J. Am. Chem. Soc. **1986**, *108*, 5683-5689 5683

saturated alkanes. It should be noted that in condensed phase studies at Pd(II) centers, carbonium ion intermediates have been previously proposed.[46] For example, oligomerization and isomerization of olefins by $Pd(CH_3CN)_4^{2+}$ have been proposed to proceed via carbonium ion intermediates.

Conclusion

The reactivities of Ru^+, Rh^+, and Pd^+ are shown to be remarkably different from their first-row congeners. Whereas Co^+ and Ni^+ dehydrogenate alkanes by a 1,4-elimination mechanism, the corresponding second-row metal ions appear to effect 1,2-dehydrogenations. The reactions of Ru^+ and Rh^+ are characterized by C–H insertions and facile β-H transfers. Unlike their first-row congeners, β-methyl transfers, and C–C insertions do not occur for Ru^+ and Rh^+. Furthermore, the barriers for reductive elimination of RH and H_2 from Rh–(olefin)$^+$ complexes are quite small, in contrast to those proposed previously for Co^+. This may result in high internal excitation of the primary dehydrogenation products for Ru^+ and Rh^+ reactions. In this case, the products themselves may undergo an exothermic elimination of a second molecule of H_2, a process not observed for the first row group 8–10 metals ions. These differences in reactivity are proposed to be due to differences in the sizes and shapes of the bonding orbitals for the first- and second-row metal ions.

The mechanism by which alkanes are activated by Pd^+ is quite distinct from any other metal ion studied to date. It is proposed that the uniquely high Lewis acidity of Pd^+ results in a hydride abstraction mechanism for C–H bond activation.

Acknowledgment. This work was supported by the National Science Foundation under Grant CHE-8407857. M.I.M. is grateful to the Bantrell Foundation for a postdoctoral fellowship.

Registry No. Ru^+, 20019-76-5; Rh^+, 20561-59-5; Pd^+, 20561-55-1; CH_4, 74-82-8; C_2H_6, 74-84-0; C_3H_8, 74-98-6; *n*-C_4H_{10}, 106-97-8; *i*-C_4H_{10}, 75-28-5; *neo*-C_5H_{12}, 463-82-1; $RhC_2H_4^+$, 103639-31-2; $RhC_3H_6^+$, 103639-32-3.

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Gas-Phase Hydration Reactions of Protonated Alcohols. Energetics and Bulk Hydration of Cluster Ions

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Abstract: The gas-phase equilibria for hydration reactions of protonated methyl alcohol, ethyl alcohol, *n*-propyl alcohol, and isopropyl alcohol, $ROH_2^+(H_2O)_{n-1} + H_2O = ROH_2^+(H_2O)_n$, were measured with a pulsed electron beam mass spectrometer. van't Hoff plots of the equilibrium constants lead to $\Delta H°_{n-1,n}$ and $\Delta S°_{n-1,n}$ up to $n = 6$. While the proton affinities increase in the order methyl alcohol < ethyl alcohol < *n*-propyl alcohol < isopropyl alcohol, the stabilities of clusters $ROH_2^+(H_2O)_n$ toward dissociation increase in the reverse order, i.e., isopropyl alcohol < *n*-propyl alcohol < ethyl alcohol < methyl alcohol. The deprotonation from the base alcohol in the cluster $ROH_2^+(H_2O)_n$ was not observed up to $n = 6$ or 7. The acid-catalyzed dehydration of alcohols was not observed either. The stepwise sums of free energy changes $\Delta G°_{n-1,n}$ for gas-phase hydration reactions of protonated alcohols and other ions are compared with the free energies of hydration. The anomalous order of basicities for H_2O and aliphatic alcohols is suggested in the gas phase and in aqueous solution. The sums of $\Delta G°_{n-1,n}$ for halide ions converge more gradually to the ultimate free energies of hydration than those for other positive ions.

There has been growing interest in the nature of cluster ions formed by the attachment of molecules to ions. This is due to the fact that the results contribute to a deeper understanding of the forces between ions and neutral molecules.[1] Furthermore, research in the cluster chemistry is very valuable for the elucidation of phenomena occurring in the condensed phase.[2]

Equilibria for the ion–solvent molecule clustering reactions involving positive or negative ions can be measured in the gas phase. The van't Hoff plots of the equilibrium constants lead to the determination of thermochemical data $\Delta G°$, $\Delta H°$, and $\Delta S°$ for the stepwise addition of solvent molecules to the ion. The present work reports the gas-phase equilibria measurements of the hydration reactions of protonated methyl alcohol, ethyl alcohol, *n*-propyl alcohol, and isopropyl alcohol. The obtained thermochemical data give some insight for the elucidation of ion hydration in the condensed phase.

Experiental Section

The measurements were made with the pulsed electron beam high-pressure mass spectrometer which has been described previously.[3,4] Small amounts of CH_3OH, C_2H_5OH, *n*-C_3H_7OH, *i*-C_3H_7OH, and H_2O were introduced into ~4 Torr of CH_4 carrier gas through stainless steel capillaries. The pressure of alcohol was ≤1 mTorr. The equilibrium constants of hydration reactions of protonated alcohols were found to be independent on the change of H_2O pressure in the range 30–300 mTorr.

Results and Discussion

1. Hydration Reactions of Protonated Alcohols. Figure 1 shows the van't Hoff plots for the hydration reactions 1–4 of protonated methyl alcohol, ethyl alcohol, *n*-propyl alcohol, and isopropyl alcohol up to $n = 6$. The equilibrium constants below −40 °C

$$CH_3OH_2^+(H_2O)_{n-1} + H_2O = CH_3OH_2^+(H_2O)_n \quad (1)$$

$$C_2H_5OH_2^+(H_2O)_{n-1} + H_2O = C_2H_5OH_2^+(H_2O)_n \quad (2)$$

$$n\text{-}C_3H_7OH_2^+(H_2O)_{n-1} + H_2O = n\text{-}C_3H_7OH_2^+(H_2O)_n \quad (3)$$

$$i\text{-}C_3H_7OH_2^+(H_2O)_{n-1} + H_2O = i\text{-}C_3H_7OH_2^+(H_2O)_n \quad (4)$$

(i.e. 1000/T(K) < ~4.3) could not be measured due to the

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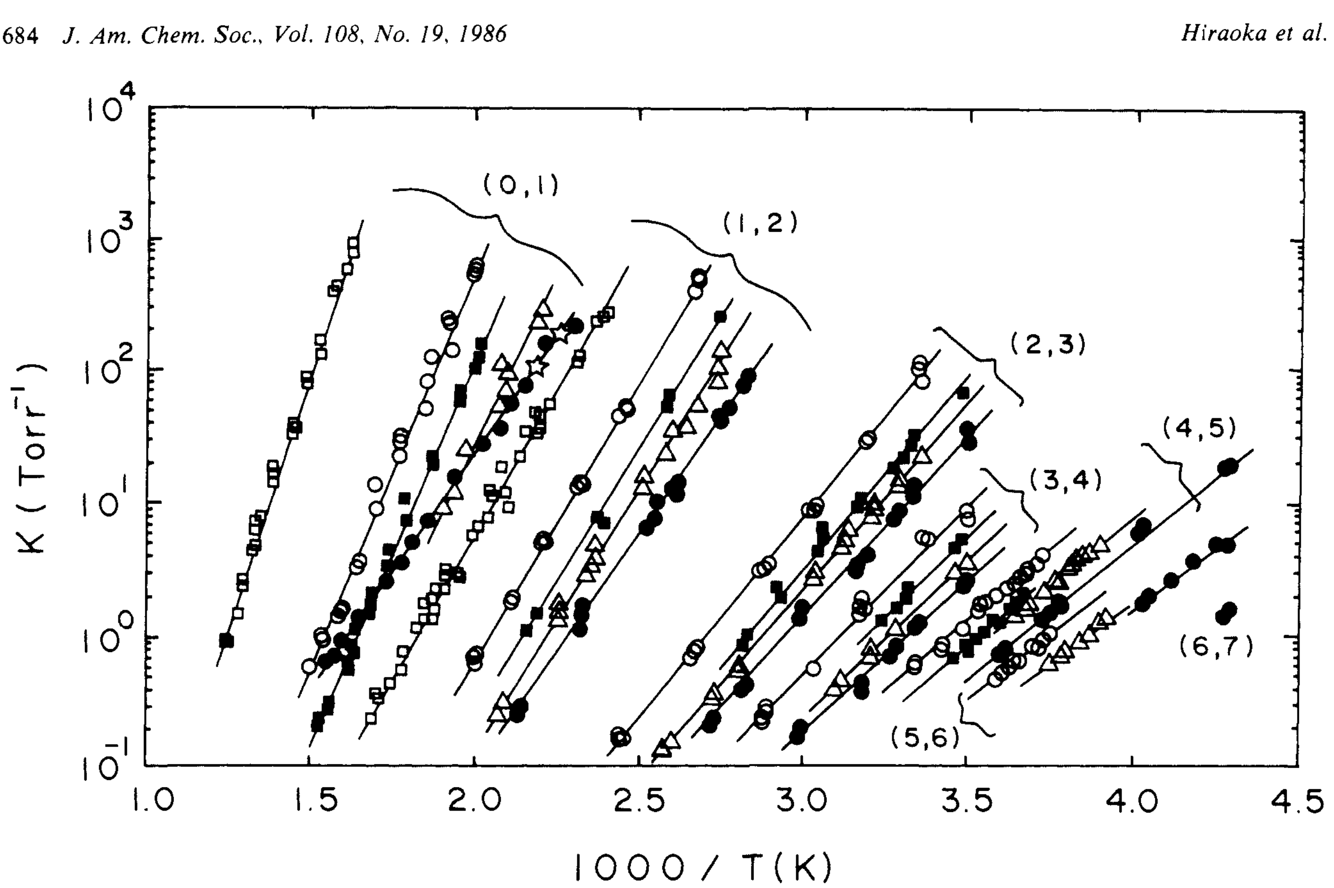

Figure 1. The van't Hoff plots for the hydration reactions of H_3O^+ and protonated alcohols: $ROH_2^+(H_2O)_{n-1} + H_2O = ROH_2^+(H_2O)_n$ (□); H_2O (○); CH_3OH (■); C_2H_5OH (△); n-C_3H_7OH (●); i-C_3H_7OH (☆); see text.

Table I. Experimentally Determined Enthalpy Changes $\Delta H°$ (kcal/mol) and Entropy Changes $-\Delta S°$ (cal/(mol·K)) for Reactions $ROH_2^+(H_2O)_{n-1} + H_2O = ROH_2^+(H_2O)_n$

ROH	H_2O		CH_3OH		C_2H_5OH		n-C_3H_7OH		i-C_3H_7OH	
n-1,n	$-\Delta H°$	$-\Delta S°$	$-\Delta H°$	$-\Delta S°$	$-\Delta H°$	$-\Delta S°$	$-\Delta H°$	$-\Delta S°$	$-\Delta H°$	$-\Delta S°$
0,1	35.0 31.6^a	30.2 24.3^a	27.6 25^b	29.4 23b	26.5 24^c	30.5 26^c	23.9	28.0	16.3	13.7
1,2	20.2 19.5a	23.6 21.9^a	19.8 21^b	27.3 28.9^b	18.7 19.2^c	26.9 28^c	17.9	26.3	16.4	24.1
2,3	17.9^a	28.4^a	14.1 14.8^b	25.1 25.9^b	13.4 14.2^c	24.7 26^c	13.0	24.4	12.5	23.6
3,4	12.7^a	23.4^a	11.6 11.6^b	23.0 22.1^b	11.3 12.5^c	22.8 26^c	11.0	22.9	10.5	21.5
4,5	11.6^a	25.0^a	9.8 9.1^b	20.7 18.5^b	9.7 *c,d*	20.9 *c,d*	9.5	20.7	9.6	21.9
5,6	10.7^a	26.1a	8.9 9.4^b	20.2 22.2^b	*d* 13.1^c	*d* 28^c	8.8	20.8	8.8	21.3
6,7			8.9^b						≃7.9	(20)

[a] Reference 6. [b] Reference 7. [c] Reference 8. [d] Equilibrium not observed. [e] Reference 9. [f] The value assumed.

condensation of water vapor on the wall of the ion source. In Figure 1 are also shown the van't Hoff plots of proton hydration reactions 5 for $n = 1$ and 2, which were measured in the separate experiments.[5] The thermochemical data obtained from these van't Hoff plots are summarized in Table I.

$$H_3O^+(H_2O)_{n-1} + H_2O = H_3O^+(H_2O)_n \qquad (5)$$

In the measurements of equilibria for reaction 3 with $n = 1$, the van't Hoff plots were found to deviate from the straight line above ~300 °C (i.e., $1000/T \leq 1.75$). It was also found that the measured van't Hoff plots almost coincide with those for reaction 4 with $n = 1$ in the temperature range of 300–340 °C. Under the present experimental conditions, the i-$C_3H_7^+$ ion which may be mainly produced from the unimolecular decomposition of protonated n-propyl alcohol was observed as one of the major ions. We think that the $C_3H_7OH_2^+$ ion observed at ≥300 °C may be more or less contaminated by i-$C_3H_7OH_2^+$ which is formed by reaction 6. We tried to increase the relative intensity of n-$C_3H_7OH_2^+$ by increasing the partial pressure of n-propyl alcohol.

$$i\text{-}C_3H_7^+ + H_2O \overset{M}{=} i\text{-}C_3H_7OH_2^+ \qquad (6)$$

However, when the pressure of n-propyl alcohol was increased, the relative intensity of dimer cation n-$C_3H_7OH_2^+$(n-C_3H_7OH) became so strong that the intensities of n-$C_3H_7OH_2^+$ and n-$C_3H_7OH_2^+(H_2O)$ ions were too weak to measure. Thus the measurements of van't Hoff plots for the clustering reaction 3 with

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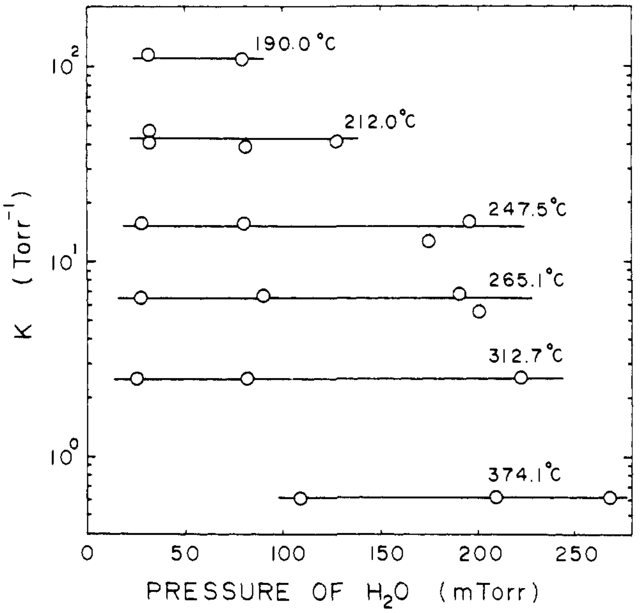

Figure 2. Some of the determinations of temperature and pressure dependences of the equilibrium constants for the reaction $i\text{-}C_3H_7OH_2^+ + H_2O = i\text{-}C_3H_7OH_2^+(H_2O)$.

$n = 1$ were limited in a rather narrow temperature range as shown in Figure 1.

When a known amount of H_2O was introduced into CH_4 carrier gas, major ions such as proton hydrates $H_3O^+(H_2O)_n$, $C_3H_7^+$, $C_3H_7OH_2^+$, and $C_3H_7OH_2^+(H_2O)$ were observed. Although the rate of reaction 6 was found to be too low to establish the equilibria of this reaction under the present experimental conditions, the equilibria between $C_3H_7OH_2^+$ and $C_3H_7OH_2^+(H_2O)$ could be observed. The obtained equilibrium constants are shown in Figure 1 as stars. They fit almost exactly to the van't Hoff plots for reaction 4 with $n = 1$. This result indicates that the associated complex of $i\text{-}C_3H_7^+$ and H_2O has the structure of the protonated isopropyl alcohol.

As shown in Figure 1, the obtained van't Hoff plot for reaction 4 with $n = 1$ is quite characteristic, namely, the slope of the van't Hoff plots is much less steep than those for reactions 1–3 with $n = 1$. The straight line leads to the thermochemical data, $-\Delta H°_{0,1} = 16.3$ kcal/mol, and $-\Delta S°_{0,1} = 13.7$ cal/(mol·K) (standard state 1 atm). The obtained $-\Delta H°_{0,1}$ is even smaller than the value of $-\Delta H°_{1,2}$ (see Table I), and the entropy change $-\Delta S°_{0,1}$ is abnormally small. These results are puzzling because, in the ion clustering reactions, the values of $-\Delta H°_{n-1,n}$ generally decrease with an increase of n due to the less availability of net charge in the cluster ion for the outermost ligand. During the experiments, we suspected that we had some problems in the measurements. We repeated the measurements under various experimental conditions. The obtained equilibrium constants were found to be independent on the change of pressures of isopropyl alcohol, methane carrier gas, and water vapor. As an example, some of the determinations of the temperature and H_2O pressure dependence of the equilibrium constants are shown in Figure 2.

It was found that the $i\text{-}C_3H_7OH_2^+$ ion decomposes above ~250 °C and its decay becomes faster at higher temperature. However, the establishment of the equilibrium for reaction 4 with $n = 1$ was much faster than the decay rate of the $i\text{-}C_3H_7OH_2^+$ ion even at the highest temperature measured (374 °C). The obtained anomalous data do not seem to be caused by an artifact such as ion decomposition. There seem to be some reasons which make the values of $-\Delta H°_{0,1}$ and $-\Delta S°_{0,1}$ of reaction 4 relatively small.

The bond energies of $R^+\cdots OH_2$ for the protonated alcohols can be estimated by using the heats of formation of carbonium ions R^+[11] and the proton affinities of alcohols ROH.[12] The

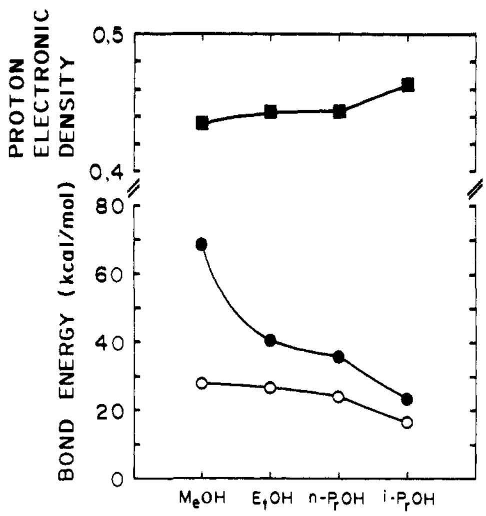

Figure 3. (○) Bond energies (kcal/mol) of singly hydrated protonated alcohols $ROH_2^+\cdots OH_2$ for ROH = CH_3OH, C_2H_5OH, $n\text{-}C_3H_7OH$, and $i\text{-}C_3H_7OH$, obtained in the present experiments. (●) Bond energies (kcal/mol) of hydrated carbonium ions, $CH_3^+\cdots OH_2$, $C_2H_5^+\cdots OH_2$, $n\text{-}C_3H_7^+\cdots OH_2$, and $i\text{-}C_3H_7^+\cdots OH_2$. (■) The electronic density on the protic hydrogens of protonated alcohols ROH_2^+ computed with MO of the 4-31G basis set (ref 5).

estimated values are 68.4, 40.4, 35.8, and 23.8 kcal/mol for $CH_3^+\cdots OH_2$, $C_2H_5^+\cdots OH_2$, $n\text{-}C_3H_7^+\cdots OH_2$, and $i\text{-}C_3H_7^+\cdots OH_2$, respectively. The bond energy of $i\text{-}C_3H_7^+\cdots OH_2$ is much smaller than those of other $R^+\cdots OH_2$ (see Figure 3). This suggests that on the protonation of isopropyl alcohol, the electron flow from $i\text{-}C_3H_7$ to OH_2 considerably neutralizes the protic hydrogens, and the positive charge is dispersed in the $i\text{-}C_3H_7^+$, i.e., the protonated isopropyl alcohol may be regarded as the complex in which $i\text{-}C_3H_7^+$ is interacting with OH_2. This is at least qualitatively verified by the result of ab initio MO calculations[5] that, as shown in Figure 3, the electronic density on the protic hydrogens of $i\text{-}C_3H_7OH_2^+$ shows a sudden increase compared to other protonated alcohols.

At the first stage of the interaction of $i\text{-}C_3H_7OH_2^+$ with H_2O, the incoming H_2O molecule interacts only weakly with the protic hydrogen atom of $i\text{-}C_3H_7OH_2^+$, because the electron density on the protic hydrogens in $i\text{-}C_3H_7^+\cdots OH_2$ is rather high.[5] However, as the ligand H_2O comes closer to the protic hydrogen atom in the cluster,

$$i\text{-}C_3H_7^+\cdots\overset{H}{O}\text{—}H\leftarrow OH_2$$

the electronic charge in the OH_2 of $i\text{-}C_3H_7^+\cdots OH_2$ will flow back to the $i\text{-}C_3H_7$ in order to strengthen the electrostatic interaction between the ligand OH_2 and the protic hydrogen atom. In the equilibrium configuration of the cluster, the positive charge of $i\text{-}C_3H_7OH_2^+$ may be more localized on the protic hydrogens, and a strong bond in the cluster $i\text{-}C_3H_7OH_2^+\cdots OH_2$ may be formed. This may be regarded as an inhibition of the charge delocalization by solvation. The net enthalpy change $-\Delta H°_{0,1}$ of reaction 4 results in the rather low value because the energy stabilization caused by the strong bond formation between $i\text{-}C_3H_7OH_2^+$ and OH_2 is partly cancelled by the energy required for the electron redistribution in the ion $i\text{-}C_3H_7^+\cdots OH_2$ during the cluster formation. Since the positive charge density in the protic hydrogens of $i\text{-}C_3H_7OH_2^+$ in the cluster $i\text{-}C_3H_7OH_2^+\cdots OH_2$ is high, the value of $-\Delta H°_{1,2}$ for reaction 4 can be reasonably high.

The small value of $-\Delta S°_{0,1}$ for reaction 4 is hard to interpret. As already described previously, the protonated isopropyl alcohol may be regarded as the complex of $i\text{-}C_3H_7^+$ interacting with OH_2. Since the positive charge is dispersed in $i\text{-}C_3H_7$, the electron density of the hydrogen atoms in two methyls may be somewhat low. The

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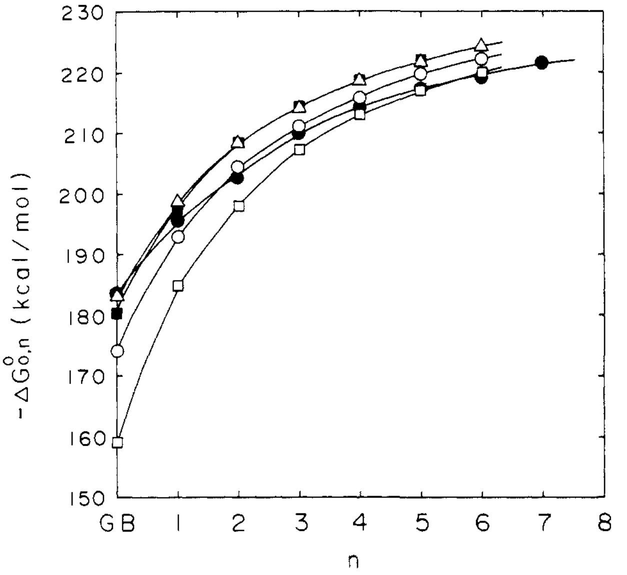
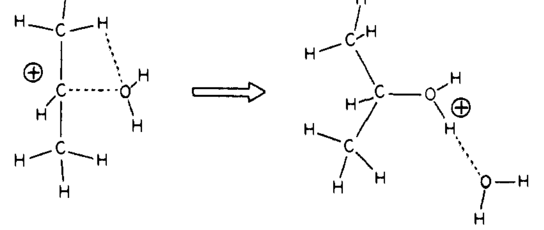


Figure 4. The n dependence of the stepwise free energy change $-\sum_{n=0}^{n=n}\Delta G_{n-1,n}$ for the hydration reaction $ROH_2^+(H_2O)_{n-1} + H_2O = ROH_2^+(H_2O)_n$: (□) H_2O; (○) CH_3OH; (■) C_2H_5OH; (△) n-C_3H_7OH; (●) i-C_3H_7OH. The value with $n = 0$ represents the gas phase basicity of the base.

negatively charged oxygen atom may experience the electrostatic attraction with a hydrogen atom in methyl. In such an intra-



molecular interaction, the free internal rotation of methyl may be more or less restricted. Besides, the distances between hydrogen atoms in methyl and OH_2 may be close enough that the internal rotation of methyls and OH_2 are also restricted, However, when the cluster i-$C_3H_7OH_2^+$- - -OH_2 is formed, the electron redistribution neutralizes i-C_3H_7 to some extent and the secondary carbon restores the sp^3 hybridization which may largely moderate the hindrance of the internal rotation of two methyls and OH_2 in i-$C_3H_7OH_2^+$. This may partly explain the less negative entropy change for reaction 4 with $n = 1$.

As shown in Figure 1 and Table I, stabilities of clusters $ROH_2^+(H_2O)_n$ toward dissociation increase in the order isopropyl alcohol < n-propyl alcohol < ethyl alcohol < methyl alcohol < H_2O. The order is opposite to the proton affinities of these compounds. The larger proton affinity means that the positive charge is more delocalized in the protonated species. This makes the electrostatic interaction between the protonated species and the ligand H_2O molecules weaker. This tendency is particularly evident for small n. With increase of n, $-\Delta H^\circ_{n-1,n}$ for reactions 1-5 are seen to become progressively similar.

It has been recognized that the gas-phase basicity of NH_3 and methylamines varies according to $NH_3 < CH_3NH_2 < (CH_3)_2NH < (CH_3)_3N$, while in aqueous solution the order is $NH_3 < CH_3NH_2 < (CH_3)_2NH > (CH_3)N$. The anomalous order of amines in aqueous solution is now known to be due to solvation. The gas-phase basicity order of H_2O and the aliphatic alcohols is $H_2O < CH_3OH < C_2H_5OH <$ n-$C_3H_7OH <$ i-C_3H_7OH. To the authors' knowledge, the basicity order of aliphatic alcohols in aqueous solution has not been determined yet. Figure 4 shows the n dependence of sums of the stepwise free energy changes $-\sum_{n=0}^{n=n}\Delta G^\circ_{n-1,n}$ for hydration reactions 1-5. The value with $n = 0$ represents the gas-phase basicity (GB) of the base.[12] The standard free energy changes $\Delta G^\circ_{n-1,n}$ are calculated from $\Delta H^\circ_{n-1,n}$ and $\Delta S^\circ_{n-1,n}$ shown in Table I. Although isopropyl alcohol is most basic in the gas phase, the value of $-\sum_{n=0}^{n=6}G^\circ_{n-1,n}$ for isopropyl alcohol is smallest compared to those for H_2O and other aliphatic alcohols. Recently Meot-Ner has pointed out that the experimentally observed fourfold specific relative hydration enthalpies simulate closely the relative bulk hydration enthalpies for most onium ions.[7] If one assumes that the rule predicted by Meot-Ner holds for H_2O and aliphatic alcohols and the entropy changes for reactions 1-5 with $n \geq 7$ are similar, the basicity order in aqueous solution may be predicted by the values of $-\sum_{n=0}^{n=6}G^\circ_{n-1,n}$, i.e., the order is i-$C_3H_7OH < H_2O < CH_3OH < C_2H_2OH \approx$ n-C_3H_7OH. It seems likely that there is also an anomalous order of aliphatic alcohol basicities in aqueous solution as is the case of aliphatic amines.

2. Acid-Catalyzed Dehydration of Alcohols. Hiraoka and Kebarle investigated the condensation reactions involving carbonium ions and Lewis bases in the gas phase.[10] They observed that the reaction of protonated *tert*-butyl alcohol with H_2O leads to the formation of isobutene, i.e., reaction 7. This reaction is

$$t\text{-}C_4H_9OH_2^+ + H_2O = H_3O^+(H_2O) + i\text{-}C_4H_8 \quad (7)$$

analogous to acid-catalyzed dehydration of alcohols in solution. It is of interest to investigate whether such reactions could be observed for lower alcohols such as ethyl alcohol and propyl alcohol.

In contrast to the clustering reactions of protonated *tert*-butyl alcohol with H_2O,[10] the equilibria were observed for reactions 1-4 with all n measured, and no sign for the occurrence of the acid-catalyzed dehydration reactions could be detected for ethyl alcohol, n-propyl alcohol, and isopropyl alcohol. The enthalpy changes for reactions 8-10 and 7 are -2.3, -2.1, 1.9, and 8.2 kcal/mol,

$$C_2H_5OH_2^+ + H_2O = H_3O^+(H_2O) + C_2H_4 \quad (8)$$

$$n\text{-}C_3H_7OH_2^+ + H_2O = H_3O^+(H_2O) + C_3H_6 \quad (9)$$

$$i\text{-}C_3H_7OH_2^+ + H_2O = H_3O^+(H_2O) + C_3H_6 \quad (10)$$

respectively. Only the most endothermic reaction (reaction 7) was observed.[10] The acid-catalyzed dehydration reaction (reaction 11) with $n = 2$ to 5 for ethyl alcohol, n-propyl alcohol, and isopropyl alcohol are more endothermic than those with $n = 1$.

$$ROH_2^+(H_2O)_{n-1} + H_2O = H_3O^+(H_2O)_n + (R\text{-}H) \quad (11)$$

For instance, the enthalpy changes of reaction 11 with $n = 5$ for ethyl alcohol, n-propyl alcohol, and isopropyl alcohol are 5.2, 2.4, and 2.9 kcal/mol, respectively. This is due to the fact that the bond energies of the cluster ions $H_3O^+(H_2O)_n$ are smaller than those of $ROH_2^+(H_2O)_{n-1}$ for small n (see Table I). It is known that the acid-catalyzed dehydration reactions occur in solution for ethyl alcohol and higher alcohols.[13] It seems likely that the acid-catalyzed dehydration reactions are affected not much by the amounts of exothermicity but by the energy required for the electron redistribution and hydrogen atom migration in the intermediated complex $[ROH_2^+$- - -$OH_2]^*$.

3. Does the Structural Isomerization of the Cluster Ions $ROH_2^+(H_2O)_n \rightarrow H_3O^+(H_2O)_{n-1}ROH$ Occur? Sensharma and Kebarle measured the hydration reaction 2 in the gas phase.[8] They found that the equilibrium for reaction 2 with $n = 5$ was not established. They also found that the binding energies pass through a minimum (see Table I). Beyond the minimum, the binding energies become similar to those for proton hydrates $H_3O^+(H_2O)_n$. They suggested that these results derive from the expulsion of the C_2H_5OH to the periphery of the cluster $H_3O^+(H_2O)_{n-1}C_2H_5OH$, i.e., the structural isomerization reaction (reaction 12) of the cluster ion $C_2H_5OH^+(H_2O)_n$. The sequence

$$C_2H_5OH_2^+(H_2O)_n \rightarrow H_3O^+(H_2O)_{n-1}C_2H_5OH \quad (12)$$

of reaction 12 suggested by Sensharma and Kebarle is shown in

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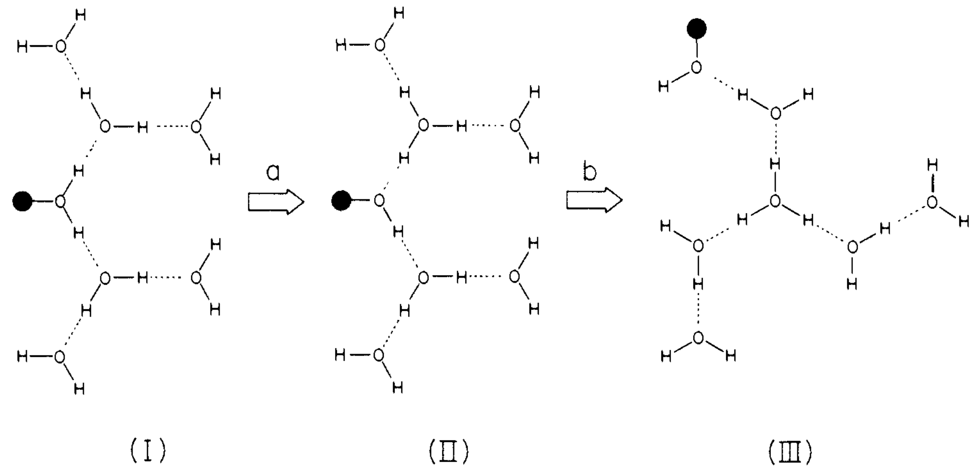

Figure 5. The sequence of the structural isomerization reaction of the cluster ion $ROH_2^+(H_2O)_6$. ● represents alkyl.

Figure 5 for $n = 6$. It is puzzling that the enthalpy change $-\Delta H_{5,6}$ for reaction 2 measured by Sensharma is larger than that for reaction 5 by 2.4 kcal/mol (see Table I). If the isomerization reaction (reaction 12) with $n = 5$ really produced the species III shown in Figure 5, the binding energy of this species should be weaker than $H_3O^+(H_2O)_6$ because the basicity of the ligand C_2H_5OH is much larger than that of H_2O, and the positive charge available for the 5th H_2O molecule in the cluster $H_3O^+(H_2O)_5(C_2H_5OH)$ is expected to be less than that for the 6th H_2O molecule in the cluster $H_3O^+(H_2O)_6$. In our measurements, the equilibria for reaction 2 with $n = 5$ could be observed. We think that Sensharma failed the observation of equilibria for reaction 2 with $n = 5$ due to the presence of impurity ion whose m/z is equal to that of $C_2H_5OH_2^+(H_2O)_5$.

We could not observe the equilibria for reaction 2 with $n = 6$. The ion whose m/z (155) corresponds to that of $C_2H_5OH_2^+(H_2O)_6$ decays more gradually than $C_2H_5OH_2^+(H_2O)_5$. This result may be interpreted as the occurrence of the structural isomerization reaction of the cluster $C_2H_5OH_2^+(H_2O)_6$ as shown in Figure 5. However, the ion with m/z 155 was also detected in the experiments of methyl alcohol and propyl alcohol as impurity ion. Thus we believe that the failure of the observation of the equilibria for reaction 2 with $n = 6$ is due to the impurity contained in the used alcohol samples.

The enthalpy and free energy changes for the cluster isomerization reactions 13 may be estimated from the thermochemical

$$ROH_2^+(H_2O)_n \rightarrow H_3O^+(H_2O)_{n-1}(ROH) \qquad (13)$$

data obtained in this experiment. For instance, the enthalpy changes (and free energy changes) for reaction 13 with $n = 5$ are estimated to be 0.9 (2.2), 4.2 (4.9), 2.2 (4.4), and -7.4 (0.1) kcal/mol for methyl alcohol, ethyl alcohol, *n*-propyl alcohol, and isopropyl alcohol, respectively. Here, the enthalpy and free energy changes for reactions 14 and 15 are assumed to be the same. The

$$H_3O^+(H_2O)_4 + H_2O = H_3O^+(H_2O)_5 \qquad (14)$$

$$H_3O^+(H_2O)_4 + ROH = H_3O^+(H_2O)_4(ROH) \qquad (15)$$

estimated free energy changes for reaction 13 with $n = 5$ are positive for all alcohols. Besides, reaction 13 with small n may experience a considerable amount of entropy barrier during the ligand reorganization as shown in Figure 5. Thus the cluster isomerization reactions seem unfavorable in the gas phase.

Similar results have been obtained by Kebarle and co-workers.[14] They observed the ions in irradiated water–methyl alcohol vapor mixtures. They found that the principal species are clusters $(CH_3OH)_m(H_2O)_nH^+$ and methyl alcohol is taken up preferentially in clusters of small size. Stace and shukla observed also the similar effects following the electron-impact ionization of neutral mixed clusters composed of water and alcohol molecules in a molecular beam.[15] Their results show that in $\{(ROH)_n \cdot H_2O\}H^+$ clusters the alcohol molecules are preferentially attached to the proton up to $n = 9$ for methyl alcohol and $n = 10$ for ethyl alcohol. It seems likely that the proton is better solvated by alcohol than water molecules for small size clusters.

The enthalpy changes for reaction 13 in water solution ($n \rightarrow \infty$) may be calculated from the proton affinities of free bases[12] and heats of hydration of free bases and those of protonated bases. With use of the heats of hydration of H_3O^+, $CH_3OH_2^+$, and $C_2H_5OH_2^+$ determined by Taft[16] (the data for *n*-propyl alcohol and isopropyl alcohol are not available), the enthalpy changes for reaction 13 in water solution are obtained to be 0.9 and 7.5 kcal/mol for methyl alcohol and ethyl alcohol, respectively. These reactions are endothermic. Similar procedures give the free energy changes for the same reactions as -1.1 and 0.1 kcal/mol for methyl alcohol and ethyl alcohol, respectively. Since the estimated free energy changes are close to zero or negative and the entropy barrier is considered to be much smaller in solution (reorganization of ligands as shown in Figure 3 is not necessary), reaction 13 in solution may be much more favorable than gas-phase reactions (for small n).

4. Stepwise and Bulk Hydration of Protonated Bases, Alkali Ions, and Halide Ions. In this section, systematic examination of gas-phase hydration and single ion enthalpies and free energies of solution in water will be given.

The stepwise hydration enthalpies $\Delta H^\circ_{n-1,n}$ and the heats of hydration ΔH°_s or stepwise hydration free energies $\Delta G^\circ_{n-1,n}$ and free energies of hydration ΔG°_s are related as[17,18] with N arbitrarily

$$\Delta H^\circ_s = \sum_{n=1}^{n=N} \Delta H^\circ_{n-1,n}(\text{ion}(H_2O)_n) - \sum_{n=1}^{n=N} \Delta H^\circ_{n-1,n}(H_2O)_n \qquad (16)$$

$$\Delta G^\circ_s = \sum_{n=1}^{n=N} \Delta G^\circ_{n-1,n}(\text{ion}(H_2O)_n) - \sum_{n=1}^{n=N} \Delta G^\circ_{n-1,n}(H_2O)_n \qquad (17)$$

large. The values of $\Delta H^\circ_{n-1,n}(\text{ion}(H_2O)_n)$ and $\Delta H^\circ_{n-1,n}(H_2O)_n$ or $\Delta G^\circ_{n-1,n}(\text{ion}(H_2O)_n)$ and $\Delta G^\circ_{n-1,n}(H_2O)_n$ converge at $n = N$.

Kebarle and co-workers found that a rapid convergence was obtained when the different energetics of the clusters around two ions are considered.[21] For example, the values of $\{\Delta G^\circ_{0,n}(X^-) - \Delta G^\circ_{0,n}(M^+)\}$ were found to converge to the single ion solvation

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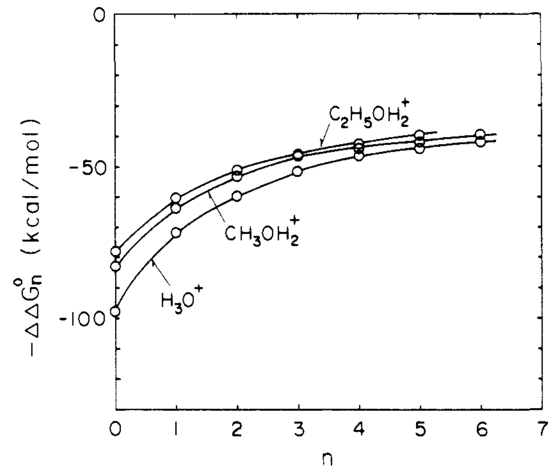

Figure 6. The n dependence of the value of $-\Delta\Delta G^\circ_n = [\Delta G^\circ_{0,n}(\text{ion-}(H_2O)_n) - \Delta G^\circ_{0,n}(H_2O)_n]$ for the protonated base. The value of $-\Delta\Delta G^\circ_n$ with $n = 0$ is taken as the value of the free energy of hydration ΔG°_s of the protonated base.

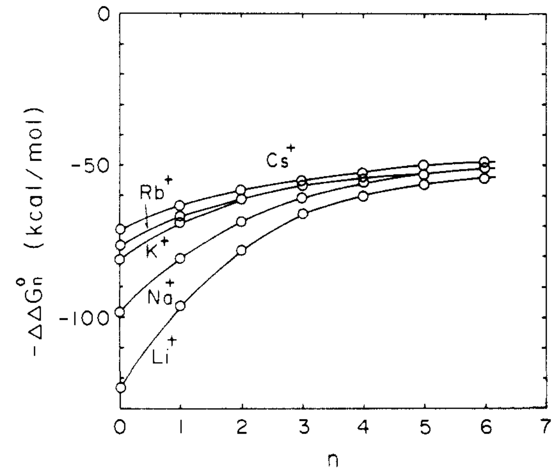

Figure 7. The n dependence of the value of $-\Delta\Delta G^\circ_n = [G^\circ_{0,n}(\text{ion}(H_2O)_n) - \Delta G^\circ_{0,n}(H_2O)_n]$ for the alkali ion. The value of $-\Delta\Delta G^\circ_n$ with $n = 0$ is taken as the value of the free energy of hydration ΔG°_s of the alkali ion.

difference $\{\Delta G^\circ_s(X^-) - \Delta G^\circ_s(M^+)\}$ for values of n as low as $n = 5$, where X^- and M^+ represent halide and alkali ions, respectively. Measurements of $\Delta H^\circ_{n-1,n}(\text{ion}(H_2O)_n)$ and $\Delta G_{n-1,n}(\text{ion}(H_2O)_n)$ are restricted to rather low values of n ($n \leq 10$) due to the condensation of solvent vapor on the wall of the reaction chamber. In this section, relationships between $\Delta G^\circ_{0,n}$ (or $\Delta H^\circ_{0,n}$) and ΔG°_s (or ΔH°_s) are studied on the ground of eq 16 and 17 with use of the presently available experimental $\Delta H^\circ_{n-1,n}$ and $\Delta G^\circ_{n-1,n}$ values.

Unfortunately not much thermochemical data are available for neutral water clusters. As a crude approximation, one may assume the enthalpy and entropy changes of reaction 18, as

$$(H_2O)_{n-1} + H_2O = (H_2O) \qquad (18)$$

$-{}^1/_2\Delta H^\circ_{\text{evap}}(\text{water})$ and -15 cal/(mol·K), respectively, for small n. With use of available $\Delta H^\circ_{\text{evap}}(\text{water}) = 10.5$ kcal/mol,[17] one obtains $\Delta G^\circ_{n-1,n}$ for reaction 18 as ca. -1 kcal/mol.

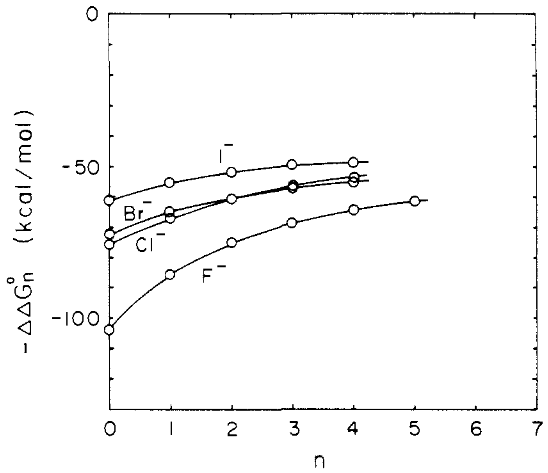

Figure 8. The n dependence of the value of $-\Delta\Delta G^\circ_n = [\Delta G^\circ_{0,n}(\text{ion-}(H_2O)_n) - \Delta G^\circ_{0,n}(H_2O)_n]$ for the halide ion. The value of $-\Delta\Delta G^\circ_n$ with $n = 0$ is taken as the value of the free energy of hydration ΔG°_s of the halide ion.

Figures 6–8 show the n dependence of the right-hand side of eq 17, $-[\Delta G^\circ_{0,n}(\text{ion}(H_2O)_n) - \Delta G^\circ_{0,n}(H_2O)_n]$ (denoted as $-\Delta\Delta G^\circ_n$) for protonated bases, alkali ions, and halide ions. Here, $\Delta G^\circ_{n-1,n}(H_2O)_n$ is assumed to be -1 kcal/mol. In these figures, the value of $-\Delta\Delta G^\circ_n$ with $n = 0$ is taken as the value of ΔG°_s for each ion. Since the value of the right-hand side of eq 17 converges to ΔG°_s with $n \to N$, all curves which start from the values ΔG°_s with $n = 0$ converge to the value 0 with an increase of n. Such a representation is useful because one can see how the stepwise hydration free energies $-\Delta\Delta G^\circ_n$ approach the ultimate free energies of hydration with an increase of n. Besides, the value of the ordinate for each curve gives the free energy released when the cluster ion$(H_2O)_n$ (with this n) is solvated into the liquid water (denoted as $-\Delta\Delta G^\circ_{n\to N}$).

It is clearly seen in Figure 6 that the values of $-\Delta\Delta G^\circ_n$ for H_3O^+, $CH_3OH_2^+$, and $C_2H_5OH_2^+$ converge each other already at $n = 6$, i.e., cluster ions $H_3O^+(H_2O)_6$, $CH_3OH_2^+(H_2O)_6$, and $C_2H_5OH_2^+(H_2O)_6$ release about the same free energies for the solvation with n from 7 to N. Similar findings also have been reported for the solvation of alkali ions, halide ions, and protonated bases.[7,19–23]

Figure 7 shows the n dependence of $-\Delta\Delta G^\circ_n$ for alkali ions.[19,24] The values of $-\Delta\Delta G^\circ_n$ also converge at $n = 6$, i.e., the values $-\Delta\Delta G^\circ_{6\to N}$ for these ions are almost independent of the kind of core alkali ions. This suggests that the charge of the core alkali ions is nearly equally shielded by about six water ligands, and the values $\Delta G^\circ_{n-1,n}$ for further solvation with $n > 6$ become more or less the same for $\mathrm{L_i^+} \sim \mathrm{C_s^+}$.

It is seen in Figures 6 and 7 that the $-\Delta\Delta G^\circ_n$ values with $n = 6$ for ROH_2^+ ions (including H_3O^+) are about 10 kcal/mol greater than those for alkali ions. This indicates that the ROH_2^+ ions are better hydrated than alkali ions with $n = 6$. One can see in Figures 6 and 7 that the ΔG°_s values (i.e., $-\Delta\Delta G^\circ_n$ with $n = 0$) for H_3O^+, $CH_3OH_2^+$, and $C_2H_5OH_2^+$ are about the same as those for Na^+, K^+, and Rb^+ ions, respectively. For these ion pairs, however, the increases in $-\Delta\Delta G^\circ_n$ with $n = 1$ are much greater for ROH_2^+ ions than for corresponding alkali ions. The increments of $-\Delta\Delta G^\circ_n$ for these ion pairs become more or less the same for $n \geq 2$. This indicates that ROH_2^+ ions are much more favorably solvated by the first H_2O molecule than alkali ions. This is due to the considerable covalent bond formation in the clusters $ROH_2^+(H_2O)$ which are absent in the clusters of alkali ions with an H_2O molecule.

As shown in Figure 6, the free energies of solvation ($-\Delta G^\circ_s$) are of the order $C_2H_5OH_2^+ < CH_3OH_2^+ < H_3O^+$, whereas the gas-phase basicities (ΔG°_g) of conjugate bases are of the order $H_2O < CH_3OH < C_2H_5OH$. This means that when the conjugate bases have lower gas-phase basicities, their conjugate acid ions have greater free energies of hydration ($-\Delta G^\circ_s$). This suggests that there is some correlation between the gas-phase basicities and free energies of hydration. Figure 9 shows a relationship between $-\Delta G^\circ_s$ for BH^+'s and ΔG°_g for B's where B's are alkyl substituted H_2O and NH_3. It appears that there is an approximate

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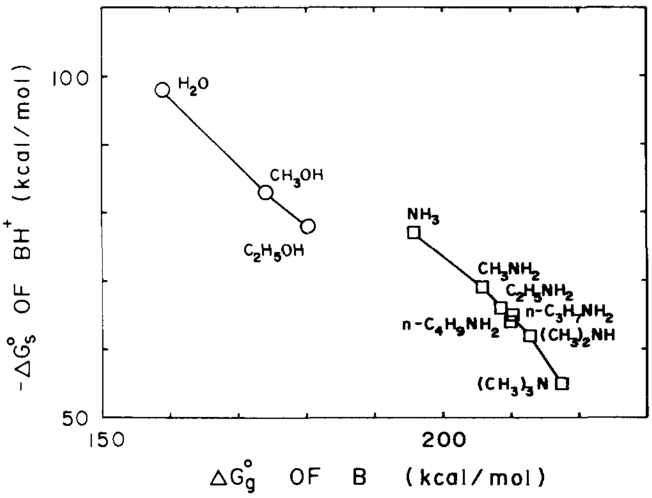

Figure 9. Relationship between the free energy of hydration $-\Delta G^\circ_s$ (kcal/mol) for BH^+'s and the gas-phase basicity ΔG°_g (kcal/mol) for B's where B's are alkyl substituted H_2O and NH_3.

linear relationship between $-\Delta G^\circ_s$ and ΔG°_g with a slope of about -1 for compounds of the same analogues, i.e.,

$$-\Delta G^\circ_s \cong -\Delta G^\circ_g + \text{constant} \qquad (19)$$

One may draw a first principle that the free energies of hydration for conjugate acid ions decrease almost linearly with an increase of gas-phase basicities for corresponding conjugate bases. We found that there is also a similar relationship between the enthalpies of hydration ($-\Delta H^\circ_s$) of conjugate acid ions and the gas-phase proton affinities (PA) of conjugate bases. Such a general rule may be useful because the free energies (or enthalpies) of transfer of conjugate acid ions from the gas phase to the dilute aqueous solutions can be roughly estimated from the available gas-phase basicities (or proton affinities)[12] of conjugate bases.

Figure 8 show the n dependence of $-\Delta\Delta G^\circ_n$ for halide ions.[20] Contrary to the case of alkali ions, the increase in the values of $-\Delta\Delta G^\circ_n$ with n is gradual and $-\Delta\Delta G^\circ_n$ for $F^- \sim I^-$ do not seem to converge at small n. This is mainly due to the large scatter of the values of $-\Delta G^\circ_s$ for $F^- \sim I^-$ ions and to the low bindng energies of the clusters $X^-(H_2O)_n$ with small n.[20] The low binding energies of halide ion hydrates may be partly due to the fact that, in the interaction of the negative ion with the ligand water molecules in the first shell, the quadrupole moment of water is repulsive when the dipole is attractive to a negative ion. The observed slow convergence of $-\Delta\Delta G^\circ_n$ for halide ions may be due to the ability of the water molecules to assume nonsymmetric positions in which only one of the hydrogen atoms touches the negative ion.[25]

In the hydrated ion, the H_2O molecules in the first shell are strongly polarized by the interaction with the core ion. The polarized H_2O molecules in the first shell would further polarize the H_2O molecules in the outer shell and thus enhance the stronger hydrogen bonding between them. This enhancement effect would extent from inner ligands to outer ligands in the shells surrounding the core ion and thus makes the value of $-\Delta G^\circ_s$ ultimately large.[26] This kind of enhancement effect may be envisaged more clearly by the donor–acceptor concept proposed by Gutmann, i.e., the spillover effect of the acceptor, and the pileup effect of the donor.[26,27] Such interactions are more effective for smaller ions. This may explain the larger values of $-\Delta\Delta G^\circ_{n\to N}$ for smaller halide ions as is observed in Figure 8.

In addition to the stepwise free energy changes $-\Delta\Delta G^\circ_n$ described above, the stepwise enthalpy changes $-\Delta\Delta H^\circ_n$ were also studied. The detailed description of the results obtained in the latter study will be omitted in the present discussion because they gave a similar results to the former. The only difference which should be noted is that the $-\Delta\Delta G^\circ_n$ values generally converge to 0 more gradually than the $-\Delta\Delta H^\circ_n$ values up to $n = 6$ or 7. This is due to the more negative entropy changes in the terms of $\Delta G_{n-1,n}(\text{ion}(H_2O)_n)$ than in those of $\Delta G_{n-1,n}(H_2O)_n$. Such an unfavorable entropy effect at small n would be greatly moderated at higher n where outer H_2O ligands belong to the structure breaking region outside the structure making one (region of immobilization of water molecules around the core ion).[28] There may be some oscillations in the values of $-\Delta\Delta G^\circ_n$ as well as $-\Delta\Delta H^\circ_n$ at higher n.

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Registry No. MeOH, 67-56-1; EtOH, 64-17-5; PrOH, 71-23-8; *i*-PrOH, 67-63-0; MeOH, 17836-08-7; EtOH, 18639-79-7; PrOH, 17456-36-9; *i*-PrOH, 18639-80-0.

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