Ab initio Molecular Orbital Calculations of Reduced Partition Function Ratios of Polyboric Acids and Polyborate Anions

Takao Oi

Department of Chemistry, Sophia University, 7-1 Kioicho, Chiyoda, Tokyo 102-8554, Japan

Reprint requests to Prof. T. O.; Fax: 81-3-3238-3361

Z. Naturforsch. **55a,** 623–628 (2000); received March 18, 2000

Molecular orbital calculations at the HF/6-31G(d) level were carried out for polyboric acids and polyborate anions up to a pentamer to estimate their ^{11}B-to-^{10}B isotopic reduced partition function ratios (RPFRs) and examine the additivity of logarithms of RPFRs. Approximate RPFR-values calculated by the use of the additivity agreed with exact RPFR-values within a margin of 1% error. This error was equivalent to a 5% error on ln(RPFR). The equilibrium constants of mono boron isotope exhange reactions between three-coordinate boron and four-coordinate boron ranged from 1.0203 to 1.0360 at 25 °C, indicating the importance of exact evaluation of RPFRs of polymers.

Key words: Ab initio Molecular Orbital Calculations; Polyborates; Reduced Partition Function Ratios; Boron Isotope Exchange; Isotope Fractionation.

1. Introduction

The boron isotope exchange reaction between the neutral boric acid molecule ($B(OH)_3$) and the monomeric borate anion ($B(OH)_4^-$),

$$^{10}B(OH)_3 + {}^{11}B(OH)_4^- = {}^{11}B(OH)_3 + {}^{10}B(OH)_4^-, \qquad (1)$$

is a reaction of great concern in boron isotope geochemistry as well as in chromatographic boron isotope separation processes because many boron isotope fractionations observed in those fields are based on it [1]. The equilibrium constant, K_B, of Reaction (1) was theoretically obtained as the ratio of the reduced partition function ratios (RPFRs) [2] of the two boron species which were calculated through the vibrational analysis in which force fields of the two species were constructed so that the experimentally observed spectroscopic data were best reproduced. The K_B-value was 1.0194 at 25 °C and has been the basis for elucidation of observed boron isotope fractionations [1].

$B(OH)_3$ and $B(OH)_4^-$ are practically the only viable boron species in aqueous solutions of very low boron concentrations. When the boron concentration is 0.025 M or higher, polymeric boron species such as $H_5B_3O_8^{2-}$ ($B_3O_3(OH)_5^{-2}$) are formed and their existence cannot be ignored any more [3]. The estimation of the RPFRs of such polymeric species is certainly indispensable for better understanding of boron isotope effects in systems containing them. The vibrational analysis of such species, however, has not yet been successful due to the scantiness of the information on their molecular vibrational frequencies. Instead, their RPFR-values were approximately estimated from those of the monomeric species by the use of additivity of the logarithms of the RPFRs (ln(RPFR)s) [1, 4]. For example, since $H_5B_3O_8^{2-}$ is composed of a triangular group containing a three-coordinate boron atom and two tetrahedral groups, each of which contains a four-coordinate boron atom, joined by three common oxygen atoms, its RPFR, (s/s') $f_{H5B3O82-}$, was approximated as

$$\ln(s/s')\, f_{H5B3O82-} = \{\ln(s/s')\, f_{B(OH)3} + 2\ln(s/s')\, f_{B(OH)4-}\}/3. \qquad (2)$$

Generally, when a polyborate contains m three-coordinate boron atoms and n four-coordinate boron atoms, its RPFR may be approximated as

$$\ln(s/s')\, f_{polyborate} = \{m \ln(s/s')\, f_{B(OH)3} + n \ln(s/s')\, f_{B(OH)4-}\}/(m+n). \qquad (3)$$

However, the degree of the goodness of this kind of approximation has not yet been verified experimentally or theoretically

With the rapid progress in computer technology it is now possible to carry out *ab initio* molecular orbital (MO) calculations of vibrational frequencies of polymeric boron species even with a personal computer in relatively short times. This enables one to verify the additivity of ln(RPFR)s. In a previous paper [5], the author reported the results of the geometry optimization and frequency calculations at the optimized structures for monomeric and dimeric boric acids and borate anions. The RPFRs of the dimers estimated from the RPFRs of the monomers

0932-0784 / 00 / 0600-0623 $ 06.00

by the use of the additivity of ln(RPFR)s agreed with those calculated by using the calculated frequencies of the dimers within a margin of 1%. This error corresponds to an error of 5% of ln(RPFR). In this paper, calculations are extended up to a hexaborate anion and the validity of Approximation (3) is discussed.

2. Theory and Procedure of Calculations

2.1. Reduced Partition Function Ratios

Isotope effects based on molecular translational, rotational and vibrational motions can be estimated by calculating the RPFRs of the chemical species participating in the considered isotope exchange reaction [2]. That reaction may be expressed, without losing any generality, as

$$AX + BX' = AX' + BX, \tag{4}$$

where X and X′ are the heavier and lighter isotopes of the element considered and A and B are polyatomic groups. The equilibrium constant, K, of Reaction (4) (strictly speaking, the equilibrium constant estimated quantum mechanically divided by that estimated classically) can be given as

$$\ln K = \ln(s/s')_{f_{BX}} - \ln(s/s')_{f_{AX}}, \tag{5}$$

where $(s/s')_{f_{AX}}$ and $\ln(s/s')_{f_{BX}}$ are the RPFRs of the chemical species AX and BX, respectively. The general formula of the RPFR of a species is given, under the Born-Oppenheimer and harmonic oscillator approximations, as

$$(s/s')_f = \prod_1^f \frac{u_i \exp(-u_i/2)/\{1-\exp(-u_i)\}}{u_i' \exp(-u_i'/2)/\{1-\exp(-u_i')\}}, \tag{6}$$

where

$$u_i = hc\,\omega_i/(kT), \tag{7}$$

and

$$u_i' = hc\,\omega_i'/(kT). \tag{7'}$$

Here, f is the degree of freedom of the vibrational motion, h Planck's constant, c the velocity of light, ω_i and ω_i' the wavenumbers of the ith molecular vibration of the heavier and lighter isotopic species, respectively, k Boltzmann's constant, and T the temperature.

2.2. ab initio Molecular Orbital Calculations

All the *ab initio* MO calculations were made with a Dell personal computer using the Gaussian 94W program package. Based on the results of a previous paper [5], the used *ab initio* MO theory and basis set were restricted to the Hartree-Fock self-consistent field (HF) method theory and the 6-31G(d) polarized basis set, respectively. A more advanced MO theory with a higher level basis set did not always yield better results of the RPFRs.

As polyboric acids and polyborate anions, three trimers, $H_3B_3O_6$ ($B_3O_3(OH)_3$), $H_4B_3O_7^-$ ($B_3O_3(OH)_4^-$) and $H_5B_3O_8^{2-}$ ($B_3O_3(OH)_5^{2-}$), one tetramer, $H_4B_4O_9^{2-}$ ($B_4O_5(OH)_4^{2-}$), one pentamer, $H_4B_5O_{10}^-$ ($B_5O_6(OH)_4^-$), and one hexamer, $H_6B_6O_{13}^{2-}$ ($B_6O_6O(OH)_6^{2-}$) were considered. The neutral $H_3B_3O_6$ is composed of a 6-membered ring of three BO_3 triangles and is found in the orthorhombic form of metaboric acid [6]. The $H_4B_3O_7^-$ trimer consists of a ring of two triangles and a BO_4 tetrahedron and occurs as an anion unit in ameghinite [7]. The third trimer $B_3O_3(OH)_5^{2-}$, consisting of a ring of a triangle and two tetrahedra, is found in such boron minerals as inderborite [8]. The tetramer $H_4B_4O_9^{2-}$ consists of two 6-membered rings, each of which being composed of a triangle and two tetrahedra with sharing of the two tetrahedra. It is a borate anion unit in borax [9]. The pentamer $H_4B_5O_{10}^-$ consists of two 6-membered rings of two triangles and a tetrahedron sharing the tetrahedron, and is the unit in sborgite [10]. The hexamer $H_6B_6O_{13}^{2-}$ consists of three 6-membered rings, each of which consisting of a triangle and two tetrahedra with each tetrahedron participating in the formation of two rings. The unique feature of this hexamer is the existence of a three-coordinate oxygen atom shared by all the three rings (cf. O1 in Fig. 1f). The $H_6B_6O_{13}^{2-}$ unit is found in nobleite [11].

The geometries of the polymers were optimized and their vibrational frequencies were calculated at the optimized geometries. Calculated frequencies were corrected using the scale factor (= 0.9590) determined for the monomers [5]. With the corrected frequencies, the RPFRs of the polymers were computed using eq. (6), and subsequently equilibrium constants of various boron isotope exchange reactions were calculated using eq. (5).

In all the frequency calculations, the isotopes of hydrogen and oxygen were ^1H and ^{16}O, respectively, and only the mono boron isotope substitutions were considered with the ^{11}B basis.

3. Results and Discussion

The most stable structures obtained are depicted in Fig. 1; a) for $H_3B_3O_6$, b) for $H_4B_3O_7^-$, c-1) for $H_5B_3O_8^{2-}$, d) for $H_4B_4O_9^{2-}$, e-1) for $H_4B_5O_{10}^-$ and f) for $H_6B_6O_{13}^{2-}$.

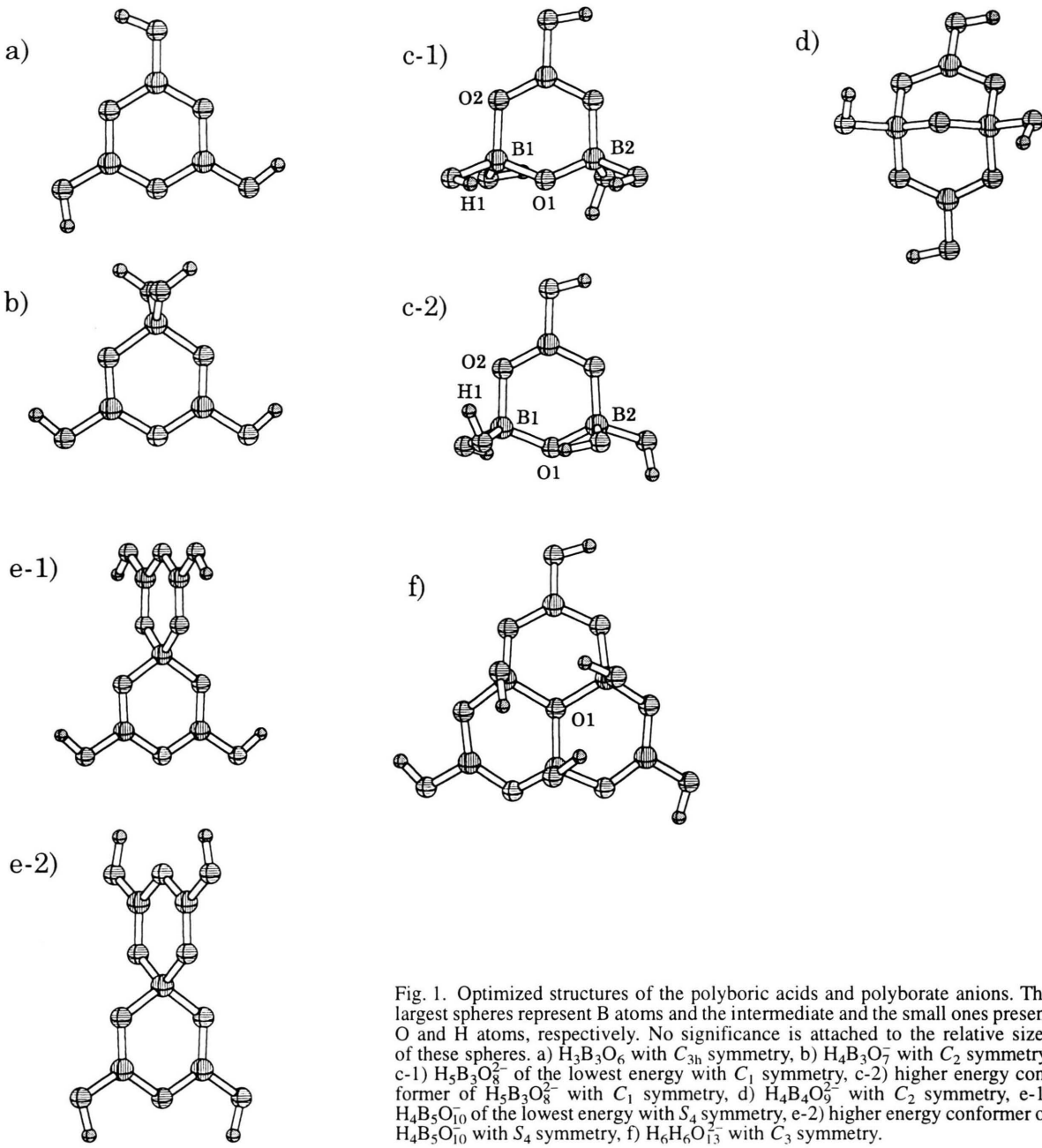

Fig. 1. Optimized structures of the polyboric acids and polyborate anions. The largest spheres represent B atoms and the intermediate and the small ones present O and H atoms, respectively. No significance is attached to the relative sizes of these spheres. a) $H_3B_3O_6$ with C_{3h} symmetry, b) $H_4B_3O_7^-$ with C_2 symmetry, c-1) $H_5B_3O_8^{2-}$ of the lowest energy with C_1 symmetry, c-2) higher energy conformer of $H_5B_3O_8^{2-}$ with C_1 symmetry, d) $H_4B_4O_9^{2-}$ with C_2 symmetry, e-1) $H_4B_5O_{10}^-$ of the lowest energy with S_4 symmetry, e-2) higher energy conformer of $H_4B_5O_{10}^-$ with S_4 symmetry, f) $H_6H_6O_{13}^{2-}$ with C_3 symmetry.

The structures of the trimers, $H_3B_3O_6$, $H_4B_3O_7^-$ and $H_5B_3O_8^{2-}$, were optimized, assuming C_{3h}, C_2, and C_1 symmetry, respectively, according to the results by Zhang et al. [12]. The structures of the tetramer, pentamer and hexamer were optimized assuming C_2, S_4 and C_3 symmetry, respectively.

For each of the polymers, the geometry optimization was also conducted assuming an other symmetry than the above one and/or starting from different initial input data. Sometimes, the calculation did not converge. In some cases, the geometry was optimized but negative frequencies were obtained for that structure. In some other

Table 1. RPFRs of the monomers and polymers at 25 °C at the HF/6-31G(d) level and additivity of RPFRs.

Species	Fig.	Triangular: Tetrahedral	Site of isotope substitution	Exact. RPFR: A	Approxi-mate RPFR: B	Error[a] (%)	Exact ln(RPFR): A′	Approxi-: mate ln(RPFR): B′	Error[b] (%)	Ref.
$B(OH)_3$		1:0	triangular	1.24711			0.22083			[5]
$B(OH)_4^-$		0:1	tetrahedral	1.21556			0.19520			[5]
$H_4B_2O_5$		2:0	triangular	1.24414	1.24711	0.2	0.21845	0.22083	1.2	[5]
$H_5B_2O_6^-$		1:1	triangular	1.24072	1.24711	0.5	0.21569	0.22083	2.4	[5]
			tetrahedral	1.20764	1.21556	0.7	0.18867	0.19520	3.5	[5]
$H_6B_2O_7^{2-}$		0:2	tetrahedral	1.20374	1.21556	1.0	0.18543	0.19520	5.0	[5]
$H_3B_3O_6$	1a)	3:0	triangular	1.24250	1.24711	0.4	0.21712	0.22083	1.7	
$H_4B_3O_7^-$	1b)	2:1	triangular	1.24421	1.24711	0.2	0.21850	0.22083	1.1	
			tetrahedral	1.21081	1.21556	0.4	0.19129	0.19520	2.0	
$H_5B_3O_8^{2-}$	1c-1)	1:2	triangular	1.24056	1.24711	0.5	0.21556	0.22083	2.4	
			tetrahedral[c]	1.20632	1.21556	0.8	0.18757	0.19520	4.1	
			tetrahedral[d]	1.20610	1.21556	0.8	0.18739	0.19520	4.2	
$H_5B_3O_8^{2-}$ (conformer)	1c-2)		triangular	1.24034	1.24711	0.5	0.21538	0.22083	2.5	
			tetrahedral[e]	1.20327	1.21556	1.0	0.18504	0.19520	5.5	
			tetrahedral[f]	1.20585	1.21556	0.8	0.18718	0.19520	4.3	
$H_4B_4O_9^{2-}$	1d)	2:2	triangular	1.24025	1.24711	0.6	0.21531	0.22083	2.6	
			tetrahedral	1.20543	1.21556	0.8	0.18684	0.19520	4.5	
$H_4B_5O_{10}^-$	1e-1)	4:1	triangular	1.24447	1.24711	0.2	0.21871	0.22083	1.0	
			tetrahedral	1.20632	1.21556	0.8	0.18758	0.19520	4.1	
$H_4B_5O_{10}^-$ (conformer)	1e-2)		triangular	1.24279	1.24711	0.3	0.21736	0.22083	1.6	
			tetrahedral	1.20459	1.21556	0.9	0.18614	0.19520	4.9	
$H_6B_6O_{13}^{2-}$	1f)	3:3	triangular	1.24285	1.24711	0.3	0.21741	0.22083	1.6	
			tetrahedral	1.20492	1.21556	0.9	0.18642	0.19520	4.7	

[a] $(B - A) \times 100/A$. [b] $(B' - A') \times 100/A'$. [c] B1 in Fig. 1c-1). [d] B2 in Fig. 1c-1). [e] B1 in Fig. 1c-2). [f] B2 in Fig. 1c-2).

cases, the geometry was optimized and no negative frequency was calculated, but the energy of that structure was higher than the energy of the structure stated in the previous paragraph. Thus, the structures in Figs. 1a), 1b), 1c-1), 1d), 1e-1) and 1f) are quite probably, although not one hundred percent sure, at the global minima of the potential energy surfaces.

For the $H_5B_3O_8^{2-}$ and $H_4B_5O_{10}^-$ borate anions, conformers with higher energies (i.e., structures at local minima) depicted, respectively, in Figs. 1c-2) and 1e-2) are also considered in order to examine the effect of the structural change on the RPFR. The largest structural difference between Figs. 1c-1) and 1c-2) is that H1 is at the cis position to O1 in Fig. 1c-1), while H1 is cis to O2 in Fig. 1c-2). The energy of the c-2) structure is higher than that of c-1) only by 0.18 kJ/mol. The e-2) structure of the pentamer is higher in energy than the e-1) structure by 28.5 kJ/mol, about the energy of a typical hydrogen bond.

The values of RPFRs of the polymers at 25 °C in this work as well as those of monomers and dimers in the previous paper [5] are summarized in Table 1. The RPFRs for mono boron isotope substitutions calculated using (6) are listed as "exact" RPFRs in the fifth column of Table 1. It is observed here that, similarly to the case of the monomers, the values of the RPFRs of the polymers containing up to six boron atoms are smaller for the boron isotope substitutions at the tetrahedral sites than those at the triangular sites, showing that ^{11}B prefers the triangular site to the tetrahedral site in those polymers. This may be generalized to include polyboric acids and polyborate anions of any size.

The RPFR-values of the polymers approximated by (3) using those of the monomers are listed as "approximate" RPFR in the sixth column of Table 1. They agree quite well with the "exact" values within 1% errors (seventh column). This seemingly shows that the RPFRs of the polymers are well approximated by using additivity of the ln(RPFR)s (3). However, this should not be taken literally, because not the RPFR itself but the deviation of the RPFR from unity is physically important, as has been pointed out in [5]. The goodness of Approximation (3) should thus be estimated as the error of (RPFR –1) or, since the value of the RPFR is usually close to unity, on ln(RPFR), instead of RPFR itself. Exact and approximate ln(RPFR)-values are listed in the eighth and ninth columns of Table 1, respectively. The percent errors of the approximate ln(RPFR)-values are listed in the tenth column. A maximum deviation of about 5% is observed. One

Table 2. Equilibrium constants (K) of mono boron isotope exchanges between various boric acid and borate monomers and polymers at 25 °C[a,b]: $^{11}X + {}^{10}Y = {}^{10}X + {}^{11}Y$ $K = ([{}^{10}X]\,[{}^{11}Y])/([{}^{11}X]\,[{}^{10}Y])$.

X(tetrahedral site) \ Y(triangular site)	$B(OH)_3$	$H_4B_2O_5$	$H_5B_2O_6^-$	$H_3B_3O_6$	$H_4B_3O_7^-$	$H_5B_3O_8^{2-}$	$H_4B_4O_9^{2-}$	$H_4B_5O_{10}^-$	$H_6B_6O_{13}^{2-}$
$B(OH)_4^-$	1.0260	1.0235	1.0207	1.0222	1.0236	1.0206	1.0203	1.0238	1.0225
		(+9.5)	(+20.2)	(+14.5)	(+9.1)	(+20.6)	(+21.7)	(+8.4)	(+13.3)
$H_5B_2O_6^-$	1.0327	1.0302	1.0274	1.0289	1.0303	1.0273	1.0270	1.0305	1.0292
	(−25.4)	(−15.9)	(−5.3)	(−11.0)	(−16.3)	(−4.9)	(−3.8)	(−17.1)	(−12.1)
$H_6B_2O_7^{2-}$	1.0360	1.0336	1.0307	1.0322	1.0336	1.0306	1.0304	1.0338	1.0325
	(−37.8)	(−28.8)	(−17.8)	(−23.5)	(−28.8)	(−17.4)	(−16.7)	(−29.5)	(−24.6)
$H_4B_3O_7^-$	1.0300	1.0275	1.0247	1.0262	1.0276	1.0246	1.0243	1.0278	1.0265
	(−15.2)	(−5.7)	(+4.9)	(−0.8)	(−6.1)	(+5.3)	(+6.5)	(−6.8)	(−2.0)
$H_5B_3O_8^{2-}$ [c]	1.0338	1.0314	1.0285	1.0300	1.0314	1.0284	1.0281	1.0316	1.0303
	(−29.5)	(−20.5)	(−9.5)	(−15.2)	(−20.5)	(−9.1)	(−8.0)	(−21.2)	(−16.3)
$H_5B_3O_8^{2-}$ [d]	1.0340	1.0315	1.0287	1.0302	1.0316	1.0286	1.0283	1.0318	1.0305
	(−30.3)	(−20.8)	(−10.2)	(−15.9)	(−21.2)	(−9.9)	(−8.7)	(−22.0)	(−17.1)
$H_4B_4O_9^{2-}$	1.0346	1.0321	1.0293	1.0308	1.0322	1.0291	1.0289	1.0324	1.0310
	(−32.5)	(−23.1)	(−12.5)	(−18.2)	(−23.5)	(−11.8)	(−11.0)	(−24.2)	(−18.9)
$H_4B_5O_{10}^-$	1.0338	1.0314	1.0285	1.0300	1.0314	1.0284	1.0281	1.0316	1.0303
	(−29.5)	(−20.5)	(−9.5)	(−15.2)	(−20.5)	(−9.1)	(−8.0)	(−21.2)	(−16.3)
$H_6B_6O_{13}^{2-}$	1.0350	1.0325	1.0297	1.0312	1.0326	1.0296	1.0293	1.0328	1.0315
	(−34.0)	(−24.6)	(−14.0)	(−19.7)	(−25.0)	(−13.6)	(−12.5)	(−25.7)	(−20.8)

[a] the upper row; the K value. [b] the lower row (in the parenthesis); percent deviation of the $\ln K_B$-value of Reaction (1) from the exact value. [c] B1 in Fig. 1c-1). [d] B2 in Fig. 1c-1).

may expect similar levels of deviations for larger polymers. The judgement on whether this deviation is acceptable or too large will depend on the accuracy of the approximation one requires.

RPFR-values of higher energy conformers of $H_5B_3O_8^{2-}$ and $H_4B_5O_{10}^-$ are also listed in Table 1. For both the polymers, the RPFRs of the more stable structures (Figs. 1c-1 and 1e-1) are larger than those of the less stable ones (Figs. 1c-2 and 1e-2) for substitutions both at tetrahedral and triangular sites. Although it is not certain whether this observation can be generalized, these results are reasonable and understandable; the curvature at the bottom of a deeper potential energy curve is usually larger than that of a shallower potential energy curve.

The equilibrium constants (K) of the boron isotope exchange reactions between boron in a BO_3 triangle of one species and boron in a BO_4 tetrahedron of another at 25 °C are summarized in Table 2. The K-value ranges from 1.0203 for the boron isotope exchange reaction of

$$^{11}B(OH)_4^- + H_4{}^{10}B^{11}B_3O_9^{2-} = {}^{10}B(OH)_4^- + H_4{}^{11}B_4O_9^{2-}$$

to 1.0360 for the reaction of

$$H_6{}^{11}B_2O_7^{2-} + {}^{10}B(OH)_3 = H_6{}^{10}B^{11}BO_7^{2-} + {}^{11}B(OH)_3\,.$$

One can expect that the range of the K-value will not be enlarged substantially even if larger polymers are included in the tabulation. All the exchange reactions of Table 2 do not occur in real systems. Table 2 thus gives a rough estimate on how polymer formations can affect the boron isotope fractionation in a system of concern. In the parentheses shown are the percent deviations from the $\ln K_B$-value for Reaction (1), which are nothing but the percent errors obtained when Approximation (3) is used for RPFR calculations of polymers. A largest deviation of about 40% is observed in Table 2, indicating that this much deviation can occur as a result of polymer formations.

As mentioned earlier, the vibrational analysis gave a K_B-value of 1.0194 at 25 °C. Experimentally, some conflicting results were presented concerning the K_B-value. In the field of boron isotope geochemistry, boron isotope fractionations between seawater and natural carbonates reported by Hemming and Hanson [13] and by Gaillardet and Allegre [14] were consistent with the K_B-value of 1.0194. Contrary to these, larger K_B-values were required to explain the boron isotope effects observed by Vengosh et al. [15] and by Palmer et al. [16]. For example, the results of Palmer et al. [16] indicated $K_B = 1.033$. In the field of boron isotope separation in aqueous systems, results indicating that the K_B-value should be larger than 1.0194 were also reported [17]. According to

the results of Table 2, the existence of polymeric boron species may elucidate the variation in boron isotope fractionation obtained experimentally.

4. Conclusions

To summarize, the following statements can be made: Geometries of polyboric acids and polyborate anions up to a hexamer were optimized at the HF/6-31G(d) level, and their RPFRs were evaluated exactly and approximately. Approximate RPFR-values by (3) agreed with exact RPFR-values within a margin of 1% error, which corresponds to a 5% error in ln(RPFR). The K values between two of various monomeric and dimeric boric acids and borate anions varied from 1.0203 to 1.0360 at 25 °C. The maximum percent deviation of an approximately evaluated K value from the exact value was about 38%, indicating the importance of accurate evaluations of the RPFRs of polymers. The present work may help to elucidate boron isotope fractionation obtained experimentally.

Acknowledgement

This study was financially supported in part by Japan Society for the Promotion of Science under the 1998–2000 Japan-China Scientific Cooperation Program.

[1] H. Kakihana, M. Kotaka, S. Satoh, M. Nomura, and M. Okamoto, Bull. Chem. Soc. Japan **50,**158 (1977).
[2] J. Bigeleisen and M. G. Mayer, J. Chem. Phys. **15,** 261 (1947).
[3] N. Ingri, Svensk Kemisk Tidskift **75,** 199 (1963).
[4] T. Oi, M. Nomura, M. Musashi, T. Ossaka, M. Okamoto, and H. Kakihana, Geochim. Cosmochim. Acta **53,** 3189 (1989).
[5] T. Oi, J. Nucl. Sci. Technol. **37,** 166 (2000).
[6] C. R. Peters and M. E. Milberg, Acta Cryst. **17,** 229 (1964).
[7] A. Dal Negro, J. M. M. Pozas, and L. Ungaretti, Amer. Mineral. **60,** 879 (1975).
[8] E. N. Kurkutova, I. M. Rumanova, and N. V. Belov, Sov. Phys. Dokl. **10,** 808 (1966).
[9] N. Morimoto, Mineral. J. (Japan) **2,** 1 (1956).
[10] S. Marlino and F. Sartori, Acta Cryst. **B28,** 3559 (1972).
[11] J. R. Clark, Amer. Mineral. **49,** 1549 (1964).
[12] Z. G. Zhang, M. B. Boisen, Jr., L. W. Finger, and G. V. Gibbs, Amer. Mineral. **70,** 1238 (1985).
[13] N. G. Hemming and G. N. Hanson, Geochim. Cosmochim. Acta **56,** 537 (1992).
[14] J. Gaillardet and C. J. Allegre, Earth Planet. Sci. Lett. **136,** 665 (1995).
[15] A. Vengosh, Y. Kolodny, A. Starinsky, A. R. Chivas, and M. T. McCulloch, Geochim. Cosmochim. Acta **55,** 2901 (1991).
[16] M. R. Palmer, A. J. Spivack, and J. M. Edmond, Geochim. Cosmochim. Acta **51,** 2319 (1987).
[17] M. M. Urgell, J. Iglesias, J. Casas, J. M. Saviron, and M. Quintanilla, Third UN Int'l. Conf. on Peaceful Uses of Atomic Energy, A/CONF.28/P/491, Spain 1964.