UC Davis

UC Davis Previously Published Works

Title

Proton-Exchange Rates on Hydroxide Bridges of Mineral-Like Metal-Hydroxide Clusters

Permalink

<https://escholarship.org/uc/item/45b4s4rr>

Journal

ChemistrySelect, 1(6)

ISSN

2365-6549

Authors

Fields, CR
Oliveri, AF
Colla, CA
et al.

Publication Date

2016-05-01

DOI

10.1002/slct.201600190

Peer reviewed

Inorganic Chemistry

Proton-Exchange Rates on Hydroxide Bridges of Mineral-Like Metal-Hydroxide Clusters

Caitlyn R. Fields⁺,^[a] Anna F. Oliveri⁺,^[b] Christopher A. Colla,^[b] Darren W. Johnson,^{*,[a]} and William H. Casey^{*,[b]}

Soluble metal-hydroxide clusters of Group 13 metals are popular in both materials chemistry and geochemistry. In geochemistry these clusters are used as experimental models for clay-like minerals. In materials chemistry these clusters are the precursors for useful thin films. However, little is known about the formation mechanisms and solution dynamics of these species or how they compare to monomer ions. In this study we use ¹H-NMR spectroscopy to estimate the exchange rates of protons on sites in the Ga₁₃(μ₃-OH)₆(μ₂-OH)₁₈(H₂O)₂₄(NO₃)₁₅ (Ga₁₃) and Ga₇In₆(μ₃-OH)₆(μ₂-OH)₁₈(H₂O)₂₄(NO₃)₁₅ (Ga₇In₆) cluster species. To date, these clusters provide the best molecular-scale models for the surface chemistry of thin films and layered minerals. Trivalent metal-hydroxide minerals are environmentally important, because of the rich acid-base chemistry that exists in the pH regions of most soils. Our data suggest millisecond timescales for the exchange of protons on the μ₂-OH bridges with bulk water in Group 13 metal-hydroxide minerals, such as tsumgallite and diaspore.

Little is known about the molecular-scale dynamics of sheet-like hydroxide materials in spite of their overwhelming importance to environmental chemistry and materials science. For example, the amorphous version of the mineral tsumgallite (GaOOH), shown in Figure 1C, is a key intermediate of solution-processed thin films before the final annealing step of dehydration to Ga₂O₃, and is isostructural with common soil minerals diaspore (AlOOH) and goethite (FeOOH).^[1–3] Table 1 includes examples of related Group 13 materials and their mineral analogues, to emphasize the links between materials chemistry and geochemistry.

Thin films can be formed from aqueous solutions of polynuclear clusters,^[10] which serve an additional role as experimental models for clay-like minerals to probe solution dy-

Figure 1. The structure of a) Ga₁₃ with capping water ligands eliminated for clarity. Metal and oxygen atoms are shown in grey. Sets of protons on hydroxide bridges are indicated by: ● μ₃-OH, ● μ₂-OH_{ext}, ● μ₂-OH_{int}. b) brucite, a sheet like mineral with μ₃-OH bridges (●) between divalent metals that resembles the planar core in these clusters. Several metal centers are removed to emphasize the structural similarity to the Ga₁₃. c) the mineral tsumgallite, GaOOH. The μ₂-OH_{GaOOH} protons (●) are structurally similar to the μ₂-OH_{int} (●) of Ga₁₃.

[a] C. R. Fields,⁺ Prof. D. W. Johnson
Department of Chemistry and Biochemistry
University of Oregon

1253 University of Oregon
Eugene, OR 97403

E-mail: dwj@uoregon.edu

[b] Dr. A. F. Oliveri,⁺ C. A. Colla, Prof. W. H. Casey
Department of Chemistry, University of California, Davis 1 Shields Ave
Davis, CA 95616
E-mail: whcasey@ucdavis.edu

[⁺] These authors contributed equally to this work.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/slct.201600190>

namics.^[11] Metal (hydr)oxide clusters have interested scientists because of their widespread uses as catalysts for water-splitting,^[12–14] sensors,^[15] pillaring agents,^[16] medical diagnostics,^[17] and precursors for the thin-film industry.^[9,10,18–20] For many years, geochemists had no good systems to estimate the dynamics of elementary processes, such as proton-exchange, electron-exchange, or ligand-substitution reactions for mineral-

Table 1. Group 13 thin films of interest and the mineral analogues.

Film	Mineral Analogue	Use in Materials Industry
Al ₂ O ₃	Corundum	Sapphire, Ruby, Solar cells ^[4–6]
Ga ₂ O ₃	-	H ₂ sensors, ^[7] Transistors ^[8]
GaInO ₃	-	Transistors
AlOOH	Diaspore, Boehmite	Intermediate in Al ₂ O ₃ film formation
GaOOH	Tsumgallite ^[1]	Intermediate in Ga ₂ O ₃ film formation ^[2]
Al(OH) ₃	Gibbsite	Soluble precursor for Al ₂ O ₃ films
Ga(OH) ₃	Söhngite	Soluble precursor for Ga ₂ O ₃ films ^[9]

like materials. The need for such data became more pressing as computational models advanced and the experimental verification lagged because it is so difficult to follow molecular processes on solids.^[21] Fortunately, methods of syntheses have advanced to provide stable, monospecific solutions of useful metal cluster ions. In this paper we employ ¹H-NMR spectroscopy to estimate rates of proton exchange from hydroxide bridges in the Ga₁₃(μ₃-OH)₆(μ₂-OH)₁₈(H₂O)₂₄(NO₃)₁₅ (**Ga**₁₃) and Ga₇In₆(μ₃-OH)₆(μ₂-OH)₁₈(H₂O)₂₄(NO₃)₁₅ (**Ga**₇In₆) cluster species. The results compare well with a geochemically important aluminum [AlO₄Al₁₂(OH)₂₄(H₂O)₁₂]⁷⁺ cluster,^[22,23] suggesting reactivity similarities among the Group 13 clusters.

We assigned ¹H-NMR signals for the isostructural set of [Ga_{13-x}In_x(μ₃-OH)₆(μ₂-OH)₁₈(H₂O)₂₄](NO₃)₁₅ (0 ≤ x ≤ 6) cluster species in wet *d*₆-dimethylsulfoxide (*d*₆-DMSO) in order to study the kinetics of proton-exchange events.^[24,25] When completely ligated with water, the **Ga**₁₃ and **Ga**₇In₆ have D_{3d} symmetry and three types of hydroxide bridges (Figure 1a).^[24] Each of the bridges (μ₃-OH, μ₂-OH_{ext} and μ₂-OH_{int}) are visible in the ¹H-NMR spectrum, are assigned, and behave uniquely in solution. The μ₂-OH_{ext} bridges bind the exterior metal ions to the planar seven-ion Ga(III) core of the clusters. Both the μ₃-OH and μ₂-OH_{int} bridges bind the cluster core. Protons on the bridges of the core are perpendicular to the surface, similar to the protons on thin-film surfaces and between sheets in minerals (e.g., brucite, boehmite, gibbsite) (Figure 1b). The μ₃-OH of the **Ga**₁₃ resemble the bridges in söhngite (Ga(OH)₃) and μ₂-OH_{int} bridges resemble those in the mineral tsumgallite (GaOOH) (Figure 1c).

The ¹H-NMR signals of the μ₃-OH bridges are the farthest downfield (6.5–6.8 ppm), and therefore the most acidic proton site on the cluster.^[26] In the ¹H-NMR spectra of **Ga**₁₃, the signal associated with the proton of this bridge disappears over time, indicating a slow, yet-unidentified, deprotonation reaction (Figure 2).^[25] This signal persists in the ¹H-NMR spectrum for anywhere from ~1 week to a few hours, depending upon the concentration of water in the *d*₆-DMSO solvent. The area of the μ₃-OH peak can be directly related to concentration of these sites in solution because we used an internal standard (1,3,5-trichlorobenzene). By plotting the normalized concentration ($\frac{C(t)}{C_0}$) of the μ₃-OH protons with respect to time (s), the resulting slope yields a reaction rate for proton exchange (Figure 3a). (Peaks with $\frac{C(t)}{C_0} \leq 0.05$ were not included.) To determine the rate constant (*k*₂₉₈) for this slow deprotonation reaction, the rates from Figure 3a were plotted as a function of water concentration (Figure 3b). The linearity of data (Figure 3b) indicates

Figure 2. ¹H-NMR spectra for the μ₃-OH bridge (●) in the seven-ion Ga(III) core of **Ga**₁₃. a) 0.007 χ_{H₂O} b) 0.045 χ_{H₂O} c) 0.123 χ_{H₂O}.

Figure 3. Kinetic data for the slow deprotonation of the μ₃-OH bridge in the **Ga**₁₃ cluster. a) The normalized concentration ($\frac{C(t)}{C_0}$) of the μ₃-OH protons as a function of time. b) Reaction rates as a function of the mole fraction of water in the solvent. This data shows that the slow deprotonation is first order with respect to water and has a rate constant *k*₂₉₈ = 1.1 × 10^{−5} ± 0.1 × 10^{−5} s^{−1}.

that the reaction is first order with respect to water, with a rate constant $k_{298} = 1.1 \times 10^{-5} \pm 0.1 \times 10^{-5} \text{ s}^{-1}$.

In contrast, ^1H -NMR signals for the $\mu_3\text{-OH}$ proton in the Ga_7In_6 cluster did not change with time. Because we see no evidence for slow elimination of this proton, we conducted VT-NMR experiments to estimate the rates of exchange. However, no broadening was observed, indicating that the proton is not exchanging on the NMR time scale, which indicates a difference in kinetic behaviors of the Ga_{13} and Ga_7In_6 clusters.

Rates of proton exchanges on the internal and external $\mu_2\text{-OH}$ bridges differed. Although we previously found that the outermost metal ions exchange slowly (days) in the mixed-metal clusters (Figure S11),^[26] no kinetic information could be acquired for the $\mu_2\text{-OH}_{\text{ext}}$. VT-NMR experiments indicate no rapid proton exchanges, therefore, we speculate that the protons may be exchanging as a unit with the oxygen and metal ion at these outer sites. We recognize, however, that the protons may be exchanging much more rapidly than the metals, but at rates that are much slower than the ^1H -NMR timescale.

The $\mu_2\text{-OH}_{\text{int}}$ bridges have the only proton signals that exhibit evidence of exchange with bulk water (Figure 4). Line-

shape analysis can be used to calculate exchange rates using modified forms of the Bloch-McConnell Equations under specific conditions that were met in this study (See SI).^[23] In this case, the difference of the full-width-at-half-maximum (FWHM) rela-

$$\frac{1}{\tau} = k = \pi(\text{FWHM} - \text{FWHM}_0) \quad (1)$$

The FWHM_0 for Ga_{13} was estimated to be $3.6 \pm 0.2 \text{ Hz}$ for all samples by averaging the lowest-temperature measurements ($25\text{--}33^\circ\text{C}$) from samples with the least amount of water present ($\chi_{\text{H}_2\text{O}} \leq 0.001$). At these conditions, the linewidths did not vary with temperature and had asymptotically reached a constant value (Figure 5a). To measure rates, ^1H -NMR spectra were collected over the temperature range 25 to 57°C with varying concentrations of water in the solvent. The maximum change in FWHM for Ga_{13} ranges from 2 to 14 Hz in this temperature range, depending on the concentration of water in the solvent (Figure 4 and 5a).

The results indicate that the lifetime of a proton at room temperature (τ_{298}) for samples where $\chi_{\text{H}_2\text{O}} > 0.001$ is $\sim 40 \text{ ms}$ (Figure 5b). The values for τ_{298} at the driest conditions ($\chi_{\text{H}_2\text{O}} \leq 0.001$) could only be estimated from experiments at relatively high temperatures, followed by back-calculation of the rates to room temperature conditions where there is no evidence of broadening (see below). To accomplish the calculation we used the Arrhenius Equation to determine activation parameters for the exchange reaction. The logarithm of the rate constants, $\ln(k)$ were plotted with respect to $1/T$ (K^{-1}) (Figure 5c). The resulting data were fit to the linear equation:

$$\ln(k) = -\frac{E_a}{R} \left(\frac{1}{T} \right) + \ln(A) \quad (2)$$

in order to estimate activation parameters, including the enthalpy of activation ($\Delta H_{298}^\ddagger$) using equation (3):

$$\Delta H_{298}^\ddagger = E_a - RT \quad (3)$$

and the entropy of activation ($\Delta S_{298}^\ddagger$), which is calculated from the intercept and Equation (4):

$$\Delta S_{298}^\ddagger = R \ln(A) - R \ln \left(\frac{k_B T}{h} \right) - R \quad (4)$$

Finally, $\Delta G_{298}^\ddagger$ can be determined using equation (5):

$$\Delta G_{298}^\ddagger = \Delta H_{298}^\ddagger - T \Delta S_{298}^\ddagger \quad (5)$$

Both $\Delta H_{298}^\ddagger$ and $\Delta S_{298}^\ddagger$ for exchange of a proton on the $\mu_2\text{-OH}_{\text{int}}$ bridges of Ga_{13} are affected by water addition (Figure 5d). However, the values quickly reach a constant value as water increases. We extrapolate the weak dependence at these concentrations to estimate rates for a purely aqueous solution. Our estimates are: $\Delta H_{298}^\ddagger = 39 \pm 4 \text{ kJ/mol}$, $\Delta S_{298}^\ddagger = -90 \pm 10 \text{ J/mol}\cdot\text{K}$, and $\Delta G_{298}^\ddagger = 66 \pm 1 \text{ kJ/mol}$. The $\Delta S_{298}^\ddagger$ changes sign as water is added to the solution, indicating that water orders the system, since hydrogen bonding may activate exchange. Using the acti-

Figure 4. VT ^1H -NMR spectra for the $\mu_2\text{-OH}_{\text{int}}$ bridge (●) in the seven-ion Ga (III) core of Ga_{13} . a) $0.001 \chi_{\text{H}_2\text{O}}$. b) $0.007 \chi_{\text{H}_2\text{O}}$. c) $0.013 \chi_{\text{H}_2\text{O}}$.

shape analysis can be used to calculate exchange rates using modified forms of the Bloch-McConnell Equations under specific conditions that were met in this study (See SI).^[23] In this case, the difference of the full-width-at-half-maximum (FWHM) rela-

Figure 5. Kinetic data for the exchange between the $\mu_2\text{-OH}_{\text{int}}$ bridge in the Ga_{13} cluster and bulk water. a) The ^1H -NMR FWHM measurements at various temperatures and concentrations of water. The FWHM_0 is approximated for all Ga_{13} samples as the asymptotic limit at low temperatures for the $\chi_{\text{H}_2\text{O}} \leq 0.001$ solutions, indicated by the line as 3.6 ± 0.2 Hz. b) Lifetime of a proton at 298 K as a function of water concentration. Circled data points were back-calculated from higher temperature measurements. c) Linear Arrhenius plot for select examples of data. d) Calculated activation parameters in respect to $\chi_{\text{H}_2\text{O}}$, distinct, but also comprise different Group 13 metal ions, which suggest that the rates of proton exchange on these hydroxyl bridges might be relatively insensitive to small changes in structure or bonding to the oxygen. We recognize that these are the only such measurements and future experiments are needed to support this hypothesis.

vation parameters, we estimate lifetimes of protons in the driest solvent at $\sim 2\text{--}3$ s. It was impossible to accurately measure FWHM_0 of the $\mu_2\text{-OH}_{\text{int}}$ bridges in the Ga_7In_6 cluster as the maximum observed change in FWHM was only 2–3 Hz, and these differences are too small to estimate rates accurately (Figures SI2–3).

To test the accuracy of our approximations, six sets of data ($0.02 \leq \tau \leq 0.0008$ s) were generated by solving the Bloch-McConnell equations for two-site exchange and for two cases where $|v_w - v_{\text{Ga}}| = 2000$ and 5000 Hz. The value $|v_w - v_{\text{Ga}}|$ is the difference in Hertz of the resonance of the ^1H -NMR signals from water and sites on the Ga_{13} , respectively. In the simulations, the intensity of the Ga_{13} signal was set 0.0005 that of the proton signals, to approximate our case where the concentrations of protons in exchanging sites are a small fraction of the total. The synthetic data were then treated as experimental results and, in each case, the approximations lead to estimates of τ that are accurate to within a factor of two. This variation is within the uncertainties given by errors in the activation parameters.

Our conclusions can link results from the Ga(III) clusters to other Group 13 polyoxocations. The lifetimes of a proton on a $\mu_2\text{-OH}_{\text{int}}$ bridge of the Ga_{13} cluster ($\tau_{298} = 0.04 \pm 0.01$ s) compare well with those measured for the two unassigned hydroxide signals of the Al_{13} Keggin ion ($\tau_{298} = 0.013$ s and $\tau_{298} = 0.201$ s)^[23] at similar conditions. These clusters are not only

structurally distinct, but also contain different Group 13 metal ions, which suggests that the rates of proton exchange on these hydroxyl bridges might be relatively insensitive to small changes in structure and bonding to the oxygen. We recognize that these are the only such measurements and future experiments are needed to support this hypothesis.

Another important question is whether the rates are affected by the overall cluster charges and solution pH. From studies of minerals, there seems to be a strong relationship between surface charge and kinetics of reactions so that any rates vary in a broad amphoteric distribution with pH as the solid develops positive or negative surface charge.^[27,28] In these clusters the surface charge would be controlled by acid-base reactions, and undoubtedly also by ion association. In our experiments, surface charge is not controllable because of the mixed-solvent systems but we can change the overall charge of a cluster via suitable choice of a ligand and examine the effect on proton lifetimes. Our data suggest millisecond timescales for the protons on the bridges of metal-hydroxide minerals, such as tsumgallite and diasporite, the most similar minerals to our cluster ion.

Acknowledgements

This work was supported by the NSF Center for Sustainable Materials Chemistry (CSMC) CHE-1102637. The University of Oregon CAMCORNMR facility, where all of the data was collected, are supported by NSF CHE-0923589 and CHE-1427987. The authors would like to particularly thank Dr. Bettye L. S. Maddux for her encouragement and help facilitating our CSMC collaboration.

Keywords: kinetics • minerals • geochemistry • clusters • NMR

- [1] J. Schluter, K. Karl-Heinz, G. Adiwidjaja, G. Gebhard, *Neues. Jb. Miner. Monat.* **2003**, 521–527.
- [2] V. Berbenni, C. Milanese, G. Bruni, A. Marini, *J. Therm. Anal. Calorim.* **2005**, 82, 401–407.
- [3] M. K. Kamunde-Devonish, D. B. Fast, Z. L. Mensinger, J. T. Gatlin, L. N. Zakharov, M. R. Dolgos, D. W. Johnson, *Inorg. Chem.* **2015**, 54, 3913–20.
- [4] Y. Bai, I. Mora-Sero, F. De Angelis, J. Bisquert, P. Wang, *Chem. Rev.* **2014**, 114, 10095–10130.
- [5] A. Hagfeldt, G. Boschloo, L. Sun, L. Kloo, H. Pettersson, *Chem. Rev.* **2010**, 110, 6595–6663.
- [6] J. Wu, Z. Lan, J. Lin, M. Huang, Y. Huang, L. Fan, G. Luo, *Chem. Rev.* **2015**, 115, 2136–2173.
- [7] G. Korotcenkov, S. Do Han, J. R. Stetter, *Chem. Rev.* **2009**, 109, 1402–1433.
- [8] S. R. Thomas, G. Adamopoulos, Y.-H. Lin, H. Faber, L. Sygellou, E. Stratakis, T. D. Anthopoulos, *App. Phys. Lett.* **2014**, 105.
- [9] L. G. Bloor, C. J. Carmalt, D. Pugh, *Coord. Chem. Rev.* **2011**, 255, 1293–1318.
- [10] Z. L. Mensinger, J. T. Gatlin, S. T. Meyers, L. N. Zakharov, D. A. Keszler, D. W. Johnson, *J. Chem. Soc. Dalton Trans.* **2008**, 120, 9626–9628.
- [11] C. A. Ohlin, E. M. Villa, J. R. Rustad, W. H. Casey, *Nat. Mater.* **2010**, 9, 11–9.
- [12] M. W. Kanan, D. G. Nocera, *Science* **2008**, 321, 1072–1075.
- [13] J. G. McAlpin, Y. Surendranath, M. Dinca, T. A. Stich, S. A. Stoian, W. H. Casey, D. G. Nocera, R. D. Britt, *J. Am. Chem. Soc.* **2010**, 132, 6882–6883.
- [14] M. W. Kanan, J. Yano, Y. Surendranath, M. Dincă, V. K. Yachandra, D. G. Nocera, *J. Am. Chem. Soc.* **2010**, 132, 13692–13701.
- [15] P. Alivisatos, P. F. Barbara, A. W. Castleman, J. Chang, D. A. Dixon, M. L. Klein, G. L. McLendon, J. S. Miller, M. A. Ratner, P. J. Rossky, et al., *Adv. Mater.* **1998**, 10, 1297–1336.
- [16] J. B. D'Espinose de la Caillerie, P. P. Man, M. A. Vicente, J. F. Lambert, *J. Phys. Chem. B* **2002**, 106, 4133–4138.
- [17] H. Wille, M. Shanmugam, M. Murugesu, J. Ollesch, G. Stubbs, J. R. Long, J. G. Safar, S. B. Prusiner, *P. Natl. Acad. Sci. USA* **2009**, 106, 3740–3745.
- [18] S. T. Meyers, J. T. Anderson, D. Hong, C. M. Hung, J. F. Wager, D. A. Keszler, *Chem. Mater.* **2007**, 19, 4023–4029.
- [19] K. Jiang, J. T. Anderson, K. Hoshino, D. Li, J. F. Wager, D. A. Keszler, *Chem. Mater.* **2011**, 23, 945–952.
- [20] J. T. Anderson, C. L. Munsee, C. M. Hung, T. M. Phung, G. S. Herman, D. C. Johnson, J. F. Wager, D. A. Keszler, *Adv. Funct. Mater.* **2007**, 17, 2117–2124.
- [21] J. Wang, J. R. Rustad, W. H. Casey, *Inorg. Chem.* **2007**, 46, 2962–2964.
- [22] G. Furrer, B. L. Phillips, K.-U. Ulrich, R. Pöthig, W. H. Casey, *Science* **2002**, 297, 2245–2247.
- [23] J. R. Houston, B. L. Phillips, W. H. Casey, *Geochim. Cosmochim. Ac.* **2006**, 70, 1636–1643.
- [24] A. F. Oliveri, L. A. Wills, C. R. Hazlett, M. E. Carnes, I.-Y. Chang, P. Ha-Yeon Cheong, D. W. Johnson, *Chem. Sci.* **2015**, 6, 4071–4085.
- [25] A. F. Oliveri, M. E. Carnes, M. M. Baseman, E. K. Richman, J. E. Hutchison, D. W. Johnson, *Angew. Chem. Int. Ed.* **2012**, 51, 10992–10996.
- [26] A. F. Oliveri, Solution Characterization of Inorganic Nanoscale Cluster Species via ¹H-NMR and DOSY, University of Oregon, **2015**.
- [27] R. Astumian, M. Sasaki, *J. Phys. Chem.* **1981**, 85, 3832–3835.
- [28] M. Ashida, M. Sasaki, H. Kan, T. Yasunaga, K. Hachiya, T. Inoue, *J. Colloid Interf. Sci.* **1978**, 67, 219–225.

Submitted: March 8, 2016

Accepted: March 11, 2016