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Dynamic NMR as a Nondestructive Method for Determination of Rates of Dissociation. XV. Dissociation of Thioether and Ether Ligands in Tin(IV) and Boron Complexes and Significance of Entropy of Activation Therein[1]

Michinori Ōki*,† and Yasuhisa Yamada
Department of Chemistry, Faculty of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113
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The rates of dissociation of thioether ligands which are imbedded in organotin(IV) compounds, such as trichloro[*o*-(ethylthiomethyl)phenyl]stannane, were determined by the dynamic NMR method. The dynamic processes of the corresponding ether ligands was too fast to detect as the change in line shapes in ^{1}H NMR spectra. All the boron compounds examined, which possessed similar structures to the stannane and were of the boronate type, failed to show dissociation of a thioether or ether ligand due to their large rates of dissociation. The rates of dissociation of a thioether-tribromoboron complex were determined by the same technique. The feature of the activation parameters was that the compounds examined exhibited fairly large positive entropy of activation in accordance with other results that involve dissociation of ionic species into covalent species.

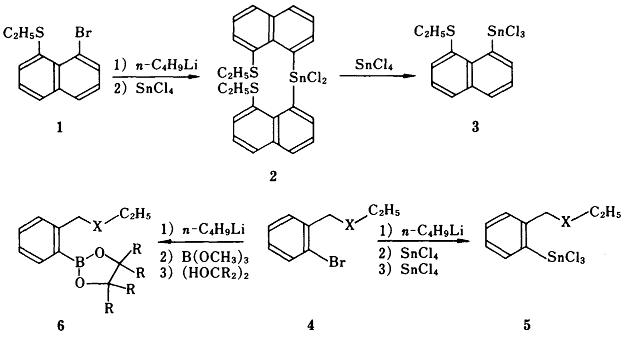
The mechanism of sulfur inversion in sulfur-ligands in platinum(II) complexes attracted interests of some investigators. It seemed generally accepted that the inversion took place without breaking the Pt-S bond.[2] However, it was shown recently that sulfur-ligands in platinum complexes could dissociate under certain circumstances.[3] We felt therefore that it would be worthwhile to provide a methodology of diagnosing the mechanism of sulfur-inversion in coordination compounds.

Our experience shows that, if dissociation takes place from an ionic ground state via more or less covalent transition state, the entropy of activation should be large positive, and, if the ground state is covalent and the transition state is ionic, the entropy of activation is large negative.[4] Since thioether-platinum(II) complexes can be considered to possess an ionic ground state and the transition state for dissociation of the ligand is of covalent character, it is expected that, if the dissociation is the rate determining step in the sulfur-inversion, the entropy of activation is large positive whereas it will be near-zero, if a simple sulfur-inversion takes place.

Indeed, there is a literature that reports the entropy of activation is very small in sulfur-inversion in a platinum(II)-thioether complex.[5] This result might be taken as evidence for the sulfur-inversion without breaking of the Pt-S bond, but there are several points to be considered before concluding in that way. Firstly, the examples that show nearly-zero entropy of activation in the sulfur-inversion in platinum-sulfur complexes are too few in literature. Secondly, the compound examined in the literature contained two thioether ligands that might affect observation of the sulfur-inversion processes. Thirdly, for not only the cases of platinum complexes, examples of reported entropy of activation are too few. Dissociation of boron-ether[6] or boron-ketone[7] complexes as investigated by the dynamic NMR technique has been reported, but the free energy of activation was obtained at only one point of temperature. There is also a literature that reports sulfur-inversion in a thioether-trichloroboron complex,[8] but the results are again obtained at one temperature.

We felt on the above backgrounds that at least some examples should be provided before concluding the relationship between the entropy of activation and the mechanism of sulfur (or oxygen) inversion that is simple and causes no ambiguity about the conclusion. Thus we have examined a case that is purely sulfur-inversion that gives near-zero entropy of activation both by classical[9] and dynamic NMR[10] methods. In this paper we wish to report that the entropy of activation for the sulfur-inversion of which mechanism is supposed to be dissociative indeed is large, positive.

The compounds of which rates of sulfur-inversion were examined by the dynamic NMR technique were prepared in the following way. 1-Bromo-8-ethylthionaphthalene (**1**) which was prepared by a standard diazotization and substitution reaction of 8-bromo-1-naphthalenamine was lithiated with butyllithium and was then treated with tin(IV) chloride. This operation afforded dichlorobis(8-ethylthio-1-naphthyl)stannane (**2**), as are observed in other similar reactions. Com-



X=O or S
R=H or CH3

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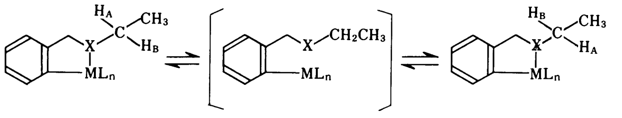
† Present address: Department of Chemistry, Faculty of Science, Okayama University of Science, Ridaicho, Okayama 700.

pound **2** was treated with excess of tin(IV) chloride to give trichloro(8-ethylthio-1-naphthyl)stannane (**3**).[11)]

The syntheses of trichloro[(*o*-ethoxymethyl)phenyl]stannane (**5**: X=O) and the thio analog (**5**: X=S) were performed similarly from *o*-bromo[ethoxy(or ethylthio)methyl]benzene (**4**). Treatment of **4** with butyllithium followed by methyl borate and then a 1,2-diol afforded 2-[*o*-ethoxy(or ethylthio)methylphenyl]-1,3,2-dioxaborolane (**6**: X=O or S, R=H or CH_3).

The selection of the compounds bases on our principle that a diastereotopic pair of protons exchange their sites on dissociation followed by racemization and recombination.[12)] The methylene or gem-dimethyl protons act as probes because they are diastereotopic as far as the ligand sticks to the metalloid center. It is possible that the sulfur-inversion takes place without breaking the sulfur-metalloid bond. But if it were the case, the entropy of activation would be close to zero as were the cases of pure sulfur-inversion.[9,10,13)]



Scheme 1. A typical site-exchange process for the diastereotopic methylene protons by dissociation.

The methylene protons of the ethyl group in compound **3** showed a typical A_2 pattern of an A_2X_3 system. When the temperature was lowered to −90 °C, the signal began to broaden at 270 MHz, but the complete decoalescence of the signal was not observed. Although it is difficult to mention the exact free energy of activation for the process without knowing the chemical shift difference of the A and B protons, the rough estimate of the free energy of activation for the process is 8—10 $\mathrm{kcal\,mol^{-1}}$ (1 cal=4.184 J) at −90 °C. In contrast, compound **5** (X=S) showed the change in line shapes at and below −65 °C and the line shapes at −90 °C and below indicated that it was in the slow exchange limit. The total line shape analysis of the spectra afforded the rate constants shown in Table 1 and putting these rate constants and temperatures into the Eyring equation afforded the following kinetic parameters: $\Delta H^{\ddagger}=12.7\pm0.2$ $\mathrm{kcal\,mol^{-1}}$, $\Delta S^{\ddagger}=13.3\pm1.0$ $\mathrm{cal\,mol^{-1}\,K^{-1}}$, $\Delta G^{\ddagger}_{273}=9.1$ $\mathrm{kcal\,mol^{-1}}$. The low energy barrier to the process observed for **3** relative to **5** can be ascribed to the strain in the coordinated form of **3** relative to **5**, because the skeleton of the molecule is more rigid because of the presence of the naphthalene nucleus than in **5**.

The oxygen compound (**5**: X=O) failed to show any line broadening even at −50 °C where compound **5** (X=S) showed the line-broadening. We judge that the dynamic process for the oxygen-tin complex is much faster than that in the sulfur compound. This is in accordance with the fact that the $(CH_3)_2O\text{-}TiCl_4$ complex is less stable than the $(CH_3)_2S\text{-}TiCl_4$.[14)]

All the boron compounds (**6**: X=O or S, R=H or CH_3) failed to show line broadening at −90 °C at 270 MHz. Therefore the barrier to the dynamic process that we expected to observe was apparently very low. We believe this observation owes to two factors. The first is that the formation of 5-membered ring will cost some energy because of the short bond distances involving the boron atom and the second is that boron acidity in boronates is lower than that of boron trihalide or trialkylborane due to the 2p-2p conjugation between the oxygen and the boron atoms.[15)] The latter factor may be more effective than the former in lowering the barrier to the process, because dissociation of amine ligands in the similar compounds has been reported.[16,17)]

Thus for the boron compound, we chose an intermolecular complex for the investigation, where boron which carries electronegative substituents can be easily used. As a sulfide, we used 3,3,4,4-tetramethylthiolane that had been made by us.[9)] Tribromoboron was our choice because of easy handling. Thus compound **7**, 3,3,4,4-tetramethylthiolane-tribromoboron complex, was made. The reason for the selection of compound **7** is that the two pairs of the gem-dimethyl protons can be used as probes for the dissociation: although the gem-protons alpha to the sulfur atom in a sulfide can be diastereotopic on ligation of the sulfide to a boron compound, they show very complex signals because of coupling with ^{10}B and ^{11}B.

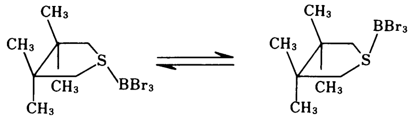


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Table 1. Rate Constants (Temperature in °C) of M-S Bond Dissociation as Determined by Dynamic NMR Spectroscopy

Compound	k/s^{-1} (Temp/°C)
5	12.0 (−80.9), 18.0 (−78.4), 28.0 (−75.9), 43.0 (−73.4), 65.0 (−70.9), 98.0 (−68.3), 142.0 (−65.8)
7[a)]	3.0 (4.8), 4.3 (7.3), 6.1 (9.9), 8.7 (12.4), 12.4 (14.8), 17.1 (17.4), 23.0 (19.9), 32.4 (22.4)
7[b)]	3.0 (4.8), 4.3 (7.2), 6.1 (9.8), 8.7 (12.3), 12.3 (14.8), 17.1 (17.4), 23.0 (19.8), 32.4 (22.4)

a) 20% excess of BBr_3 added. b) 10 molar excess of BBr_3 added.

Compound **7** dissociated to ca. 5% into the sulfide and tribromoboron in chloroform-*d* at −50 °C, as found by ^{1}H NMR spectrum at 270 MHz. Since excessive sulfide can cause S_N2 type substitution in addition to dissociative mechanisms, as was the case of ether-borane complexes,[6] we added excess of tribromoboron to the solution: if the excess of the boron compound affects the dissociation rates, extrapolation to the zero excess of the Lewis acid should give intrinsic rates of dissociation of the sulfur-boron complex. The results are given in Table 1, where only two extreme values are shown. At other points of excess of the boron compound, the rate constants were the same with those listed in the table. Putting these parameters to the Eyring equation, we obtain the following activation parameters: $\Delta H^{\neq}=21.5\pm0.4$ kcal mol^{-1}, $\Delta S^{\neq}=21.0\pm1.4$ cal mol^{-1} K^{-1}.

The feature of the kinetic parameters for both compounds **5** (X=S) and **7** is that the entropy of activation is both large positive, although the enthalpy of activation is different. This makes a sharp contrast to the case of pure sulfur-inversion that gives near-zero entropy of activation. The results are in agreement with others in that the entropy of activation is positive when the ground state is of ionic character and the transition state for dissociation reduces the ionic character. The generality of the rule thus encompasses the coordination complexes that contain sulfur ligands.

Experimental

Dynamic NMR Spectroscopy. All the ^{1}H NMR spectra were recorded on a JEOL GX-270 NMR spectrometer operating at 270 MHz. The temperature indicated on the temperature setting of the machine was calibrated by a thermocouple. A sample was dissolved in an appropriate solvent to make up ca. 50 mmol L^{-1} solutions. The solvent was dichloromethane-d_2 in the case of intramolecularly ligating stannane and borane compounds and it was chloroform-*d* for compound **7**. When 20% excess of tribromoboron was added to the chloroform-*d* solution of **7**, no signal attributable to the free sulfide was observed. The spin exchange was treated as AB $\rightleftarrows$ BA with no coupling for compound **7** and $ABX_3 \rightleftarrows BAX_3$ for compound **5** and the line shapes were simulated with the use of DNMR3 program.[18] The chemical shift differences of the methyl signals (A and B) in compound **7** drifted a little according to temperatures of observation and the linear relation was obtained between the former and the latter in the slow exchange limit: $\Delta\nu/\mathrm{Hz}=0.016t/{}^\circ\mathrm{C}+12.5$ for the cases of small excess of tribromoboron and $\Delta\nu/\mathrm{Hz}=0.016t/{}^\circ\mathrm{C}+12.3$ for the case where tribromoboron was of 10 molar excess. In the case of compound **5**, the chemical shift differences between A and B protons and between A and X protons were constant in the slow exchange limit at 99.6 and 364 Hz, respectively. The coupling constants, J_{AB} and $J_{AX}=J_{BX}$, for compound **5** were constant at −13.6 and 7.3 Hz, respectively, throughout the temperature range examined. These results were extended to the temperature range, where line broadening and coalescence took place, in calculation of the spectra. T_2 was estimated to be 0.10 s for compound **5** and 0.16 s for **7** and these values were used throughout the simulation of the line shapes. The best fit between the observed and the calculated spectra were obtained by visual fitting. The agreement between them was satisfactory. The rate constants thus obtained were put into the Eyring equation to produce the activation parameters.

1-Bromo-8-ethylthionaphthalene (1). 1-Amino-8-bromonaphthalene[19] (5.00 g or 22.5 mmol) was dissolved in 50 mL of water and 6 mL of concentrated hydrochloric acid by heating. To the cooled mixture, was added a solution of 1.6 g (23 mmol) of sodium nitrite in 10 mL of water with shaking. The diazotized solution was neutralized by adding aqueous sodium acetate with cooling and filtered. The solution was added at 40 °C to an aqueous solution of sodium ethanethiolate prepared from 1.0 g (25 mmol) of sodium hydroxide, 50 mL of water and 1.6 mL (22 mmol) of ethanethiol. The mixture was heated to 90 °C and stirred at that temperature for 2 h. The cooled mixture was extracted with benzene, and the extract was washed with water. After drying over magnesium sulfate, the solvent was evaporated and the residue was submitted to chromatography on silica gel with hexane as an eluent. The desired product was obtained in 46.7% yield after recrystallization from hexane, mp 47.0—48.0 °C. Found: C, 53.75; H, 4.08%. Calcd for $C_{12}H_{11}BrS$: C, 53.95; H, 4.08%. ^{1}H NMR ($CDCl_3$) $\delta=1.36$ (3H, t, $J=7.6$ Hz), 2.93 (2H, q, $J=7.6$ Hz), 7.1—7.9 (6H, m).

Dichlorobis(8-ethylthio-1-naphthyl)stannane (2). To a solution of 2.40 g (8.98 mmol) of the bromo compound **1** in 80 mL of ether was added 7.5 mL (11 mmol) of a ca. 1.5 mol L^{-1} hexane solution of butyllithium at −30 °C under a nitrogen atmosphere. The mixture was allowed to stand so that the temperature slowly rose until the temperature became ambient. The solution was transfered to a dropping funnel through a Teflon tube and added to a solution of 2 mL (17 mmol) of tin(IV) chloride in 100 mL of benzene at room temperature. After the reaction was continued for an additional hour at the temperature, the solvent was evaporated. Recrystallization of the residue from dichloromethane-hexane afforded the desired compound, mp 225.5—226.5 °C, in 67% yield. Found: C, 50.83; H, 3.66; Cl, 12.57; S, 11.47%. Calcd for $C_{24}H_{22}Cl_2S_2Sn$: C, 51.10; H, 3.93; Cl, 12.57; S, 11.37%. ^{1}H NMR ($CDCl_3$) $\delta=0.89$ (6H, t, $J=7,7$ Hz), 2.70 and 3.00 (4H, AB part of ABX_3, $J_{AB}=12.0$ Hz, $J_{AX}=J_{BX}=7.7$ Hz), 7.4—8.1 (10 H, m), 8.86 (2H, dd, $J=6.9$ and 1.3 Hz).

Trichloro(8-ethylthio-1-naphthyl)stannane (3). A solution of 1.70 g (3.01 mmol) of the diaryldichlorostannane (**2**) and 1 mL (9 mmol) of tin(IV) chloride in 80 mL of toluene was heated under reflux for 12 h under a nitrogen atmosphere. The solvent was evaporated and the residue was extracted with hot hexane. Cooling the hexane extract afforded crystals. Recrystallization of the product from dichloromethane-hexane gave a pure sample, mp 108.5—109.5 °C. Found: C, 34.89; H, 2.76; Cl, 25.99; S, 7.85%. Calcd for $C_{12}H_{11}Cl_3SSn$: C, 34.96; H, 2.69; Cl, 25.79; S, 7.78%. ^{1}H NMR ($CDCl_3$) $\delta=1.23$ (3H, t, $J=7.4$ Hz), 2.96 (2H, q, $J=7.4$ Hz), 7.5—8.2 (5H, m), 8.58 (1H, d, $J=7.2$ Hz).

Dichlorobis[2-(ethylthiomethyl)phenyl]stannane, mp 174.5—175.5 °C, was obtained by similar treatment of 1-bromo-2-(ethylthiomethyl)benzene[20] as described in the preparation of **2** in 45% yield. Found: C, 43.44; H, 4.50; Cl, 15.42%. Calcd for $C_{18}H_{22}Cl_2S_2Sn$: C, 43.93; H, 4.51; Cl, 14.41%. ^{1}H NMR ($CDCl_3$) $\delta=0.99$ (6H, t, $J=7.5$ Hz), 2.37 (4H, q, $J=7.5$ Hz), 4.11 (4H, s), 7.2—7.5 (6H, m), 8.2—8.3 (2H, m).

Trichloro[2-(ethylthiomethyl)phenyl]stannane (**5**: X=S), mp 108.5—109.5 °C, was similarly obtained by treating the diaryldichlorostannane with $SnCl_4$ in 79% yield. Found: C, 28.49; H, 2.95; Cl, 27.92%. Calcd for $C_9H_{11}Cl_3SSn$: C, 28.73; H, 2.95; Cl, 28.26%. ^{1}H NMR ($CDCl_3$) δ=1.28 (3H, t, J=7.4 Hz), 2.40 (2H, q, J=7.4 Hz), 4.10 (2H, s), 7.4—7.7 (3H, m), 8.1—8.2 (1H, m).

Dichlorobis[2-(ethoxymethyl)phenyl]stannane was similarly prepared from 1-bromo-2-(ethoxymethyl)benzene.[21] The product was recrystallized from dichloromethane-hexane to give 46% of the desired product, mp 194.0—195.0 °C. Found: C, 46.78; H, 4.92; Cl, 15.45%, Calcd for $C_{18}H_{22}Cl_2O_2Sn$: C, 47.00; H, 4.82; Cl, 15.42%. ^{1}H NMR ($CDCl_3$) δ=0.92 (6H, t, J=6.9 Hz), 3.37 (4H, q, J=6.9 Hz), 4.70 (4H, s), 7.1—7.5 (6H, m), 8.3 (2H, m).

Trichloro[2-(ethoxymethyl)phenyl]stannane (**5**: X=O), mp 130.5—132.0 °C, was similarly prepared as for the preparation of **3** in 67% yield. The analytical sample was obtained by recrystallization from hexane. Found: C, 29.73; H, 3.21; Cl, 29.44%. Calcd for $C_9H_{11}Cl_3OSn$: C, 30.01; H, 3.08; Cl, 29.52%. ^{1}H NMR ($CDCl_3$) δ=1.44 (3H, t, J=7.0 Hz), 4.15 (2H, q, J=7.0 Hz), 4.81 (2H, s), 7.4 (1H, m), 7.5—7.6 (2H, m), 8.0—8.1 (1H, m).

2-[2-(Ethylthiomethyl)phenyl]-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**6**: X=S, R=CH_3). To a solution of 4.03 g (17.4 mmol) of 1-bromo-2-(ethylthiomethyl)benzene[21] in 50 mL of ether was added 12.2 mL (18.3 mmol) of a ca. 1.5 mol L^{-1} hexane solution of butyllithium at −78 °C under a nitrogen atmosphere. The mixture was allowed to warm slowly up to room temperature and then transferred to a dropping funnel through a Teflon tube. The mixture was added to 3.4 mL (30 mmol) of trimethyl borate in 50 mL of ether at −78 °C and allowed to warm slowly up to the room temperature. Water (10 mL) and then 10 mL of dilute sulfuric acid were added to the mixture and the ether layer was separated. The aqueous layer was extracted with ether and the combined ether layers were washed with water. The solvent was evaporated and the residue was mixed with 2.0 g (17 mmol) of 2,3-dimethyl-2,3-butanediol and 150 mL of toluene. The mixture was heated with a Dean-Stark apparatus for 2 h. The mixture was then fractionally distilled to give the desired product, bp 128.0—130.0 °C/3 mmHg (1 mmHg=133.322 Pa). The yield was 1.8 g (37%). Found: C, 64.85; H, 8.51; S, 11.66%. Calcd for $C_{15}H_{23}BO_2S$: C, 64.76; H, 8.33; S, 11.52%. ^{1}H NMR ($CDCl_3$) δ=1.17 (3H, t, J=7.5 Hz), 2.38 (2H, q, J=7.5 Hz), 1.40 (12H, s), 4.01 (2H, s), 7.2—7.3 (3H, m), 7.7—7.8 (1H, m).

2-[2-(Ethylthiomethyl)phenyl]-1,3,2-dioxaborolane (**6**: X=S, R=H), bp 114—115 °C/3 mmHg, was similarly prepared by treating 2-(ethylthiomethyl)phenyllithium with trimethyl borate and then with acidic water followed by ethylene glycol in 55% yield. Found: C, 59.45; H, 6.94; S, 14.09%. Calcd for $C_{11}H_{15}BO_2S$: C, 59.48; H, 6.81; S, 14.09%. ^{1}H NMR ($CDCl_3$) δ=1.19 (3H, t, J=7.4 Hz), 2.40 (2H, q, J=7.4 Hz), 4.00 (2H, s), 4.37 (4H, s), 7.1—7.3 (3H, m), 7.7—7.8 (1H, m).

2-[2-(Ethoxymethyl)phenyl]-1,3,2-dioxaborolane (**6**: X=O, R=H), bp 95—105 °C/4 mmHg, was similarly prepared from 1-bromo-2-(ethoxymethyl)benzene[21] as for the preparation of **6** (X=S, R=CH_3) in 46% yield. The distillate solidified and was recrystallized from dichloromethane-hexane to afford a pure sample, mp 50.0—51.0 °C. Found: C, 64.23; H, 7.06%. Calcd for $C_{11}H_{15}BO_3$: C, 64.12; H, 7.34%. ^{1}H NMR ($CDCl_3$) δ=1.24 (3H, t, J=6.9 Hz), 4.56 (2H, q, J=6.9 Hz), 4.38 (4H, s), 4.74 (2H, s), 7.2—7.5 (3H, m), 7.8 (1H, m).

3,3,4,4-Tetramethylthiolane-Tribromoboron Complex (7). To a solution of 0.20 g (0.14 mmol) of the thiolane[9] in 1 mL of dichloromethane was added 0.15 mL (0.16 mmol) of tribromoboron at −78 °C and then dry hexane to give precipitates. The supernatant liquid was removed by a syringe and the residue was recrystallized from dichloromethane-hexane. This compound began to decompose at 118 °C, as indicated by the sublimed crystals of the thiolane, and then the decomposition was complete at 170—192 °C. Found: S, 7.76%. Calcd for $C_8H_{16}BBr_3S$: S, 8.12%. ^{1}H NMR ($CDCl_3$, −50 °C) δ=1.10 (6H, s), 1.14 (6H, s), 3.1—3.6 (4H, m). An additional peak attributable to free thiolane at δ 0.96 (ca. 5%) was observed under the conditions.

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