Polyoxometalates

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# Reaction Dynamics of the Decaniobate Ion $[H_xNb_{10}O_{28}]^{(6-x)-}$ in Water**

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Key questions in geo- and environmental chemistry concern interactions between water and metal-oxide/mineral surfaces as these are responsible for weathering and for the elimination of pollutants. Large oxide ions could be enormously useful to geochemists in testing hypotheses about reaction pathways at mineral surfaces, but most dissociate rapidly, exchange oxygen atoms too quickly, or have such complicated acid–base chemistry that they are not helpful. Simultaneously, information about reaction pathways in polyoxometalate (POM) ions is needed to understand the degradation of catalysts and the structural evolutions among different POMs. The nanometer-size decaniobate[1] ion ($[H_xNb_{10}O_{28}]^{(6-x)-}$) is unique in aqueous niobate chemistry as it does not strongly protonate when dissolved in water and is stable at near-neutral pH. We report here the rates of steady isotope exchange at all seven different oxygen sites in this ion (labeled A–G in Figure 1 a) as a function of solution composition. Separately, we follow the pathways for dissociation and identify the reaction products. Our results indicate that the entire structure is involved in the reaction dynamics. For example, rates of steady oxygen-isotope exchanges also increase with pH, even when these processes are much more rapid than dissociation. Furthermore, base-induced dissociation leaves much of the molecule intact, illustrating pathways for interconversion of all isopolyniobate types known to occur in aqueous media.

We prepared $^{17}$O-enriched crystals of $[N(CH_3)_4]_6[Nb_{10}O_{28}]\cdot 6H_2O$ and dissolved about 20 mg into 2 mL of isotopically normal electrolyte containing an anionic pH buffer and 0.1 M $[N(CH_3)_4]Cl$. The decline in intensity of the $^{17}$O NMR signals as a function of time yields rates of isotopic exchange for all seven different oxygen sites with the bulk solution (Figure 1 b). Under most pH conditions, the intensity of the $^{17}$O NMR signal from the central $\mu_6$-O site remains constant, indicating that the decaniobate ion does not dissociate as the other oxygen atoms equilibrate with isotopically normal water. Loss of $^{17}$O NMR peak intensity for the central $\mu_6$-O site occurs only as the molecule dissociates and the central oxygen atoms become accessible to bulk water.

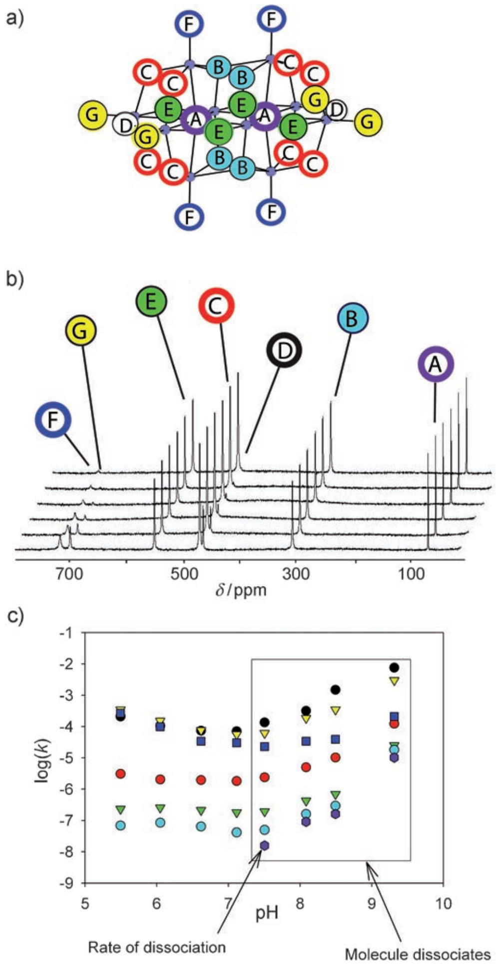

***Figure 1.*** A) Structure of the decaniobate ion, which has one set of two $\mu_6$-O (sites A), one set of four $\mu_3$-O (sites B), three sets of $\mu_2$-O sites (sites C, D, and E), and two sets of $\eta$=O (sites F and G). B) $^{17}$O NMR spectra of $[H_xNb_{10}O_{28}]^{(6-x)-}$ at pH 6.6 and 308.5 K. Times range from 25 min to 15.5 h. C) Rates of steady oxygen isotopic exchange at 308.5 K as a function of pH, with $k = 1/\tau$, the characteristic time. The rate of exchange at the $\mu_6$-oxo site A is proportional to the rate of dissociation of the molecule.

We compared the $^{17}$O NMR spectra with electrospray-ionization mass spectra (ESI-MS) to identify dissociation pathways. The reactivity trends for steady isotope exchanges at all seven structural oxygen sites are surprising:

1) The rates span a range of approximately $10^4$ and are not predictable from simple structural considerations (see the

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Supporting Information for X-ray crystal structure data). The reactivity trend at near-neutral pH is: D($\mu_2$-oxo) > G($\eta$=oxo) > F($\eta$=oxo) > C($\mu_2$-oxo) ≫ E($\mu_2$-oxo) ≫ B($\mu_3$-oxo) ≫ A($\mu_6$-oxo), and all oxygen sites except site A, and possibly site B, increase rates of isotopic substitution at pH ≤ 7.0. Notably, the relative rates of isotopic exchange in the three $\mu_2$-O sites (C, D, and E) differ by about $10^4$. One $\mu_2$-O site (D) even exchanges more rapidly than either terminal oxygen (sites F and G) at pH ≥ 6.6. Furthermore, another $\mu_2$-O site (E) is extraordinarily slow to exchange (Figure 1 c) at these conditions.

2) Most oxygen sites become labile to isotopic exchange as the molecule is protonated, probably at a single oxygen site. Approximate equilibrium constants are assigned from $^{51}$V NMR and potentiometry studies of the isostructural and isovalent $[H_xV_{10}O_{28}]^{(6-x)-}$,[2,3] with p$K_x$ values of: p$K_1 = 6.0$; p$K_2 = 3.74$, and p$K_3 = 1.6$ ($I = 0.6$ M). Using these equilibrium constants, the $[Nb_{10}O_{28}]^{6-}$ species dominates at most pH conditions of this study, with the monoprotonated form $[HNb_{10}O_{28}]^{5-}$ becoming important at pH < 6.5, consistent with the pH variation of isotope-exchange rates. We do not, however, observe $^{17}$O NMR signals to change positions with changes in pH, consistent with very weak protonation.

Site F is the most basic oxygen atom and probably the site of protonation, which explains why the dimer $[Nb_{20}O_{54}]^{8-}$ is formed at two adjacent F sites.[4] Site F also has the highest calculated proton affinity of all the structural oxygen sites and exhibits strong hydrogen bonds to water molecules in the solid state (see the Supporting Information). However, site F is neither the most rapid to exchange nor the only structural oxygen site affected by changes in pH. At pH > 7, the rates of isotopic exchange of sites F, G, and D differ by a factor of around $10^2$. At pH < 7, however, these rates are nearly equal. Even the relatively inert equatorial $\mu_2$-oxygen atoms (site E) exhibit a pH dependence, albeit reduced, for isotopic exchange that is similar to most of the other structural oxygen sites. In no case do we find integer rate orders. Thus, the dynamics of the entire molecule control isotopic-exchange rates; the effects are not local.

We separately followed dissociation of the $[Nb_{10}O_{28}]^{6-}$ ion into product ions from the slow decline in the $^{17}$O NMR signal for the $\mu_6$-oxo site and from changes in the ESI mass spectrum. Dissociation is clearly detectable at pH ≥ 7.5, and the rate increases with pH (Figure 1 c). There are two key results from the dissociation experiments:

1) All oxygen sites exhibit increased rates of isotopic exchange as pH increases, as though the entire nanometer-size cluster is responding to increased $OH^-$ concentrations. Some of these isotope-exchange rates are orders of magnitude higher than rates of base-induced dissociation, which indicates that the molecule as a whole is labilized.

2) The molecule initially dissociates to leave an intact fragment. At pH 12.5, the decaniobate ion dissociates to yield $[H_xNb_6O_{19}]^{(8-x)-}$. If the $[Nb_{10}O_{28}]^{6-}$ ion dissociates to yield an intact hexaniobate and a tetraniobate species in isotopically normal water, 1.0 equivalent of the formed hexaniobate would retain a $^{17}$O label in the inert $\mu_6$-oxo position. By integrating the $\mu_6$-O signals, we observed that 0.8 equivalents of hexaniobate retained an isotopically labeled $\mu_6$-oxygen site, which is close to the anticipated value.

At pH < 9.3, dissociation of the decaniobate molecule is significantly slower than isotopic exchange at most oxygen sites (Figure 1 c). At a much higher pH value of 12.5, however, dissociation is much faster than isotope exchanges at some—or most—oxygen sites in the decaniobate ion. This is clear because the $[H_xNb_6O_{19}]^{(8-x)-}$ product retains $^{17}$O enrichments originally in the $[Nb_{10}O_{28}]^{6-}$ ion.

At pH 9.3, we observe that the $\mu_6$-oxo from the $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion transforms intact into the $\mu_6$-oxo of the smaller $[H_xNb_6O_{19}]^{(8-x)-}$ ion during dissociation (Figure 2). Previous work[5] showed that this site is inert to exchange if the molecule remains intact.

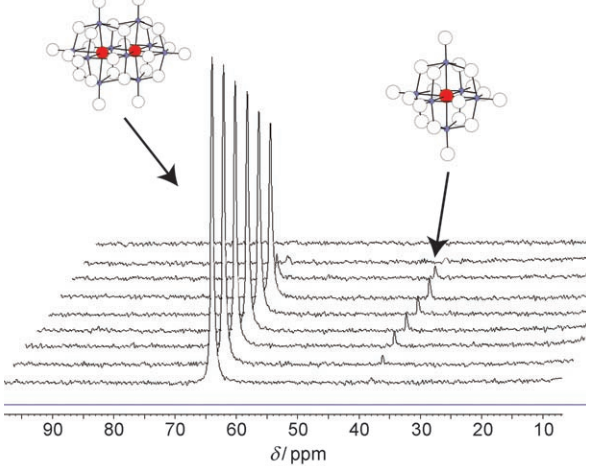

*Figure 2.* Stacked $^{17}$O NMR spectra at pH 9.3 showing the disappearance of the signal for $\mu_6$-oxo (red) in the decaniobate ion and the appearance and subsequent disappearance of the signal for $\mu_6$-oxo in the hexaniobate ion. The transient signal for $\mu_6$-oxo in the hexaniobate ion is due to the reversibility of the dissociation of the decaniobate ion. The first spectrum was collected at 50 min and the last at 10.5 days.

Disappearance of the $^{17}$O NMR signal for this $\mu_6$-oxo suggests that the $[Nb_{10}O_{28}]^{6-}$ and $[H_xNb_6O_{19}]^{(8-x)-}$ ions interconvert, diminishing the signal from both ions with time as isotopically normal oxygen is repeatedly incorporated (see the Supporting Information for the ESI-MS data). To support this idea, we found that we can obtain the decaniobate ion from hexaniobate ion at near-neutral pH.

Thus, a major pathway for base-enhanced dissociation transfers a $\mu_6$-oxo group intact from the dissociating $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion to a $\mu_6$-oxo site in the newly formed $[H_xNb_6O_{19}]^{(8-x)-}$ ion (Figure 3). This pathway is consistent with one suggested for the isostructural decavanadate ion,[6,7] which was inferred from experiments over a much narrower range of rates and conditions. The tetraniobate fragment remaining after dissociation of the $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion

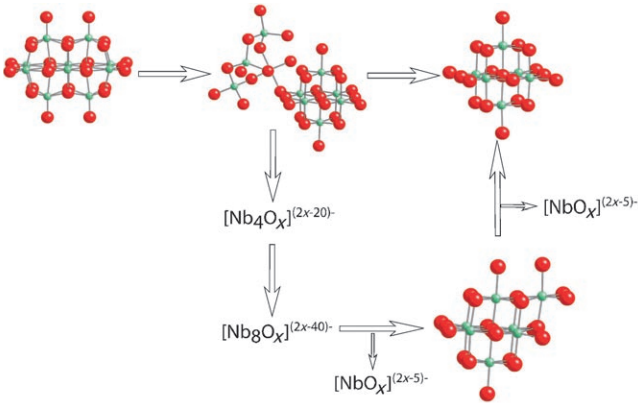

**Figure 3.** The suggested mechanisms for the base-promoted dissociation of the decaniobate ion. One pathway involves dissociation of the $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion at the $\mu_3$-oxo site, releasing a tetrameric fragment.[6,7,10] Subsequent reaction of the tetrameric fragment yields a heptaniobate ion.

subsequently forms higher oligomers, one of which is detectable both by $^{17}O$ NMR spectroscopy and ESIMS. This transient species was identified as heptaniobate, $[Nb_7O_{22}]^{9-}$, based on the spectroscopic data (see the Supporting Information). The ion has been structurally characterized as a subunit of larger clusters or supermolecular structures by two different groups,[8] both of which used the hexaniobate ion as a precursor.

Geochemists investigate the surface chemistry of minerals at the molecular scale using computational models.[9] Their predictions are usually for slow reactions in complicated settings and the important features during mineral growth and dissolution are often nanometer-scale kinks in surface steps or etch pits. Similarly, the products of metal hydrolysis at mineral surfaces are often nanometer-size polymers. The conceptual models of these reactions involve truncated versions of the extended structure, such as using metal–hydroxo dimers as shorthand for the surface of quartz or the basal sheet of a clay.

We here show that even the simplest single-bond-rupture reactions cannot be considered in isolation from the motions of other atoms in nanometer-size structures. Computational models must be structurally faithful to the surface to an extraordinary degree or they will miss the essential chemical features. Furthermore, the results presented here indicate that the decaniobate ion is a keystone of isopolyniobate chemistry since it interconverts to all structural types known to occur in aqueous media.

## Experimental Section

Details of synthesis and spectroscopy are presented in the Supporting Information. To estimate rates, $^{17}O$ NMR peak intensities, relative to a standard, were fit to $I(t) = I_0 \cdot \exp(-kt)$, where $I_t$ and $I_0$ are the peak intensities at times $t$ and zero, respectively. Assignment of the decaniobate $^{17}O$ NMR signals in solution was guided by previous work on decaniobate and decavanadate ions[6,11,12] with the exception of the $\eta{=}O$ peak at 722 ppm, which was assigned to site F based on DFT calculations of $^{17}O$ NMR chemical shifts. Electrospray-ionization mass spectrometry (ESIMS) charge assignments were confirmed by a study of isotopically substituted compounds created by equilibrating $[N(CH_3)_4]_6[Nb_{10}O_{28}]\cdot 6H_2O$ or $[N(CH_3)_4]_8[Nb_6O_{19}]\cdot{\sim}16H_2O$ salts with $H_2{}^{18}O$. Further details on the crystal structure investigations on $[N(CH_3)_4]_6[Nb_{10}O_{28}]\cdot 14H_2O$ may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz--karlsruhe.de), on quoting the depository number CSD-419266.

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