Polyoxometalates

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Distinctly Different Reactivities of Two Similar Polyoxoniobates with Hydrogen Peroxide**

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Niobium oxides are used as photocatalysts[1] and also used to sequester radionuclides from waste.[2] Hydrogen peroxide is a common byproduct from these applications, and herein we examine how isopolyoxoniobates, the hexaniobate $[H_xNb_6O_{19}]^{(8-x)-}$ and the decaniobate $[H_xNb_{10}O_{28}]^{(6-x)-}$ ions, react with hxdrogen peroxide. Both the isopolyoxoniobate and the peroxopolyoxoniobate species can be detected by using electrospray-ionization mass spectrometry (ESI-MS) and ^{17}O NMR spectroscopy. Interestingly, we observed that although the decaniobate anion rapidly picks up peroxide, the peroxodecaniobate clusters can dissociate over time and yield the peroxohexaniobate species, and sometimes in the presence of reformed and peroxy-free decaniobate ion. In both isopolyoxoniobate structures, the reaction proceeds by the replacement of niobium terminal oxygen atoms with η^2-$O^{(I)}{}_2{}^{2-}$. The peroxohexaniobate species are extraordinarily stable and we have determined the crystal structure of $[N(CH_3)_4]_5[H_3Nb_6O_{13}(O^{(I)}{}_2)_6]\cdot 9.5\,H_2O$, in which all six terminal oxygen atoms are replaced by η^2-$O^{(I)}{}_2{}^{2-}$. This crystal structure us the first example of an isolated peroxo-isopolyoxoniobate cluster.

The solution chemistry of isopolyoxoniobates is dominated by the decaniobate ion $[H_xNb_{10}O_{28}]^{(6-x)-}$ at near-neutral pH and by the hexaniobate ion $[H_xNb_6O_{19}]^{(8-x)-}$ at higher pH (Figure 1). The rates of the isotopic equilibration of the structural oxygen atoms in both ions were recently determined.[3,4] The central μ_6-oxo sites in the molecules are normally inert to exchange unless the molecule fully dissociates and allows access of unlabeled water to all sites; the ^{17}O NMR signals from the μ_6-oxo sites are typically constant as long as the molecule is intact. Because so much is known about the reactivity of these structures in water, they are good candidates for examining peroxide substitutions. Discrete niobium–peroxide species that involve extended niobium–oxygen networks have not yet been described; however several monomeric $[Nb(O^{(I)}{}_2)_4]^{3-}$ species are described in the literature,[5] as well as some polyoxotungstate complexes that have been functionalized with niobium–peroxo moieties.[6]

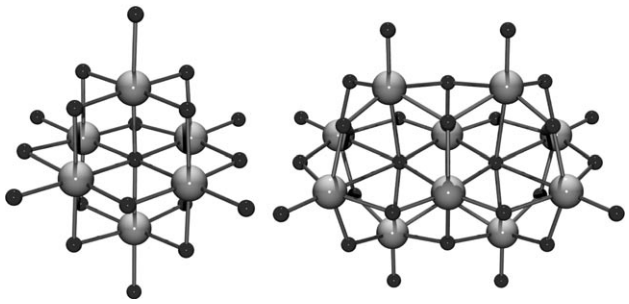

Figure 1. Structures of the decaniobate $[Nb_{10}O_{28}]^{6-}$ (right) and hexaniobate $[Nb_6O_{19}]^{8-}$ (left) ions. Nb gray, O dark gray.

For this study we employed the complementary methods of ESI-MS and ^{17}O NMR spectroscopy. Whereas ESI-MS is a convenient method for monitoring reactions and resolving mixtures of species, it does not yield structural information or reliable quantitative information. This information can, however, be obtained from ^{17}O NMR spectroscopy.

We first monitored the peroxidation of the $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion, which was used as a 1 mM solution of the tetramethylammonium salt at pH 7.3–7.4 at 24 °C. One to six equivalents of hydrogen peroxide were added to the solution, and the reaction was monitored as a function of time by ESI-MS analysis and ^{17}O NMR spectroscopy. Subsequently, we examined the reaction of the $[H_xNb_6O_{19}]^{(8-x)-}$ Lindqvist ion with H_2O_2 at a slightly higher pH value (pH $\approx$ 8.8–9.2). By analogy with the isostructural and isovalent decavanadate ion, the decaniobate ion is unprotonated at these experimental conditions. The hexaniobate Lindqvist ion, in contrast, has two to three protons on the bridging oxygen atoms under these pH conditions.[4]

The peroxide was rapidly incorporated into the decaniobate ion with no change in the pH, this being consistent with one terminal oxygen atom being replaced with η^2-O_2 as H_2O is eliminated for every H_2O_2 added to the structure. When one equivalent of H_2O_2 was added, the reaction was complete within 30 minutes (Figure 2, top), and the reaction rates increased as the peroxide concentration increased. At all peroxide concentrations (1–6 mM), mono- and disubstituted peroxodecaniobate species dominated, and tetra-, penta-, or hexasubstituted species were not observed.

However, whereas peroxide is rapidly incorporated into the decaniobate ion, it is also slowly lost over a matter of days. The reformation of peroxide-free decaniobate ion is clear from the ^{17}O NMR spectra (Figure 2, bottom), which shows an initial signal corresponding to the central μ_6-oxo sites, then the appearance of new signals as the peroxyl group is

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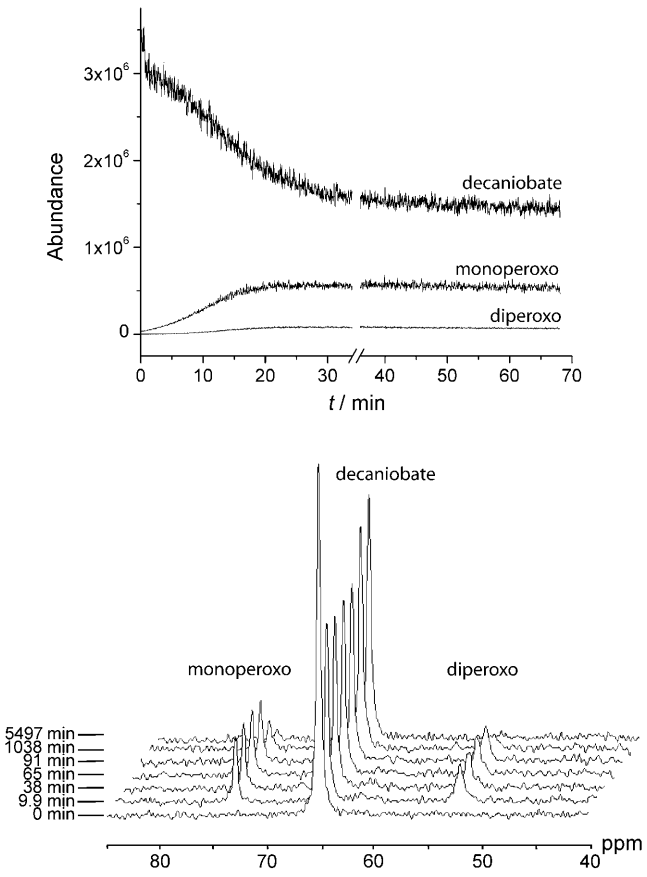

Figure 2. Time course of ESI-MS signals (top) of a solution of the $[Nb_{10}O_{28}]^{6-}$ ion after addition of one equivalent of H_2O_2. Peroxy derivatives of the $[H_xNb_{10}O_{28}]^{(6-x)-}$ become evident after minutes ($[H_xNb_{10}O_{28}]^{(6-x)-}$, $[H_xNb_{10}O_{27}(O^{(l)}{}_2)]^{(6-x)-}$, and $[H_xNb_{10}O_{26}(O^{(l)}{}_2)_2]^{(6-x)-}$). The ^{17}O NMR spectra (bottom) initially show only a single peak arising from the central μ_6-oxo site in the $[Nb_{10}O_{28}]^{6-}$ ion. After addition of one equivalent of H_2O_2, other μ_6-oxo signals become evident as $[Nb_{10}O_{27}(O^{(l)}{}_2)]^{6-}$ and $[Nb_{10}O_{26}(O^{(l)}{}_2)_2]^{6-}$ form. Over time, evidence for the substituted ions disappears and the $[Nb_{10}O_{28}]^{6-}$ ion reforms.

substituted into the structure, and finally it reverts to the initial spectrum with a single signal for the μ_6-oxo in the $[H_xNb_{10}O_{28}]^{(6-x)-}$ ion. This ingrowth of new peaks and then reversion to the original spectrum was only observed during the reaction of one or two equivalents of hydrogen peroxide with the decaniobate ion. If more equivalents of peroxide were added, isotopic labeling was lost rapidly in all oxygen sites in the decaniobate ion, including the μ_6-oxo site, indicating that the ion was dissociating. The upfield and downfield peaks in the ^{17}O NMR spectrum were assigned to the μ_6-oxo signal from the diperoxo-substituted and monoperoxo-substituted decaniobate ions, respectively, based on DFT calculations and ESI-MS spectra (see the Supporting Information).

Consistent with evidence of dissociation of the decaniobate ion, we found that peroxidation of the decaniobate ion is accompanied by formation of peroxy-substituted derivatives of the $[H_xNb_6O_{19}]^{(8-x)-}$ Lindqvist ion. In the presence of one to three equivalents of hydrogen peroxide, only minor amounts of peroxohexaniobates are formed. However, in the presence of six equivalents of peroxide, the decaniobate ion is completely converted into peroxy-substituted hexaniobate species. The hexaniobate species corresponding to the highest abundances in the ESI-MS spectrum for these solutions contained four to six peroxy groups.

In contrast, the $[H_xNb_6O_{19}]^{(8-x)-}$ Lindqvist ion reacts more slowly with hydrogen peroxide. In the presence of one equivalent of peroxide it took approximately 100 minutes before the reaction was complete (Figure 3). The stepwise

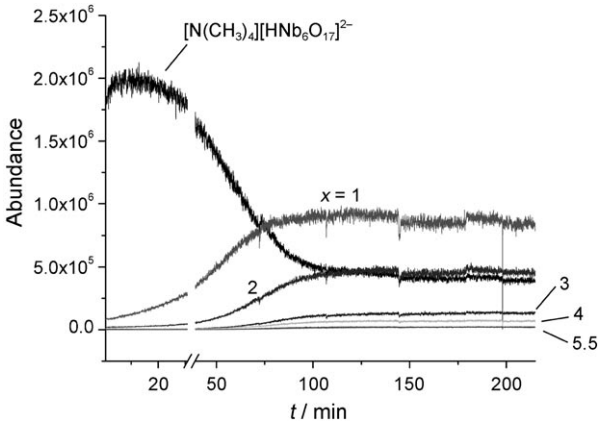

Figure 3. Time course of the ESI-MS signals showing that the hexaniobate ion, $[Nb_6O_{19}]^{8-}$, converts into the peroxy derivatives of the form $[H_yNb_6O_{19-x}(O^{(l)}{}_2)_x]^{(8-y)-}$ (traces correspond to $x=1$, 2 etc.) in the presence of one equivalent of H_2O_2. See the Supporting Information.

formation of the mono- to the hexaperoxohexaniobate species was monitored by using ESI-MS methods (Figure 4) and apart from the monoperoxohexaniobate, we observed species with an even number of peroxo units incorporated. Consistent with the ESI-MS data, the ^{17}O NMR spectra of the solutions of the hexaniobate and hydrogen peroxide showed the formation of the range of mono- to hexasubstituted peroxohexaniobates, depending on the number of equivalents of peroxide added. The assignments were based on μ_6-oxo NMR shifts, and on the order of appearance these signals over time as they correlated with the ESI-MS data. The assignments were also correlated with the relative shifts obtained by DFT calculations (see the Supporting Information). The pentasubstituted peroxohexaniobate is likely to be present only in small amounts based on the ESI-MS data; additionally the μ_6-oxo signal for this ion is expected to overlap with that of the solvent signal (see the Supporting Information) and was therefore not observed.

The peroxy-substituted $[H_xNb_6O_{19}]^{(8-x)-}$ Lindqvist ion is extraordinarily stable. Long-term studies showed that whereas the hexaniobate reacted more slowly than decaniobate with peroxide, the resulting peroxide species exhibited no significant loss of peroxide, even after three months of storage. The peroxy species can also be precipitated by the addition of acetonitrile, isolated, and redissolved. The ^{17}O signal for the μ_6-oxo site of the peroxy-substituted molecules is retained when one equivalent of peroxide is reacted with the $[H_xNb_6O_{19}]^{(8-x)-}$ Lindqvist ion. In this case, as indicated in the ^{17}O NMR spectra, the mole ratios of di-,

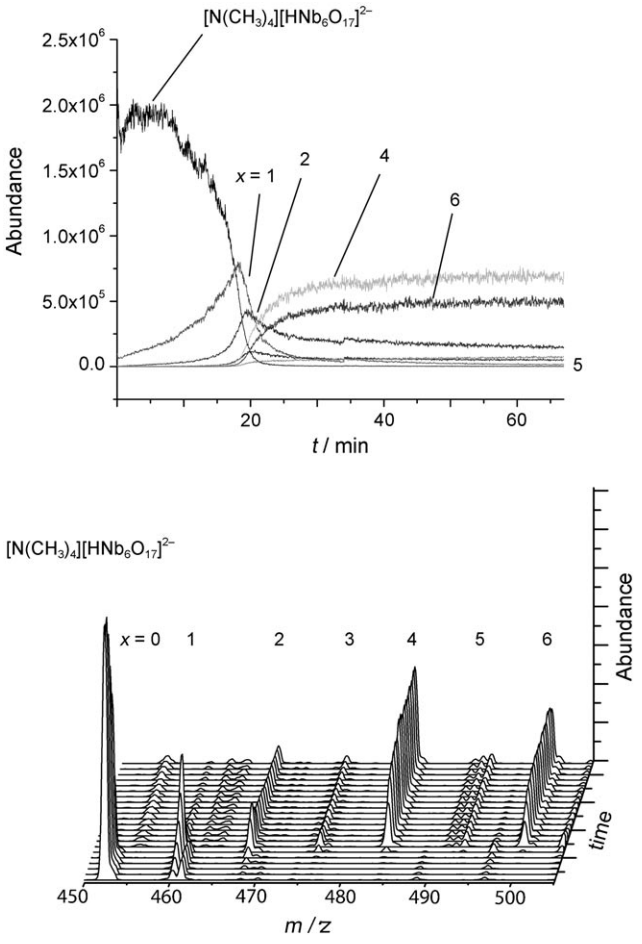

Figure 4. Time course of ESI-MS signals (top) and a stacked plot of spectra (bottom) showing the reaction of the hexaniobate ion with six equivalents of hydrogen peroxide at 24 °C The stoichiometries are $[N(CH_3)_4][HNb_6O_{17-x}(O^{(I)}_2)_x]^{2-}$, where $x=0$ for $[N(CH_3)_4][HNb_6O_{17}]^{2-}$; $x=1$ for $[N(CH_3)_4][HNb_6O_{16}(O^{(I)}_2)]^{2-}$ etc. The stacked plot covers the initial 35 min of the reaction.

mono-, and unsubstituted hexaniobates are stabilized at approximately 0.25, 0.50, and 0.25, respectively, which is in agreement with the ESI-MS data. However, in the presence of six equivalents of hydrogen peroxide, all the ^{17}O isotopic labeling is lost from the structure in a few hours, indicating the presence of a dynamic process leading to exposure of the central μ_6-oxygen atom to unlabeled water which was used as the solvent.

To determine the mode of coordination of the peroxide moieties we prepared crystals of $[N(CH_3)_4]_5[H_3Nb_6O_{13}(O^{(I)}_2)_6]\cdot 9.5\,H_2O$ (**1**, Figure 5, bottom), which are the first isolated examples of a peroxoisopolyoxoniobate, as well as the first example of a triply protonated Lindqvist-type polyoxoniobate. The asymmetric unit is composed of one triply protonated peroxohexaniobate anion along with five tetramethylammonium cations and 9.5 water molecules. This modified Lindqvist-type anion therefore possesses a charge of −5 and is composed of six NbO_7 pseudo-octahedra. The protons are located at three bridging oxygen atoms, which were located based on difference-Fourier maps and additionally supported by the internal structural perturbations

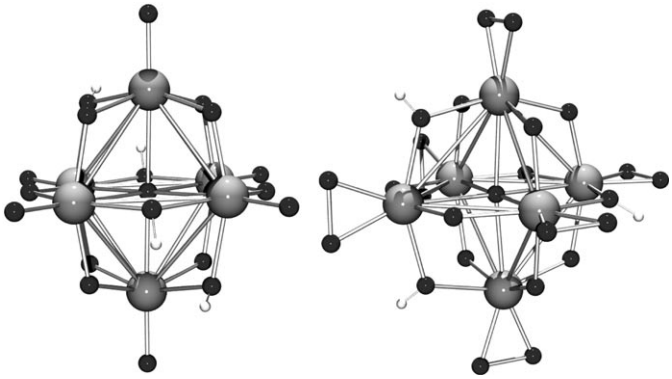

Figure 5. Ball-and-stick models of the $[H_3Nb_6O_{19}]^{5-}$ (left) and the $[H_3Nb_6O_{13}(O^{(I)2})_6]^{8-}$ (right) ions generated from X-ray crystallographic structures of the $[N(CH_3)_4]^+$ salts. Nb gray, O dark gray, H white. See the Supporting Information.

reported by Ozeki et al.[7] and Nyman et al.[8] The structure of $[N(CH_3)_4]_5[H_3Nb_6O_{19}]\cdot 20\,H_2O$ (**2**, Figure 5, top), also reported herein, provides additional support.

The dry, crystalline peroxohexaniobate was stable over at several weeks at room temperature, as determined by redissolving it in water and then subjecting it to ESI-MS analysis. The peroxide moieties were found to coordinate as η^2 ligands in the terminal positions.

In summary, we see that reaction between the decaniobate anion and H_2O_2 is almost instantaneous, reaching near-completion in a matter of minutes, whereas the hexaniobate Lindqvist ion reacts more slowly. The decaniobate anion dissociates in the presence of several equivalents of peroxide to yield peroxohexaniobate species with rapid and complete loss of the isotopic labelling. This loss of the isotopic signal indicates that the peroxy group induces enough dissociation of the structure such that isotopic exchange occurs between the solution and all the oxygen atoms. In contrast, the hexaniobate Lindqvist ion is stable towards high concentrations of hydrogen peroxide without dissociation. In the presence of peroxide the decaniobate ion reacts to yield mono- and diperoxo species. In contrast, tetra- and hexaperoxohexaniobate species dominate for the hexaniobate, and degrees of substitution ranging from one to six are all observed. Finally, solutions of the peroxodecaniobate species slowly lose peroxide over a period of days to yield decaniobate. In contrast, peroxohexaniobates can be stored for months with little loss of peroxide. The cause of the difference in reactivity at the terminal oxo groups on the hexaniobate and decaniobate ions is not known. Differences in dissociation may relate to the overbonded μ_3-oxo, which was shown to be important to dissociation of the decaniobate ion.[3] Overbonding here refers to a sum of Pauling bond valence substantially different than two at the oxygen. If so, experiments with a titanium(IV)-substituted version of this molecule may be helpful as it reduces the overbonding, and perhaps the rates of dissociation.

These results are particularily relevant to the use of niobates as water-splitting catalysts, since the terminal niobium-bound oxygen atoms can be so easily replaced by peroxy groups, a product of water oxidation.

Experimental Section

Electrospray-ionization mass spectrometry (ESI-MS) was carried out on an Agilent 1956b single quadrupole spectrometer equipped with a syringe pump for direct injection. Typically, aqueous solutions of 1 mM of the niobate salts were injected at room temperature at a rate of 40 μL min^{-1}, and the cone voltage set to −20 V. The ^{17}O NMR data were acquired on a Bruker Avance 500 MHz spectrometer on solutions prepared by dissolution of either ^{17}O-enriched $[N(CH_3)_4]_6[Nb_{10}O_{28}]$, which was prepared according to Villa et al.,[3] or ^{17}O-enriched $K_7[HNb_6O_{19}]$ as described by Black et al.[4] $[N(CH_3)_4]_8[Nb_6O_{19}]$ and $[N(CH_3)_4]_6[Nb_{10}O_{28}]$ were synthesized according to Ohlin et al.[9] H_2O_2 (3% aq) solutions were standardized by titration with $KMnO_4$. Crystals of **1** were grown by adding 0.8 mL 30% H_2O_2(aq) to 400 mg $[N(CH_3)_4]_8[Nb_6O_{19}]$, and then slowly evaporatins the solvent at room temperature. All ESI-MS and ^{17}O NMR spectra, DFT NMR-shift calculations, and the details of structure determination and refinement of $[N(CH_3)_4]_5[H_3Nb_6O_{19}]\cdot 20\,H_2O$ and $[N(CH_3)_4]_5[H_3Nb_6O_{13}(O^{(1)}{}_2)_6]\cdot 9.5\,H_2O$ are supplied in the Supporting Information. Additional details on the crystal structure investigation may be obtained from the Fachinformationszentrum Karlsruhe, 76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666; e-mail: crysdata@fiz-karlsruhe.de), upon quoting the depository numbers CSD-419732 and CSD-419733.

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