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Oxygen-exchange pathways in aluminum polyoxocations

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Abstract—Using molecular dynamics simulations and electronic structure methods, we postulate a mechanism to explain the complicated reactivity trends that are observed for oxygen isotope exchange reactions between sites in aluminum polyoxocations of the ϵ -Keggin type and bulk solution. Experimentally, the molecules have four nonequivalent oxygens that differ considerably in reactivity both within a molecule, and between molecules in the series: Al_{13} , GaAl_{12} , and $\text{GeAl}_{12}[\text{MO}_4\text{Al}_{12}(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{n+}$ (aq); with $M = \text{Al(III)}$ for Al_{13} , $n = 7$; $M = \text{Ga(III)}$ for GaAl_{12} , $n = 7$; $M = \text{Ge(IV)}$ for GeAl_{12} , $n = 8$. We find that a partly dissociated, metastable intermediate molecule of expanded volume is necessary for exchange of both sets of μ_2 -OH and that the steady-state concentration of this intermediate reflects the bond strengths between the central metal and the μ_4 -O. Thus the central metal exerts extraordinary control over reactions at hydroxyl bridges, although these are three bonds away.

This mechanism not only explains the reactivity trends for oxygen isotope exchange in μ_2 -OH and η -OH₂ sites in the ϵ -Keggin aluminum molecules, but also explains the observation that the reactivities of minerals tend to reflect the presence of highly coordinated oxygens, such as the μ_4 -O in boehmite, α -, and γ -Al₂O₃ and their Fe(III) analogs. The partial dissociation of these highly coordinated oxygens, coupled with simultaneous activation and displacement of neighboring metal centers, may be a fundamental process by which metals atoms undergo ligand exchanges at mineral surfaces. Copyright © 2004 Elsevier Ltd

1. INTRODUCTION

The disequilibrium exchange of oxygen between water molecules in bulk solution and individual sites at a mineral surface is the most fundamental expression of water-rock interaction. These hydrolysis reactions are central to a wide variety of geochemical processes, including dissolution, sorption, and colloid formation, yet little is known about the actual molecular pathways for exchange or even about the relative exchange rates at different coordination sites. Because there is so little information about mineral surface reactions at the molecular scale, the mechanisms have always been interpreted loosely using a vocabulary that derives from studies of simple octahedral substitutions in monomeric aqueous complexes (e.g., Lasaga, 1992). Yet the coordination chemistry of oxygens at a mineral surface is much more complicated than in a simple monomeric ion. A richer detail is needed.

Studies were recently undertaken on oxygen isotope-exchange reactions in small aqueous clusters using nuclear magnetic resonance (NMR) spectroscopy (Phillips et al., 2000; Casey et al., 2000; Casey and Phillips, 2001; Lee et al., 2002; Phillips et al., 2003; Loring et al., 2004). Because the structures of the aqueous clusters are known, these studies allow reactions to be followed at individual sites. Rates of exchange of bound water molecules (η -OH₂) and hydroxyl bridges (μ_2 -OH) with water molecules in the bulk solution were separately measured in these clusters. The clusters are 1–2 nm in size and were chosen because they expose functional groups that resemble

those on aluminum-hydroxide mineral surfaces. In fact, one of the clusters may be a precursor molecule in the formation of solid aluminum-hydroxide floc in polluted streams (Furrer et al., 2002; see also Bertsch and Parker, 1996). These clusters have a close link to aluminum-hydroxide solids (see Casey et al., 2001; Casey and Swaddle, 2003).

The experimental results were jarring. Rates of exchange of the two hydroxide bridges in each ϵ -Keggin structure were found to be independent of pH and to differ dramatically from one another by as much as a factor of $\sim 10^3$. More startling was the fact that the rates were enormously sensitive to a single metal substitution in the center of the ion and that these substitutions cause rates to differ by at least a factor of 10^5 . Since the central tetrahedral metal is three bonds away from the exchanging oxygen in these structures, and is unchanged by exchange of the μ_2 -OH bridges, it is surprising that there is such a strong effect. Conversely, the rates of exchange of η -OH₂ sites on all of the ϵ -Keggin structures were nearly independent of the metal substitution, yet were also three bonds away. These bound water sites, of course, are closely analogous to water molecules bound to the surface of a mineral that can deprotonate and create surface charge.

The experimental data indicate that the exchange mechanisms are much more complicated than the community of geochemists would have anticipated. Given the similarity between the functional groups on these ϵ -Keggin structures and those thought to occur on oxide surfaces, it seems prudent to explain the reactivity trends on this system, where the rate data are unambiguous and the molecular structure is known, before moving on to the much more complex (experimentally and computationally) oxide surface simulations.

Using molecular dynamics simulations and electronic struc-

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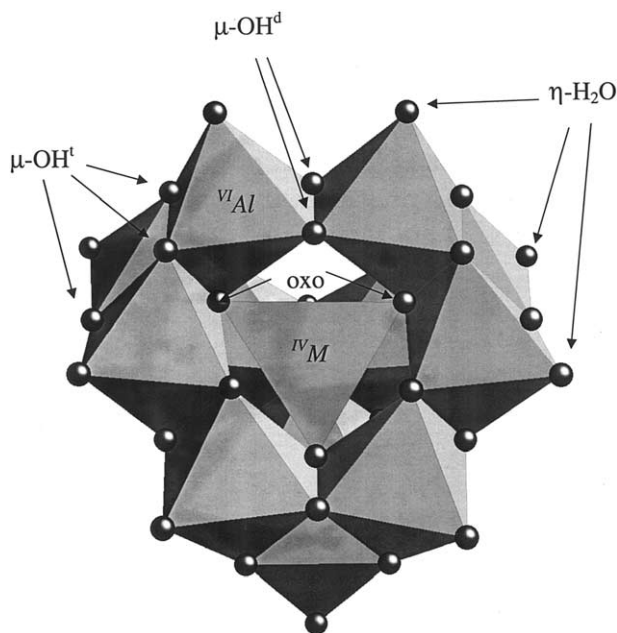


Fig. 1. Polyhedral representation of the ϵ -Keggin structures of the MAI_{12} molecules. The structure has a central MO_4 tetrahedron surrounded by 12 AlO_6 octahedra arranged in four trimeric subunits. There are 12 equivalent η - OH_2 (bound water) sites and two distinct sets of μ_2 -OH sites connecting the edges of the AlO_6 octahedra. One set of μ_2 -OH bridges connect AlO_6 octahedra within the same trimeric subunit (OH^t), and the other set of μ_2 -OH (OH^d) connect octahedra from different trimeric subunits.

ture calculations, we show here that the observed reactivity trend arises because the central metal in the Keggin ion controls the formation of a hydrated metastable intermediate through polarization of the fourfold coordinated oxygen atoms (μ_4 -O) in each ϵ -Keggin structure. The mechanism involves bond rupture at two metal centers and the resulting surface structure is made stable by $H_3O_2^-$ bridges. This $H_3O_2^-$ bridge is known from studies of oxygen exchange in dimers (e.g., Springborg, 1988; van Eldik et al., 1987; Bino and Gibson, 1982) and is probably common to many ligand-exchange reactions at the surfaces of metal-hydroxide minerals.

In contrast to previous ideas, where the metal ion was thought to remain fixed during variations in coordination state, this new mechanism shows that dynamic surface metal rearrangements, involving dislodgment of the metal ions through dissociation at μ_4 -O sites, are intimately involved in the exchange events. The mechanism explains the reactivity trends and indicates that dissociation of surface metal ions from highly coordinated oxygens may be a key factor in mineral-fluid interaction.

2. BACKGROUND

The ϵ -Keggin aluminum molecular ions (Fig. 1) have the stoichiometry: $MAI_{12} = MO_4Al_{12}(OH)_{24}(H_2O)_{12}^{n+}$ (aq); [$M = Al(III)$ for Al_{13} , $n = 7$; $M = Ga(III)$ for $GaAl_{12}$, $n = 7$; $M = Ge(IV)$ for $GeAl_{12}$, $n = 8$]. These molecular ions expose two sets of 12 bridging hydroxyls (μ_2 -OH) and 12 terminal boundwaters (η - OH_2) that deprotonate near $pH = 6$ (Furrer et al.,

1992; Lee et al., 2002; Casey et al., 2001). The surface charge density of these ions is similar to that of aluminum (hydr)oxide minerals at near-neutral to slightly acidic conditions (compare Phillips et al., 2000 and Hiemstra et al., 1999).

The structure consists of a central metal (^{IV}M) in tetrahedral coordination to fourfold-coordinated oxygens (μ_4 -O) that bond to four trimeric $^{VI}Al_3O(OH)_3(H_2O)_9$ groups (Johansson, 1960; Parker et al., 1997; Lee et al., 2001). These μ_4 -O are apparently inert to exchange. One of the two sets of μ_2 -OH connects aluminum atoms within each $^{VI}Al_3O(OH)_3(H_2O)_9$ trimer and these are abbreviated: OH^t (for "trimer" OH). The second set of μ_2 -OH links the $^{VI}Al_3O(OH)_3(H_2O)_9$ trimers to one another and these are abbreviated OH^d (for "dimer" OH), because of their similarity to the μ_2 -OH in doubly hydroxy-bridged metal dimers (see below).

The rates of exchange of oxygen atoms between the μ_2 -OH and η - OH_2 sites and bulk solution have been measured for Al_{13} , $GaAl_{12}$, and $GeAl_{12}$ via ^{17}O -NMR and exhibit several surprising results, as mentioned above (Phillips et al., 2000; Casey et al., 2000; Casey and Phillips, 2001; Lee et al., 2002). First, the exchange rates of the OH^d and OH^t hydroxyl bridges within a $GaAl_{12}$ or Al_{13} molecule differ by a factor of 44 ($GaAl_{12}$) and 1000 (Al_{13}). Secondly, the exchange rates for the $GaAl_{12}$ and Al_{13} molecules are virtually independent of pH ($4.0 < pH < 5.5$). Thirdly and most surprisingly, the hydroxide-exchange rates increase by a factor greater than 10^5 as the central tetrahedral ion is changed from $Ga(III)$ to $Al(III)$ to $Ge(IV)$. Thus, in addition to the notable difference in rate between OH^d and OH^t bridges within a given molecule, the variations among substituted molecules are enormous.

This result is surprising because the ^{IV}M is three bonds removed from both the OH^d and OH^t bridges and would not be expected to have such a strong influence on the exchange rates. Substitutions at ^{IV}M , for example, have a negligible effect on the Al-O bond lengths at the exchanging oxygens in crystallographic studies (Johansson, 1960; Parker et al., 1997; Lee et al., 2001). This sensitivity is a crucial piece of evidence concerning the molecular nature of the exchange process and indicates that the mechanism is more complex than, for example, simple protonation and exchange for a bulk water molecule via a fivefold or sevenfold coordinated surface metal atom. For these ϵ -Keggin aluminum molecules, the process of getting to the transition state for oxygen exchange in a μ_2 -OH evidently depends on bonding well inside the ion and is not simply an octahedral-substitution mechanism that varies in the associative/dissociative character. Conversely, the rates of exchange of the η - OH_2 are relatively unaffected by substitutions at ^{IV}M , for these molecules vary within a range of ~ 5 .

3. MATERIAL AND METHODS

This paper reports two sets of calculations. The first is a series of molecular dynamics calculations on a model Keggin ion in aqueous solution. These calculations reveal a possible mechanism for exchanging a solvating water molecule with an OH^d hydroxide ion. The influence of ^{IV}M substitution on this mechanism was then explored through density-functional electronic structure calculations using methods previously shown to reproduce important reactivity trends for aqueous trivalent metal ions and oxyacids (Rustad et al., 1999; Rustad et al., 2001).

3.1. Molecular Dynamics Methods

To understand the possible mechanisms, we carried out molecular dynamics (MD) simulations of an M_{13} ion embedded in a periodic box of water molecules ($28.04 \text{ \AA} \times 28.04 \text{ \AA} \times 28.04 \text{ \AA}$) with solvent coordinates generated from an equilibrated simulation of pure water. Five simulations were carried out, each lasting 4×10^6 time steps and each using different initial conditions for the water coordinates. The simulations were conducted using potentials developed for the Fe(III)-(hydr)oxide-aquo systems with parameters originally fitted to a quantum-mechanical calculation of the interaction between a water molecule and Fe(III). The details of the model are discussed in Rustad et al. (1995) and Rustad (2001).

The potential parameters were fitted to ab initio calculations on the Fe^{3+} -OH₂ potential surface and, hence, the M^{3+} -O bond lengths are closer to Fe-O bonds than Al-O bonds, but there is little real justification for distinguishing between Al(III) and Fe(III) using a molecular dynamics model such as this one. Bond lengths correlate poorly with many important reactivity trends in the geochemically trivalent metal ions (Brown et al., 1985; Rustad et al., 1999). The gas-phase acidity of the model $M(H_2O)_6^{3+}$ complex is 40 kcal/mol, which is much closer to ab initio calculations on $Al(H_2O)_6^{3+}$ (40-45 kcal/mol) than $Fe(H_2O)_6^{3+}$ (17-28 kcal/mol). Finally, the use of the Fe(III) potentials has the desirable effect of accelerating the frequency of reaction, and hence shortening the computer simulations, because Fe(III) is approximately 10^2 - 10^3 times more reactive than Al(III) in similar ligand exchanges (Richens, 1997). In reality, the force field is of course neither "iron" nor "aluminum" but should be regarded as broadly appropriate for reactions between water and several hard Lewis acid trivalent metals such as Fe(III), Al(III), Ga(III), and Cr(III).

3.2. Electronic Structure Calculations

Although the MD calculations are (as we shall show) accurate enough to identify a compelling overall mechanism, they cannot be used to calculate the influence of ^{IV}M substitution. As we have discussed, correct description of the differences in chemical behavior between the trivalent ions (Al^{3+} and Ga^{3+} in this case) appears to be outside the capability of any electrostatic model. The calculations involving ^{IV}M substitutions were carried out using electronic structure methods. We used the density-functional module in NWChem (Harrison et al., 2002) with the DZVP atomic-orbital basis and the A1 charge-density fitting basis (Godbout et al., 1992). The structure optimizations were done in the local density approximation (LDA) because of the systematically long Al-O bond lengths using nonlocal density functional theory (DFT) methods with practical basis sets (Wasserman et al., 1997; Rustad et al., 1999). Within this approximation, the exchange functional is the Slater $\rho^{1/3}$ functional (Slater, 1974), and the correlation functional is the Vosko-Wilk-Nusair (VWN5) functional (Vosko et al., 1980). The μ_4 -O- ^{VI}Al distance was constrained and varied from its fully relaxed distance of 201 pm to 300 pm while allowing optimization of the remaining degrees of freedom. These structures were used for energy evaluation with the B3LYP exchange-correlation functional (Becke, 1993).

4. RESULTS

4.1. Identification of the Exchange Mechanism

The molecular dynamics simulations yielded a stable $MO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ Keggin-like ion in solution, with no deprotonation of the bound water molecules or bridging hydroxide ions. Given that an error of 1.4 kcal/mol in the acidity of an η -OH₂ surface functional group would correspond to an order of magnitude change in the pK_a , this result is rather remarkable and to some extent fortuitous, given the errors inherent in the MD approach which are clearly larger than a few kcal/mol. In other words, a small error in the acidity of the MOH₂ functional groups could easily have resulted in the

complete conversion into MOH + H⁺ and probable collapse of the Keggin structure. The stability of the model ion in the model aqueous solution means that the molecule's dynamics can guide our interpretations of oxygen exchange in the real Keggin ion.

The simulations (Fig. 2) show that oxygen exchange at the OH^d begins with expansion of the stable $MO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+}$ into a conformer having two adjacent, but transient, five-coordinated metal ions (VM). Consider the doubly-bridged dimeric $^{VI}M(OH^d)_2^{VI}M$ situated on top of the molecule shown in Figure 2a. In Figure 2b, two ^{VI}M - μ_4 -O bonds dissociate to form a transient doubly-bridged $^{VM}(OH^d)_2^{VM}$ unit at the top of the complex. This group is stabilized by the addition of two water molecules, restoring the VM to ^{VI}M , and forming the hydrated $MO_4Al_{12}(OH)_{24}(H_2O)_{12}^{7+} \cdot 2H_2O$ intermediate in Figure 2c. This intermediate is not an activated complex (in the sense of having a negative vibrational eigenvalue) because it persists for timescales of tenths to tens of picoseconds in the simulation and appears to be metastable.

Two reaction paths were observed from the structure in Figure 2c. The first path simply involves the loss of two water molecules from the ^{VI}M sites, returning the ion to the original structure (Fig. 2a). The second path involves dissociation of one of the M-OH^d in the upward-pointing M-OH^d-M bridge. This dissociation results in transient fivefold coordination for one of the aluminums in the dimeric structure (Fig. 2d). Hydration of this VM results in the formation of dibridging structure (Fig. 2e) with OH^d (downward-pointing) and H₃O₂⁻ (upward-pointing) bridges between the ^{VI}M . Because one of the oxygens in the H₃O₂⁻ moiety was originally a bulk water molecule, the dewatering results in hydroxide exchange with 50% probability.

4.2. Establishing the Reactivity Trends

In light of this fundamental mechanism involving the metastable intermediate, the experimental reactivity trends become clear and can be understood in terms of simple size/charge arguments. Exchange is initiated by breaking the ^{VI}M -O bonds in Figure 2a, yielding the intermediate shown in Figure 2b. Why then would substitution at the ^{IV}M site affect this initiation step and accelerate the transition defined by Figure 2a to Figure 2b? We hypothesize that it is controlled by polarization of the μ_4 -O ion. The more the ^{IV}M polarizes the μ_4 -O ion, the more frequent the μ_4 -O- ^{VI}Al dissociation attempts and the faster the exchange rate. In the ϵ -Keggin structure, the ^{IV}Ga -O bond length is approximately 0.05 Å longer than the ^{IV}Al -O bond length (Parker et al., 1997). The bond valence contributed to the oxide ion by ^{IV}Ga is thus less than that contributed by the ^{IV}Al . Because the Pauling bond strength at the oxygen is less, there is less of a tendency for the sixfold-coordinated ^{VI}Al in the $GaAl_{12}$ molecule to dissociate from the ^{IV}Ga -O than for the ^{VI}Al to dissociate from the ^{IV}Al -O in the Al_{13} molecule. Hence, the rate of hydroxide exchange should be slower for the $GaAl_{12}^{7+}$ than for the Al_{13}^{7+} , as observed experimentally. The high reactivity of $GeAl_{12}^{8+}$ is consistent with this interpretation as the Ge(IV) ion polarizes the oxide ion even more strongly than Al(III).

To verify this hypothesis, we carried out electronic structure calculations of the energy barrier between the stable Keggin ion

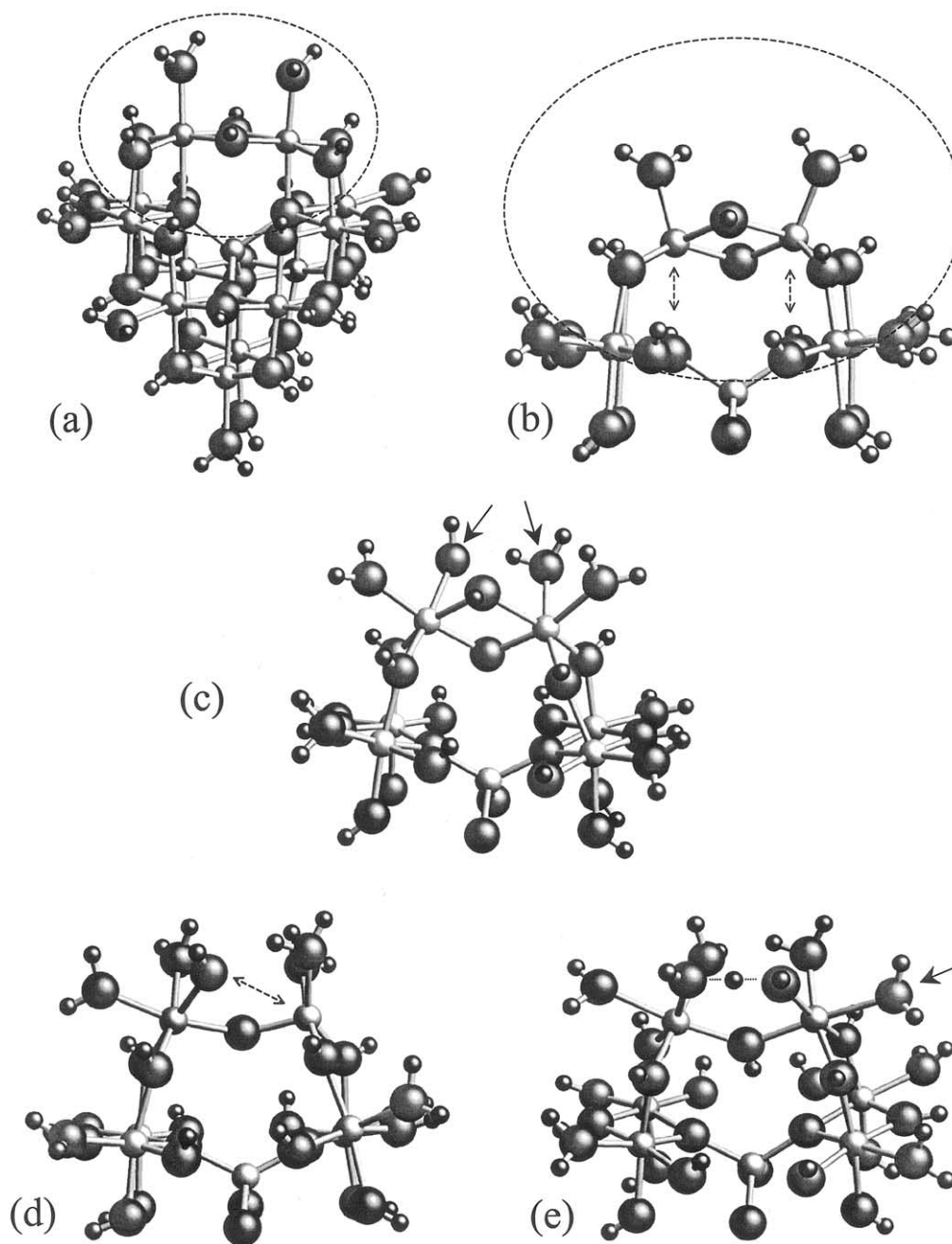


Fig. 2. Stages in hydroxide exchange in the $MA_{12}^{7+/8+}$ cation. (a) Stable ion with active groups encircled by the dotted line, (b) first step involves dissociation of μ_4 -O-Al bonds, (c) stabilization of precursor in (b) through conversion of ^VAl to $^{\text{VI}}\text{Al}$ by addition of two water molecules from solution, (d) second step involving rupture of upward-pointing hydroxide bridge, (e) addition of a third water molecule, and creation of an μ_2 - H_3O_2^- bridge. Dewatering of μ_2 - H_3O_2^- bridge results in hydroxide exchange with 50% probability.

(Fig. 2a) and the fivefold precursor to the hydrated intermediate (Fig. 2b) for GaAl_{12} , Al_{13} , and GeAl_{12} . This initiation step is the only step in Figure 2 likely to be sensitive to substitution at the tetrahedral site.

The energy transects (Fig. 3) indicate large differences among the energetics of forming the intermediate molecule for the GaAl_{12} , Al_{13} , and the GeAl_{12} ions. The intermediate molecule for the GaAl_{12} is the least favored, and the structure with

$M=\text{Ge}$ becomes slightly more stable than the basic Keggin structure. The trend in reactivity, from least- to most-extensive is: $\text{GaAl}_{12} < \text{Al}_{13} < \text{GeAl}_{12}$, which is the experimental sequence for rates of oxygen isotope exchange into the μ_2 -OH sites. While these surfaces will change quantitatively with the presence of solvent, the calculations are consistent with the simple interpretation that increasing the charge/size ratio of the central metal decreases the energy required to partly dissociate

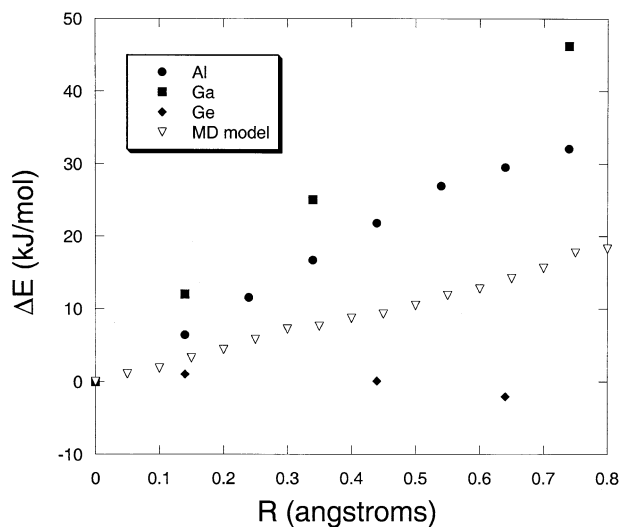


Fig. 3. Gas-phase potential energy surfaces for the first activation step (Fig. 2a to Fig. 2b) for MAI_{12} ($GaAl_{12}$, Al_{13} , and $GeAl_{12}$), from density-functional electronic structure calculations. The order $Ga > Al > Ge$ follows size/charge ratio. The higher the polarization of the μ_4 -O, the more facile the transformation from Figure 2a to Figure 2b, and the more rapid the hydroxide exchange rate. Additional calculations indicate that the results are not changed substantially, in a relative sense, if a dielectric medium is used to simulate the solvent.

the Keggin ion into the $\nabla Al(OH)_2-\nabla Al$ structure in Figure 2b. The energy barrier for the molecular dynamics model, as parameterized from Fe^{3+} , is ~ 18 kJ/mol at $R = 0.8$ Å, considerably lower than the ab initio calculations on Al^{3+} or Ga^{3+} , which is probably part of the reason why the relatively rare dissociation event is observable on our time scales.

Although the OH^t bridges are unreactive on our simulation time scales, a similar $H_3O_2^-$ intermediate can be imagined that controls OH^t exchange within the trimeric units via a similar pH-independent pathway. Instead of Figure 2d, one would obtain an analogous structure involving replacement of one of the rearmost OH^t by an $H_3O_2^-$ bridge. The slower rate of exchange of the OH^t likely arises because of the decreased strain within the three-membered $Al_3(OH^t)_3$, which contains the activated OH^t bridge. The OH^d , on the other hand, occur in two-membered $Al(OH^d)_2Al$ “rings” and are more highly strained, with the Al-O distances being $\sim 5\%$ longer than the OH^t bridges in LDA calculations of the intermediate.

5. DISCUSSION

The fundamental hypothesis derived from these simulations is that a hydrated metastable intermediate forms at steady state and is necessary for exchange of the μ_2 -OH on the Keggin ion. Because the intermediate forms without proton transfer from the aqueous solution, a mechanism for oxygen exchange that involves this intermediate is consistent with the observed pH-independence of exchange rates. Because the formation is controlled by bonds between the μ_4 -O and the central metal, the extent to which this intermediate forms varies in the order $GaAl_{12} < Al_{13} < GeAl_{12}$, the observed trend in rates of isotopic exchange into μ_2 -OH.

This fundamental hypothesis can be tested experimentally. The reaction to form the hydrated intermediate has a high positive reaction volume (ΔV_{rxn}) relative to the stable ϵ -Keggin structure. This ΔV_{rxn} includes removal of two water molecules from the bulk solution that return the five-coordinated aluminums to their six-coordinated state. Usually, removal of water molecules from the bulk solution and packing them into hydration spheres causes a net negative volume change because bulk water molecules are more loosely packed (~ 18 cm³/mol) than those in hydration spheres (~ 9 cm³/mol for octahedral ions; Swaddle, 1981, 1993). However, expansion of the ϵ -Keggin molecule to form the hydrated intermediate exceeds the negative volume change that arises from removal of two water molecules from the bulk solution.

To estimate the sign of the ΔV_{rxn} , we carried out calculations on the LDA structures using the Connolly excluded-volume method (Connolly, 1985). The volume of the Al_{13} hydrated intermediate (~ 796 Å³; probe radius 1.4 Å) exceeds the volume of the stable Al_{13} ion, (~ 666 Å³) by 130 Å³. This is more than twice the volume lost from removing two waters from the solution, ($\sim 2 \times 30$ Å³ = 60 Å³), so the net reaction to form the intermediate has $\Delta V_{rxn} > 0$. The ΔV^\ddagger value for activated exchange, of course, will be added to the ΔV_{rxn} , but it is unlikely that ΔV^\ddagger will be so large and negative as to change the sign of the net reaction. Thus, our proposed mechanism predicts that rates of oxygen exchange in μ_2 -OH sites in the Al_{13} will decrease with increased pressure and will be dominated by the large increase in volume to form the intermediate.

A second corollary is that solvation forces are important in stabilizing the hydrated intermediate. If the electrolyte distribution around the highly charged ion ties up water molecules needed for the stabilization of the intermediate in Figure 2c, activation of the stable Keggin ion into the expanded intermediate will be inhibited. Therefore, ionic strength and the type of electrolyte would have a significant influence on exchange rates through the effects on local fluctuations in water concentration and shielding.

Additionally, it is important to appreciate the $H_3O_2^-$ bridge that forms by hydrogen bonding between a bound η -OH₂ and a η -OH. These μ_2 - $H_3O_2^-$ are well documented for doubly bridged hydroxo dimers of metals (see Springborg, 1988; Ardon and Bino, 1985) where they dramatically affect the stability of the dimer and the Brønsted acid-base properties. It seems likely that similar bridges will be observed on mineral surfaces.

The experimental data indicate that the ¹⁷O-NMR signal is dominated by rates of exchange of η -OH₂ from the stable ϵ -Keggin molecule, and not from the intermediate molecule. Although the rates of exchange of η -OH₂ at sites in the intermediate structures are probably more rapid than for the stable ϵ -Keggin molecules, the concentrations of the intermediates are too small to detect via the ¹⁷O-NMR line-broadening method. Thus, η -OH₂ exchange, unlike μ_2 -OH exchange, is measured to be virtually independent of substitution into the central tetrahedral site.

Details of the η -OH₂ exchange also indicate that important features are missing from the molecular dynamics force field. Because we observe η -OH₂ exchanges during the simulations only during the conversion from Figure 2c to 2a, we would predict that the ^{IV}M substitutions should have a significant effect on the η -OH₂ water exchange as well as for the μ_2 -OH

site. In fact, the IVM substitutions have a relatively small effect on the $\eta\text{-OH}_2$ exchange rates. The molecular dynamics simulations failed to find the predominant mechanism for water exchange which evidently does not involve the hydrated intermediate. The implications of this discrepancy may become clearer as activation volume data become available for both the $\mu_2\text{-OH}$ and $\eta\text{-OH}_2$ sites.

How will this basic mechanism be modified on a mineral surface? In simulations of solvated $\alpha\text{-M}_2\text{O}_3$ (012) surfaces, we have observed similar hydrated intermediates. Here the metals are activated singly, not in pairs as is the case for the Keggin ion. Experimentally, it is known that even in high vacuum environments, involving monolayer coverages of water on hematite (012) surfaces, nearly complete mixing of oxygen between lattice ($\mu_3\text{-O}$) and adsorbed ($\eta\text{-OH}_2$) water molecules was observed on hour-long time scales, indicating the dynamic nature of the surface environment (Henderson et al., 1998). Similarly puzzling surface lability involving extensive mixing of lattice oxygens and adsorbed waters has been observed on alumina surfaces (Elam et al., 1998). One cannot help but speculate that this exchange process involves $\mu_4\text{-O-M}$ dissociation similar to what we have observed on the Keggin ions in solution, probably involving coactivation of two adjacent metal centers. Such coactivation would transform a triply bridging oxygen into a doubly bridging oxygen, which could then exchange by a process analogous to that in Figure 2d and 2e. Otherwise the exchange process must somehow directly lift a $\mu_3\text{-O}$ site out of the lattice and exchange it with an $\eta\text{-OH}_2$ adsorbed water molecule. Once the idea of *metals* dynamically moving between their lattice sites and their hydrated intermediate states is understood, the process becomes far easier to envision.

A few remarks on the pH dependence of the exchange rate are in order. As mentioned above, our mechanism does not involve a protonation step and to first order is independent of pH. Deprotonation of the $\eta\text{-OH}_2$ sites would decrease the barrier to forming the hydrated intermediate in the same way as deprotonation of an $\eta\text{-OH}_2$ site on a monomeric Al^{3+} complex enhances the exchange rates of the remaining water molecules (Richens, 1997). This effect is not observed experimentally for the ε -Keggin system because the ε -Keggin ion is not stable at the pH at which the $\eta\text{-OH}_2$ begin to deprotonate. An oxide surface, however, probably will be stable at the pH at which its $\eta\text{-OH}_2$ begin to deprotonate, and it is likely that exchange rates will increase with increasing pH in the surface environment.

The reactivities of minerals may be controlled by highly coordinated oxygens, such as the $\mu_4\text{-O}$ in boehmite, α -, and $\gamma\text{-Al}_2\text{O}_3$ and their Fe(III) analogs, even though these highly coordinated oxygens represent a small fraction of the total exposed oxygens and do not contribute considerably to the acid-base chemistry. The partial dissociation of these highly coordinated oxygens, coupled with simultaneous activation and displacement of neighboring metal centers, is likely to be a fundamental process by which metals atoms undergo ligand exchanges at mineral surfaces.

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