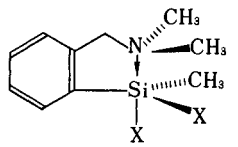

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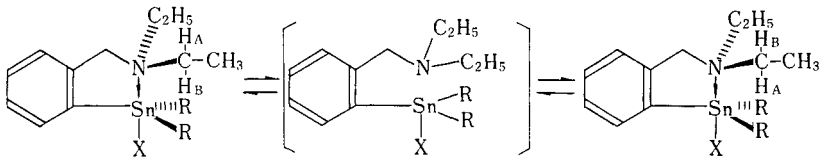
Our method allows the determination of rates of dissociation without having center of chirality in the central metal: if for example an amine, which carries two ethyl groups and another which is different from ethyl, ligates to a metal the methylene protons of the ethyl group will be diastereotopic and the dissociation process should be followed by this technique (eq. 10).



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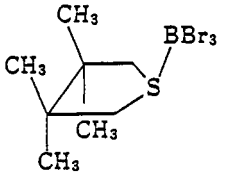
Indeed, the coordinated form of o-(diethylaminomethyl)dialkylstannyl halides (13) showed the dynamic process (ref. 15). With the use of this principle, the effect of halogen atoms on the rates of dissociation of N-Sn bond was

examined. As are shown in Table 5, the electronegative halogen atom tends to enhance the barrier to dissociation. This is consistent with the idea that a strong acid forms a more stable amine-acid complexes than a weak acid, if the amine is fixed. Again, the entropy of activation is large, positive.

TABLE 5. Activation Parameters for the Sn-N Bond Dissociation in Compound 13 (R=CH_3) in Chloroform-d

X	F	Cl	Br	I
$\Delta H^{\ddagger}$/kcal mol^{-1}	21.0±0.8	21.1±0.8	23.4±0.9	22.8±0.3
$\Delta S^{\ddagger}$/e. u.	20.5±2.5	22.3±2.7	30.9±1.1	30.5±1.1
$\Delta G^{\ddagger}_{283}$/kcal mol^{-1}	15.2	14.8	14.7	14.1

Using the same principle, we were able to determine the rates of dissociation of thioether complexes of some Lewis acids (ref. 16). The coordination compound between tribromoborane and 3,3,4,4-tetramethylthiolane (14) possesses a necessary pair of diastereotopic methyls and its rates of dissociation were suitable for the dynamic spectrosocopy. The activation parameters for this process in chloroform-d were obtained as follows: $\Delta H^{\ddagger}$ 21.5±0.4 kcal mol^{-1}, $\Delta S^{\ddagger}$ 21.0±1.4 e. u.. Similarly, an intramolecular complex (15) between thioether and tin gave $\Delta H^{\ddagger}$ 12.7 kcal mol^{-1} and $\Delta S^{\ddagger}$ 13.3±1.0 e. u.. The positive entropy of activation is the feature of the process.



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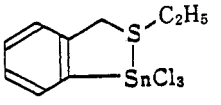

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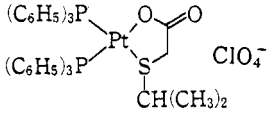
According to literatures (ref. 17 and 18), thioether-platinum(II) complexes show sulfur inversion much more easily than sulfonium ions (ref. 19). The mechanism of the inversion in the platinum complexes have been assumed to be simple sulfur inversion. However, the ease of the sulfur inversion in the platinum complexes might suggest that the thioether dissociates prior to inversion. Although this possibility was excluded by observing the persistent spin-couplings between the platinum and the proton in the ligand in the literature, apparently broad signals which were attributed to the coupling allured us to reinvestigate the case. The entropy of activation will be the clue in diagnosing the mechanism of sulfur-inversion. Accordingly, sulfur inversion in thioether complexes (16 and 17) of platinum(II) was investigated (ref. 20). The activation parameters were as follows: $\Delta H^{\ddagger}$ 18.0±0.4 kcal mol^{-1} and $\Delta S^{\ddagger}$ 4.0±1.4 e. u. for compound 16, and $\Delta H^{\ddagger}$ 17.2 kcal mol^{-1} and $\Delta S^{\ddagger}$ 4.7±1.4 e. u. for compound 17 in chloroform-d. The entropy of activation suggests that the sulfur inversion in the thioether-platinum complexes proceeds without bond breaking.



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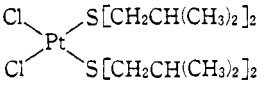

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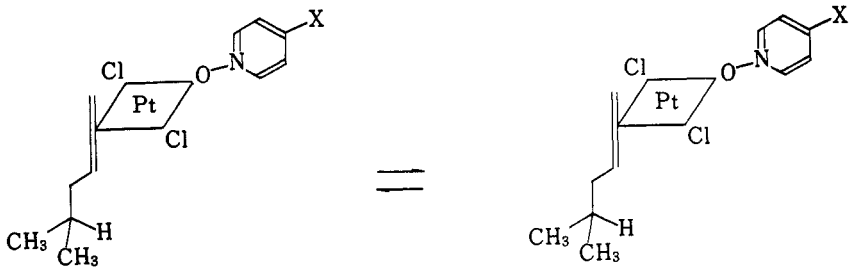
APPLICATION TO ORGANOMETALLIC CHEMISTRY

Olefins are known to form enantiomers (ref. 21) if they are properly substituted and ligate to a metal center. One of the examples of this sort is found in platinum-olefin complexes. In order to facilitate the bond dissociation between the olefin and the platinum center, it was necessary to place a very weak base trans to the olefin in platinum-olefin complexes. Thus trans-dichloro(4-methyl-1-pentene)(4-substituted pyridine 1-oxide)platinum(II) (18) were made. These complexes possess diastereotopic probes, the isopropyl group in the olefin. If the platinum-to-olefin bond is broken and the platinum recoordinate to the olefin from the rear, then the racemization takes place (eq. 11) and the diastereotopic protons exchange their sites.



18 (11)

The results are shown in Table 6, which clearly indicate that the trans effect is important: the weaker the base, the more facile is the dissociation of the platinum-olefin bond.

TABLE 6. Activation Parameters for the Dissociation of the Olefin in Compound 18 in Bromoform-d

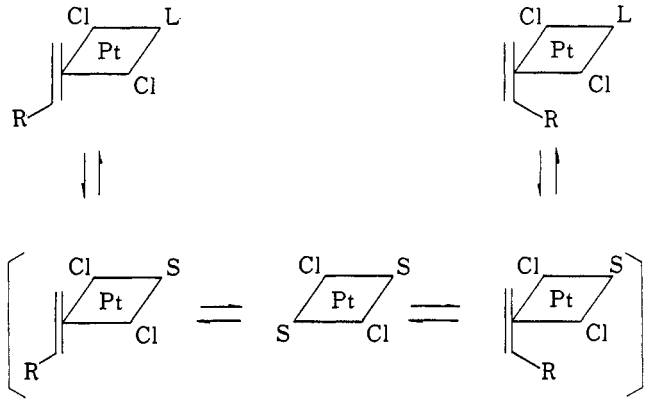
Substituent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/ e. u.	$\Delta G^{\ddagger}_{353}$/kcal mol^{-1}
CH_3			20.4
H			19.6
Cl	18.1±0.6	-2.8±1.9	19.1
CH_3OCO	17.6±0.5	-2.7±1.3	18.5
NO_2	13.8±0.7	-9.0±2.1	17.0

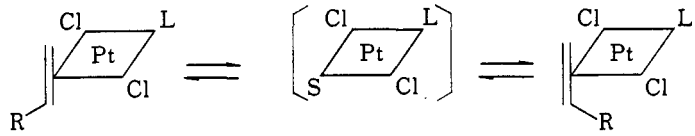
Solvent assistance in the dissociation of ligands in platinum complexes is very common. Unfortunately, the complexes decomposed very easily in polar solvents, majority of which possess high affinity to platinum. However, it was possible to observe the solvent effect on the dissociation by comparing the rates in aromatic hydrocarbons and in halogenated hydrocarbons. The results are shown in Table 7.

TABLE 7. Solvent Effects on the Kinetic Parameters for the Dissociation of the Olefin Ligand in Compound 18

Solvent	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/e. u.	$\Delta G^{\ddagger}_{323}$/kcal mol^{-1}
$CDBr_3$	17.6±0.5	-2.7±1.3	18.4
$Cl_2CDCDCl_2$	19.0±0.9	2.7±2.7	18.2
C_6D_6	16.3±0.5	-3.8±1.4	17.5
$C_6D_5CD_3$	16.7±0.3	-3.1±1.7	17.7

Seeing the distinct solvent effects on the dissociation of the platinum complexes, we can write two mechanisms of racemization (eq. 12 and 13). Equation 12 is suggesting that the solvent molecule is substituting the pyridine oxide ligand prior to the dissociation of the olefin ligand. This is possible because in some olefin-platinum complexes the dissociation of basic ligand(s) is observed (ref. 22). Equation 13 suggests that the solvent molecule replaces the olefin simply during the course of racemization. How-

 (12)



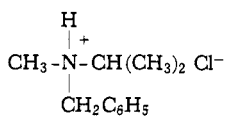
(13)

ever, the observation of the substituent effects on the rates of dissociation (Table 6) strongly support that the case of eq. 13 is more likely than eq. 12.

RELIABILITY OF THE DATA OBTAINED BY DYNAMIC NMR SPECTROSCOPY

Although the reliability of the data obtained by line shape analysis of the NMR spectra was questioned in earlier days (ref. 23), it is commonly accepted today that the data obtained by total line shape analysis is acceptable, esecially the line shapes used for the analysis are complicated (ref. 24 and 25). However, the reliability of the data are dependent on not only the complexity of the line shapes but the nature of the site exchange process. Therefore, we carried out investigations on the reliability of the data obtained by dynamic NMR spectra of various sources.

N-Isopropyl-N-methylbenzylamine hydrochloride (**19**) possesses three kinds of probes in one molecule. The isopropyl-methyl protons will have negligible coupling with the ammonium proton, thus providing a simple site exchange in the dyanmic process. The methyl protons will show coupling with the ammonium proton if the exchange is slow, whereas they will lose the coupling if the rates of dissociation becomes fast. The benzylic methylene protons are the probes which simultaneously lose coupling with the ammonium proton and exchange sites on topomerization. N,N-Diethylmethylamine hydrochloride (**20**) is another example which have multiple probes, the methyl-protons which lose coupling and the methylene-protons which exchange their sites as well as losing coupling on topomerization. The activation parameters for the topomerization obtained by three probes of compound **19** are summarized in Table 8. As are seen in the table, the agreement is satisfactory among the probes. Observation of the line shapes due to benzylic protons with decoupling with the ammonium proton followed by simulation of the spectra also afforded satisfactory results and the quality of the data were even better than those obtained by direct simulation without decoupling. Compound **20** gave the similar results (ref. 26).



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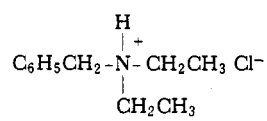

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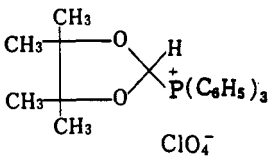
TABLE 8. Activation Parameters for the Rate Processes Observed in Compound 19 in $Cl_2CDCDCl_2$

Probe	$\Delta H^{\ddagger}$/kcal mol^{-1}	$\Delta S^{\ddagger}$/ e. u.	$\Delta G^{\ddagger}_{363}$/kal mol^{-1}
$(C\underline{H}_3)_2CH$	35.7±0.8	46.1±2.1	19.0
$C\underline{H}_3N$	35.2±2.2	44.4±6.1	19.0
$C_6H_5C\underline{H}_2$	33.5±5.4	40.1±14.7	18.9
$C_6H_5C\underline{H}_2$*	34.6±2.0	43.0±5.4	19.0

*Data obtained with decoupling

Our choice, if various probes are available, is again complex signals which provide multitude of points which are used for matching the observed and the calculated spectra. Thus the isopropyl-methyl proton signals are the most preferred and the loss of coupling of the methyl signals least preferred.

Similar investigation for comparison of the data were carried out with the use of loss of coupling between proton and phosphorus and site exchange of the diastereotopic pairs of methyl groups in triphenyl-4,4,5,5-tetramethyl-1,3-dioxolan-2-ylphosphonium perchlorate (**21**). Apparently both probes give satisfactory agreement.



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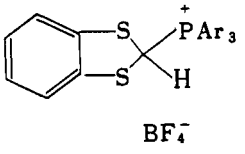

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Finally, we compared the kinetic data obtained by loss of coupling between the proton and the phosphorus with those obtained by the exchange between the free and the coordinated phosphines with the use of triarylbenzo-1,3-dithiol-2-ylphosphonium tetrafluoroborate (22), where aryl is preferably p-chlorophenyl. This comparison is interesting because there are wealth of literatures which report the dynamics in the presence of excess of ligand (ref. 28). The agreement between the two probes were good. The small excess of ligands does not seem to harm the kinetic data obtained by this technique.

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