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Borate Accelerates Rates of Steady Oxygen-Isotope Exchange for Polyoxoniobate Ions in Water

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Understanding simple oxygen-exchange reactions is important to a variety of communities concerned with the chemistry of oxides with water. Limitations in the methods available for studying reactions at these oxide–water interfaces, as well as difficulties in characterizing their structures, have led to the use of polyoxometalates (POMs) as model molecules. POMs are metal oxide ions composed of Group 5 and 6 metals. These ions constitute discrete and often soluble clusters than can be spectroscopically probed with great confidence. In addition, POMs are interesting in their own right, owing to their structural and chemical diversity, and are finding an increasing number of applications.[1–5] We have been investigating the oxygen-isotope-exchange kinetics in these ions and aqueous solution by ^{17}O-nuclear magnetic resonance (NMR) spectroscopy to help better recognize what controls the molecule–water interface processes on the level of individual oxygen sites.[6–10] These structures were chosen because the isotope-exchange reactions could be followed separately from dissociation or condensation of the structure.

Borate is widely used as a pH buffer owing to its low cost and conveniently located pK_a. In general, borate buffers are assumed to be inert. Most POMs are anions, as is borate, and it is reasonable to assume that the negative charges of the POM and the borate will minimise interactions in solution. Here we describe the interactions between borate and three different niobium-based POMs. These interactions are interesting in their own right, but also allow us to reconcile observed differences in the oxygen exchange rates between the hexaniobate and hexatantalate ions.[6,7]

We observed a large increase in the rates of oxygen-isotope exchange when a borate buffer was employed in experiments on the sodium salt of the dititanoniobate ion $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$.[9] This observation led us to further investigate this phenomenon in other systems. The rates of oxygen exchange for three separate POMs were discovered to be enhanced by having borate in solution: the potassium salt of the hexaniobate ion $[H_xNb_6O_{19}]^{(8-x)-}$, the tetramethylammonium salt of the decaniobate ion $[H_xNb_{10}O_{28}]^{(6-x)-}$, and sodium salt of the dititanoniobate $[H_xTi_2Nb_8O_{28}]^{(8-x)-}$ ion (hereafter represented by Nb_6, Nb_{10}, and Ti_2Nb_8, respectively, for clarity).

After noticing this rate-enhancing effect, we repeated experiments on the Nb_6 ion. In the original work, we employed borate as a buffer at $10.1 \leq pH \leq 10.7$, a pH region in which rates increase dramatically (Figure 1) and the bridging and terminal oxygen atoms reach similar values for rates of oxygen-isotope exchange.[6] To check whether the increased rates resulted from pH buffer, we replicated the experiments with CAPS (3-cyclohexylamino-1-propanesulfonic acid) buffer. Rates for oxygen-isotope exchange for both reacting structural oxygen atoms decreased dramatically, by at least a factor of 10 (Figure 1, bottom, that is, both the terminal oxygen atoms and μ_2-oxo bridges). Borate buffer clearly had a significant effect on the rates of oxygen-isotope exchange. The effects of carbonate ion were also examined and a difference was apparent here too.

This enhancement of rates of oxygen-isotope exchange caused by the buffer clarifies our previous results for the hexatantalate ion $[H_xTa_6O_{19}]^{(8-x)-}$ (abbreviated Ta_6).[7] For the Ta_6 ion, we found a small increase in rates as the pH was lowered and the molecule became protonated. However, the increase was nowhere near as dramatic as was found for Nb_6 ion in borate buffer (Figure 1; top). The experiments with CAPS show that the faster rates of oxygen exchange were due to dissolved borate in solution.

We then measured rates of isotope exchanges for the Nb_{10} and Ti_2Nb_8 ions in the presence of borate. The latter ion is stable between pH 7.5 and at least pH 13.[9] Isotope exchange rates for sites in the Ti_2Nb_8 ion in sulfonate and amine buffers (see Supporting Information) were measured at $7 \leq pH \leq 10.5$. This pH range was chosen to span across

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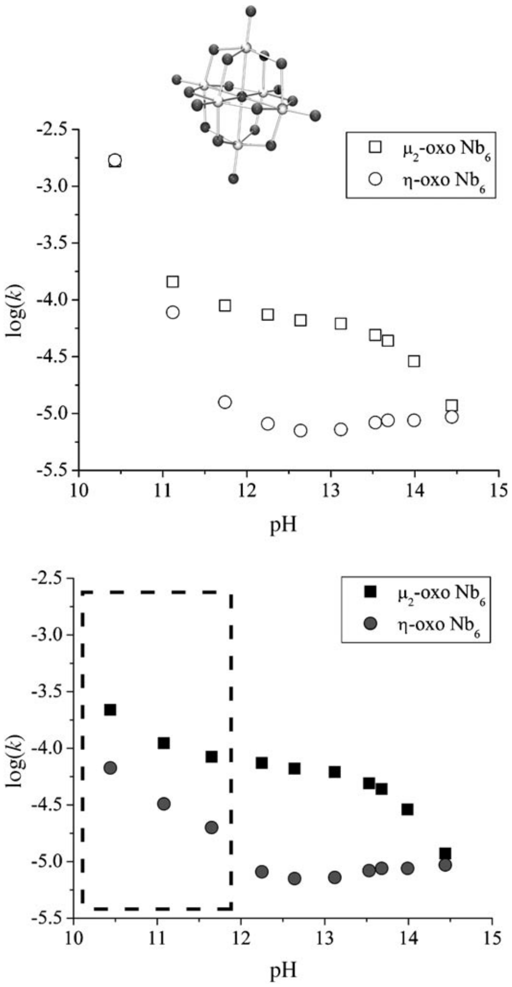

Figure 1. Re-examination of the pseudo-first-order rate coefficients for oxygen exchange for the $[H_xNb_6O_{19}]^{(8-x)-}$ ion. Top: original data published for the Nb_6 ion using borate and carbonate as pH buffers (pH 10.44 for borate; pH 11.65 and 11.08 for carbonate).[6] Bottom: boxed area indicating where new experiments were conducted, replacing borate and carbonate with CAPS (3-cyclohexylamino-1-propanesulfonic acid). The rates of oxygen exchange are heavily influenced by these small anions in solution.

the first pK_a of borate (≈9.14). At all pH conditions, borate accelerates the rates of oxygen-isotope exchange, with a somewhat larger increase close to pH≈9.1 (see Supporting Information for rates and plots). We cannot state confidently that the rate-enhancement is due only to interactions of the polyoxoniobate ions with a monomeric borate complex, because rates are enhanced across a broad range in pH. Polyborate species are also present at these concentrations and may influence the exchange rates. Such polyborate species are known to form in solutions where the borate concentration is above 50 mм.[11–14]

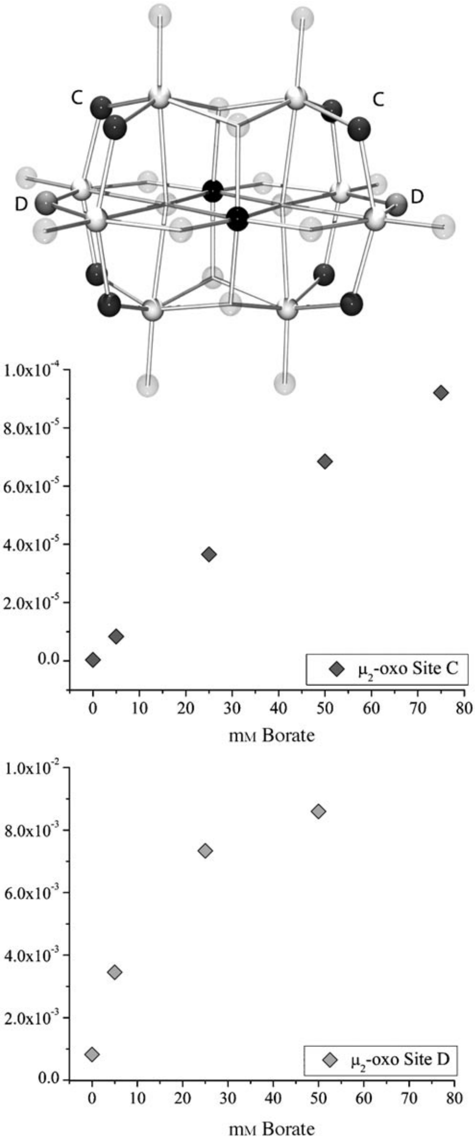

Figure 2. The pseudo-first-order rate coefficients for oxygen exchange of sites C and D, shown in dark gray and light gray respectively, in the Ti_2Nb_8 ion (in which the titanium atoms are black, niobium atoms are white, and all other oxygen atoms are gray and transparent). The rates linearly increase with the borate concentration for site C, but apparently approach a maximum for site D; however, the final datum for site C at 75 mм borate could be approaching a maximum as well. In all cases, the concentration of the Ti_2Nb_8 ion is constant at about 2.8 mм, save the experiment with 50 mм borate for which the concentration of Ti_2Nb_8 was ≈4.2 mм. Rates were too fast to be estimated above 50 mм borate for μ2-oxo site D.

The rates of oxygen-isotope exchange increase for most, but not all, structural oxygen atoms in the Ti_2Nb_8 ion as the amount of borate increases in solution. In Figure 2, the rates of oxygen-isotope exchange for sites C (in dark gray) and site D (in light gray) in the Ti_2Nb_8 ion are shown with respect to total dissolved borate concentration. The rates for site C linearly increase with the amount of borate in solution, a trend that is also seen for the terminal oxygen atoms in the Ti_2Nb_8 ion (see Supporting Information for all rate data); however, the rate for site C at 75 mм borate may exhibit signs of rate saturation, whereby the rates are no longer linearly increasing, as is seen for site D. This saturation of rates of oxygen exchange at sites C and D may help to indicate the preferred interaction sites on the ion. The rates of oxygen exchange for the terminal oxygen atoms increase linearly and might indicated a different, weaker interaction with borate in solution. The rates for some sites, such as the μ_3-oxygen atoms, are unaffected by the presence of borate, but these sites are inert to exchange for the Ti_2Nb_8 ion.[9] One set of slowly exchanging equatorial μ_2-oxygen atoms, along the long side of the ion, are uninfluenced by borate in solution (Figure 3).

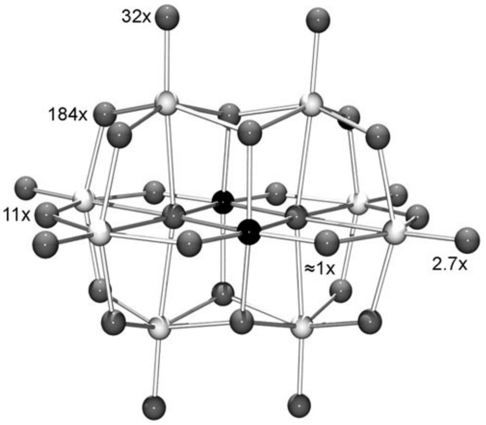

Figure 3. All reacting oxygen atoms are shown with the increase in rates that is observed when the amount of total dissolved borate in solution is increased from 0 to 50 mM. These increases correspond to a ratio so that ≈1× increase means that the rates are virtually unaffected by borate in solution (see Supporting Information for actual rates).

In Figure 3, structural oxygen atoms are shown with the relative increases in rates of oxygen-isotope exchange in the presence, and absence, of borate buffer. The increases correspond to the ratio of the rates so that ≈1× means that the rates are virtually unaffected. The oxygen atoms that are most influenced correspond to the distal face on the short side of the ion, including two sets of μ_2-oxygen atoms and two sets of terminal oxygen atoms.

Richens and co-workers isolated a reduced niobate species in which borate is coordinated to three μ_2-bridging oxygen atoms.[15,16] Here the complex has a stable orthoborate cap above three niobium atoms. This coordination looks similar to the most highly affected oxygen atoms in the Ti_2Nb_8. The authors of that study did not examine the oxygen-exchange kinetics. However, we found no shifts or broadening of lines in the ^{17}O-NMR spectra in the presence of borate for the compounds. No borate coordination was indicated by electrospray-ionization mass spectrometry of the solutions either, suggesting that the interaction is weak or transient or both, which is, however, different from the stable compound made by Richens and co-workers.

Finally, borate accelerated base-induced dissociation of the Nb_{10} ion to the Nb_6 products, which is even evident pH ≈7, at which it was previously unsuspected.[8] A separate side reaction, not dissociation, affects the Ti_2Nb_8 ion at pH ≈7.1 (possibly a dimerization) and this reaction too was accelerated by borate buffer.[9]

Borate and carbonate both rapidly equilibrate with forms that have a reduced coordination number. Boric acid is trigonal and rapidly adds an oxygen atom to form a borate ion $H_3BO_3 \leftrightarrow B(OH)_4^-$,[11,17–20] while trigonal carbonate ions equilibrate with hydrated CO_2, which is linear. We speculate that this interconversion and oxygen addition is key to the rate enhancement. The niobates are large anions and would repel borate or carbonate anions electrostatically. The facile interconversion of the anion to a neutral form, followed by oxygen addition and ejection, is a reasonable hypothesis to explore. Anions that are not able to lose an oxygen tend to be inert (namely, phosphate and sulfate) and are expected to have little to no effect on niobates.

In conclusion, borate enhances rates of oxygen-isotope exchange of polyoxometalate oxygen atoms. Borate also accelerates dissociation and perhaps dimerization side reactions. The exact nature of the interaction of the polyoxometalate ion with the buffer is unclear, but we suspect that borate, and perhaps other small anions that can rapidly add and lose oxygen atoms, interact preferably with the distal face of the large polyoxometalate ions and stabilize intermediate forms of the structure. These interactions are well suited for simulation and may be general to other POMs, and perhaps even solid oxide surfaces.

Experimental Section

Synthesis and ^{17}O-enrichment of $K_8Nb_6O_{19}$, $[N(CH_3)_4]_6[Nb_{10}O_{28}]$, and $Na_8Ti_2Nb_8O_{28}$ were carried out according to published procedures.[6,8,9] $H_2{}^{17}O$ (40%) was purchased from Isotec Laboratories. The solution-state ^{17}O NMR experiments were conducted on a 500 MHz Bruker Avance spectrometer located at the UCD NMR facility. A solution of $TbCl_3$ in water (0.3 M) was employed as an external intensity standard, which was included in the 10 mm NMR tube as a coaxial insert. More details on synthesis, ^{17}O spectroscopy, ^{17}O NMR stack plots, and rates of oxygen exchange provided as Supporting Information. The intensities for ^{17}O NMR signals decrease exponentially with time according to a pseudo-first-order equation; k has units of s^{-1}.

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