Dynamic NMR as a Nondestructive Method for the Determination of Rates of Dissociation. XX. Secondary Isotope Effect on Kinetic Basicity of Amine Ligands in Boronate-Amine Complexes and Ammonium Salts[1)]

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(Received March 11, 1992)

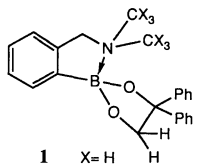
Secondary isotope effects on the kinetic basicity of amine ligands in boronate-amine complexes and ammonium salts were first determined by taking advantage of the rate constants of the dissociation of the amine ligands measured by the dynamic NMR method. The basicities of amine ligands are enhanced by the α-deuterations in the both compounds and the isotope effect caused by a deuterium is larger in the boronate complexes than the ammonium salts. These isotope effects are discussed on the basis of the inductive and steric effects.

The dynamic NMR spectroscopy has been extensively applied to problems on bond dissociation.[2,3)] Dissociation of an amine ligand in a coordination compound is one of the well-investigated areas and kinetic parameters for dissociation of amine ligands could be determined in intramolecular tin–amine[4)] and boron–amine[5,6)] complexes as well as ammonium salts.[7,8)] Useful information on kinetic basicity of amine ligands is obtained from the rates of dissociation of the amines in the acid-base complexes. During the investigations on dissociation of amine ligands in boron-amine complexes, the barrier to dissociation of the N–B bond was found to be significantly influenced by substituents at the nitrogen atom.[5,6)] Bulky substituents reduce Lewis basicity of the amine ligands due to the steric effects, F-strain.

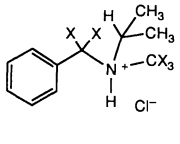
Basicities of alkylamines are known to be affected by α-deuteration at the nitrogen atom; this is the secondary isotope effect (SIE).[9,10)] The literatures have shown that a deuterated amine is a slightly stronger base than the corresponding nondeuterated one.[11–14)] All of these results were obtained by differential potentiometric measurements in an aqueous solution system, namely secondary equilibrium isotope effects (SEIE). There are, however, no reports on SIE on kinetic basicity of amines.

Though the dynamic NMR method can provide important information on the kinetic basicity of amine ligands, it seems difficult to use this technique in the field of SIE because of small changes in rate constants when one or two deuterium atoms are introduced; the same situation would prevail in determination of SEIE. The differences in the rates of dissociation are, however, expected to be enhanced to an extent observable by the method when several protons are replaced by deuterons. Therefore the dynamic NMR method can contribute to studies on SIE on kinetic basicity of amine ligands if we design appropriate compounds.

A boronate–amine complex **1**[5)] and an ammonium salt **2**,[8)] of which the kinetic parameters for the dissociation had been reported, were selected as compounds for the purpose. The corresponding highly deuterated



1 X=H
1-d_6 X=D



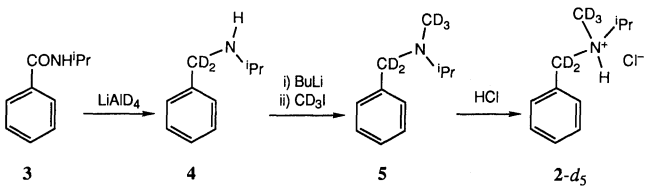
2 X=H
2-d_5 X=D

compounds, **1**-d_6 and **2**-d_5 were synthesized and submitted to the measurement of the kinetics of dissociation. We report here the first observation of SIE on kinetic basicity of amine ligands by the use of the dynamic NMR method and the obtained results are discussed from various points of view.

Results

Syntheses of Deuterated Compounds. The deuterated boronate complex (**1**-d_6) was synthesized in the same manner as for the preparation of **1** described in the previous paper[5)] except that dimethyl-d_6-amine was used instead of dimethylamine. ^{1}H NMR of **1**-d_6 exhibited a very small residual signal due to *N*-methyl protons at δ=2.48, while that signal appeared at δ=2.51 in **1** with 6H intensities. Mass spectra gave a molecular ion peak (M^+) at 363 for **1**-d_6, this value being larger than that in **1**(M^+ 357) by 6 mass units. These spectral data indicate that six protons in the *N*-methyl groups are deuterated and its isotopic purity is more than 98% in **1**-d_6.

The deuterated ammonium salt (**2**-d_5) was prepared according to the route described in Scheme 1. Two



3 **4** **5** **2**-d_5

Scheme 1.

deuterium atoms at the benzylic position were introduced by reduction of amide **3** with $LiAlD_4$. The secondary amine thus obtained was treated with iodomethane-d_3 to afford the desired tertiary amine (**5**). ^1H and ^{13}C NMR and mass spectra of the amine indicate that the five hydrogens at the benzylic methylene and the *N*-methyl group are deuterated in more than 97% purity. This amine was converted to the corresponding hydrochloride by treatment with HCl gas. ^1H NMR of the ammonium salt (**2**-d_5) showed a double-doublet due to a pair of diastereotopic methyl protons in the isopropyl group at δ=1.34 and 1.49 and a broad signal due to the N–H proton at δ 12.2.

Determination of Rates of Dissociation. Rates of dissociation of the N–B bond in the boronate complexes and the N–H bond in the ammonium salts were determined by the dynamic NMR method. Total line shape analyses were performed with DNMR3K program[15] by using exchanging signals due to the methylene protons at the 5-position in the 1,3,2-dioxaborolane ring of the boronates and the methyl protons in the isopropyl group in the ammonium salts as a probe. It had been confirmed that the rates of topomerization as obtained from the line shape analysis were equal to just a half of the rates of bond dissociation in the both systems.[5,8] The kinetic parameters for dissociation of the N–B bond were determined in four solvents for **1** and **1**-d_6 listed in Table 1. For the ammonium salts **2** and **2**-d_5, 1,1,2,2-tetrachloroethane-d_2 was used as a solvent and the results are shown in Table 2. Relative rate constants

Table 1. Kinetic Parameters for Dissociation of the N–B Bond in Boronate–Amine Complexes **1** and **1**-d_6 in Various Solvents[a]

Compound	Solvent	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}_{233}$	k_{233}	r[b]
		kcal mol^{-1}	cal mol^{-1} K^{-1}	kcal mol^{-1}	s^{-1}	
1	Toluene-d_8	13.8±0.2	11.9±0.5	11.0_4	218	0.9998
	CD_2Cl_2	14.4±0.3	12.0±1.3	11.5_6	70.4	0.9997
	Acetone-d_6	13.5±0.2	8.9±0.8	11.3_9	101	0.9998
	DMF-d_7	13.9±0.2	9.0±0.6	11.8_5	37.4	0.9999
1-d_6	Toluene-d_8	14.0±0.4	11.8±1.6	11.2_2	145	0.9996
	CD_2Cl_2	14.7±0.2	12.4±0.8	11.7_6	45.6	0.9999
	Acetone-d_6	13.6±0.2	8.7±0.8	11.5_9	66.4	0.9999
	DMF-d_7	14.2±0.2	9.3±0.6	12.0_6	23.7	0.9999

a) 1 cal=4.184 J. Concentration ca. 40 mmol dm^{-3}. b) Correlation coefficient.

Table 2. Kinetic Parameters for Dissociation of the N–H Bond in Ammonium Salts **2** and **2**-d_5 in 1,1,2,2-Tetrachloroethane-d_2[a]

Compound	$\Delta H^{\neq}$	$\Delta S^{\neq}$	$\Delta G^{\neq}_{390}$	k_{390}	r
	kcal mol^{-1}	cal mol^{-1} K^{-1}	kcal mol^{-1}	s^{-1}	
2	32.1±0.4	33.1±0.9	19.1_4	153	0.9999
2-d_5	32.5±0.4	33.7±0.9	19.3_2	121	0.9999

a) Concentration ca. 65 mmol dm^{-3}.

Table 3. Secondary Isotope Effects on Basicity of Amines in Various Isotopomer Pairs

Amine pair (solvent)	Isotope effect[a]	Isotope effects per D[b]	Ref.
1/**1**-d_6 (toluene-d_8)	1.50±0.08	1.070±0.010	This work
1/**1**-d_6 (CD_2Cl_2)	1.54±0.08	1.075±0.010	This work
1/**1**-d_6 (acetone-d_6)	1.52±0.08	1.072±0.010	This work
1/**1**-d_6 (DMF-d_7)	1.58±0.08	1.079±0.010	This work
2/**2**-d_5 ($C_2D_2Cl_4$)	1.26±0.07	1.047±0.011	This work
CH_3NH_2/CD_3NH_2	1.13	1.042	12)
$(CH_3)_2NH/(CD_3)_2NH$	1.32	1.047	12)
$(CH_3)_3N/(CD_3)_3N$	1.61	1.054	13)
$PhCH_2NH_2/PhCD_2NH_2$	1.077±0.003	1.038±0.002	14)
$RNHCH_3/RNHCD_3$[c]	1.14±0.01	1.044±0.003	11)
$R'NHCH_3/R'NHCD_3$[d]	1.11±0.02	1.037±0.004	11)

a) Relative rate constants (k_H/k_D) of dissociation of the amine ligand determined in this work, and relative equilibrium constants (K_H/K_D) in the literatures. b) This value is overall isotope effect powered by reciprocal of the number of deuterium. c) R=2,4-dinitrophenyl. d) R′= 2,4,6-trinitrophenyl.

between the nondeuterated and the deuterated compounds, secondary kinetic isotope effects (SKIE), are shown in Table 3.

In order to reduce errors in rate constants, especially in relative rate constants, we paid following attentions in the measurements because differences in the rate constants were expected to be small. The kinetic parameters in the nondeuterated compounds were redetermined under the same conditions as in the deuterated compounds; concentrations of solution, temperature control, and so on. Measurement and line shape analyses of NMR signals were individually performed at least three times for each entry and their reproducibilities were confirmed. Errors involved in the relative rate constants are estimated to be less than 5% of the values.

The kinetic parameters for the dissociation of the N–B bond in compound **1** are in agreement with the data obtained previously.[5] The rate constants of dissociation for the deuterated compound **1**-d_6 are smaller than those for the nondeuterated compound **1** in all solvents. The relative rate constants, $k(\mathbf{1})/k(\mathbf{1}\text{-}d_6)$, are 1.50—1.58 as shown in Table 3 and these values are significant in view of the experimental errors mentioned above. These findings indicate that the kinetic basicity of the nitrogen atom in **1**-d_6 is stronger than that in **1**. If we assume that every deuterium contributes to the changes in the rate constants in the same proportion, the isotope effect per a deuterium, which is overall isotope effect powered by reciprocal of the number of deuterium, is calculated to be 1.070—1.079.

Dissociation is more facile in **2** than in **2**-d_5 and the basicity of the deuterated amine (**2**-d_5) is again stronger than the nondeuterated one (**2**). The isotope effect on dissociation of the N–H bond is 1.26 (overall) and 1.047 (per D) in the isotopomer pair of the ammonium salts **2** and **2**-d_5. Strictly speaking, deuteriums at the benzylic position and in the methyl groups should contribute to the overall isotope effect to a different degree. We neglect this difference because such a dichotomy is not possible at present and the difference should not be large.

Enhancement in basicity of amines by α-deuteration was reported in some methylamines and benzylamines.[11–14] All of these data are SEIE's, being determined in an equilibrium between an amine and its conjugate acid in a water system. Therefore, our results are, to the best of our knowledge, the first example of SKIE on basicity of amines. Evidently the SKIE's are different from one complex to another.

Discussion

As seen in Table 3, SKIE's could be obtained for **1** and **1**-d_6 in various solvents. The SKIE values obtained for various solvents did not significantly differ from each other although the dissociation of the N–B bond is generally slow in polar solvents due to stabilization of the polar ground state by solvation of the solvent. On the other hand, the kinetic data for the ammonium salts, **2** and **2**-d_5, could be determined only for 1,1,2,2-tetrachloroethane-d_2 solutions due to limitations of the technique, solubility and rates of dissociation at an appropriate temperature range. For the same reasons, it was not possible to determine SKIE in the **1**/**1**-d_6 pair in 1,1,2,2-tetrachloroethane-d_2. This may seem to prevent from direct comparison of the data for the two pairs of compounds, but we believe it is possible for the following reasons.

Firstly, the solvents were selected from among a wide variety of them, from nonpolar to strongly polar, for the determination of rates of dissociation of the N–B bond in compounds **1** and **1**-d_6. The absence of the solvent effects on SKIE's indicates that the deuteration hardly affects the solvation energy in the boronate complexes in a given solvent. This is also true for dichloromethane-d_2, as is seen in Table 1. Secondly, we have reported that dichloromethane-d_2 and 1,1,2,2-tetrachloroethane-d_2 gave almost the same rates of the N–B bond dissociation in a borane-amine complex.[6] These solvent effects are attributed to the fact that solvent parameters of the two solvents are similar. This will mean that SKIE's observed in these two solvents should not be different to a significant extent in a pair of a compound and a deuterated isotopomer. On these grounds, SKIE's observed for the pairs, **1**/**1**-d_6 and **2**/**2**-d_5, may be directly compared, though there is no common solvent for the two pairs.

Ruling out the solvent effects for the difference in SKIE's for the sets of **1**/**1**-d_6 and **2**/**2**-d_5, we can now discuss the origins of the difference. Different cationic species are present in **1** from **2** including their isotopomers. The size of the cationoid may be important. Another difference is the number of deuterons present in **1**-d_6 and **2**-d_5. Their electronic as well as steric effects may be important.

The SIE's on basicity of amines have been commonly interpreted in terms of inductive effects and steric interactions in published papers.[17] According to these discussions, a CD_3 group is more electron-donating than a CH_3 group by inductive effects. On the other hand, a CD_3 group is less able to donate electrons to the attached atom through hyperconjugation than a CH_3 group. Since we discuss the electron density on the amine-nitrogen, not a cation with an empty orbital, in the present case, the effect of hyperconjugation should be small, however. Therefore, the basicity of an amine is enhanced by deuteration through the inductive effects.

From the steric point of view, a CD_3 group is said to be slightly smaller than a CH_3 group, as evidenced by the fact that the CD_3 group prefers the axial position than the CH_3 group in a cyclohexane.[18] Namely the steric effect (F-strain) is smaller in a deuterated compound than a nondeuterated compound; the basicity of an amine is enhanced in the deuterated compound if the steric demand is important.

Which effect, inductive or steric, is important in SKIE

on the basicity of amines? We wish to discuss this point by comparing our results with other data reported previously. The SEIE's on basicity of amines in various isotopomer pairs are also listed in Table 3. We notice that the isotope effects in the ammonium salts, **2** and **2**-d_5, are comparable to those in other amine pairs (4—5% per D). These compounds have a common feature of that a proton is an acid. This indicates that SKIE's are comparable to SEIE on basicity of the amine for a given acid.

The isotope effects in the boronate compounds (7—8% per D) are slightly but significantly larger than that in the isotopomer pair of the ammonium salts, in which a proton is an acid. The difference in structures is that a borane, which is much larger than a proton, is a Lewis acid in the complex. Since the larger an acid, the more important the steric effects become in coordination,[19] the large isotope effects in the boronate compounds with respect to the ammonium salts are attributed to the steric effects; the size of the deuterium atom plays a dominant role in the difference.

The importance of the steric effect in SIE's has been referred to in some literatures. Bartell reported that the nonbonded repulsion was important rather than the hyperconjugation in SIE on the association of trimethyl-d_9-borane with trimethylamine from theoretical approaches.[20] These compounds have a borane as a Lewis acid as in boronate complex **2**. H. C. Brown et al. insisted that the steric effect was a dominant factor in SIE on the basis of experimental data of some reactions in 2,6-dimethylpyridine and 2,6-dimethyl-d_6-pyridine.[21]

The following facts support the significance of the steric effects as well. The isotope effects per a deuterium on the basicity of amines increase as the number of methyl-substitution increases, as shown in Table 3; methylamine<dimethylamine<trimethylamine. If this tendency is significant, it indicates that the steric effects in the isotope effect became important as the size of an amine becomes large. Barnes and Scott calculated SIE's on the basicity of a dimethylamine/dimethyl-d_6-amine pair using Taft's equation to be 1.18 (1.028 per D);[22] this value is much smaller than the observed one, 1.32.[12] Since the steric effect is scarcely taken into considerations in Taft's σ^* values, it is possible that the small calculated value is the result of neglect of the steric effect.

Quantitative discussion on SKIE on basicity of amine ligands is difficult from available data. At least, the steric effects and the inductive effects operate with comparable contributions in the boronate system. In the ammonium salts, steric effects must be less important than in the boronates but cannot be neglected. Finally, we should like to point out the followings. The effect of the number of deuteriums on SKIE will be cancelled if we take SKIE per a deuterium, as far as inductive effects concern. However, if the steric effects are important, the number of deuterons should affect SKIE.

Experimental

Melting points are uncorrected. Elemental analyses were performed by a Perkin Elmer 240C analyzer. Electron impact mass spectra were measured with a JEOL JMS-DX303 spectrometer. ^{1}H and ^{13}C NMR spectra were measured on a Varian Gemini-300 spectrometer operating at 300.1 and 75.0 MHz, respectively. ^{1}H NMR at various temperatures was measured on a JEOL GSX-400 spectrometer at 399.8 MHz. 2-[2-(Dimethylaminomethyl)phenyl]-4,4-diphenyl-1,3,2-dioxaborolane (**1**) was prepared by the known method and analytical and ^{1}H NMR data were reported in the literature (M^+ 357, Calcd for $C_{23}H_{24}{}^{11}BNO_2$: M^+ 357).[5] Benzylisopropylmethylammonium chloride was prepared from *N*-isopropyl-*N*-methylbenzylamine and HCl gas by a conventional method.[8] (^{1}H NMR ($CDCl_3$) δ=1.36 (3H, d, J=6.6 Hz), 1.52 (3H, d, J=6.6 Hz), 2.62 (3H, d, J=5.1 Hz), 3.48 (1H, d septet, J=2.7 and 6.6 Hz), 4.14 and 4.16 (1H, the AB part of an ABX system, J_{AB}=13.0 Hz, J_{AX}=6.3 Hz, J_{BX}=6.0 Hz), 7.40—7.50 (3H, m) 7.72—7.80 (2H, m), 12.3 (1H, br, the X of the ABX). ^{13}C NMR ($CDCl_3$) δ=15.2, 17.5, 34.5, 54.3, 56.4, 128.8, 128.9, 129.5, 130.8.)

2-[2-(Dimethyl-d_6-aminomethyl)phenyl]-4,4-diphenyl-1,3,2-dioxaborolane (1-d_6). A solution of dimethyl-d_6-amine in 10 cm^3 of benzene was prepared by treatment of 300 mg (3.43 mmol) of dimethyl-d_6-amine hydrochloride (Aldrich Co., Inc.) with aqueous solution of sodium hydroxide in the presence of benzene. This amine solution was added to a solution of 2,4,6-tris[2-(bromomethyl)phenyl]boroxin[23] (157 mg or 0.266 mmol) in 10 cm^3 of benzene and the mixture was stirred for 30 min at room temperature. The resulting salt was removed by filtration and the filtrate was evaporated. The residue was refluxed with 150 mg (0.700 mmol) of 1,1-diphenyl-1,2-ethanediol[24] in 20 cm^3 of toluene for 2 h with a Dean-Stark apparatus for removing water by azeotropic distillation. The solvent was evaporated and recrystallization of the residue from hexane-dichloromethane afforded 170 mg of colorless crystals in 64% overall yield. Isotope purity was better than 98% from its mass and ^{1}H NMR spectra. Mp 127.0—128.0 °C. Found: C, 76.05; N, 3.61%, M^+ 363. Calcd for $C_{23}H_{18}D_6BNO_2$: C, 76.07; N, 3.86%, M^+ 363. ^{1}H NMR ($CDCl_3$) δ=3.91 (s, 2H), 4.59 (s, 2H), 7.01—7.35 (m, 10H), 7.54 (m, 4H). The signal due to the residual *N*-methyl protons was observed at δ=2.48 and its intensity was less than 2%.

***N*-Isopropylbenzyl-α,α-d_2-amine (4).** To a solution of 2.00 g (47.6 mmol) of lithium aluminium tetradeuteride (LAD) in 100 cm^3 of dry ether was added 5.38 g (35.7 mmol) of *N*-isopropylbenzamide, which was prepared from benzoyl chloride and isopropylamine in an ordinary method, in small portions during the course of 30 min under a nitrogen atmosphere. The mixture was stirred for 1 day at room temperature. An excess of LAD was decomposed by addition of ethyl acetate and then 50 cm^3 of water. The ether layer was separated and the water layer was extracted with ether. The combined organic solution was treated with 100 cm^3 of 1 mol dm^{-3} hydrochloric acid. The water layer was then made basic, pH>11, with sodium hydroxide and the resulting oil was extracted with ether. The ether solution was dried and evaporated. The residue was distilled under a reduced pressure to give 4.66 g (65 %) of colorless liquid. Bp 44—47 °C/0.3 mmHg (1 mmHg=133.322 Pa). Found: m/z 151.1311. Calcd for $C_{10}H_{13}D_2N$: M^+, 151.1330. ^{1}H NMR ($CDCl_3$)

δ=1.09 (6H, d, J=6.4 Hz), 1.2 (1H, br), 2.85 (1H, septet, J=6.4 Hz), 7.20—7.33 (5H, m). ^{13}C NMR ($CDCl_3$) δ=22.8, 47.8, 51.7 (quintet, J=20.5 Hz), 126.7, 128.0, 128.2, 140.6.

***N*-Isopropyl-*N*-methyl-d_3-benzyl-α,α-d_2-amine (5).** To a solution of *N*-isopropylbenzyl-α,α-d_2-amine (4.50 g or 29.8 mmol) in 40 cm^3 of dry ether was added 21.0 cm^3 of 15% solution of butyllithium (32.8 mmol) in hexane at −78 °C under a nitrogen atmosphere. The solution was stirred for 2 h at room temperature and 5.18 g (35.7 mmol) of iodomethane-d_3 (Merck) was added. The mixture was stirred for 1 h at room temperature and then refluxed for 2 h. After cooling the mixture was quenched by addition of 40 cm^3 of water. The organic layer was separated, dried, and evaporated. Distillation of the residual oil gave 4.14 g (83%) of the desired amine. Isotopic purity was better than 97% from mass and NMR spectra. Bp 41—44 °C/0.3 mmHg. Found: m/z, 168.1693. Calcd for $C_{11}H_{12}D_5N$: M^+ 168.1675. ^{1}H NMR ($CDCl_3$) δ=1.06 (2H, d, J=6.6 Hz), 2.88 (1H, septet, J=6.6 Hz), 7.18—7.35 (5H, m). ^{13}C NMR ($CDCl_3$) δ=17.9, 36.0 (septet, J=20.4 Hz), 52.9, 56.7 (quintet, J=20.2 Hz), 126.6, 128.1, 128.8, 140.0.

Benzyl-α,α-d_2-isopropylmethyl-d_3-ammonium Chloride 2-d_5). *N*-Isopropyl-*N*-methyl-d_3-benzyl-α,α-d_2-amine (1.00 g or 5.94 mmol) was treated with hydrogen chloride gas in a hexane solution (20 cm^3). The resulting viscous solid was recrystallized from THF to give 0.90 g (74%) of white solid. The material was recrystallized for two more times for the sample of dynamic NMR measurements. Mp 126.0—127.0 °C. Found: C, 64.86; N, 6.78%. Calcd for $C_{11}H_{13}D_5NCl$: C, 64.57; N, 6.85%. ^{1}H NMR ($CDCl_3$) δ=1.34 (3H, d, J=6.6 Hz), 1.49 (3H, d, J=6.6 Hz), 3.45 (1H, d septet, J=2.7 and 6.6 Hz), 7.37—7.46 (3H, m), 7.69—7.78 (2H, m), 12.2 (1H, br). ^{13}C NMR ($CDCl_3$) δ=15.1, 17.4, 33.7 (septet, J=21.7 Hz), 54.2, 55.6 (quintet, J=21.7 Hz), 128.6, 128.9, 129.4, 130.7.

Dynamic NMR Measurements. ^{1}H NMR was measured on the 400 MHz spectrometer with a variable temperature apparatus. Temperatures were read from a thermometer and calibrated by using chemical shift differences of signals due to methanol and 1,2-ethanediol. Concentration of the solution was ca. 40 and 65 mmol dm^{-3} for the boronate complexes and the ammonium salts, respectively. Total line shape analyses were performed with the DNMR3K program.[15]

For the boronate complexes, the methylene protons at the 5-position in the 1,3,2-dioxaborolane ring were used as a probe and the line shapes were simulated as the AB⇆BA system. The signals due to the methylene protons were measured at the slow exchange limits to estimate following input parameters: chemical shift differences ($\Delta\nu$), coupling constants (J), and spin-spin relaxation times (T_2). The chemical shift differences were linearly correlated with temperature and the coupling constants were independent of temperature for every measurement. These input parameters for the calculation were listed in Table 4. The rate constants of the dissociation of the N–B bond, which are twice of those obtained by the line

Table 4. Temperature Dependence of the Chemical Shift Difference, Coupling Constant, and T_2 of the Methylene Protons at 5-Position in 1,3,2-Dioxaborolane Ring in Compounds **1** and **1**-d_6

Compound	Solvent	$\Delta\nu_{AB}$/Hz[a]	J_{AB}/Hz[b]	T_2/s[c]
1	Toluene-d_8	$-0.191t+192.3$	−8.5	0.14—0.15
	CD_2Cl_2	$-0.509t+75.9$	−8.9	0.17—0.18
	Acetone-d_6	$-0.865t+146.5$	−8.6	0.17—0.20
	DMF-d_7	$-0.890t+174.7$	−8.7	0.13—0.16
1-d_6	Toluene-d_8	$-0.216t+192.8$	−8.5	0.16—0.17
	CD_2Cl_2	$-0.511t+77.9$	−8.9	0.17—0.19
	Acetone-d_6	$-0.864t+148.3$	−8.6	0.17—0.19
	DMF-d_7	$-0.868t+176.9$	−8.7	0.16—0.19

a) Chemical shift difference between methylene protons (AB signal): $\Delta\nu_{AB}$/Hz=xt/°C+y. b) Coupling constant between AB protons. c) Spin–spin relaxation times for the signals.

Table 5. Rate Constants of Dissociation of the N–B Bond in Compounds **1** and **1**-d_6

Compound	Solvent	k/s^{-1} (temperature/°C)
1	Toluene-d_8	19.6(−57.0), 34.8(−53.0), 66(−48.7), 108(−45.1), 216(−40.2), 410(−35.2), 750(−30.2), 1340(−25.2), 2500(−20.1)
	CD_2Cl_2	22.0(−48.2), 38.0(−44.2), 69(−40.2), 122(−36.2), 200(−32.1), 340(−28.2), 520(−24.2), 860(−20.2)
	Acetone-d_6	14.2(−54.3), 23.6(−50.5), 49(−45.5), 96(−40.5), 184(−35.6), 320(−30.6), 570(−25.5), 1020(−20.7), 1720(−15.6)
	DMF-d_7	13.4(−47.5), 24.0(−43.4), 39.2(−39.5), 74(−34.5), 144(−29.6), 260(−24.6), 460(−19.7), 800(−14.7), 1340(−9.7), 2200(−4.8)
1-d_6	Toluene-d_8	24.0(−53.0), 39.6(−48.9), 70(−45.1), 144(−40.2), 290(−35.1), 520(−30.2), 920(−25.1), 1640(−20.2)
	CD_2Cl_2	14.0(−48.1), 24.8(−44.2), 44(−40.2), 80(−36.2), 130(−32.2), 224(−28.2), 370(−24.2), 580(−20.2), 1040(−15.2)
	Acetone-d_6	9.2(−54.3), 15.4(−50.5), 31.2(−45.5), 64(−40.5), 120(−35.6), 220(−30.6), 390(−25.5), 680(−20.7), 1160(−15.7)
	DMF-d_7	8.4(−47.5), 14.6(−43.5), 24.8(−39.5), 48.8(−34.6), 92(−29.6), 172(−24.5), 310(−19.7), 540(−14.7), 920(−9.7), 1500(−4.8)

shape analyses because the topomerization of the signals takes place with a half probability of the dissociation, are listed in Table 5.

The NMR spectra at various temperatures were obtained in 1,1,2,2-tetrachloroethane-d_2 dried over molecular sieve 4A for the measurements of the ammonium salts. Signals due to the two methyl groups in the isopropyl group were used for the line shape analyses. The calculation was performed as an ABX⇆BAX system which was an approximation of the $A_3B_3X \leftrightarrows B_3A_3X$ site exchange process. The coupling constants and the chemical shift differences were constant throughout the temperature ranges for each compound. Input parameters and rate constants follow: **2**: $\Delta\nu_{AB}$=54.1 Hz, $\Delta\nu_{AX}$=781.9 Hz, J_{AB}=0 Hz, J_{AX}=J_{BX}=6.7 Hz, T_2=0.22 s; $k/s^{-1}(t/°C)$ 8.4(92.1), 12.2(95.1), 17.6(98.1), 25.2(101.1), 36.0(104.1), 52(107.1), 73(110.1), 102(113.1), 140(116.1), 192(119.2), 264(122.2), 360(125.3). **2**-d_5: $\Delta\nu_{AB}$=53.7 Hz, $\Delta\nu_{AX}$=780.3 Hz, J_{AB}=0 Hz, J_{AX}=J_{BX}=6.7 Hz, T_2=0.20 s; $k/s^{-1}(t/°C)$ 9.4(95.1), 13.6(98.1), 19.2(101.1), 28.8(104.1), 40(107.1), 57(110.1), 80(113.1), 110(116.1), 154(119.2), 212(122.2), 292(125.3).

This work was supported by Grants-in-Aid for Scientific Research Nos. 03214107 and 04740305 from the Ministry of Education, Science and Culture. The 400 MHz NMR and mass spectra were measured at the Analytical Center in Okayama University of Science.

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