require several configurations even for their basic description, and the simplest way to allow for the necessary flexibility is to use an averaged Fock hamiltonian. In this section, we provide more details about such calculations for the representative case of HfH^+, comparing the energy spectrum obtained by using different SCF and CI methods at the internuclear distance of 1.830 Å.

The expected low-lying states of HfH^+ are ${}^3\Delta(\sigma^1\delta^1)$, ${}^3\Pi(\pi^1\delta^1,\sigma^1\pi^1)$, ${}^3\Phi(\pi^1\delta^1)$, and ${}^3\Sigma^-(\pi^1\pi^1,\delta^1\delta^1)$, where the dominant configuration(s) of nonbonding electrons are given in parentheses but with the σ bond pair omitted for clarity. Orbitals based, say, on the GVB wave function for the ${}^3\Delta$ state would bias against all other states since they all involve a π orbital that would not be optimized self-consistently. In addition, the ${}^3\Pi$ and ${}^3\Sigma^-$ states require several types of reference configurations in the CI. Several averaged-field calculations were performed, and the resulting spectra are compared in Table IX at the CCCI/S and CCCI/D levels of CI. (As indicated, full CI (FCI) leads to essentially the same results.) Hamiltonian 1 consists of placing one electron in a σ orbital and 0.25 electron in each of the four remaining δ and π orbitals, while hamiltonian 2 involves 0.4 electron in each of the five orbitals. From Table X we see that the state splittings are not sensitive to the type of orbital since the variation (0.02 eV) is within the range of uncertainty due to using a truncated AO basis. It is encouraging that the calculational level used throughout this work (GVB orbitals adapted to each individual state plus CCCI/D) reproduces the full CI results to 0.01 eV. Lone-pair electron correlation effects in late transition metals might lead to less perfect matching, but the agreement is expected to remain satisfactory.

For some late metals, CCCI/S (which ignores the pair correlation of nonbonding electrons) leads to results significantly different from those obtained with CCCI/D. Thus, for IrH^+, CCCI/S leads to $R_e = 1.572$ Å and $D_e = 64.9$ kcal/mol, while CCCI/D leads to $R_e = 1.560$ Å and $D_e = 69.2$ kcal/mol.

D. Relativistic Effects and Spin-Orbit Coupling. The quantitative importance of relativistic effects grows very rapidly going down a column of the periodic table, and they are quite significant for the third transition row and beyond. The effective potentials[20,21] used in this study include the dominant relativistic terms (mass-velocity and Darwin) for the core electrons. Previous tests[20,21] and the present calculations of atomic splittings (Table I) and orbital sizes (Table II) indicate that these potentials are successful in taking into account the bulk of core relativistic effects. Thus Table II shows that both s and d orbitals undergo a spectacular tightening from La^+ to Hf^+, with the effect for the s orbital being larger than for d orbitals, as expected. On the other hand, for molecules formed from sixth-row atoms, valence spin-orbit effects are significant for states that are both orbitally degenerate *and* spin degenerate.[29] For such systems, our calculations represent the average over the spin-orbit sublevels. One can estimate these corrections by using the experimental spin-orbit splitting of the atom (M^+), which could be used to extract a spin-orbit coupling parameter $\{E_{JLS}(M^+) = \lambda[J(J+1) - L(L+1) - S(S+1)]\}$, which would be used as a perturbation, $\delta H = \lambda \hat{L}\cdot\hat{S}$ added to the normal electronic Hamiltonian to estimate the spin-orbit coupling of the molecular state (MH^+). Unfortunately, for the third row atoms the experimental atomic spectra are generally quite incomplete, and we have not attempted such corrections here.

Spin-orbit coupling can affect the ordering of the low-lying excited states. Generally states with high orbital angular molecular (Ω) and large spin will be favored. For example, the ${}^4\Phi$ state of TaH^+ is calculated only 0.9 kcal/mol above the predicted ground state ${}^4\Sigma^-$ (see Table VII). Thus we would expect that spin-orbit coupling would stabilize the ${}^4\Phi_{9/2}$ state sufficiently for it to become the ground state. Similarly IrH^+ has the ${}^4\Phi$ state just 3.8 kcal/mol above the predicted ground state ${}^4\Sigma^-$. Here again, ${}^4\Phi_{3/2}$ would be stabilized by spin-orbit coupling, probably becoming the ground state.

For PtH^+ the ${}^1\Delta$ state is found to be just 1 kcal/mol above the predicted ground state (${}^1\Sigma^+$), so that ${}^3\Delta_1$ will become the ground state after including spin-orbit coupling. In addition, for WH^+ (where ${}^5\Delta$ is 1.5 kcal/mol higher than the predicted ground state of ${}^5\Pi$) spin-orbit coupling might change the ground-state symmetry.

Acknowledgment. The calculations and discussions rest heavily on the approaches and conclusions from systematic studies on the first two rows of transition-metal hydrides carried out by Dr. J. B. Schilling (now at Amoco Research Center) in collaboration with Professor J. L. Beauchamp (Caltech) and one of the authors (W.A.G.). The calculations were supported by the National Science Foundation (Grant No. CHE-8318041). One of the authors (G.O.) is grateful to NATO for a fellowship supporting part of his stay at Caltech. In addition, the computer resources (Alliant FX8/8 and DEC VAX 8650) were funded by ONR/DARPA, NSF-MRG, ONR-SRO, and DOE-ECUT.

Molecular Orbital Study on the Mechanism of Oxidation of a Beryllium Atom in Acidic Solution

Kenro Hashimoto,[†] Nobuyuki Yoda, Yoshihiro Osamura,* and Suehiro Iwata

Contribution from the Department of Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohokuku, Yokohama 223, Japan. *Received December 7, 1989*

Abstract: To elucidate the mechanism of metal hydrolysis in acidic solution, we have studied the reaction of a beryllium atom in acidic aqueous solution with ab initio molecular orbital theory. The oxidation process from Be^0 to Be^{II} via Be^I can be regarded as the successive reaction between a Be atom and H_3O^+ ions, assisted by the surrounding water molecules. Although the apparent reacting species are a Be atom and hydronium ions, it is shown that the hydration by water molecules is essential in stabilizing the reacting system at every step. The intermediate species corresponding to Be^I is found to be a solvated protonated beryllium ($[BeH(H_2O)_n]^+$). In the second stage of the oxidation process, the reaction should involve the interaction between the Be^I species and H_3O^+ to produce an H_2 molecule and a hydrated Be^{2+} ion. The molecular interaction to overcome Coulombic repulsion between these two positively charged species is analyzed in terms of electron-population analysis. It is concluded that the large exothermicity due to the hydration of Be^{II} leads to the oxidation of solvated Be^0 and to the production of a hydrogen molecule.

Introduction

A standard textbook of electrochemistry tells us that if the standard reduction potential of a metal is more negative than that of the hydrogen electrode, the metal is oxidized in aqueous solution to produce hydrogen gas. The reaction can be expressed by the following redox equation

$$M + nH^+ + aq \rightarrow M^{n+}aq + (n/2)H_2 \qquad (1)$$

which is formally the reaction among a metal, protons, and solvent waters to form a solvated metal ion and molecular hydrogens.[1]

[†] Present address: Special Researcher, Basic Science Program, The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-01, Japan.

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The reaction involves the successive oxidation and reduction processes of the metal atom and protons as

$$M + aq \rightarrow M^+aq + e^- \qquad (2)$$

$$\begin{array}{c} M^+aq \rightarrow M^{2+}aq + e^- \\ \hline H^+ + e^- \rightarrow \frac{1}{2}H_2 \end{array}$$

The successive reactions (2) are, however, merely formal elemental reactions. In reality, more complex ionic species are involved in the reactions. Although these electrochemical reactions are basic and fundamental in chemistry, the detailed reaction mechanism and the nature and structure of the chemical species involved are not well-known. This is because most of the experimental studies have used electrochemical techniques, and thus the results obtained can only give information on macroscopic quantities. There is also the reason that it is difficult to apply molecular spectroscopy to such complicated electrochemical reactions.

In light of the recent advances in ab initio molecular orbital (MO) methods, in particular with regard to the great progress in energy gradient techniques, these methods have now attained broader applicability to more realistic chemistry.[2] Quantum chemical calculations enable us to explore the detailed mechanisms of chemical reactions, not only for isolated gas-phase processes but also for several complex catalytic reactions.

In the present paper, we describe a study of the reaction mechanism for a beryllium atom as an example of the reaction (2). The Be^{2+} ion has a very large negative standard reduction potential between those of Mg^{2+} and Al^{3+}.[3] The questions that we would like to answer are the following: (a) What is the chemical species for each oxidation stage, Be^0, Be^I, and Be^{II}? In particular, what is the Be^I species? (b) What role do protons play in the oxidation process? (c) In what way do the active species and solvent molecules interact with each other? (d) How is molecular hydrogen produced? (e) What is the effect of the surrounding solvent molecules on the structures of the ionic species, and how do they influence the relative energies of all intermediates in the process? Although a number of water molecules should be taken into account in order to describe solution chemistry, the present model calculations consider the reaction in a water cluster, thus allowing us to understand the essential electronic factors involved in the oxidation process at the molecular level.

Computational Procedure

The molecular structures and the energies of the chemical species discussed in this paper were calculated with the closed-shell SCF method with the GAUSSIAN82 program package.[4] The molecular geometries were optimized with the energy gradient technique. The STO-3G[5] and 3-21G[6] basis sets were used. Through a series of theoretical studies[7-11] on molecular systems containing the Be atom and Be^{2+} ion, we have examined the basis set dependence of the bonding nature of Be. From the calculations with more flexible basis sets, such as double ζ (DZ),[12] 6-31G,[13] or a basis set with polarization functions (3-21G*), we found that the 3-21G basis set describes the chemical bonding of the Be atom properly, provided that the p functions of Be are included. The analytical second-derivative method is used to identify the intermediates and the transition states. The values cited in the text are those obtained with the 3-21G basis set.

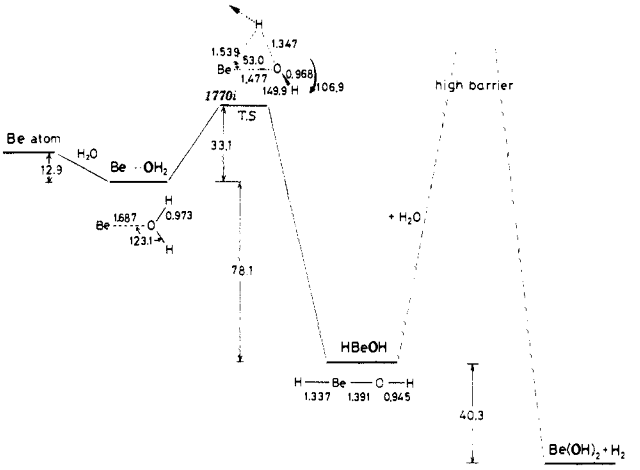

Figure 1. Energy diagram related to reactions 4 and 5 with the optimized geometries of the complex, transition state, and products calculated with 3-21G basis set. The dotted arrow in the transition state indicates the reaction coordinate with one imaginary frequency (cm^{-1}). The energies are given in kilocalories per mole. The units for optimized structures are angstroms and degrees.

Results and Discussion

It is well-known that the processes of oxidation and reduction of a transition metal in solution generally take place at different sites on the metal surface. The metal itself acts as an anode or a cathode by forming a partial electrode. Although one should consider such an electrode reaction from the macroscopic point of view, we will discuss the oxidation process of a single Be atom in this paper, assuming that all metal atoms finally dissolve into aqueous solution as metal ions.

During the course of the oxidation process of a Be atom, we assume that a finite number of water molecules interact with a Be atom or a Be ion. In our approach, we first focus on the reacting moiety with only a single water molecule and then take into account the participation of other water molecules. As a consequence, we may be able to find the essential number of water molecules necessary for the overall reaction to proceed.

The oxidation process of a Be atom may be assumed to involve the following two ionization steps:

$$Be^0 \rightarrow Be^I \rightarrow Be^{II} \qquad (3)$$

The atomization process of bulk Be is not considered in this study. Note that the first and second ionization potentials of an isolated Be atom are 9.322 and 18.211 eV.[14] The oxidation up to Be^{II} requires a large stabilization, not only by solvation of the ions but also by the formation of strong chemical bonds in the intermediate and product ions.

One of the questions we would like to solve involves the chemical species corresponding to Be^I and Be^{II}. Although chemical equilibrium would exist among many intermediate species in solution, we would like to find the principal chemical species in order to understand the reaction mechanism of the oxidation process. We will examine the possible reacting species in subsections A–C. The next question to be answered is how the reaction occurs in acidic solution. We will discuss the first oxidation process in subsection D. The successive oxidation reaction leading to the formation of an H_2 molecule is discussed in subsections E–G.

A. Do Beryllium Hydroxides Take Part in the Oxidation Process? Since beryllium is amphoteric in nature, as is the case

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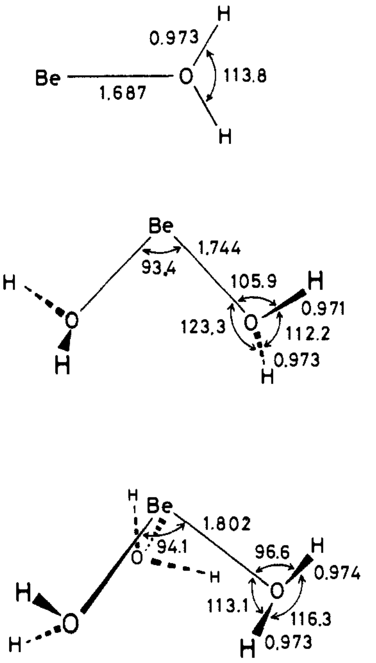

Figure 2. Optimized structure of the hydrated Be atom (Be^0) calculated with the 3-21G basis set. The values are given in angstroms and degrees.

with boron and aluminum, the beryllium hydroxides HBeOH and $Be(OH)_2$ may be considered as good candidates corresponding to the Be^I and Be^{II} species, respectively. In this subsection, we examine the possibility of the direct reaction of a Be atom and H_2O molecules:

$$Be + H_2O \rightarrow HBeOH \tag{4}$$

$$HBeOH + H_2O \rightarrow Be(OH)_2 + H_2 \tag{5}$$

Figure 1 summarizes the energy diagram and optimized structures relating to reactions 4 and 5. In the initial stage of reaction 4, a Be atom and H_2O weakly interact by forming an electron donor–acceptor complex [$Be\cdots H_2O$]. The calculated energy barrier of the isomerization from this complex to the hydroxide is very high (33.1 kcal/mol), though the product HBeOH is a very stable molecule due to formation of a strong Be–O bond.[7,8] Reaction 5 is less favorable because a four-centered transition state is required for the reaction to proceed from a relatively stable $HBeOH{\cdot}H_2O$ complex. The energy barrier to form an H_2 molecule from the $HBeOH{\cdot}H_2O$ complex is extremely large, and the transition state in this reaction path cannot be obtained at the Hartree–Fock level of calculation.

Hydronium ions, not as bare protons, may catalyze reactions 4 and 5 under acidic conditions by participating in the oxidation process, as is discussed in the later subsections. It is certain that beryllium hydroxides exist[15] and are stable[10] in aqueous solution, but we will show that they do not take part in a series of reactions to form the H_2 molecule.

B. Are the Hydrated Be Atom and Be^{2+} Ion Stable? It is important to examine the interaction of both a Be atom (reactant) and a Be^{2+} ion (product) with water molecules. Since we have to treat reactions that take place in aqueous solution, we should consider the situation where a Be atom is surrounded by a number of water molecules.

Figure 2 shows the optimized structures of a Be atom hydrated with up to three water molecules. Since a Be atom has low-lying vacant 2p orbitals, the electron donor–acceptor complexes are formed by charge-transfer from the lone-pair orbitals of the H_2O molecules to the 2p orbitals of the Be atom. The consecutive stabilization energies[16] are calculated to be −12.9, −11.0, and −14.7 kcal/mol by adding H_2O molecules one by one. No stabilization is found for the fourth H_2O molecule binding directly to the Be atom of $Be(H_2O)_3$.

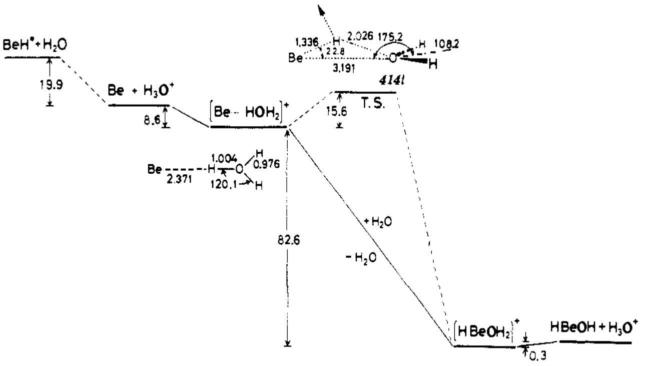

Figure 3. Energy diagram for the interaction between Be atom, H_3O^+, and H_2O. The structural parameters are given in angstroms and degrees. The energies are given in kilocalories per mole. The dotted arrow in the transition state indicates the reaction mode with one imaginary frequency.

The structures in Figure 2 clearly show that the lone-pair orbitals of the water molecules are directed toward the three 2p orbitals (p_x, p_y, and p_z). Since the 2s orbital of the Be atom is already occupied by two electrons, the valency of Be is saturated by 8 electrons. Thus, we can conclude that the maximum hydration number of a Be atom is 3. If the two electrons in the 2s orbital are removed from a Be atom, one might expect that further hydration would become possible to form the $[Be(H_2O)_4]^{2+}$ ion.[10]

In fact, we have already reported the structures and stabilization energies for the hydrated Be^{2+} ion obtained from ab initio MO calculations.[9] Both experimental evidence[17] and theoretical results[9] show that the coordination number of H_2O molecules is 4 for a Be^{2+} ion. The position of the oxygen atoms binding to a Be ion in $[Be(H_2O)_4]^{2+}$ is almost tetrahedral, and a fifth water molecule starts to form the second shell around the $[Be(H_2O)_4]^{2+}$ cluster. Since all 2s and 2p orbitals are vacant for Be^{2+}, the lone-pair electrons of the H_2O molecules bind strongly to the positively charged Be by means of sp^3 hybridization. We have shown that the $Be^{2+}\cdots O$ bond is nearly covalent and that the positive charge is dispersed onto the H atoms of the ligand H_2O's.[9] Note that the hydration energy of Be^{2+} is extremely large:

$$Be^{2+} + 4H_2O \rightarrow [Be(H_2O)_4]^{2+} \qquad \Delta E = -493\ \text{kcal/mol} \tag{6}$$

We can evaluate the energy difference between the reactants, $Be(H_2O)_3 + 2H_3O^+$, and the products, $[Be(H_2O)_4]^{2+} + H_2O + H_2$; it is as large as −176 kcal/mol. The large *exo*thermicity suggests the possibility of a fierce oxidation reaction from Be^0 to Be^{II}.

C. What is the Species Corresponding to Be^I? The reactant and product corresponding to Be^0 and Be^{II} can be reasonably assumed to be $Be(H_2O)_n$ and $[Be(H_2O)_n]^{2+}$. In this subsection, we discuss the possible intermediate Be^I species. In principle, it is possible that some radical species are involved in the reaction because a Be^+ ion has an odd electron. Since we are treating the ionic reaction in aqueous solution starting from closed-shell molecules, we may exclude a radical intermediate in the present stage.

Because the oxidation is initiated in acidic conditions, it is natural to expect that the hydronium ion H_3O^+ plays an important role in the reaction generating Be^I species. Figure 3 shows the energy diagram in the following reaction:

$$Be + H_3O^+ \rightarrow HBeOH_2^+ \tag{7}$$

When a Be atom approaches an oxygen atom of H_3O^+, the potential energy curve is found to be repulsive. On the other hand, the interaction between a Be atom and an H atom of H_3O^+ is attractive. The interaction energy of the [$Be\cdots H_3O$]$^+$ complex is calculated to be −8.6 kcal/mol. In this case, the Be atom acts

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[15] Brown, P. L.; Ellis, J. *J. Chem. Soc., Dalton Trans.* **1983**, 2001.

[16] Calculated by $E(Be(H_2O)_n) - E(Be(H_2O)_{n-1}) - E(H_2O)$.

[17] Yamaguchi, T.; Ohtaki, H.; Spohr, E.; Palinkas, G.; Heinzinger, K.; Probst, M. M. *Z. Naturforsch., A* **1986**, *41*, 1175.

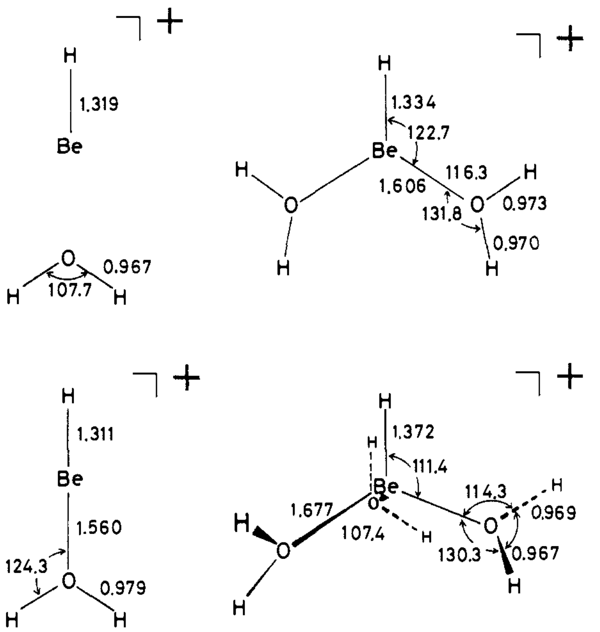


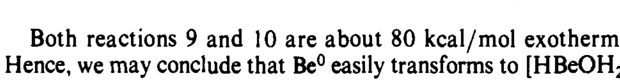
Figure 4. Structures of the hydrated BeH^+ ion (Be^I) optimized with the 3-21G basis set. The values are given in angstroms and degrees.

as an electron donor, in contrast to the case of the Be- - -OH_2 interaction. This demonstrates the amphoteric nature of Be.

In order to form more stable species having a strong Be- - -O bond, the Be atom should insert into the H–O bond of H_3O^+. In the unimolecular rearrangement

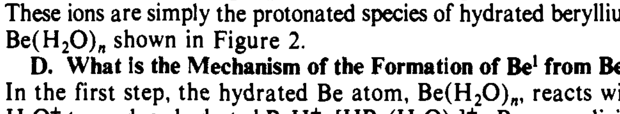
$$\mathrm{Be}\cdots\mathrm{H_3O^+} \rightarrow \mathrm{H{-}Be{-}OH_2^+} \qquad (8)$$

a moderate energy barrier (16 kcal/mol) is found, in contrast to the huge stabilization (−91 kcal/mol) to produce $HBeOH_2^+$. In aqueous solution, however, the assistance of solvent H_2O molecules should make reaction 8 more favorable. If an H_2O molecule approaches the complex [Be- - -H_3O^+] from the opposite side of H_3O^+, the following water exchange reaction 9 takes place without energy barrier as shown in Figure 3.



(9)

An alternative pathway to produce $HBeOH_2^+$ from the neutral Be- - -OH_2 complex is also found to have no energy barrier.



(10)

Both reactions 9 and 10 are about 80 kcal/mol exothermic. Hence, we may conclude that Be^0 easily transforms to $[HBeOH_2]^+$ in acidic aqueous solution. Since the product $[HBeOH_2]^+$ is regarded as an HBe^+ ion hydrated with a water molecule, more water molecules can hydrate it. The optimized molecular structures of $[HBe(H_2O)_n]^+$ (n = 0–3) are given in Figure 4. These ions are simply the protonated species of hydrated beryllium $Be(H_2O)_n$ shown in Figure 2.

D. What Is the Mechanism of the Formation of Be^I from Be^0? In the first step, the hydrated Be atom, $Be(H_2O)_n$, reacts with H_3O^+ to produce hydrated BeH^+, $[HBe(H_2O)_n]^+$. By generalizing reaction 10, the first oxidation reaction is written as

$$\mathrm{Be^0(H_2O)_{\mathit{n}} + H_3O^+ \rightarrow [HBe^I(H_2O)_{\mathit{n}}]^+ + H_2O} \qquad (11)$$

for n = 1–3. Figure 5 summarizes the energy relation of the first oxidation process from the Be atom to BeH^+. In contrast to the small stabilization for the hydration of Be^0, the formation of a Be–H^+ bond induces strong coordination of H_2O. This leads to an extremely large exothermicity (ΔE for reaction 11): −138 kcal/mol for n = 2 and −171 kcal/mol for n = 3.

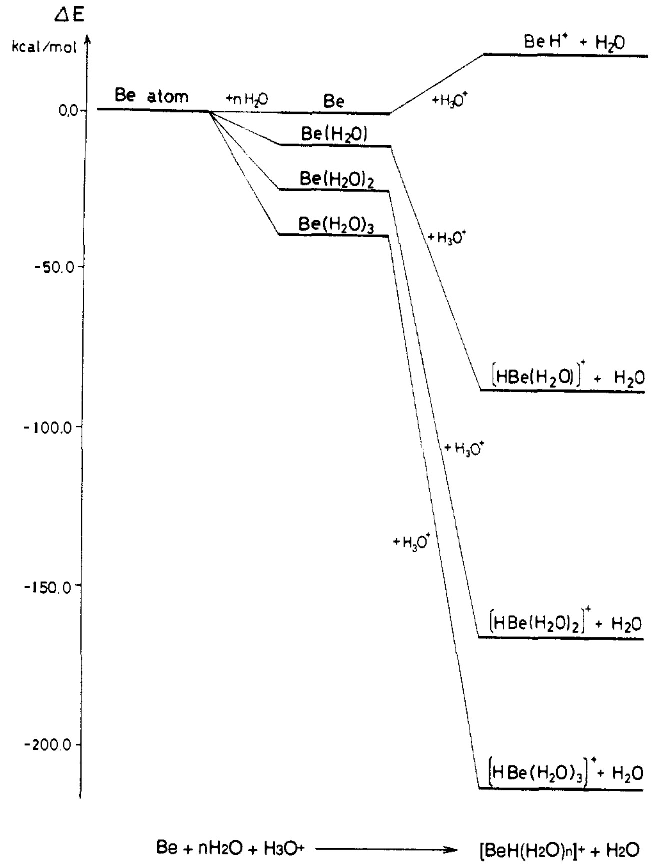


Figure 5. Relative energy diagram of the first oxidation stage from Be^0 to Be^I.

Note that reaction 11 from Be^0 to Be^I is a simple proton transfer. As indicated in Figure 5, the proton affinity of a hydrated Be atom substantially increases with the hydration number. Since the electron populations on the Be atom in $Be(H_2O)_n$ are 4.17 (n = 1), 4.27 (n = 2), and 4.25 (n = 3), the large proton affinity implies that an electron-rich Be atom in the hydrated complex is more strongly attracted by the proton. Furthermore, the orbital energy of the highest occupied molecular orbital (HOMO) becomes close to zero with increasing hydration number. This result suggests that charge transfer from water molecules to Be, as well as an electrostatic interaction, which we have already analyzed in a previous paper,[9] plays an important role in stabilizing ionic hydrated complexes. The shape of the HOMO in $Be(H_2O)_3$ is more similar to a 2s atomic orbital of the Be atom than to an sp^3 hybrid orbital. The electrons in the HOMO can be used to form a strong Be–H bond by abstracting a proton from H_3O^+.

In addition to strong Be–H bond formation, the large exothermicity also indicates that the proton-transfer reaction strengthens the Be–O bonds. The bond distances between Be and O in $[HBe(H_2O)_n]^+$ are 1.560 Å (n = 1), 1.606 Å (n = 2), and 1.677 Å (n = 3); they are much shorter than the corresponding ones in $Be(H_2O)_n$ (1.687 Å (n = 1), 1.744 Å (n = 2), and 1.802 Å (n = 3)). The Be–O bond lengths in the hydrated Be^I species are intermediate in value between the values in the Be^0 and Be^{II} species of the same hydration number. Note also that the change of the bond angles ∠O–Be–O is remarkable (see Figures 2 and 4). The bond angle around Be in $[HBe(H_2O)_n]^+$ takes a nearly ideal value corresponding to sp, sp^2, and sp^3 hybridization for n = 1–3, respectively. Complete sp^3 hybridization could be another reason for the stabilization in $[HBe(H_2O)_3]^+$.

Since we have identified the chemical species of Be^0, Be^I, and Be^{II}, we may construct the reaction scheme for the essential parts of the overall oxidation process, which is summarized in Figure 6.

E. How Can a Positive Ion BeH^+ React with a Positively Charged H_3O^+? The second step of the oxidation process may

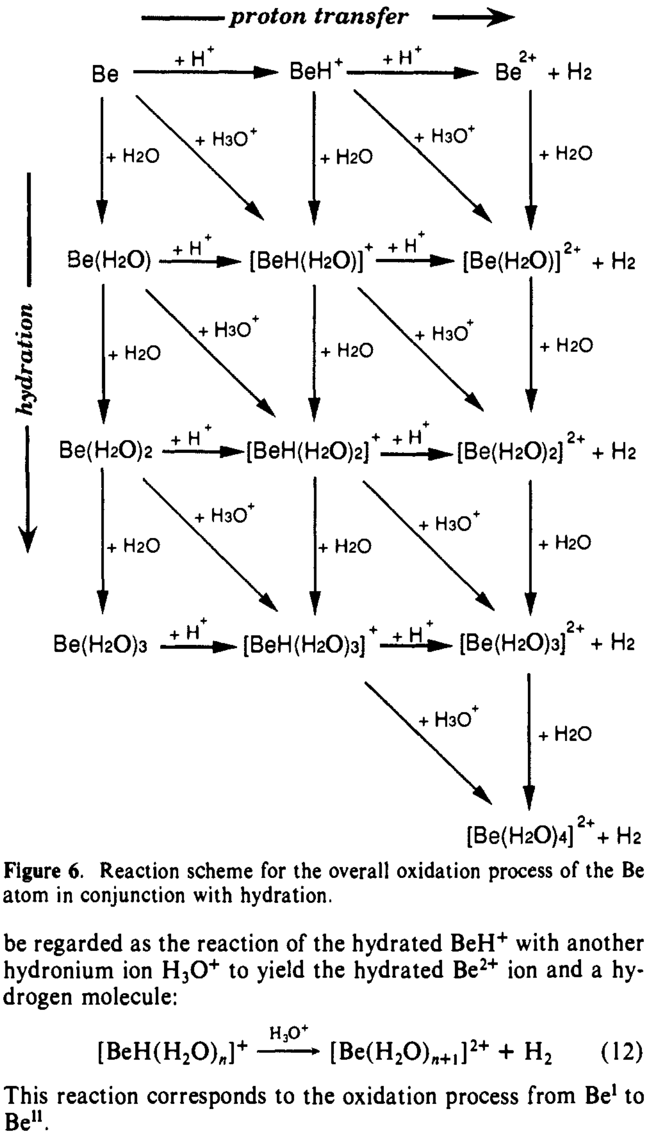


Figure 6. Reaction scheme for the overall oxidation process of the Be atom in conjunction with hydration.

be regarded as the reaction of the hydrated BeH^+ with another hydronium ion H_3O^+ to yield the hydrated Be^{2+} ion and a hydrogen molecule:

$$[BeH(H_2O)_n]^+ \xrightarrow{H_3O^+} [Be(H_2O)_{n+1}]^{2+} + H_2 \qquad (12)$$

This reaction corresponds to the oxidation process from Be^{I} to Be^{II}.

Since only the hydrated Be^{2+} ion can exist at low pH (strong acid),[15] we consider it as one of the final products of the reaction (12). In previous work,[9] we have shown that more than 80% of the enthalpy change for the hydration of a Be^{2+} ion results from the first hydration shell. Thus, we may assume that a limited number of water molecules around Be^{2+} is sufficient to describe the essential effects of hydration on the reaction.

In eq 12, the positive charge of H_3O^+ is transferred to the Be^{I} species to produce a Be^{2+} ion and a neutral H_2 molecule. Since both hydrated BeH^+ and H_3O^+ are positively charged, it is apparent that the interaction between these two ions is energetically unfavorable. Reaction 12, however, must take place in order to produce the final products.

Before discussing the reaction mechanism of 12, we first search for the possible attractive interaction between the hydrated BeH^+ and H_3O^+. Figure 7 shows the Mulliken net charge[18] for various Be^{I} species. Note that the positive charge mostly localizes on the Be atom in bare BeH^+. As was discussed by Takano et al.,[19] the net charge on an atom is well correlated with the oxidation number. The charge distribution of BeH^+ supports the notion that the oxidation number of Be is +1 in BeH^+. When a single H_2O molecule coordinates to BeH^+, the positive charge on the Be atom decreases from +0.99 to +0.76 and the charge is dispersed onto the H atoms of the ligand H_2O molecule. It is most notable that the H of BeH^+ becomes almost neutral because the hydrogens of the H_2O molecule act as a buffer of positive charge. This tendency continues as the number of coordinating waters increases. Consequently, the hydrogen atom bonded to the Be atom in $[HBe(H_2O)_3]^+$ has a negative charge, −0.23, and becomes an attractive site to other positive species. We can, therefore, guess the structure of the complex as being

$$(H_2O)_nBeH^+\cdots H\text{–}OH_2^+ \qquad (13)$$

which leads to the reaction to produce an H_2 molecule in the second oxidation step, eq 12. This reaction is, however, expected to have an energy barrier, because the cleavage of two bonds (an OH bond of H_3O^+ and a Be–H bond of $[HBe(H_2O)_n]^+$) and the formation of a single H–H bond are involved. In the following subsection, we will explore the reaction mechanism of the second oxidation process for each hydrated Be^{I} species by determining the transition-state structure.

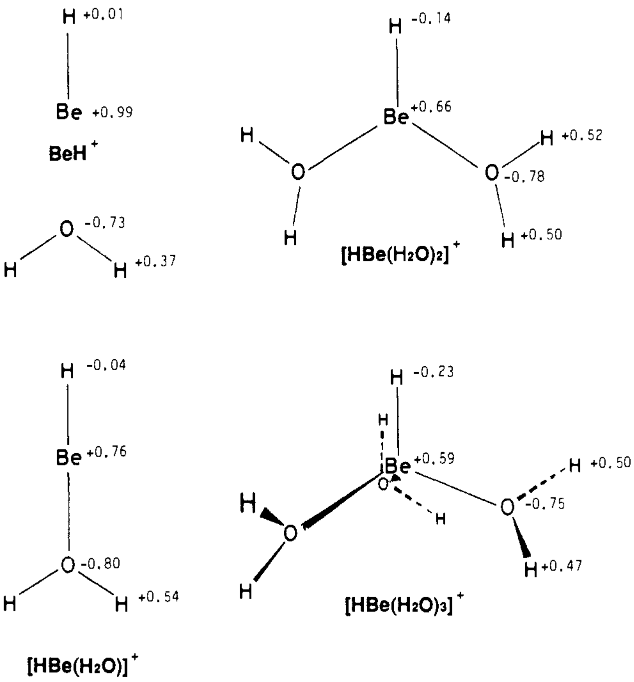


Figure 7. Charge distribution of the hydrated BeH^+ species obtained with the 3-21G basis set.

F. How is an H_2 Molecule Formed in the Oxidation from Be^{I} to Be^{II}? We examine first the direct reaction between BeH^+ and H_3O^+ without solvation. Figure 8 shows the geometry of the transition state and the energy profile of this reaction. The imaginary frequency at the transition state is also given in Figure 8. The final product in this model reaction is not a bare Be^{2+} ion but a hydrated Be^{2+}, $[BeOH_2]^{2+}$, because of the large hydration energy of the Be^{2+} ion. Thus, the reaction is written as

$$BeH^+ + H_3O^+ \rightarrow [Be(H_2O)]^{2+} + H_2 \qquad (14)$$

Since the energy of the products $[Be(H_2O)]^{2+} + H_2$ is 90 kcal/mol higher than that of the reactants $BeH^+ + H_3O^+$, this model reaction is energetically impossible. As indicated with dotted arrows in Figure 8, however, the reaction coordinate at the transition state clearly shows the formation of an H_2 molecule. The transition state is a typical four-centered structure, which suggests that the reaction is nearly of 2 + 2 type in the sense of the Woodward–Hoffmann rules.[20] In other words, the energy barrier is very high, as suggested by the general rule that this type of reaction requires the formation of two bonds simultaneously with the cleavage of two bonds.

Now we examine the hydration effect of a single H_2O molecule in reaction 14:

$$[H_2OBeH]^+ + H_3O^+ \rightarrow [Be(H_2O)_2]^{2+} + H_2 \qquad (15)$$

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[18] Mulliken, R. S. *J. Chem. Phys.* **1955**, *23*, 1833.

[19] Takano, K.; Hosoya, H.; Iwata, S. *J. Am. Chem. Soc.* **1984**, *106*, 2787.

[20] Woodward, R. B.; Hoffmann, R. *The Conservation of Orbital Symmetry*; Academic Press: New York, 1970.

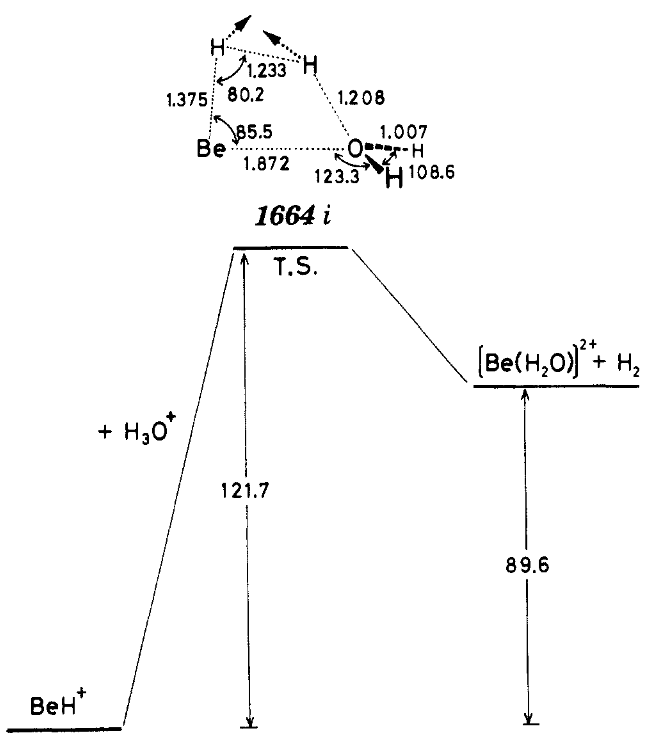


Figure 8. Energy diagram for the reaction between BeH^+ and H_3O^+ calculated with the 3-21G basis set. The dotted arrows in the transition state represent the reaction coordinate to produce an H_2 molecule with one imaginary frequency of 1664*i* cm^{-1}. Relative energies are in kilocalories per mole, and the geometrical parameters are in angstroms and degrees.

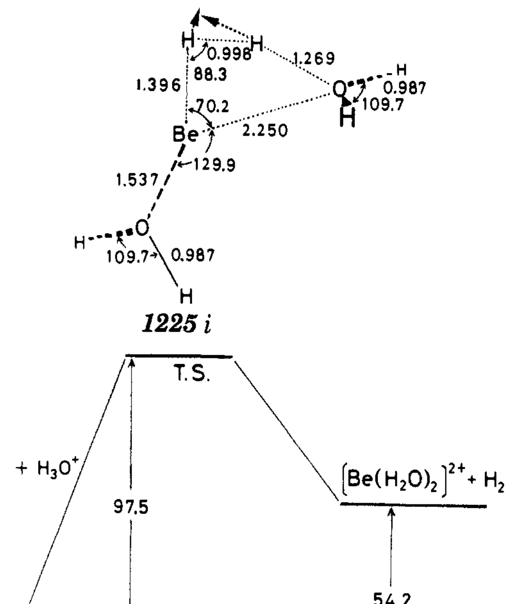


Figure 9. Energy diagram for the reaction between $[BeH(H_2O)]^+$ and H_3O^+. The dotted arrows in the transition state represent the reaction mode to produce an H_2 molecule with one imaginary frequency of 1225*i* cm^{-1}. Units for energy and structural parameters are kilocalories per mole, angstroms, and degrees.

As shown in Figure 9, the structure of the transition state deviates from the four-centered geometry. The H–H interaction becomes more favorable than that of the previous no-hydration case, as is seen in the shorter distance for the newly formed H–H bond. The energy of both the product and the transition state decreases by about 30 kcal/mol from the corresponding energy in reaction 14.

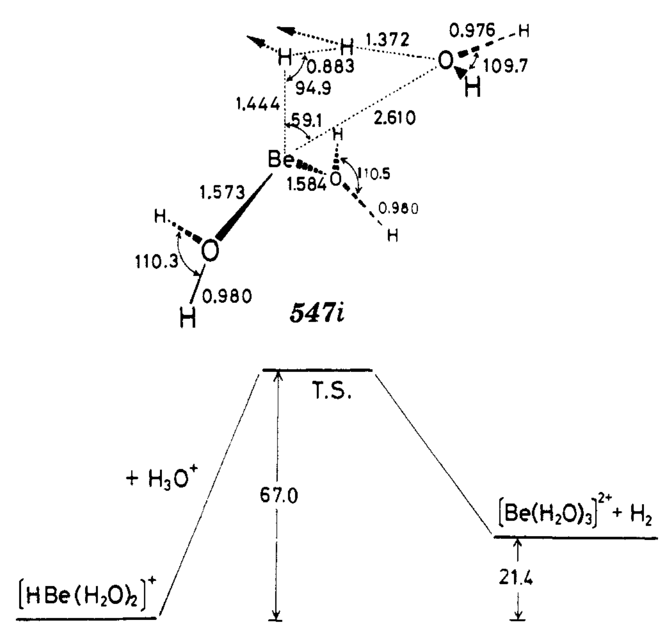


Figure 10. Energy diagram for the reaction between $[BeH(H_2O)_2]^+$ and H_3O^+. The dotted arrows in the transition state indicate the reaction mode to produce an H_2 molecule with one imaginary frequency of 547*i* cm^{-1}. Units for energy and structural parameters are kilocalories per mole, angstroms, and degrees.

Table I. Mulliken Net Charge on Be and H Atoms at Reactants,[a] Transition States (Figures 8–11), and Products[b] in the Reaction $[(H_2O)_nBeH]^+ + H_3O^+ \rightarrow [Be(H_2O)_{n+1}]^{2+} + H_2$ Calculated by the SCF Method with the 3-21G Basis Set

	reactants[a] $[BeH(H_2O)_n]^+$		transition states $[(H_2O)_nBe\text{-}H\cdots H\text{-}OH_2]^{2+}$			product ions[b] $[Be(H_2O)_{n+1}]^{2+}$
n	Be	H[c]	Be	H(Be)[c]	H(O)[d]	Be
0	+0.99	+0.01	+1.23	−0.12	+0.48	+1.60
1	+0.76	−0.04	+1.10	−0.15	+0.39	+1.28
2	+0.66	−0.14	+1.03	−0.20	+0.33	+1.11
3	+0.59	−0.23	+1.00	−0.37	+0.39	+1.00

[a] See Figure 7. [b] Taken from ref 9. [c] The hydrogen atom binding to Be. [d] The leaving hydrogen atom from H_3O^+ to form an H_2 molecule.

When two H_2O molecules are solvated to BeH^+, further stabilization is found for the reaction

$$[(H_2O)_2BeH]^+ + H_3O^+ \rightarrow [Be(H_2O)_3]^{2+} + H_2 \quad (16)$$

The results are shown in Figure 10. Since the net charge on the H atom of BeH^+ is negative for $[(H_2O)_2BeH]^+$, an H atom of H_3O^+ can directly attack the H atom of BeH^+. The barrier height of reaction 16 is 67 kcal/mol, which is about half that in reaction 14. Note that the H–H distance in the forming H_2 molecule is already 0.883 Å at the transition state. The product Be^{II} is significantly stabilized by three H_2O molecules after releasing H_2. The energy of the product, however, is still 21 kcal/mol higher than that of the reactants in reaction 16.

Finally, we show the results for the reaction of a fully hydrated $[(H_2O)_3BeH]^+$ with H_3O^+:

$$[(H_2O)_3BeH]^+ + H_3O^+ \rightarrow [Be(H_2O)_4]^{2+} + H_2 \quad (17)$$

$$\Delta E = -5 \text{ kcal/mol}$$

Figure 11 clearly shows that the barrier height is reduced again to half of that in reaction 16, and the reaction becomes *exothermic*. It should be noted that the coordination of the fourth water molecule from the reagent H_3O^+ produces a fully hydrated species of the Be^{2+} ion, $[Be(H_2O)_4]^{2+}$.

The energy profile in the second oxidation step, $Be^I \rightarrow Be^{II}$, is summarized in Figure 12. As the number of coordinating H_2O molecules increases, the energy barrier successively decreases together with the energy lowering of the products, Be^{II} and H_2. This fact may be interpreted by analyzing the character of each chemical bond taking part in the reaction.

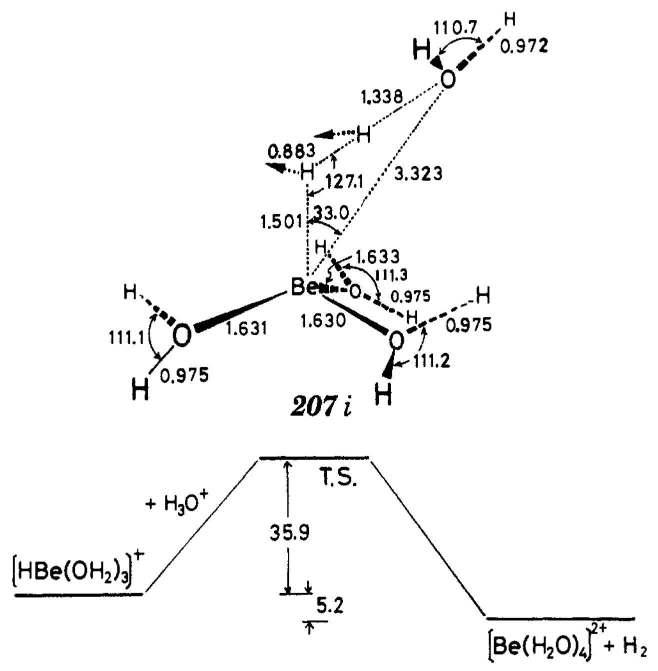


Figure 11. Energy diagram for the reaction between $[BeH(H_2O)_3]^+$ and H_3O^+. The dotted arrows in the transition state indicate the reaction mode to produce an H_2 molecule with one imaginary frequency of 207*i* cm^{-1}. Units for energy and structural parameters are kilocalories per mole, angstroms, and degrees.

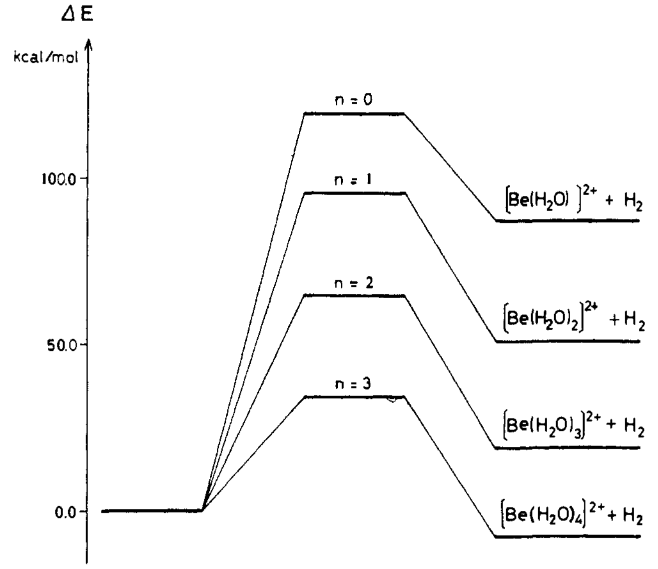


Figure 12. Relative energy diagram for the second oxidation stage from Be^I to Be^{II} involving the reaction between hydrated BeH^+ and H_3O^+.

Table I lists the net charge on Be and H atoms of forming H_2 in reactants, transition states, and products. It is noticeable, from the sum of the net charge on the two H atoms, that the leaving H_2 part becomes neutral in the case of full hydration. The hydrating water molecules play an important role in supplying the electrons to form a new H–H bond. Note also that the hydrogen atom binding directly to Be becomes more negative at the transition state than in the reactant. This electronic effect is amplified with hydration so that the proton of H_3O^+ can easily encounter the negatively charged hydrogen atom of hydrated BeH^+. On the other hand, the net charge on Be at the transition state is very close in value to that in the product, since the water molecule for H_3O^+ has already begun to hydrate the Be^{II} species. This favorable situation to form the products is also seen in the geometries illustrated in Figures 8–11, in particular in the bond distance of the leaving H_2. It is clearly shown that the transition state becomes "late" in the reaction path with the increasing hydration number.

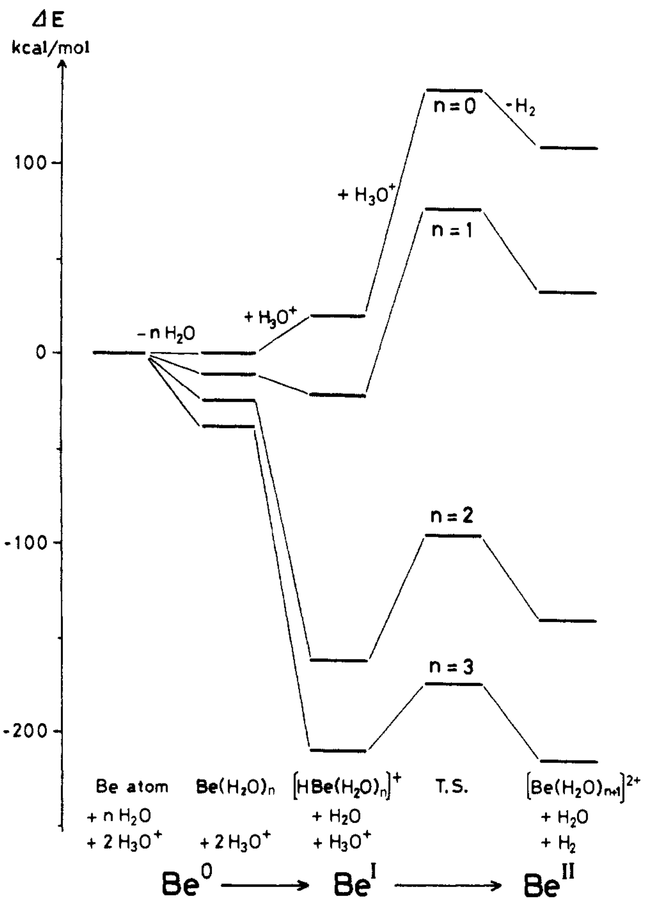


Figure 13. Energy diagram for the total oxidation process from Be^0 to Be^{II} via Be^I.

G. Are Solvent Water Molecules Important? As we have seen from the study of the reaction mechanism in subsections D and F, the oxidation proceeds in stepwise fashion from Be^0 to Be^{II} via Be^I. Figure 13 summarizes the overall energy diagram of the reactions from Be^0 to Be^{II} with evolution of H_2.

At the very first stage of the reaction, water molecules hydrate a Be atom. The stabilization energy is about 39 kcal/mol when a Be atom is fully hydrated by three H_2O molecules:

$$Be + 3H_2O \rightarrow Be(H_2O)_3 \qquad \Delta E = -39 \text{ kcal/mol} \quad (18)$$

The hydration of a Be atom makes it possible for the Be atom to be easily ionized by abstracting a proton from an H_3O^+ ion. The importance of the water molecules in the first oxidation step is clearly seen by the fact that the proton abstraction reaction is *endo*thermic without water molecules. The exothermicity of the reaction (11) increases with the hydration number. A large amount of energy (~200 kcal/mol) is released in the reaction by forming a fully hydrated Be^I species, $[HBe(H_2O)_3]^+$:

$$Be + 3H_2O + H_3O^+ \rightarrow [HBe(H_2O)_3]^+ + H_2O \quad (19)$$

$$\Delta E = -209 \text{ kcal/mol}$$

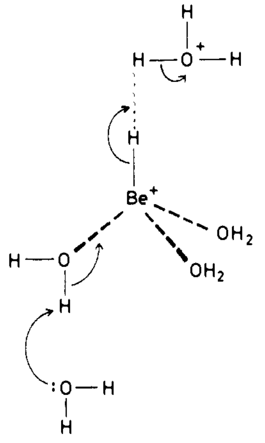
This exothermicity is mainly attributed to stabilization by the formation of strong covalent Be–O bonds.

The hydrating H_2O molecules play another important role as an electrostatic buffer of the positive charge. Since the positive charge is dispersed onto the H atoms in the hydrating water molecules, the second H_3O^+ ion can approach the Be^I species by overcoming the Coulombic repulsion; this approach is the starting point of the oxidation reaction $Be^I \rightarrow Be^{II}$.

As mentioned in the previous subsection, both the energy barrier of the second oxidation step and the total energy of the final products (hydrated Be^{2+} ion + H_2 molecule) are lowered with the increase in hydration number. In the fully hydrated system, the second oxidation reaction would be much more exothermic than in the model calculation (17). Although the Be^{II} species do not gain much stabilization by hydration in comparison with the Be^{I} species, as seen in Figure 13, the hydration energy generated in the first oxidation step surmounts the barrier height of the second oxidation reaction (12) for $n \geq 2$.

In the present work, we have not taken into account the entropy factor at all, but only considered the enthalpy changes. The former might be important in the formation reaction of gaseous H_2. The other limitation of the present work is that only the minimum solvation is considered in order to describe the oxidation reaction. The H_2O molecules coordinating to reacting species may be regarded as forming the first-shell structure in the cluster model. Since the maximum coordination number is 3 for Be^0 and is 4 for Be^{II}, further H_2O molecules would be more weakly attached to the solvated H_2O of the first shell through hydrogen bonding. The stabilization energy by such solvation in the second shell will be much less than that obtained from the first-shell structure. In more realistic models, the modified potential energy surface must be built by considering the effect of an infinite number of H_2O molecules.

The solvation of the second shell also contributes to dispersing the positive charge of the Be^{I} species. Moreover, the following electron movement is expected to make the energy barrier of H_2 formation small. It might also be possible to reduce the activation energy of reaction 17 by the assistance of negatively charged counterions, though we have not considered such an effect in the present study.



(20)

Conclusion

We have discussed the reaction mechanism of the oxidation process of a Be atom at the molecular level by using ab initio MO theory. The reaction of Be in acidic solution is treated as the molecular interaction among Be, H_2O, and H_3O^+, so that the essential reacting species are taken into account.

The conclusions that we have reached from the present quantum chemical calculation are as follows:

(1) The chemical species of Be corresponding to the oxidation numbers 0, I, and II are the hydrates of the Be atom, BeH^+, and Be^{2+} ions, respectively.

(2) The oxidation process from Be^0 to Be^{II} via Be^{I} can be divided into three reactions. The initial stage of this reaction is the solvation of a Be atom. The first oxidation step, following the hydration of a Be atom, would be the proton transfer reaction 11 from an H_3O^+ ion to form a Be^{I} species. The final step is the formation of an H_2 molecule and a hydrated Be^{2+} ion from another H_3O^+ ion and the Be^{I} species.

(3) By utilizing the large difference between the hydration energy of a neutral Be atom and that of the Be^{I} species in the $Be^0 \rightarrow Be^{I}$ reaction, the second oxidation reaction proceeds in spite of a significant energy barrier (see Figure 13). More than two water molecules are needed to generate the exothermicity of the overall reaction.

(4) The successive oxidation reactions proceed with ionic character. The neutral Be atom dissolves by ionizing with the assistance of the water molecules so that the Be^{2+} ion turns out to be the final product for the Be^{II} species.

(5) Water in the reactions is not just a solvent but should be regarded as one of the reagents. It plays an essential role in the energetic, electronic, and structural nature of the overall reaction.

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