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# Relevance of Protons in Heterolytic Activation of H<sub>2</sub>O<sub>2</sub> over Nb(V). Insights from Model Studies on Nb-substituted Polyoxometalates

Nataliya V. Maksimchuk,<sup>†, ‡</sup> Gennadii M. Maksimov,<sup>†</sup> Vasilii Yu. Evtushok,<sup>†, ‡</sup> Irina D. Ivanchikova,<sup>†</sup> Yuriy A. Chesalov,<sup>†, ‡</sup> Raisa I. Maksimovskaya,<sup>†</sup> Oxana A. Kholdeeva,<sup>†, ‡,</sup>\* Albert Solé-Daura,<sup>§</sup> Josep M. Poblet,<sup>§</sup> and Jorge J. Carbó<sup>§,</sup>\*

<sup>†</sup>Boreskov Institute of Catalysis, Pr. Lavrentieva 5, Novosibirsk 630090, Russia

<sup>‡</sup> Novosibirsk State University, Pirogova str. 2, Novosibirsk 630090, Russia

<sup>§</sup> Departament de Química Física i Inorgànica, Universitat Rovira i Virgili, 43005 Tarragona, Spain

**ABSTRACT:** Nb-monosubstituted Lindqvist-type polyoxometalates (POM),  $(Bu_4N)_4[(NbW_5O_{18})_2O]$ (1)and  $(Bu_4N)_3[Nb(O)W_5O_{18}]$  (2), catalyze epoxidation of alkenes with hydrogen peroxide and mimic the catalytic performance of heterogeneous Nb-silicate catalysts. Dimer 1 is more active than monomer 2, but the catalytic activity of the latter increases in the presence of acid. Kinetic and spectroscopic studies suggest a mechanism that involves generation of monomer (Bu<sub>4</sub>N)<sub>2</sub>[Nb(OH)W<sub>5</sub>O<sub>18</sub>] (3), interaction of 3 with  $H_2O_2$  leading to a protonated peroxo niobium species,  $(Bu_4N)_2[HNb(O_2)W_5O_{18}]$  (4), followed by oxygen transfer to a C=C bond in alkene. The previously unknown peroxo complex 4 has been isolated and characterized by elemental analysis, UV-vis, FT-IR, Raman, <sup>93</sup>Nb, <sup>17</sup>O and <sup>183</sup>W NMR spectroscopy, cyclic voltammetry, and potentiometric titration. The physicochemical techniques support a monomeric Lindqvist structure of 4 bearing one peroxo ligand attached to Nb(V) in a  $\eta^2$ coordination mode. While the unprotonated peroxo complex  $(Bu_4N)_3[Nb(O_2)W_5O_{18}]$  (5) is inert toward alkenes under stoichiometric conditions, 4 readily reacts with cyclohexene to afford epoxide and 1,2-trans-cyclohexane diol, which proves the key role of protons for heterolytic activation of  $H_2O_2$  over Nb(V). The IR, Raman, UV-vis, and <sup>17</sup>O NMR spectroscopic studies along with DFT calculations showed that the activating proton in 4 is predominantly located at a Nb-O-W bridging oxygen. However, DFT calculations revealed that the protonated peroxo species 'HNb( $O_2$ )' is present in equilibrium with a hydroperoxo species 'Nb( $\eta^2$ -OOH)', which has a lower activation barrier for the oxygen transfer to cyclohexene and is, therefore, the main epoxidizing species. The calculations indicate that protonation is crucial to generate the active species and to increase POM electrophilicity. KEYWORDS: epoxidation, hydrogen peroxide, niobium, peroxo complex, polyoxometalate, Lindqvist structure, DFT

#### INTRODUCTION

On the way to sustainable production of valuable chemicals, a challenging goal is the development of economic and ecologically sound oxidation processes which employ green, cheap and readily available oxidizing agents.<sup>1-4</sup> Along with molecular oxygen, hydrogen peroxide is the most environmentally friendly oxidant since it is atom-efficient, easy to handle and safe (<60 wt% in water and <20% wt% in organic solvent) and produces water as the sole byproduct.<sup>5-7</sup> Likewise dioxygen, H<sub>2</sub>O<sub>2</sub> itself is inert toward most organic substrates and its use in selective oxidation processes requires employment of catalysts. Redox transition metals readily perform homolytic activation of  $H_2O_2$ , leading to the formation of radical species and Fenton-type chemistry.<sup>8,9</sup> However, in this case, unproductive decomposition of H<sub>2</sub>O<sub>2</sub> with evolution of molecular oxygen competes with the target oxygenation reaction, leading to very low oxidant utilization efficiency. Moreover, the formation of radicals (HO $\cdot$ , HO<sub>2</sub> $\cdot$ ) is detrimental for selectivity of oxidation processes.

The selective catalytic epoxidation of alkenes with hydrogen peroxide is of both academic and industrial interest.<sup>10-13</sup> To accomplish oxygen atom transfer from H<sub>2</sub>O<sub>2</sub> to alkenes and to avoid the formation of intermediate radical species, heterolytic activation of the oxidant is required. Several highly effective homogeneous catalysts, including specific complexes of

W(VI),<sup>11,14-17</sup> Re(VII),<sup>18-20</sup> Ti(IV),<sup>21-23</sup> Mn(II),<sup>12,24-26</sup> and Fe(II/III)<sup>12,20,27,28</sup>, have been reported for epoxidation of a wide range of alkenes. Among heterogeneous catalysts, the microporous titanium–silicalite TS–1 developed by the ENI group at the beginning of the 1980s remains a unique material that enables efficient transformations of linear olefins into epoxides using dilute  $H_2O_2$ .<sup>29,30</sup> The development of mesoporous Ti-silicates in the 2000s was targeted at oxidative transformations of large organic molecules; however, the hydrophilic nature of these materials favors adsorption and unproductive decomposition of hydrogen peroxide, which deteriorates selectivity of epoxidation, with the exception of some specific cases.<sup>31,32</sup>

In recent years, niobium-containing materials have attracted growing interest as selective oxidation catalysts. In particular, mesoporous Nb-silicates turned out to be active and recyclable catalysts for alkene epoxidation using dilute  $H_2O_2$ .<sup>33-42</sup> Several research groups noticed that Nb,Si-catalysts reveal superior selectivity in  $H_2O_2$ -based epoxidation relative to their Ti counterparts.<sup>37,38,41,42</sup> The reasons for this are not completely clear. While high levels of understanding mechanisms of alkene epoxidation have been reached for W, Re and Ti,<sup>30,43-45</sup> as well as biomimetic Fe and Mn catalysts,<sup>24-27,43,46,47</sup> epoxidation catalyzed by Nb is still poorly understood. A few attempts at rationalizing the catalytic behavior of Nb(V) have been reported.<sup>42,48-51</sup> Nevertheless, the nature of the active epoxidizing

species still remains under debate. Our recent kinetic and spectroscopic studies on mesoporous Nb-silicates implicated a protonated, presumably hydroperoxo niobium species Nb– OOH as the active form responsible for epoxidation of electron-rich C=C double bonds in alkenes.<sup>42,52</sup> On the other hand, Bregante et al. proposed that a superoxo Nb species is responsible for alkene epoxidation over Nb-substituted Betazeolite.<sup>50,51</sup> More recently, they discarded superoxo Nb and suggested that, in sharp contrast to Ti single-site catalysts for which hydroperoxo species TiOOH has become a widely accepted concept,<sup>30,53,54</sup> simply Nb( $\eta^2$ –O<sub>2</sub>) surface intermediates epoxidize alkenes on Nb-based catalysts.<sup>55</sup> To shed more light on the nature of active Nb peroxo species, detailed experimental and theoretical model studies using soluble molecular compounds are needed.

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Anionic metal-oxygen clusters or polyoxometalates (POMs), owing to their metal oxide like structure, thermodynamic stability to oxidation and hydrolysis as well as tunable acidity and redox properties, have found applications in a wide range of research areas, covering catalysis, molecular magnetism, electronics and medicine.<sup>56-66</sup> The evident structural analogy between POMs and metal oxide surfaces makes possible considering POMs as discrete, soluble fragments of extended metal oxide lattices, which can be characterized and investigated at the atomic/molecular level.<sup>67–72</sup> Since lacunary polyanion frameworks can function as totally inorganic, hydrolytically and oxidation-resistant multidentate ligands toward a heterometal M, transition-metal mono-substituted POMs (M-POMs) meet the criteria of an important class of single-site catalysts<sup>73</sup> and can serve as tractable molecular models for studying mechanisms of oxidation catalysis.74-80 Earlier, some of us demonstrated that Ti-substituted POMs mimic well the catalytic performance of mesoporous titanium-silicate catalysts in a range of selective oxidations with H<sub>2</sub>O<sub>2</sub>.<sup>76-78</sup> Alkene epoxidation mediated by two different POMs, the Timonosubstituted Keggin type POM [PTi(OH)W11O39]4- and the sandwich type POM [Ti<sub>2</sub>(OH)<sub>2</sub>As<sub>2</sub>W<sub>19</sub>O<sub>67</sub>(H<sub>2</sub>O)]<sup>8-</sup>, containing well-defined 6- and 5-coordinated titanium atoms, respectively, have been studied in detail using experimental and computational techniques.<sup>45,78,81</sup> The higher selectivity of the sandwich anion was attributed to the larger energy cost of homolytic O-O bond breaking in the hydroperoxo intermediate 'TiOOH'.45 It was also demonstrated that electrophilicity and reactivity of the peroxo titanium derivative of the Keggin Ti-POM can be increased through polyanion protonation.<sup>8</sup>

Although a large number of Nb-containing POMs have been reported in the literature,<sup>84</sup> in particular in relation to their antitumor and antiviral activity,<sup>84,85</sup> potential of Nb-POMs in catalysis is much less explored compared to Ti-POMs. Among them, very few works were devoted to oxidation catalysis.<sup>86-</sup> Nb-trisubstituted POMs, (Bu<sub>4</sub>N)<sub>5</sub>H<sub>2</sub>[(NbO<sub>2</sub>)<sub>3</sub> SiW<sub>9</sub>O<sub>37</sub>]<sup>86</sup> and (Bu<sub>4</sub>N)<sub>4</sub>H<sub>2</sub>[(NbO<sub>2</sub>)<sub>3</sub>PW<sub>9</sub>O<sub>37</sub>],<sup>87</sup> could accomplish epoxidation of unsaturated allylic alcohols to the corresponding diols with aqueous H<sub>2</sub>O<sub>2</sub>, but they were inert toward unfunctionalized alkenes.<sup>86</sup> On the basis of kinetic and NMR data, the authors concluded that the Nb-POMs function primarily as catalyst precursors that produce active W, Nb or polyoxoanion fragments.<sup>86,87</sup> More recently, Mizuno and coworkers reported synthesis and catalytic properties of a di-Nb-substituted silicodecatungstate,  $(Bu_4N)_5[\gamma$ -HSiW<sub>10</sub>O<sub>38</sub>Nb<sub>2</sub>( $\eta^2$ -O<sub>2</sub>)<sub>2</sub>].<sup>88</sup> This POM was able to catalyze oxidation of some organic substrates (cyclooctene, thioanisole, 1-phenylethanol, and allyl

alcohol) with  $H_2O_2$  in the presence of 2 equiv. of protons source.



**Figure 1.** 3D representation for several monosubstituted Nbtungtates of the Lindqvist structure.

In the present work, we first explored the catalytic performance of Nb-monosubstituted Lindqvist tungstates, i.e.  $\mu$ -oxo dimer  $(Bu_4N)_4[(NbW_5O_{18})_2O]$  ((NbW\_5)<sub>2</sub>O, 1) and monomer  $(Bu_4N)_3[Nb(O)W_5O_{18}]$  (Nb(O)W<sub>5</sub>, 2) in alkene epoxidation with hydrogen peroxide. Hydrolysis of dimer 1 was anticipated to produce a monomer,  $(Bu_4N)_2[Nb(OH)W_5O_{18}]$ (Nb(OH)W<sub>5</sub>, **3**) with terminal Nb–OH bond. Figure 1 shows the 3D molecular structures of anions 1, 2 and 3. Given that both Nb=O and Nb-OH surface groups are present in Nbsilicates and zeolites<sup>89-91</sup> and both may potentially lead to an active peroxo niobium species,<sup>42,49,52,92,93</sup> it was interesting to compare their reactivity towards H<sub>2</sub>O<sub>2</sub> using well-defined molecular compounds. To elucidate the role of protons in the activation of the peroxo niobium group, we first synthesized a niobium complex, protonated peroxo  $(Bu_4N)_2[HNb(O_2)W_5O_{18}]$  (HNb(O<sub>2</sub>)W<sub>5</sub>, 4), and fully characterized it by elemental analysis, potentiometric titration, cyclic voltammetry, UV-vis, FT-IR, Raman, and <sup>183</sup>W, <sup>93</sup>Nb, and <sup>17</sup>O NMR spectroscopy. The structure and reactivity of 4 have been investigated by experimental and computational techniques in comparison with the unprotonated peroxo complex  $(Bu_4N)_3[Nb(O_2)W_5O_{18}]$  (Nb(O<sub>2</sub>)W<sub>5</sub>, 5).

## EXPERIMENTAL

Materials. Acetonitrile (Panreac, HPLC grade) was dried and stored over activated 3Å molecular sieves. Cyclohexene and cyclooctene were purchased from Sigma-Aldrich and purified prior to use by passing through a column filled with neutral alumina to remove traces of possible oxidation products. All the other compounds were the best available reagent grade and used without further purification. A solution of 77% H<sub>2</sub>O<sub>2</sub> was obtained by concentration of a commercial 30% aqueous solution in vacuum. The concentration of hydrogen peroxide was determined iodometrically prior to use. Semiquantitative Quantofix peroxide test sticks were used for estimation of the amount of H<sub>2</sub>O<sub>2</sub> at the end of catalytic reactions. Tetra-n-butylammonium hydroxide (TBAOH) (0.39 M in water) was titrated with HCl (0.1 M) prior to use. All the other compounds were the best available reagent grade and were used without further purification.

## Synthesis and Characterization of POMs

 $Na_7HNb_6O_{19}\cdot xH_2O$  was prepared according to the known procedure.<sup>94</sup> Nb<sub>2</sub>O<sub>5</sub> (25.5 g) was fused with 31 g of NaOH

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(1:8 molar ratio) in a nickel crucible at 600 °C for 5 h. The reaction product was dissolved in water (1.5 L) under heating (90 °C). The resulting solution was slowly evaporated to 200 mL at ambient temperature and the precipitate was washed with ethanol and recrystallized from water. The white product was washed with ethanol and air-dried overnight. The recrystallization yielded an analytical sample with 90% yield. FTIR (KBr, 1200–400 cm<sup>-1</sup>): 860, 772, 677, 534.

 $(Bu_4N)_3[Nb(O_2)W_5O_{18}]$  (Nb(O<sub>2</sub>)W<sub>5</sub>, 5). The synthesis of ref.95 peroxo complex 5 was adapted from Na7HNb6O19.15H2O (3.55 g, 2.7 mmol) was dissolved in 140 mL of water (20 °C) and 5 mL of 30% aqueous H<sub>2</sub>O<sub>2</sub>. The resulting turbid solution was stirred overnight, then heated to 50 °C followed by the addition of 20 g (60.6 mmol) of Na<sub>2</sub>WO<sub>4</sub>·2H<sub>2</sub>O in 50 mL H<sub>2</sub>O and 15% HNO<sub>3</sub> (slowly) to adjust the pH at 2.3. After 1 h of stirring at 100 °C, a turbid yellow solution was centrifuged to remove precipitate of unreacted peroxoniobate. Then 12 g (37 mmol) of TBABr was added to the clear solution to afford a yellow precipitate which was collected by suction filtration, washed with 100 mL of water, dried at 100 °C, and purified by reprecipitation with water from CH<sub>3</sub>CN. The resulting yellow solid (13.3 g) was dissolved in 100 mL of dichloroethane, centrifugated to remove insoluble impurities, evaporated in air, and then reprecipitated with the aqueous solution of H<sub>2</sub>O<sub>2</sub> (2 mL of 30% H<sub>2</sub>O<sub>2</sub> in 160 mL H<sub>2</sub>O) from CH<sub>3</sub>CN (80 mL). The resulting yellowish solid (11.2 g, yield 44% on W) was dried in air at 30 °C overnight and at 90 °C for 1 h. The presence of one peroxo group per molecule of 5 was confirmed by titration with triphenylphosphine (PPh<sub>3</sub>) followed by monitoring with <sup>31</sup>P NMR.<sup>87</sup> Anal. calcd (%) for C<sub>48</sub>H<sub>108</sub>N<sub>3</sub>NbW<sub>5</sub>O<sub>20</sub>: C, 27.99; H, 5.29; N, 2.04; O, 15.54; Nb, 4.51; W, 44.63. Found: C, 27.71; H, 5.40; N, 1.96; O, 14.34; Nb, 4.16; W, 44.60. IR (KBr 1000–400 cm<sup>-1</sup>): 980 (w, sh), 960 (s,W–Ot), 885 (w, TBA), 857 (sh), 806 (vs), 735 (sh, TBA), 639 (m), 602 (m), 586 (w), 567 (w), 546 (w), 442 (w), 428 (s). <sup>183</sup>W NMR (ppm, in CH<sub>3</sub>CN): 62  $(4W_{eq})$ , 101  $(1W_{ax})$ . <sup>93</sup>Nb NMR (ppm, in CH<sub>3</sub>CN): -1045. <sup>17</sup>O NMR (ppm, in CH<sub>3</sub>CN): 734 (W=O), 725 (NbO<sub>2</sub>), 460 (NbOW), 396 (WOW), 390 (WOW), -72 (µO).

 $(Bu_4N)_3[Nb(O)W_5O_{18}]$  (Nb(O)W<sub>5</sub>, **2**). Monomeric Nbsubstituted tungstate 2 was synthesized by reduction of Nb(O<sub>2</sub>)W<sub>5</sub> with PPh<sub>3</sub>. To a solution of 5 (3.8 g, 1.8 mmol) in 20 mL CH<sub>3</sub>CN, PPh<sub>3</sub> (0.56 g, 2.1 mmol) dissolved in 10 mL of CH<sub>3</sub>CN was added, and the reaction mixture was stored for 1 h. A white solid was precipitated by a two-fold excess of water, isolated by filtration, washed with ethanol and dried in air at 30 °C. Yield 83%. Anal. calcd (%) for C<sub>48</sub>H<sub>108</sub>N<sub>3</sub>NbW<sub>5</sub>O<sub>19</sub>: C, 28.21; H, 5.33; N, 2.06; O, 14.88; Nb, 4.55; W, 44.98. Found: C, 28.06; H, 6.06; N, 2.12; O, 14.98; Nb, 4.34; W, 45.0. IR (KBr 1000–400 cm<sup>-1</sup>): 977(w, sh), 957 (s, W-Ot), 915 (m, Nb-Ot), 883 (w, TBA), 804 (vs), 735 (sh, TBA), 589 (m), 572 (m). <sup>183</sup>W NMR (ppm, in CH<sub>3</sub>CN): 71  $(4W_{eq})$ , 27  $(1W_{ax})$ . <sup>93</sup>Nb NMR (ppm, in CH<sub>3</sub>CN): -899. <sup>17</sup>O NMR (ppm, in CH<sub>3</sub>CN): 732 (W=O), 730 (sh, W=O), 455 (NbOW), 392 (WOW), 390 (sh, WOW), -68 (µO).

 $(Bu_4N)_4[(NbW_5O_{18})_2O]$  ((NbW\_5)<sub>2</sub>O), **1**). The synthesis of dimer **1** was adapted from ref.<sup>96</sup> Acetylchloride (0.11 mL, 1.5 mmol) was added to a solution of Nb(O)W<sub>5</sub> (3.0 g, 1.5 mmol) in 20 mL CH<sub>3</sub>CN. The reaction mixture was stirred for 15 min at room temperature (20 °C), and the resulting white precipitate was isolated by filtration and washed with 50 mL of ether

to give 1.8 g of product in 70% yield. Anal. calcd (%) for  $C_{64}H_{144}N_4Nb_2W_{10}O_{37}$ : C, 21.44; H, 4.05; N, 1.56; O, 16.51; Nb, 5.18; W, 51.26. Found: C, 21.64; H, 4.07; N, 1.69; O, 16.37; Nb, 5.13; W, 50.2. IR (KBr, 1000-400 cm<sup>-1</sup>): 994 (w, sh), 974 (s), 877 (m), 835 (w, sh), 812 (s), 733 (w, sh), 720 (m, sh), 695 (s, NbONb), 588 (m), 547 (m), 447 (s). <sup>93</sup>Nb NMR (ppm, in CH<sub>3</sub>CN): –950 (broad).

(Bu<sub>4</sub>N)<sub>2</sub>[HNb(O<sub>2</sub>)W<sub>5</sub>O<sub>18</sub>] (HNb(O<sub>2</sub>)W<sub>5</sub>, **4**). Protonated peroxo complex **4** was synthesized by the addition of 30% H<sub>2</sub>O<sub>2</sub> (0.2 mL, 2.3 mmol) to a suspension of (NbW<sub>5</sub>)<sub>2</sub>O (2.8 g, 0.7 mmol) in 20 mL CH<sub>3</sub>CN. The yellow solution was stored for 30 min at room temperature and diluted with 120 mL of ether. The resulting yellowish solid (2.7 g, ca. 95% yield) was isolated by decantation and dried in air at room temperature. Anal. calcd (%) for C<sub>32</sub>H<sub>73</sub>N<sub>2</sub>NbW<sub>5</sub>O<sub>20</sub>: C, 21.14; H, 4.05; N, 1.54; O, 17.60; Nb, 5.11; W, 50.57. Found: C, 21.22; H, 3.51; N, 1.68; O, 17.37; Nb, 4.96; W, 48.4. IR (KBr, 1000–400 cm<sup>-1</sup>): 984 (w, sh), 973 (vs), 883 (w, TBA), 870 (w), 848 (m), 816 (m), 770 (m), 739 (w, TBA), 621 (w), 595 (m), 567 (w), 541 (w), 455 (m). <sup>93</sup>Nb NMR (ppm, in CH<sub>3</sub>CN): -1015. <sup>17</sup>O NMR (ppm, in CH<sub>3</sub>CN): 754 (W=O), 742 (NbO<sub>2</sub>), 414 (NbOW), 409 (WOW), 402 (WOW), and -63 (µO).

 $(Bu_4N)_2[W_6O_{19}]$  (W<sub>6</sub>O<sub>19</sub>) was prepared and characterized as described elsewhere.<sup>97</sup>

 $(Bu_4N)_4PW_{11}NbO_{40}$  (PW<sub>11</sub>Nb). H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub>·6H<sub>2</sub>O (9 g, 3 mmol) was dissolved in 20 mL of water. Then 0.9 mL of 0.325 M H<sub>3</sub>PO<sub>4</sub>, 50 mL of hot aqueous solution of Na<sub>7</sub>HNb<sub>6</sub>O<sub>19</sub>·15H<sub>2</sub>O (0.702 g, 0.5 mmol), and 1 mL of 30% H<sub>2</sub>O<sub>2</sub> (11 mmol) were subsequently added and the reaction mixture was stirred upon heating during 1 h. The resulting yellow solution of the peroxo species (Bu<sub>4</sub>N)<sub>4</sub>PW<sub>11</sub>Nb(O<sub>2</sub>)O<sub>29</sub> (<sup>31</sup>P NMR: -13.7 ppm) was evaporated until dryness and then dried in air at 140 °C for 2 h. The white residue was dissolved in water (20 mL), an insoluble precipitate was separated by centrifugation, and TBA salt was precipitated by the addition of TBABr (4.5 g). The resulting white solid was isolated by filtration, washed with water, dried at 100 °C and then recrystallized from CH<sub>3</sub>CN. Large colorless crystals were dried in air at room temperature and then at 90 °C. Yield ca. 50%. The number of TBA cations (4) was determined by ignition. IR (KBr, 1100–400 cm<sup>-1</sup>): 1082, 1070, 965, 890, 805, 600, 510. <sup>31</sup>P NMR (ppm, in CH<sub>3</sub>CN): -13.2. <sup>183</sup>W NMR (ppm, in CH<sub>3</sub>CN): -67, -88, -93, -99, -106.

**Interaction with H<sub>2</sub>O<sub>2</sub>.** Interaction of Nb-POMs with 30%  $H_2O_2$  was performed by the addition of  $H_2O_2$  (0.1–50 equiv., taken as 30% solution in water) to a 0.01 M (<sup>93</sup>Nb NMR monitoring) or 0.0005 M (UV-vis monitoring) solution of POM in dry CH<sub>3</sub>CN at 20 °C.

**Catalytic reactions.** Catalytic oxidations were performed under vigorous stirring (500 rpm) in thermostated glass vessels. Typical reaction conditions were as follows: alkene 0.2 mmol, H<sub>2</sub>O<sub>2</sub> 0.2 mmol, POM 0.004 mmol (0.002 mmol for (NbW<sub>5</sub>)<sub>2</sub>O), CH<sub>3</sub>CN 1 mL, 50 °C. Reactions were started by the addition of 30% H<sub>2</sub>O<sub>2</sub> to the reaction mixture containing acetonitrile solvent, alkene, POM and, in some cases, 1 equiv. (0.004 mmol) of HClO<sub>4</sub>. Samples of the reaction mixture (0.5  $\mu$ L) were withdrawn periodically during the reaction course by a syringe. The oxidation products were identified by gas chromatography–mass spectrometry (GS–MS). The product yields and substrate conversions were quantified by gas chromatography (GC) using an internal standard, biphenyl. For GC analysis, the method described by Shul'pin<sup>98</sup> was used, which involves treatment of the reaction mixture with PPh<sub>3</sub> in order to reduce unreacted  $H_2O_2$  and possible organic peroxides formed and comparison of chromatograms of the reaction mixture before and after the reduction of peroxides with PPh<sub>3</sub>. Each experiment was reproduced at least 2 times.

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**Kinetic experiments.** Kinetic experiments were performed in temperature-controlled glass vessels under vigorous stirring (600 rpm). Reactions were initiated by the addition of 30 or 77% H<sub>2</sub>O<sub>2</sub> to a CH<sub>3</sub>CN solution containing CyOct substrate, catalyst (NbW<sub>5</sub>)<sub>2</sub>O, and internal standard for GC (biphenyl). The total volume of the reaction mixture was 1 mL. The reaction temperature was kept at 50 °C. Samples (0.5  $\mu$ L) of the reaction mixture were withdrawn periodically during the reaction with a syringe and analyzed by GC. Each experiment was reproduced at least 2–3 times. To rule out the possibility of evaporative losses of the substrate, blank experiments without catalyst and oxidant were carried out at the reaction temperature using the internal standard.

*Reaction order in catalyst.* The catalyst (NbW<sub>5</sub>)<sub>2</sub>O concentration was varied in the range 0.0006–0.004 M. Concentrations of other reactants were held constant: [CyOct] = 0.1 M,  $[H_2O_2] = 0.1$  M.

*Reaction order in substrate.* The initial substrate concentration was varied between 0.02 and 0.3 M while maintaining constant concentrations of  $H_2O_2$  (0.1 M) and catalyst (0.002 M).

*Reaction order in*  $H_2O_2$ . The initial oxidant concentration was varied in the range of 0.1–0.9 M. The concentration of water in these experiments was kept constant by the addition of corresponding amounts of  $H_2O$ . To reduce the amount of water in the reaction mixture, 77%  $H_2O_2$  was employed. The concentrations of other reactants were as follows: [CyOct] = 0.1 M, [(NbW<sub>5</sub>)<sub>2</sub>O] = 0.002 M.

*Reaction order in*  $H_2O$ . The initial concentration of water was varied from 0.08 to 1.8 M. Other parameters were held constant: [CyOct] = 0.1 M, [H<sub>2</sub>O<sub>2</sub>] = 0.1 M, and [(NbW<sub>5</sub>)<sub>2</sub>O] = 0.001 M.

Determination of activation energy. Temperature dependence of the reaction rate was studied in the range of 30-80 °C in CH<sub>3</sub>CN using the following reaction conditions: [CyOct] = 0.1 M, [H<sub>2</sub>O<sub>2</sub>] = 0.1 M, and [(NbW<sub>5</sub>)<sub>2</sub>O] = 0.002 M.

Stoichiometric interaction with CyH. Stoichiometric reactions between CyH and peroxo complexes  $Nb(O_2)W_5$  and  $HNb(O_2)W_5$  were performed under Ar in thermostated glass vessels equipped with a magnetic stirrer at [POM] = 0.016 M, [CyH] = 0.08 M, and [HCIO<sub>4</sub>] = 0.016 M (if any) in dry CH<sub>3</sub>CN (1 mL) at 50 °C. The reaction course was monitored by UV-vis and GC. The oxidation products were identified by GC–MS and quantified by GC using internal standard.

**Instrumentation and Methods.** GC analyses were performed using a gas chromatograph Tsvet-500 equipped with a flame ionization detector and a quartz capillary column (30  $m \times 0.25$  mm) filled with Agilent DB–5MS. GC–MS analyses were carried out using an Agilent 7000B system with a triple– quadrupole mass–selective detector Agilent 7000 and a GC Agilent 7890B apparatus (quartz capillary column 30m×0.25mm/HP–5ms). <sup>93</sup>Nb, <sup>17</sup>O, and <sup>183</sup>W NMR spectra were recorded at 97.94, 54.24, and 16.67 MHz, respectively, on an Avance-400 Brüker spectrometer using a high resolution multinuclear probe head with 10 mm o.d. (3 mL solution volume) sample tubes. <sup>17</sup>O NMR spectra were measured at natural <sup>17</sup>O abundance (0.037 %). Chemical shifts,  $\delta$ , were referenced to NbCl<sub>5</sub>, H<sub>2</sub>O, and Na<sub>2</sub>WO<sub>4</sub> for <sup>93</sup>Nb, <sup>17</sup>O, and <sup>183</sup>W NMR spectra, respectively. For convenience, secondary external standards were used: 0.4 M H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> for <sup>183</sup>W NMR (-103.6 ppm) and 0.05 M H<sub>5</sub>SiW<sub>11</sub>NbO<sub>40</sub> (-975 ppm) for <sup>93</sup>Nb NMR. Infrared spectra were recorded as 0.5–2.0 wt % samples in KBr pellets on an Agilent Cary 600 FTIR spectrometer. Electronic absorption spectra were run on a Carv-50 spectrophotometer using a 0.2 cm quartz cells. FT-Raman spectra (3600–100 cm<sup>-1</sup>, 300 scans, resolution 4 cm<sup>-1</sup>, 180° geometry) were recorded using a RFS 100/S spectrometer (Brüker). Excitation (1064 nm) was provided by a Nd-YAG laser (100 mW power output). Cyclic voltammetric measurements were performed under Ar using a P-8nano voltammetric analyzer (Elins Electrochemical Instruments), a threeelectrode cell, a Pt working electrode, a Pt auxiliary electrode, and an Ag/AgCl reference electrode (BAS). TBAClO<sub>4</sub> (0.1 M) was used as a supporting electrolyte. The analysis of W and Nb content was done by ICP-OES using a Perkin Elmer Optima-430 DV instrument. The concentrations of C, H, N and O in the samples were determined with a CHNSO analyzer Vario EL Cube (Elementar Analysensysteme GmbH).

Computational details. The DFT analysis of the reaction pathway was carried out with Gaussian09 rev. C01 software.<sup>5</sup> Geometry optimization of reagents, intermediates, transition states and products was made using B3LYP density functional.  $^{100-102}$  LANL2DZ pseudopotential  $^{103}$  was used for W and Nb atoms and 6-31g(d,p) basis set  $^{104-106}$  was used for other atoms. The geometry optimization was full and without any symmetry constrains, and solvent effects of acetonitrile were included using the IEF-PCM implicit solvation model as implemented in Gaussian09. This level of theory has been proved to be accurate and reliable enough to study the reactivity concerning POMs and their transition metal-substituted analogues, always showing a high degree of consistency with experimental outcomes and kinetic studies.<sup>107-109</sup> Timedependent DFT (TD-DFT) calculations were performed with the long-range corrected CAM-B3LYP functional<sup>110</sup> as implemented in Gaussian 09 using the same basis set. In order to compute protonation energies ( $\Delta G_{H+}$ ), we took the experimental standard free energy of a proton in aqueous solution 272.2 kcal·mol<sup>-1,111</sup> NMR calculations were performed with ADF2107 package using a TZVP Slater type all-electron basis set and the OPBE functional<sup>112</sup> with spin-orbit (SO) corrections.113

## **RESULTS AND DISCUSSION**

**Catalytic performance of Nb-POMs in alkene oxidation.** The catalytic properties of the well-known Lindqvist type dimer  $(NbW_5)_2O$  and monomer Nb(O)W<sub>5</sub> were first assessed in the oxidation of cyclohexene (CyH) with hydrogen peroxide using equimolar amount of the oxidant (Table 1). CyH possesses highly reactive H atoms in the allylic position, which can be easily abstracted by radical species. Hence, the formation of allylic oxidation products, viz. cyclohexenyl hydroperoxide (HP), 2-cyclohexene-1-ol (enol) and 2-cyclohexene-1-one (enone), is a clear indication of a homolytic oxidation mechanism. Contrary, the selective formation of epoxide along with the ring opening product transcyclohexane-1,2-diol (diol) and its overoxidation product 2-hydroxycyclohexanone (ketol) points to heterolytic oxidation mechanism.

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**Table 1.** CyH oxidation with  $H_2O_2$  in the presence of Nb-POMs<sup>*a*</sup>

Entry	РОМ	Time,	CyH conv.,%	H <sub>2</sub> O <sub>2</sub> eff., <sup>b</sup> %	Product selectivity, <sup>c</sup> %					
Ē		h			epoxide	diol	ketol	HP	enol	enone
1	Nb(O)W <sub>5</sub>	5	55	64	53	25	14	2	3	3
2	$W_{6}O_{19}$	5	2	n.d. <sup>d</sup>	traces	-	-	n.d. <sup>d</sup>	traces	traces
3	PW <sub>11</sub> Nb	5	20	n.d. <sup>d</sup>	8	20	5	50	10	5
4	$Nb(O)W_5 + 1 eq. H^+$	2	74	98	3	43	37	4	7	1
5	$(NbW_5)_2O^e$	1.5	76	97	3	51	33	3	3	1
6	$Nb(O)W_5 + 0.1 eq. H^+$	3	74	92	20	40	27	4	4	1
7	No catalyst	5	5	n.d. <sup>d</sup>	21	traces	-	33	33	11
8	1 eq. H <sup>+</sup>	5	8	n.d. <sup>d</sup>	25	44	-	-	25	traces

<sup>*a*</sup> Reaction conditions: 0.2 M CyH, 0.2 M H<sub>2</sub>O<sub>2</sub> (30%), 0.004 M POM, 0.004 M HClO<sub>4</sub> (if any), 50 °C, 1 mL CH<sub>3</sub>CN. <sup>*b*</sup> H<sub>2</sub>O<sub>2</sub> utilization efficiency = total yield of products based on the oxidant consumed. <sup>*c*</sup> Based on substrate consumed. <sup>*d*</sup> Not determined. <sup>*e*</sup> Concentration of dimer (NbW<sub>5</sub>)<sub>2</sub>O was 0.002 M.

In the presence of Nb(O) $W_5$ , CyH conversion attained 55% after 5 h at 50 °C. Total selectivity toward heterolytic oxidation products (epoxide, diol, and ketol) and efficiency of hydrogen peroxide utilization were 92% and 64%, respectively (Table 1, entry 1). Epoxide prevailed among the oxidation products. Importantly, the Nb-free tungstate  $(Bu_4N)_2[W_6O_{19}]$ was almost inactive in this reaction, indicating that the substitution of W(VI) for Nb(V) is indispensable for the observed activity (Table 1, entry 2). It is noteworthy that the Nbsubstituted Keggin phosphotungstate (Bu<sub>4</sub>N)<sub>4</sub>[PW<sub>11</sub>NbO<sub>40</sub>] revealed very poor activity and selectivity, producing HP as the main oxidation product and thereby indicating predomination of a homolytic oxidation pathway (Table 1, entry 3), which was also confirmed by reduction of the reaction rate in the presence of the conventional radical scavenger ionol. The reaction in the presence of Nb(O)W<sub>5</sub> was greatly accelerated with the addition of 1 equiv. of acid (Figure S1). Moreover, H<sub>2</sub>O<sub>2</sub> utilization efficiency increased reaching 98% (Table 1, entry 4). A similar result was observed with dimer (NbW<sub>5</sub>)<sub>2</sub>O (Table 1, entry 5; Figure S1). In contrast to the reaction with  $Nb(O)W_5$ , the epoxide ring-opening product, diol, predominated among the oxidation products and the yield of the overoxidation product, ketol, also increased. Even minor (0.1 equiv.) additives of acid produced a significant effect on CyH oxidation rate and selectivity in the presence of Nb(O)W<sub>5</sub> (Table 1, entry 6). If 1 equiv. of acid was used as the sole catalyst, the selectivity toward heterolytic oxidation products (epoxide and diol) increased in the blank experiment either (Table 1, compare entries 7 and 8), but the reaction rate was insignificant relative to the Nb-POM-catalyzed reaction.

Importantly, the stability of the Lindqvist structure under the turnover conditions of CyH oxidation was confirmed. The IR spectra of the catalysts recovered by precipitation with ether revealed all the main vibrations of the Lindqvist tungstate and were very close to those of peroxo complex Nb(O<sub>2</sub>)W<sub>5</sub> (Figure S2, compare spectra E and F with C). This is indicative that peroxo species participates in the reaction mechanism. The <sup>93</sup>Nb NMR spectrum of the reaction mixture after 24 h of the CyH oxidation revealed a sole resonance with  $\delta$  –900 ppm, which is very close to that of Nb(O)W<sub>5</sub> (Figure S3, A and B), as one could expect after complete consumption of the oxidant. In turn, the <sup>93</sup>Nb NMR spectrum of the reaction mixture after the CyH oxidation in the presence of 1 equiv. of HClO<sub>4</sub> showed a resonance slightly shifted upfield (Figure S3, C),

which is, most likely, a manifestation of a partial protonation of  $Nb(O)W_5$  (see Figure S4).

The catalytic properties of Nb(O)W<sub>5</sub> and (NbW<sub>5</sub>)<sub>2</sub>O were also tested in epoxidation of various alkenes with aqueous H<sub>2</sub>O<sub>2</sub> (Table S1). For cyclic alkenes, such as cyclooctene (CyOct) and caryophillene, selectivity toward corresponding epoxides reached >99%. In the oxidation of methyl oleate and cis-stilbene, only cis-epoxides were formed, indicating a concerted mechanism of oxygen atom transfer that involves no radical or ionic intermediate capable of rotation around C-C bond. Note that stereospecificity in epoxidation of cis-alkenes is typical of mesoposous niobium-silicates.<sup>42,114,115</sup> Styrene and stilbene produced, along with epoxides, a significant amount of benzaldehyde, the product of the oxidative C=C bond cleavage, which is also characteristic of heterogeneous Nbcatalysts.<sup>40,42</sup> Therefore, the catalytic performance of the Lindqvist Nb-substituted tungstates is very similar to that of mesoporous niobium-silicates, which justifies use of the Nb-POMs as soluble molecular models for studying activation of H<sub>2</sub>O<sub>2</sub> over Nb(V) sites.

Since unproductive decomposition of hydrogen peroxide is the main side reaction that competes for  $H_2O_2$  with the target selective oxidation, activity of  $(NbW_5)_2O$  and  $Nb(O)W_5$  was also evaluated in decomposition of  $H_2O_2$  in the absence of any organic substrate. While monomer  $Nb(O)W_5$  revealed rather low activity, the addition of acid strongly enhanced the  $H_2O_2$ degradation rate (Figure S5). Dimer  $(NbW_5)_2O$  exhibited activity similar to that of monomer  $Nb(O)W_5$  in the presence of 1 equiv. of acid. Therefore, protons accelerate both the target (epoxidation) and side  $(H_2O_2$  degradation) reactions. However, given that a significant improvement of the oxidant utilization efficiency was observed in the presence of acid (Table 1, compare entries 1 and 4), we conclude that the effect of acid on epoxidation is more pronounced.

**Kinetic Studies.** To shed more light on the epoxidation mechanism over Nb-POM, the kinetics of CyOct oxidation with  $H_2O_2$  in the presence of dimer  $(NbW_5)_2O$  was studied. CyOct was chosen as a model substrate because it is less volatile than CyH and its epoxide is more stable toward ring opening and overoxidation (compare data in Table 1 and Table S1). Typical kinetic curves of CyOct consumption and epoxide product accumulation showed no induction period, autocatalysis or inhibition behavior. The absence of effect of light, oxygen or conventional chain radical scavengers, e.g., ionol, on

the reaction rate discarded radical chain oxidation mechanism, which is consistent with the minor amount of allylic oxidation products formed in the oxidation of CyH (*vide supra*).

The rate of CyOct oxidation in the presence of  $(NbW_5)_2O$  exhibited a typical Arrhenius dependence (Figure 2), which implies that there was no change in the rate-limiting step over the evaluated temperature range. The value of the apparent activation energy (11.7 kcal mol<sup>-1</sup>) turned out close to that previously found for CyOct epoxidation over mesoporous Nb-catalysts (11–12 kcal mol<sup>-1</sup>).<sup>42</sup> It is also noteworthy that the  $E_a$  for epoxidation is significantly lower than the  $E_a$  established for decomposition of H<sub>2</sub>O<sub>2</sub> in the absence of organic substrate: 11.7 vs 16.3 kcal mol<sup>-1</sup> (Figure 2). The same trend was recently observed for mesoporous niobium-silicates.<sup>42</sup>



Figure 2. Arrhenius plots for  $(NbW_5)_2O$ -catalyzed CyOct epoxidation and  $H_2O_2$  decomposition in CH<sub>3</sub>CN. Reaction conditions: CyOct 0.1 M,  $H_2O_2$  0.1 M, and  $(NbW_5)_2O$  0.002 M (for CyOct epoxidation) and  $H_2O_2$  0.2 M,  $(NbW_5)_2O$  0.004 M (for  $H_2O_2$  decomposition).

The CyOct epoxidation reaction showed a first-order dependence on alkene substrate (Figure S6a). The reaction order in oxidant and catalyst depended on the concentration of H<sub>2</sub>O. With 30% H<sub>2</sub>O<sub>2</sub> ([H<sub>2</sub>O] was adjusted to 1.4 M in all experiments), the reaction was first order in oxidant (Figure S6b). While using 77% H<sub>2</sub>O<sub>2</sub> ([H<sub>2</sub>O] = 0.35 M), the reaction was slower and its rate exhibited a saturation behavior, indicating the formation of an active peroxo niobium intermediate (Figure S7a). In turn, the reaction was first order in catalyst with 30% H<sub>2</sub>O<sub>2</sub> (Figure S6c) while the order changed to the fractional value (close to 0.5) when concentrated H<sub>2</sub>O<sub>2</sub> was employed (Figure S7b). Finally, the rate of CyOct oxidation revealed a complicated, bell-shaped dependence on the concentration of water (Figure S8).

The observed kinetic trends allowed us to suggest a reaction mechanism that involves hydrolysis of  $(NbW_5)_2O$  to form monomeric species  $Nb(OH)W_5$  (Eq. 1), interaction of  $Nb(OH)W_5$  with  $H_2O_2$  generating a peroxo species  $HNb(O_2)W_5$ (Eq. 2), followed by oxygen transfer from  $HNb(O_2)W_5$  to alkene, producing epoxide (Eq. 3).

Interconversions between  $(NbW_5)_2O$ ,  $Nb(O)W_5$  and  $Nb(OH)W_5$  in CH<sub>3</sub>CN solution can be followed by <sup>93</sup>Nb NMR spectroscopy. The addition of water to a solution of  $(NbW_5)_2O$  causes the narrowing of the <sup>93</sup>NMR resonance indicating the formation of Nb(OH)W<sub>5</sub> (Figure S9, spectrum B). After the addition of 1 equiv of acid to Nb(O)W<sub>5</sub>, an upfield shift is initially observed (Figure S9, spectrum D) followed by broad-

ening of the <sup>93</sup>Nb NMR signal (Figure S9, spectrum E), which reflects the process of condensation of Nb(O)W<sub>5</sub> in the presence of acid. The formation of HNb(O<sub>2</sub>)W<sub>5</sub> in the presence of H<sub>2</sub>O<sub>2</sub> is discussed in more detail in the next section.

$$[(NbW_5O_{18})_2O]^{4_*} + H_2O \xrightarrow{\longrightarrow} 2[Nb(OH)W_5O_{18}]^{2_*}$$
(1)  
(1) (3)

$$[Nb(OH)W_5O_{18}]^{2-} + H_2O_2 \longrightarrow [HNb(O_2)W_5O_{18}]^{2-} + H_2O$$
(2)  
(3) (4)

 $[HNb(O_2)W_5O_{18}]^2 + alkene \longleftrightarrow [Nb(OH)W_5O_{18}]^2 + epoxide$ (3) (4) (3)

The first reaction order in (NbW<sub>5</sub>)<sub>2</sub>O found for 30% H<sub>2</sub>O<sub>2</sub> implies that, at high concentration of water, dissociation of the dimer is not involved in the rate-limiting step of the oxidation process otherwise one would anticipate ca. 0.5 reaction order in (NbW<sub>5</sub>)<sub>2</sub>O, as it was observed earlier for thioether oxidation catalyzed by a Ti-monosubstituted µ-hydroxo Keggin dimer.116 Indeed, the reaction order in catalyst became close to 0.5 when the amount of water in the system was reduced (see Figure S7b). In turn, at low concentration of water, the overall reaction rate is proportional to H<sub>2</sub>O concentration since water accelerates of the formation of Nb(OH)W<sub>5</sub> via Eq. 1. However, when water concentration becomes significant and all the Nb-POM is present in the form of monomer, the oxidation rate tends to decrease, most likely, because equilibrium (Eq. 2) shifts left, thereby decreasing the concentration of the active peroxo Nb species. The linear dependence of the reaction rate on the concentration of H<sub>2</sub>O<sub>2</sub> at high concentration of water and saturation dependence at low water concentration are also consistent with the proposed mechanism. Note that stages similar to those described by Eq. 2 and Eq. 3 were recently suggested for epoxidation of electron-rich alkenes over mesoporous niobium-silicates on the basis of product, kinetic and spectroscopic data.42

Interaction of dimer 1 and monomer 2 with  $H_2O_2$ . To confirm and understand the formation of the active peroxo niobium species, we studied the interaction of dimer  $(NbW_5)_2O$  and monomer  $Nb(O)W_5$  with hydrogen peroxide by using UV-vis and <sup>93</sup>Nb and <sup>183</sup>W NMR spectroscopy. Scheme 1 summarizes possible equilibriums between various Nb-POM species in the presence of aqueous hydrogen peroxide.



Scheme 1. Possible Nb-POM species and interconversion in the presence of aqueous  $H_2O_2$ .

First, after the addition of  $H_2O_2$  to Nb(O)W<sub>5</sub>, the solution slowly turned pale yellow and a shoulder at 309 nm appeared

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in the UV-vis spectrum (Figure 3a). Note that yellow or light yellow color is characteristic of several Nb(V) peroxo complexes for which bidentate ( $\eta^2$ ) coordination of the peroxo ligand has been proved by X-ray analysis.<sup>87,117,118</sup> Hence, the shoulder at 309 nm can be assigned to peroxo ligand-to-metal charge transfer.



Figure 3. UV-vis spectra of Nb(O)W<sub>5</sub> (0.0005 M) after addition of (a) 5 equiv. of  $H_2O_2$  and (b) 1 equiv. of  $HClO_4$  and 5 equiv. of  $H_2O_2$ . CH<sub>3</sub>CN, 20°C.

<sup>93</sup>Nb NMR spectroscopy is very useful to characterize the Nb(V) compounds both in solids<sup>119</sup> and solution. <sup>93</sup>Nb has the high NMR sensitivity, high spin (9/2) and the large electric quadrupolar moment which, coupling to the local electric field gradients in typical for Nb(V) distorted environments, accelerates the nuclear magnetic relaxation, significantly broadening the signal. In solution, the signal widths increase also with the complex dimension and concentration. The Lindqvist-type Nb-substituted tungstates are appropriate for studying by <sup>93</sup>Nb NMR.<sup>96,120</sup> The width of the <sup>93</sup>Nb NMR signal of anion Nb(O)W<sub>5</sub> in its 0.008M CH<sub>3</sub>CN solution (δ -898 ppm) is about 1000 Hz, and it is the sharpest signal among those of the derivative anions studied in this work. Niobium in the composition of this anion has a distorted  $C_{4v}$ -like octahedral oxygen environment with one terminal unshared oxygen atom. A significant signal broadening observed for dimer (NbW<sub>5</sub>)<sub>2</sub>O (Figure S9, A) can be explained by almost two-fold increase of the anion dimensions which results in a larger correlation time of molecular rotation,96 although the symmetry of the <sup>93</sup>Nb environment in the dimer is similar to that in monomers Nb(O)W<sub>5</sub> and Nb(OH)W<sub>5</sub>.

Upon addition of  $H_2O_2$  to Nb(O)W<sub>5</sub>, a new broad signal ( $\delta$  – 1048 ppm) appeared in the <sup>93</sup>Nb NMR spectrum (Figure 4a). A

similar high field shift was recently observed for peroxoniobate (Bu<sub>4</sub>N)[NbO(O<sub>2</sub>)(OH)<sub>2</sub>] as compared to the spectrum of  $(Bu_4N)[NbO(OH)_2R]$ .<sup>121</sup> The intensity of this resonance increased with increasing concentration of H<sub>2</sub>O<sub>2</sub> and, after the addition of 2 equiv., the initial signal of Nb(O)W<sub>5</sub> ( $\delta$  -898 ppm) disappeared completely (Figure 4, spectrum D). Evidently, the resonance at -1048 ppm belongs to peroxo complex  $Nb(O_2)W_5$  formed via reaction of  $Nb(O)W_5$  with  $H_2O_2$ . The correctness of this process was confirmed by experiments with additives of water. Indeed, the resonance of initial Nb(O)W<sub>5</sub> ( $\delta$ -898 ppm) appeared if 10 vol% of H<sub>2</sub>O was added to the equilibrated mixture of Nb(O)W5 and H2O2 (Figure 4a, spectrum E). The approximately five-fold broadening of the signal of Nb(O)W<sub>5</sub> indicates that the <sup>93</sup>Nb quadrupolar relaxation rate in it is five times faster,<sup>120</sup> which is due to the increase of the Nb coordination number from six to seven and consequently to the increase of the electric field gradients, produced by more distorted oxygen environment. The Lindquist structure of the peroxo Nb-POM (Nb(O<sub>2</sub>)W<sub>5</sub>) proved to be stable toward excess of hydrogen peroxide. No signs of the structure degradation were detected by <sup>93</sup>Nb NMR even after exposure to a 50-fold excess of H<sub>2</sub>O<sub>2</sub> during one week. DFT calculations on Nb(O)W<sub>5</sub> and Nb(O<sub>2</sub>)W<sub>5</sub> also showed an upfield shift of the <sup>93</sup>Nb NMR signal when the oxo ligand in the Lindqvist structure was replaced by peroxo group with  $\eta^2$  coordination, although the computed upfield shift of 106 ppm was somewhat lower than the observed one of 150 ppm.



**Figure 4.** (a) <sup>93</sup>Nb NMR spectra of Nb(O)W<sub>5</sub> (A); Nb(O)W<sub>5</sub> in the presence of 0.5, 1 and 2 equiv. of  $H_2O_2$  (B, C and D, respectively) and spectrum D after addition of 10 vol%  $H_2O$  (E). (b) <sup>93</sup>Nb NMR spectra of Nb(O)W<sub>5</sub> in the presence of 1 equiv. of  $H_2O_2$  and 1 equiv. of HClO<sub>4</sub> (A), (NbW<sub>5</sub>)<sub>2</sub>O in the presence of 1 equiv. of  $H_2O_2$  (B), Nb(O<sub>2</sub>)W<sub>5</sub> (C), Nb(O<sub>2</sub>)W<sub>5</sub> in the presence of 1 equiv. of HClO<sub>4</sub> (D), and HNb(O<sub>2</sub>)W<sub>5</sub> (E). Nb-POM 0.01 M, CH<sub>3</sub>CN, 20 °C.

In the presence of 1 equiv. of acid, the shoulder in the UV spectrum of H<sub>2</sub>O<sub>2</sub>-treated Nb(O)W<sub>5</sub> displayed a substantial red shift (Figure 3b). The TD-DFT simulated spectra for Nb-peroxo species Nb(O<sub>2</sub>)W<sub>5</sub> shows one peak centered around 305 nm, as shown in Figure S10. The absorption arises from the HOMO to LUMO excitation, which has a  $\pi^*_{O-O} \rightarrow d(M)$  nature. The protonation of Nb(O<sub>2</sub>)W<sub>5</sub> at the bridging Nb–O–W

oxygen to give HNb(O<sub>2</sub>)W<sub>5</sub> shifts the peak for  $\pi^*_{O-O} \rightarrow d(M)$ excitation to 315 nm, reproducing nicely the experimental red shift. The analysis of molecular orbitals revealed that upon protonation at the POM framework the d-type orbitals of W suffer a larger stabilization than the  $\pi^*_{O-O}$ -type orbital of peroxo moiety reducing the energy gap. Moreover, the addition of protons greatly accelerated generation of the peroxo species, which completed within few minutes (compare Figures 3a and 3b). Dimer (NbW<sub>5</sub>)<sub>2</sub>O reacted with H<sub>2</sub>O<sub>2</sub> very fast and the UV-vis spectrum of (NbW<sub>5</sub>)<sub>2</sub>O after interaction with  $H_2O_2$  was similar to the spectrum of Nb( $O_2$ )W<sub>5</sub> in the presence of acid (Figure S11). A pronounced bathochromic shift was earlier observed in the UV-vis spectra of the H<sub>2</sub>O<sub>2</sub>-Nb<sub>2</sub>O<sub>5</sub>-H<sub>2</sub>SO<sub>4</sub> system as the concentration of sulfuric acid was increased.<sup>122</sup> It is noteworthy that a blue shift of the DR UV-vis band, which was preliminary assigned to a 'NbOOH' species (307 nm), was detected upon addition of base to an H<sub>2</sub>O<sub>2</sub>treated mesoporous Nb-silicate.42 Hence, we may conclude that the UV-vis absorption associated with the peroxo Nb species generated in mesoporous Nb-silicate and homogeneous Nb-POM reveal a similar response to acid/base additives.

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The protonation of the Nb-POM peroxo species was also manifested in the <sup>93</sup>Nb NMR spectra (Figure 4b). In the presence of 1 equiv. of acid, the resonance of H<sub>2</sub>O<sub>2</sub>-treated Nb(O)W<sub>5</sub> shifted downfield relative to the proton-free system ( $\delta$  –1015 versus –1048 ppm). A resonance with the same chemical shift ( $\delta$  –1015 ppm) was observed in the <sup>93</sup>Nb NMR spectrum of dimer (NbW<sub>5</sub>)<sub>2</sub>O upon interaction with hydrogen peroxide (Figure 4b, spectrum B). In turn, the broad <sup>95</sup>Nb NMR resonance of peroxo complex Nb(O<sub>2</sub>)W<sub>5</sub> ( $\delta$  –1048 ppm) narrowed significantly in the presence of protons and moved to –1015 ppm (Figure 4b, spectrum D). Thus, the observed changes in the UV-vis and <sup>93</sup>Nb NMR spectra allowed us to suggest that the same protonated niobium peroxo species could be generated via interaction of H<sub>2</sub>O<sub>2</sub> with either (NbW<sub>5</sub>)<sub>2</sub>O or Nb(O)W<sub>5</sub> in the presence of H<sup>+</sup> (see Scheme 1).

Importantly, the <sup>183</sup>W NMR spectrum of  $(NbW_5)_2O$  in the presence of 3 equiv. of  $H_2O_2$  (Figure S12, spectrum D) showed two resonances with the intensity ratio of 4:1 typical of monosubstituted Lindqvist tungstates.

**Characterization and reactivity of Nb-peroxo species.** While our attempts to isolate a protonated peroxo niobium complex from a solution of Nb(O)W<sub>5</sub> in the presence of acid and an excess of  $H_2O_2$  failed, we managed to synthesize it starting from dimer (NbW<sub>5</sub>)<sub>2</sub>O and  $H_2O_2$  (Scheme 1).

The presence of one peroxo group per Nb atom was confirmed by titration with PPh<sub>3</sub> monitored by <sup>31</sup>P NMR according to the procedure described in the literature.<sup>87</sup> The elemental analysis data agreed with the formulation of (Bu<sub>4</sub>N)<sub>2</sub>[HNb(O<sub>2</sub>)W<sub>5</sub>O<sub>18</sub>]. Although attempts to grow X-ray quality crystals of HNb(O<sub>2</sub>)W<sub>5</sub> failed, this compound could be comprehensively characterized using various analytic and spectroscopic techniques. Potentiometric titration of HNb(O<sub>2</sub>)W<sub>5</sub> in CH<sub>3</sub>CN with aqueous Bu<sub>4</sub>NOH showed a sharp breakpoint at 0.73 equiv. of OH<sup>-</sup> (Figure S13), indicating that the exact [H<sup>+</sup>]/[Nb] ratio is a little less than 1. Cyclic voltammetry indicated a significant increase in the oxidation potential of HNb(O<sub>2</sub>)W<sub>5</sub> relative to Nb(O<sub>2</sub>)W<sub>5</sub> (Figure S14). The UVvis spectrum of  $HNb(O_2)W_5$  differed from that of  $Nb(O_2)W_5$ , but it practically coincided with the spectrum of  $Nb(O_2)W_5$  in

the presence of 1 equiv. of acid (Figure S11), corroborating the presence of proton in  $HNb(O_2)W_5$ .

The purity of HNb(O<sub>2</sub>)W<sub>5</sub> was verified by using <sup>93</sup>Nb NMR spectroscopy. The only peak detected in the <sup>93</sup>Nb NMR spectrum was located at  $\delta$  –1015 ppm (Figure 4b, spectrum E). The same chemical shift was observed for the peroxo species generated *in situ* upon addition of 1 equiv. of H<sup>+</sup> to Nb(O<sub>2</sub>)W<sub>5</sub> (Figure 4b, spectrum D). <sup>93</sup>Nb NMR monitoring of the stepwise addition of HClO<sub>4</sub> to Nb(O<sub>2</sub>)W<sub>5</sub> (Figure S15a) and Bu<sub>4</sub>NOH to HNb(O<sub>2</sub>)W<sub>5</sub> (Figure S15b) clearly indicated that species HNb(O<sub>2</sub>)W<sub>5</sub> and Nb(O<sub>2</sub>)W<sub>5</sub> are in fast exchange on the <sup>93</sup>Nb NMR time scale, which implies that both peroxo complexes have a similar structure and differ only in their protonation state. As one can judge from Figure S15, the interconversion between HNb(O<sub>2</sub>)W<sub>5</sub> and Nb(O<sub>2</sub>)W<sub>5</sub> is reversible and the Lindqvist structure of the NbW<sub>5</sub> peroxo complexes is stable toward, at least, 3 equiv. of acid and 1.5 equiv. of base.

The structure of HNb(O<sub>2</sub>)W<sub>5</sub>, in particular a possible site of the proton localization, was probed by vibrational spectroscopic techniques. No IR bands were observed for solid HNb(O<sub>2</sub>)W<sub>5</sub> in the characteristic 1800–1600 cm<sup>-1</sup> region (Figure S16), indicating that no  $H_3O^+$  was present and that the proton is directly attached to the POM surface.<sup>123,124</sup> The FT-IR spectra of  $HNb(O_2)W_5$  and  $Nb(O_2)W_5$  confirm the retention of the Lindqvist structure (see Figure S2). The absence of the vibration stretches of Nb=O and Nb-O-Nb at 915 and 695  $cm^{-1}$  present in the parent compounds Nb(O)W<sub>5</sub> and (NbW<sub>5</sub>)<sub>2</sub>O, respectively, clearly indicates changes at the terminal position of the Nb atom. The FT-IR spectrum of Nb(O<sub>2</sub>)W<sub>5</sub> revealed new bands at 857, 638 and 602 cm<sup>-1</sup>. On the basis of the literature data reported for various peroxo niobium complexes,  $^{86,95,125-131}$  the band at 857 cm<sup>-1</sup> can be assigned to the stretching fundamental of the O-O bond while the couple at 638 and 602 cm<sup>-1</sup> is associated with symmetric and asymmetric Nb-peroxide stretches. The IR spectrum of HNb(O<sub>2</sub>)W<sub>5</sub> revealed some important distinctive features relative to that of Nb(O<sub>2</sub>)W<sub>5</sub>. First, the frequencies of v(W=O) and v(O-O) are shifted to higher energy: 973 vs 960  $\text{cm}^{-1}$  and 870 vs 857  $\text{cm}^{-1}$ , respectively, which reflects a decrease in the corresponding bond lengths due to the contraction of the structure via reduction of the negative charge. This indicates that protonation of the peroxo derivative occurs at Nb-O-W bridging oxygen rather than at the peroxo group, because, in the latter case, one would expect a lower-energy shift due to lengthening of the O–O bond. A higher energy shift of v(W=O) was observed earlier upon protonation of the di-Nb-substituted Lindqvist tungstate  $[Nb_2W_4O_{19}]^{4-.132}$ 

The assignment of the IR bands in the peroxo Nb species and the hypothesis about protonation of the Nb–O–W bridging oxygen were further supported by Raman spectroscopy. In comparison with the spectra of peroxo-free compounds (NbW<sub>5</sub>)<sub>2</sub>O and Nb(O)W<sub>5</sub>, new bands appeared in the Raman spectra of the peroxo derivatives at 860–863 and 603–623 cm<sup>-1</sup> (Figure S17) and can be assigned to v(O–O) and v(NbO<sub>2</sub>) vibrations, respectively.<sup>118,125,126,133–135</sup> Similarly to the IR spectra, a higher-energy shift of the stretching vibrations of terminal W=O groups was clearly observed in the Raman spectrum of solid HNb(O<sub>2</sub>)W<sub>5</sub> as compared to the spectra of Nb(O<sub>2</sub>)W<sub>5</sub> generated *in situ* from Nb(O<sub>2</sub>)W<sub>5</sub> and 1 equiv. of H<sup>+</sup> in CH<sub>3</sub>CN solution (Figure 5) showed shearing of v(W=O) and v(NbO<sub>2</sub>) to higher energies (*ca.* 13 and 7 cm<sup>-1</sup>, respective-

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ly). Thus, both IR and Raman spectroscopy provided evidence in favor of the side-on  $(\eta^2)$  bonding mode of the peroxo ligand in HNb(O<sub>2</sub>)W<sub>5</sub> and Nb(O<sub>2</sub>)W<sub>5</sub>, with proton located at Nb–O– W oxygen site in the former. In agreement with this interpretation, the DFT-simulated Raman spectra of Nb(O<sub>2</sub>)W<sub>5</sub> and HNb(O<sub>2</sub>)W<sub>5</sub> (Figure S18) revealed a shift to higher energies for v(W=O) and v(NbO<sub>2</sub>) bands of complex HNb(O<sub>2</sub>)W<sub>5</sub> by 14 and 5 cm<sup>-1</sup>, respectively, which is close to what was observed experimentally. Moreover, DFT calculations (*vide infra*) showed that in HNb(O<sub>2</sub>)W<sub>5</sub> protonation at Nb–O–W is thermodynamically favored relative to protonation at the W–O–W bridging oxygen and at the peroxo moiety by 3.0 and 8.7 kcal·mol<sup>-1</sup>, respectively.



Figure 5. Raman spectra of  $CH_3CN$  (A) and  $CH_3CN$  solutions of  $Nb(O)W_5$  (B),  $Nb(O_2)W_5$  (C), and  $Nb(O_2)W_5$  in the presence of 1 equiv. of  $HClO_4$  (D). POM 0.1 M,  $CH_3CN$ , 20 °C.



**Figure 6.** <sup>17</sup>O NMR spectra of Nb(O)W<sub>5</sub> (A), Nb(O<sub>2</sub>)W<sub>5</sub> (B), and HNb(O<sub>2</sub>)W<sub>5</sub> (C). 0.1 M POM, CH<sub>3</sub>CN, 20 °C. The spectrum of HNb(O<sub>2</sub>)W<sub>5</sub> was accumulated in the presence of a 10-fold excess of 30% H<sub>2</sub>O<sub>2</sub>. Peaks corresponding to H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O are marked with asterisks \* and \*\*, respectively.

The protonation site in HNb(O<sub>2</sub>)W<sub>5</sub> was also confirmed by <sup>17</sup>O NMR spectroscopy. As shown in Figure 6 and Table S2, the <sup>17</sup>O NMR spectrum of HNb(O<sub>2</sub>)W<sub>5</sub> revealed a pronounced upfield shift of the Nb–O–W signal ( $\delta$  414 ppm) relative to its position in the <sup>17</sup>O NMR spectra of Nb(O)W<sub>5</sub> ( $\delta$  456 ppm)<sup>97,120</sup> and Nb(O<sub>2</sub>)W<sub>5</sub> (460 ppm). This shift in combination with downfield shifts for the rest of signals is, according to the literature, <sup>132,136</sup> an unambiguous prove for the protonation of Nb–O–W bond in solution.<sup>137</sup> Hence, IR, Raman, and <sup>17</sup>O NMR spectroscopic techniques along with DFT calculations (see below) all support the conclusion that in HNb(O<sub>2</sub>)W<sub>5</sub> the proton is preferably located at the Nb–O–W bridging oxygen site rather than at the peroxo ligand.

Finally, we investigated the stoichiometric interaction of  $Nb(O_2)W_5$  and  $HNb(O_2)W_5$  with CyH as model alkene substrate. The results on the substrate conversion and product selectivity are shown in Table 2. Peroxo complex Nb(O<sub>2</sub>)W<sub>5</sub> was found to be completely inert toward CyH. However, it became reactive and produced heterolytic oxidation products, epoxide and diol, if 1 equiv. of protons was added. In turn, protonated peroxo complex HNb(O<sub>2</sub>)W<sub>5</sub> was also able to oxidize CyH under stoichiometric conditions, leading to epoxide and diol. The amount of the oxygenated products corresponded to the amount of active oxygen (i.e., peroxo oxygen activated by proton) in HNb(O2)W5. These experiments unambiguously prove that protons play a crucial role in the activation of the peroxo niobium moiety and that namely protonated Nb peroxo species is responsible for heterolytic oxidation of C=C bond in alkene.

Table 2. Interaction of HNb(O<sub>2</sub>)W<sub>5</sub> and Nb(O<sub>2</sub>)W<sub>5</sub> with CyH<sup>a</sup>

Entry	POM	СуН	Product yield, <sup>b</sup> %		
		conv. %	epoxide	diol	
1	$Nb(O_2)W_5$	0	0	0	
2	$Nb(O_2)W_5 + 1 eq. H^+$	19.5	13.5	6	
3	HNb(O <sub>2</sub> )W <sub>5</sub>	16	10	6	

<sup>*a*</sup> Reaction conditions: 0.016 M POM, 0.016 M HClO<sub>4</sub> (entry 2), 0.08 M CyH, CH<sub>3</sub>CN, 50 °C, 2 h. <sup>*b*</sup> Based on substrate.

The stoichiometric reaction can be easily followed by UVvis. The decrease in the characteristic absorption region due to the ligand-to-metal charge transfer (310-350 nm) in the UVvis spectra of HNb(O<sub>2</sub>)W<sub>5</sub> (Figure 7) or HNb(O<sub>2</sub>)W<sub>5</sub> generated in situ from  $Nb(O_2)W_5$  and H<sup>+</sup> (Figure S19) is much slower than in the presence of CyH. This implies that thermal decomposition of HNb(O<sub>2</sub>)W<sub>5</sub> is rather slow and that the observed decay of the absorption is due to the reaction with CyH. <sup>93</sup>Nb NMR monitoring of the reaction between HNb(O<sub>2</sub>)W<sub>5</sub> and CyH revealed transformation of the sharp resonance at  $\delta$  – 1015 ppm into the broad resonance at ca. -950 ppm attributed to  $(NbW_5)_2O_5^{96}$  which appeared at the end of the reaction as a result of dimerization of Nb(OH)W<sub>5</sub>. Importantly, interaction of HNb(O<sub>2</sub>)W<sub>5</sub> with cis-stilbene produced exclusively cisepoxide along with the C-C cleavage product benzaldehyde, corroborating a concerted oxygen transfer mechanism.





We have analyzed the heterolytic oxygen transfer to CyH from both side-on Nb-hydroperoxo (4b) and -peroxo (4) species. Figure 9 collects the geometries of the reactants and the transition states, as well as, the corresponding free energy barriers. The less stable hydroperoxo anion 4b shows a lower free energy barrier than the peroxo anion 4 (17.6 vs 27.1  $kcal \cdot mol^{-1}$ ). In Nb-hydroperoxo species 4b, the alkene attack occurs preferably at the proximal, non-protonated  $\alpha$ -oxygen because the  $\sigma^*O-O$  orbital is polarized toward  $O\alpha$ , favoring the donation from the nucleophilic double bond.<sup>45</sup> In this case, the transition state for  $\beta$ -oxygen transfer (see Figure S20) is 2.3 kcal·mol<sup>-1</sup> higher than the corresponding transition state for a-oxygen transfer  $TS_{4b-P}$ . Nevertheless, the  $\beta$ -oxygen transfer could be favored in complexes with metal ions in sterically hindered or strongly embedded in non-flexible environment that make the  $O\beta$  more accessible to the substrate.<sup>139</sup>



**Figure 8.** Calculated Gibbs free energy profile  $(\text{kcal} \cdot \text{mol}^{-1})$  for the epoxidation of cyclohexene (CyH) with H<sub>2</sub>O<sub>2</sub> catalyzed by Nb(OH)W<sub>5</sub> (**3**).

Another important feature of the potential free-energy profile (Figure 8) is the relative rates between the hydrogen and the oxygen transfer from 4b to form the peroxo species 4  $(TS_{4b-4})$  and the epoxide  $(TS_{4b-P})$ , respectively. The hydrogen transfer is computed to be faster, its free energy barrier being 2.5 kcal·mol<sup>-1</sup> lower in energy. Thus, it is reasonable to assume that a large proportion of the reacting species, reaching the Nb-hydroperoxo 4b intermediate, evolve to the Nb-peroxo complex 4, which becomes the resting-state of the catalytic process. From Nb-peroxo species 4, the reaction can proceed directly to oxygen transfer to the alkene through  $TS_{4-P}$  structure, overcoming a computed free-energy barrier of 27.1 kcal·mol<sup>-1</sup>, or it can come back to the less stable but more reactive Nb-hydroperoxo species 4b, overcoming an overall free-energy barrier (4  $\rightarrow$  TS<sub>4b-P</sub>) of 26.3 kcal·mol<sup>-1</sup>. In summary, our calculations indicate that most of the reaction proceeds via heterolytic oxygen transfer from Nb- $\eta^2$ -hydroperoxo species 4b, involving a previous formation of protonated Nbperoxo species 4, which acts as the resting-state of the catalyst. However, other two energetically accessible paths can contribute to the formation of epoxides: (i) the direct oxygen transfer from 4b without the formation of peroxo species 4, and (ii) the heterolytic oxygen transfer from the Nb-peroxo



**Figure 7.** UV-vis spectra of  $HNb(O_2)W_5$  (a) in time and (b) in time in the presence of 5 equiv. of CyH. Reaction conditions: 0.0005 M HNb(O<sub>2</sub>)W<sub>5</sub>, 0.0025 M CyH, CH<sub>3</sub>CN, 50 °C.

DFT study of reaction mechanism. To understand the reaction mechanism at atomistic level and identify the active species of the oxygen transfer process, we have performed DFT calculations on Nb-substituted Lindqvist anions using CyH as substrate. Our previous study on the effect of the metal nature on the oxygen transfer mechanism showed that when we move from Ti to Nb (down in the periodic table), both peroxo and hydroperoxo energy barriers decrease, but the latter does it more appreciably.<sup>45</sup> However, in order to obtain a complete picture of the reaction, one should also evaluate the effect of the larger radius of Nb(V) ion on the stabilization of 7coordinated species such as  $\eta^2$ -peroxo and  $\eta^2$ -hydroperoxo ones.<sup>138</sup> Figure 8 depicts the calculated free energy profile for the epoxidation of CyH with H2O2 catalyzed by  $[Nb(OH)W_5O_{18}]^{2-}$  (3) anion. In the first step, the interaction of H<sub>2</sub>O<sub>2</sub> with the Nb-hydroxo moiety of **3** results in the hydroperoxo species 4a, in which the OOH group is  $\eta^{1}$ -coordinated, and the release of a water molecule. The H2O2 activation proceeds through transition state  $TS_{3-4a}$  (see Figure S20), and the computed free-energy barrier is moderate, 15.3 kcal mol<sup>-1</sup>. The generated  $\eta^1$ -OOH species (4a) can evolve to the more stable  $\eta^2$ -OOH species **4b** because the size of the second-row Nb(V) ion allows to accommodate 7-fold coordination. The  $\eta^2$ -hydroperoxo species **4b** is lower in energy (-3.5 kcal·mol<sup>-</sup> <sup>1</sup>) than the corresponding  $\eta^1$ -hydroperoxo **4a**, but higher in energy (+8.7 kcal·mol<sup>-1</sup>) than the corresponding  $\eta^2$ -peroxo complex 4 in agreement with experimental data. Nb-peroxo complex 4 can be formed from 4b via hydrogen transfer from the hydroperoxo moiety to a bridging W-O-Nb oxygen overcoming a moderate free energy barrier of 15.1 kcal·mol<sup>-1</sup> (see transition state structure  $TS_{4b-4}$  in Figure S20). As commented

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species 4. According to the computed values, at 50° C, the contribution of the two latter paths is approximately 2 and 21%, respectively.



**Figure 9.** Combined balls-and-sticks and polyhedral representation of some of the most relevant intermediates (**4b** and **4**) and transition states ( $TS_{4b-P}$  and  $TS_{4-P}$ ) in reaction mechanism. Main distances are shown in Å. Free energy barriers for the electrophilic O-transfer step occurring from **4b** and **4** are shown in kcal mol<sup>-1</sup>.

To further validate our proposed mechanism, we analyzed the zero-point corrected energy profile (Figure S21) for CyOct epoxidation by dimer (NbW<sub>5</sub>)<sub>2</sub>O and compared it with the experimental  $E_a$  (11.7 ± 0.8 kcal·mol<sup>-1</sup>) in Figure 2. In the absence of entropic effects, the computed overall energy barrier for direct oxygen transfer from hydroperoxo species **4b** is 8 kcal·mol<sup>-1</sup> (too low) while those involving the formation of peroxo species **4** are about 16 kcal·mol<sup>-1</sup> (too high). However, assuming that several paths contribute to the reaction, the weighted average of the computed energy barriers should be close to experimental  $E_a$  value.

Next, to understand the role of protons on the reactivity, we evaluated feasibility of the epoxidation process using the nonprotonated peroxo species  $[Nb(O_2)W_5O_{18}]^{3-}$  (5). The free energy barrier for the oxygen transfer from 5 to CyH was computed to be 31.6 kcal mol<sup>-1</sup>, which is larger than that for the epoxidation by protonated peroxo species 4, 26.3 kcal·mol<sup>-1</sup> (from 4 to **TS**<sub>4b-P</sub>). This is consistent with lack of reactivity observed over species 5. Moreover, the free-energy barrier for  $H_2O_2$  activation by the non-protonated species 2 is ~4 kcal mol<sup>-1</sup> higher than that from the protonated species **3** (see Figure 8) in full agreement with the accelerated generation of peroxo species observed upon addition of protons (Figure 3). Thus, protonation has two important consequences in the catalytic performance of Nb-substituted anions: (i) it allows forming the more reactive Nb-hydroperoxo species, and (ii) it reduces the overall negative charge of the POM favoring the electrophilic oxygen transfer to the alkene as observed also for Ti-substituted POMs.83

**Table 3.** Calculated protonation free-energies ( $\Delta G_{H^+}$ ) and freeenergy barriers for oxygen transfer ( $\Delta G^{\ddagger}_{Otrans}$ ) from Lindqvist (Nb(O<sub>2</sub>)W<sub>5</sub> **5** and HNb(O<sub>2</sub>)W<sub>5</sub> **4**) and Keggin (**5k** and **4k**) anions in kcal·mol<sup>-1</sup>.

Catalyst	$\Delta G_{\rm H^+}$	Active species	q/M	$\Delta G^{\ddagger}_{Otrans}$
5	-	5	0.50	31.6
5k	-	5k	0.33	29.6
$5 + 1 \mathrm{H}^+$	-3.7	4	0.33	26.3 <sup><i>a</i></sup>
$5\mathbf{k} + 1\mathbf{H}^+$	+2.7	4k	0.25	23.8 <sup><i>a</i></sup>

<sup>*a*</sup> Free-energy barriers through hydroperoxo path.

Finally, we analyzed computationally the reactivity of Nbsubstituted Keggin anions  $[PW_{11}O_{39}Nb(O_2)]^{4-}$  (5k) and  $[HPW_{11}O_{39}Nb(O_2)]^{3-}$  (4k), which also display a poor performance in alkene epoxidation (Table 1). Two main trends are observed in Table 3, which collects the computed protonation energies ( $\Delta G_{H+}$ ) and the free-energy barriers for oxygen transfer ( $\Delta G_{\text{Otrans}})$  through peroxo (5/5k  $\rightarrow$  TS\_{5-P}/TS\_{5k-P}) and hydroperoxo  $(4/4k \rightarrow TS_{4b-P}/TS_{4bk-P})$  paths. First, ongoing from Lindqvist to Keggin anion the charge density decreases as reflected in the total charge per metal ratio (q/M).<sup>107,140–142</sup> Consequently, the POM becomes better electrophile favoring the oxygen transfer to the nucleophilic alkene by  $\sim 2 \text{ kcal} \cdot \text{mol}^-$ <sup>1.83</sup> Second, the less basic Keggin anion is more difficult to protonate resulting in an endergonic process according to our calculations (+2.7 kcal·mol<sup>-1</sup> for  $5\mathbf{k} + 1\mathbf{H}^+ \rightarrow 4\mathbf{k}$ ). The computed atomic charge from electrostatic potential at the bridging Nb-O-W oxygen for 5k (-.74 au) is less negative than that of the corresponding oxygen for Lindqvist species 5 (-.86 au). Thus, although Keggin structures are more reactive as oxygen transfer agents than Lindqvist ones, they are more difficult to be activated via protonation. Overall, these opposite trends might result in a loose of reactivity for Keggin structures. In summary, for the alkene epoxidation by Nb-substituted POMs the art consists of tuning the charge density of the anion. The POM should have low electron density in order to favor the electrophilic oxygen transfer to alkenes, but basic enough to be protonated and enable the hydroperoxo path.

## CONCLUSIONS

Nb-substituted tungstates of the Lindqvist structure are highly active and selective catalysts for H2O2-based oxidation of alkenes via heterolytic pathway. In this work, we demonstrated that the Lindqvist Nb-POMs mimic well the catalytic performance of heterogeneous Nb-silicate catalysts and can be successfully employed as soluble molecular models for studying mechanism of H<sub>2</sub>O<sub>2</sub> activation on Nb(V). Product, spectroscopic and computational studies revealed that protons play a crucial role in the catalytic activity of niobium sites. While a suitable source of protons is required to accelerate interaction of the terminal Nb=O bond in monomer Nb(O)W<sub>5</sub> with H<sub>2</sub>O<sub>2</sub>,  $\mu$ -oxo dimer (NbW<sub>5</sub>)<sub>2</sub>O is highly active without any additives. Interaction of  $(NbW_5)_2O$  (alternatively Nb(O)W<sub>5</sub> + H<sup>+</sup>) with H<sub>2</sub>O<sub>2</sub> affords protonated Nb peroxo derivative HNb(O<sub>2</sub>)W<sub>5</sub> which, in contrast to proton-free peroxo complex  $Nb(O_2)W_5$ , is able to epoxidize alkenes under stoichiometric conditions. Therefore, protons are important not only for the generation of peroxo niobium species but also for its reactivity. Spectroscopic (UV-vis, IR, Raman, and <sup>17</sup>O NMR) and computational techniques strongly support a monomeric Lindqvist structure of HNb(O<sub>2</sub>)W<sub>5</sub> with one peroxo ligand attached to Nb(V) in a  $\eta^2$ -coordination mode and proton located at a Nb–O–W bridging oxygen. DFT calculations also revealed that  $\eta^2$ -hydroperoxo niobium species, which is present in equilibrium with the protonated peroxo species HNb(O<sub>2</sub>)W<sub>5</sub> in CH<sub>3</sub>CN solution, is the main epoxidizing species since it drives the reaction by a less energy-demanding reaction path. The protonation of the Nb-POMs plays a crucial role in activating the oxidant by allowing the formation of the more reactive hydroperoxo intermediate and increasing its electrophilicity that favors the oxygen transfer to nucleophiles. Future catalyst designs should fine-tune its electrostatic properties reducing electron density but allowing protonation in order to enable the hydroperoxo path.

## **AUTHOR INFORMATION**

### Corresponding Author

\* E-mails: khold@catalysis.ru; j.carbo@urv.cat

## Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

#### Notes

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The authors declare no competing financial interests.

## ASSOCIATED CONTENT

**Supporting Information**. Data on product yields for various alkenes, <sup>183</sup>W and <sup>93</sup>Nb NMR, IR, Raman, and UV-vis spectra, <sup>17</sup>O NMR data, potentiometric titration, cyclic voltammograms, kinetic data on CyOct epoxidation, structures of transition state, energy profile.

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