EurJIC
European Journal of Inorganic Chemistry

A Journal of ChemPubSoc Europe

Accepted Article

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To be cited as: *Eur. J. Inorg. Chem.* 10.1002/ejic.201801108

Link to VoR: http://dx.doi.org/10.1002/ejic.201801108

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Thioether oxidation with H_2O_2 catalyzed by Nb-substituted polyoxotungstates. Mechanistic insights

Olga V. Zalomaeva,[a] Nataliya V. Maksimchuk,[a,b] Gennadii M. Maksimov,[a] and Oxana A. Kholdeeva *[a,b]

Abstract: Nb-monosubstituted polyoxotungstates of the Lindqvist and Keggin structures, $(Bu_4N)_3[Nb(O)W_5O_{18}]$ (**1**) and $(Bu_4N)_4[PW_{11}NbO_{40}]$ (**2**), respectively, catalyze oxidation of organic sulfides with aqueous H_2O_2 in acetonitrile. The corresponding peroxocomplexes $(Bu_4N)_3[Nb(O_2)W_5O_{18}]$ (**3**) and $(Bu_4N)_4[PW_{11}Nb(O_2)O_{39}]$ (**4**) formed upon interaction of **1** and **2** with H_2O_2 are able to oxidize sulfides to sulfoxides and sulfones under stoichiometric conditions. The product analysis of the oxidation of thianthrene 5-oxide, competitive sulfide-sulfoxide oxidation and Hammett plot implicated electrophilic oxidative properties of **4** and a complex oxidative nature of **3**. Protonation of peroxo complex **3** leading to the formation of the peroxo species $(Bu_4N)_2[HNb(O_2)W_5O_{18}]$ (**5**) strongly increases its electrophilicity, which has a great impact on its reactivity and sulfoxidation selectivity.

Introduction

In recent years, various niobium-containing materials have attracted increasing attention as catalysts for important H_2O_2-based selective oxidations, such as epoxidation of alkenes[1] and sulfoxidation of thioethers.[2] While several attempts of rationalizing the catalytic performance of Nb(V) in alkene epoxidation have been published,[2j, 3] the mechanism of Nb-catalyzed thioether sulfoxidation remains practically unexplored.

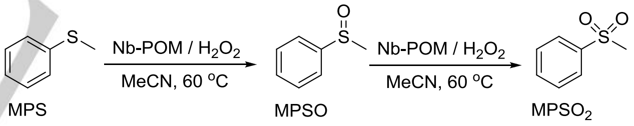
Transition-metal-substituted polyoxometalates (POMs) are well-known homogeneous catalysts for a range of selective oxidations[4] and they can also serve as tractable soluble models for heterogeneous catalysts in mechanistic studies.[5] Our recent work showed that Nb-monosubstituted tungstates of the Lindqvist structure mimic well the catalytic performance of mesoporous Nb-silicate catalysts in epoxidation of alkenes with H_2O_2 and that protons play a crucial role in heterolytic activation of the oxidant and selectivity of epoxidation.[6]

In the present work, we first explored catalytic properties of the Lindqvist and Keggin type Nb-monosubstituted polyoxotungstates, $(Bu_4N)_3[Nb(O)W_5O_{18}]$ (**1**) and $(Bu_4N)_4[PW_{11}NbO_{40}]$ (**2**), in the oxidation of thioethers with H_2O_2 and also studied reactivity of peroxo complexes $(Bu_4N)_3[Nb(O_2)W_5O_{18}]$ (**3**), $(Bu_4N)_4[PW_{11}Nb(O_2)O_{39}]$ (**4**) and $(Bu_4N)_2[HNb(O_2)W_5O_{18}]$ (**5**) toward a range of organic S-compounds under stoichiometric conditions. The oxidation mechanism has been investigated using kinetic and spectroscopic tools, product studies on the test substrate thianthrene 5-oxide, competitive experiments, and Hammett correlations.

Results and Discussion

Catalytic oxidations

The oxidation of methyl phenyl sulfide (MPS) with 1 equiv. of H_2O_2 was studied in the presence of catalytic amounts (2 mol%) of tetrabutylammonium (TBA) salts of Nb-substituted polyoxo- and peroxopolyoxotungstates with the Lindqvist (**1**, **3** and **5**) and Keggin (**2** and **4**) structures (Scheme 1). The stoichiometry of MPS oxidation with H_2O_2 to produce sulfoxide (MPSO) and sulfone ($MPSO_2$) is 1:1 and 1:2, respectively.



Scheme 1. Catalytic oxidation of MPS in the presence of Nb-POM.

The results on the catalytic MPS oxidation are presented in Table 1. Catalytic activity of the Lindqvist **1** and Keggin **2** POMs having terminal oxo group (Nb=O) was found to be close: TOF 0.4 and 0.3 min^{-1}, respectively (Table 1, entries 1 and 2). However, in the presence of **1**, the overoxidation product $MPSO_2$ was obtained with a higher yield (16 vs 10% for **2**). Both **2** and its peroxocomplex **4** revealed similar activity and selectivity (Table 1, compare entries 2 and 4). For Lindqvist **1** and its peroxocomplex **3**, the product yields were also close: 66-68% MPSO and 16% $MPSO_2$ (Table 1, entries 1 and 3). However, the activity of corresponding peroxo derivative **3** was significantly higher (TOF 2 vs 0.4 min^{-1} for **1**). At the same time, protonated peroxocomplex **5** was more active than **3** and revealed higher selectivity toward MPSO (Table 1, compare entries 3 and 5). Recently, some of us reported that **5** is formed from μ-oxo dimer $(Bu_4N)_4[(NbW_5O_{18})_2O]$ (**6**) upon hydrolysis and interaction with H_2O_2.[6] Indeed, if we compare catalytic properties of the protonated peroxo species **5** and dimer **6**, we can see that both compounds demonstrate practically the same activity and selectivity in MPS oxidation (Table 1, entries 5 and 6), which

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indicates that **5** is most likely the active species responsible for the catalysis observed with **6**.

Table 1. Catalytic oxidation of MPS with H_2O_2 in the presence of Nb-POMs.[a]

Entry	POM	MPS conversion [%]	Yields [%][b]		Time [h]	TOF, [min^{-1}][c]
			MPSO	MPSO$_2$		
1	**1**	82	66 (80)	16 (20)	3	0.4
2	**2**	87	77 (89)	10 (11)	4	0.3
3	**3**	84	68 (81)	16 (19)	1	2
4	**4**	91	79 (87)	11 (13)	4	0.4
5	**5**	87	76 (87)	11 (13)	0.5	4
6	**6**	85	74 (87)	11 (13)	0.5	4

[a] Reaction conditions: [MPS] 0.2 M, [H_2O_2] 0.2 M, [Nb-POM] 0.004 M, MeCN 1 mL, 60 °C. [b] Yield based on initial MPS. Yield based on converted MPS is given in paretheses. [c] TOF = (moles of substrate consumed)/(moles of Nb x time), determined from initial rates of substrate consumption.

Reaction kinetics

Kinetics of sulfide oxidation with H_2O_2 in the presence of **1** was investigated using 4-bromothioanisole (Br-MPS) as a model substrate. Typical kinetic curves showed no induction period, autocatalysis or inhibition behavior. The reaction rate was not affected by light and by the presence of molecular oxygen. All these indicate that neither photochemical nor autoxidation processes are involved. The first-order dependence of the reaction rate on the concentration of sulfide and catalyst was observed (Figures 1a and 1b). The linier dependence of the reaction rate on the concentration of **1** confirms stability of the Nb-POM under the turnover conditions, which was also corroborated by IR and ^{93}Nb NMR techniques.The order in the oxidant changed from first to zero with increasing H_2O_2 concentration (Figure 1c).

Such kinetic behavior implies Michaelis-Menten-type kinetics and suggests a two-step mechanism: a) the first step is a reversible interaction of H_2O_2 with **1** with the production of peroxocomplex **3** (Equation 1) and b) the second step is an interaction between **3** and organic substrate (Equation 2).

$$\underset{\mathbf{1}}{[Nb(O)W_5O_{18}]^{3-}} + H_2O_2 \overset{K}{\rightleftharpoons} \underset{\mathbf{3}}{[Nb(O_2)W_5O_{18}]^{3-}} + H_2O \qquad (1)$$

$$[Nb(O_2)W_5O_{18}]^{3-} + MPS \xrightarrow{k_2} [Nb(O)W_5O_{18}]^{3-} + MPSO \qquad (2)$$

In the framework of this mechanism, the reaction rate law can be described by Equation (3), which is consistent with the experimental data.

$$W_0 = k_2 \cdot K \frac{[\mathbf{1}]\cdot[MPS]\cdot[H_2O_2]}{[H_2O] + K\cdot[H_2O_2]} \qquad (3)$$

The values of the equilibrium constant *K* and rate constant k_2 can be estimated using a plot of $1/W_0$ versus $1/[H_2O_2]$ (Figure 1d). The following values were found: K = 14 ± 5 and k_2 = 0.06 ± 0.01 $M^{-1}\cdot s^{-1}$.

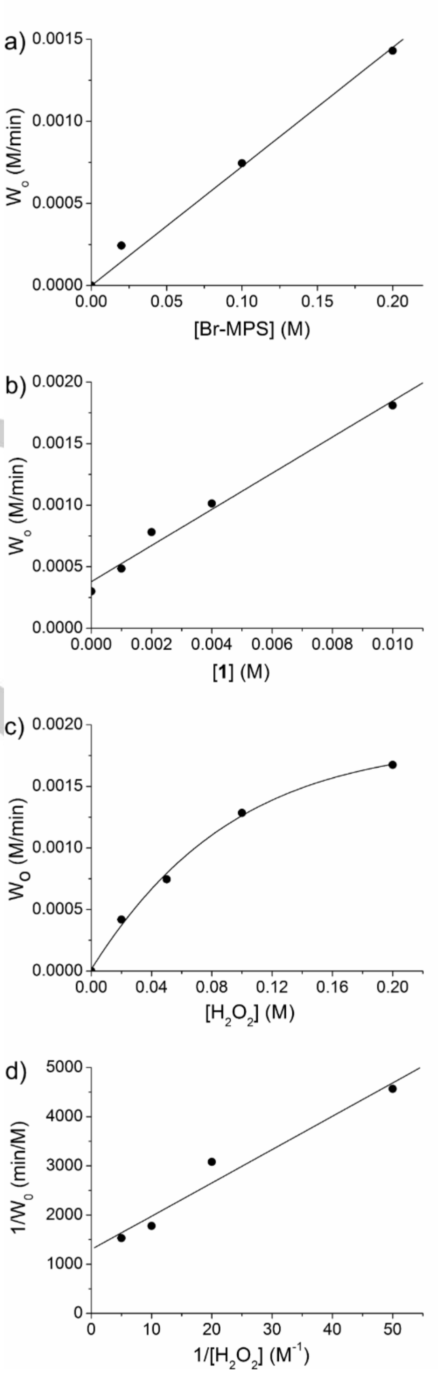


Figure 1. Initial reaction rates vs concentrations of (a) Br-MPS, (b) **1**, and (c) H_2O_2. Reaction conditions: [H_2O] 0.7 M, MeCN 1 mL, 60 °C; (a) [H_2O_2] 0.05 M, [**1**] 0.002 M; (b) [Br-MPS] 0.1 M, [H_2O_2] 0.05 M; (c) [Br-MPS] 0.1 M, [**1**] 0.002 M. (d) Plot of $1/W_0$ vs $1/[H_2O_2]$.

Stoichiometric oxidations

Sulfides, which are strong nucleophiles, can be oxidized to corresponding sulfoxides by using only electrophilic oxidants.

Sulfoxides in its turn have biphilic nature; therefore sulfoxide oxidation to sulfones can be accomplished with both nucleophilic and electrophilic oxidants. Typically, the rate-determining step in organic sulfide oxidation is either (1) a single electron transfer (SET) from sulfide to metal ion[7] or (2) an electrophilic oxygen atom transfer from oxidant (active form of a catalyst) to the sulfur atom of sulfide (concerted mechanism).[7a,b,h,k,8] The consequent oxidation of sulfoxide to sulfone, besides electrophilic paths,[7a,e,f, 9] can also occur through a nucleophilic attack of oxidant on the sulfur atom of sulfoxide. [8f,10]

To verify the nature of the active species in Nb-POM-catalyzed thioether oxidation and to investigate their electrophilic properties, we studied MPS oxidation with **3** in stoichiometric conditions ([MPS]/[**3**] = 5/1) without addition of H_2O_2. Indeed, peroxo complex **3** was able to oxidize MPS to MPSO and $MPSO_2$ with selectivities of 95 and 5%, respectively (Table 2, entry 1). Unlike the oxidation of alkenes,[6] additional protonation of the peroxocomplex was not necessary, most likely,because sulfides are more nucleophilic compounds than olefins. With **3**, MPS conversion achieved a maximum of the possible value (19%) in 24 h. However, the addition of 1 equiv. of H^+ or the use of the protonated peroxo complex **5**, which is more electrophilic,[6] led to a significant increase in the reaction rate and the formation of sulfoxide as the sole product (Table 2, entries 2 and 3, respectively). In sharp contrast to the epoxidation of alkenes,[6] peroxocomplex **4** with the Keggin structure was also active in MPS oxidation under stoichiometric conditions. In this case, MPSO formed with 99% selectivity (Table 2, entry 4), thus pointing to electrophilic behavior of the oxidizing species. The addition of H^+ to **4** also led to increasing the reaction rate but did not affect significantly the product distribution (Table 2, entry 5). All these results collectively allowed us to suggest that sulfide oxidation with **4** and **5** occurs by an electrophilic concerted mechanism, while the oxidation with **3** may have a more complicated nature. The difference in the oxidation properties of the Lindqvist and Keggin polyanions is most likely related to the difference in their charge density, which is higher for the former, making Lindqvist peroxo complex more prone to protonation.[6]

Table 2. Stoichiometric oxidation of MPS with Nb-POMs.[a]

Entry	POM	MPS conversion [%]	Selectivity [%][b]		Time [h]
			MPSO	$MPSO_2$	
1	**3**	19	95	5	24
2	**3**+H^+	20	100	0	0.08
3	**5**	18	100	0	0.08
4	**4**	14.5	99	1	24
5	**4**+H^+	15	98	2	0.5

[a] Reaction conditions: [MPS] 0.05 M, [Nb-POM] 0.01 M, MeCN 1 mL, 30 °C. [b] Yield based on converted MPS; calculated as the average of 2-3 experiments.

To confirm the oxidizing capability of the Nb-POM peroxocomplexes, the interaction of **3** and **4** with MPS was studied by ^{93}Nb NMR (**3** and **4**) and ^{31}P NMR (**4**). After the addition of MPS to the solution of **3** in MeCN, we observed a simultaneous disappearance of the ^{93}Nb NMR signal at -1048 ppm corresponding to the Lindqvist Nb peroxocomplex,[6] and appearance of the signal at -898 ppm, corresponding to **1** (Figure 2). After the reaction of **4** with MPS, thebroad ^{93}Nb NMR signal at -910 ppm attributed to **4** revealed a significant shift to ca. -958 ppm (Figure 3a), indicating the formation of **2**. In turn, the ^{31}P NMR signal slightly shifted from -13.1 to-13.2 ppm (Figure 3b), which also corresponds to the fransfornation of **4** to **2** (see Supporting Information, Table S1).

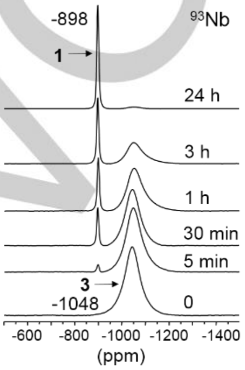


Figure 2. ^{93}Nb NMR spectra of **3** after the addition of 5 equiv. of MPS. Reaction conditions: [Nb-POM]/[MPS] = 1/5, MeCN, [**3**] 0.04 M; 20 °C.

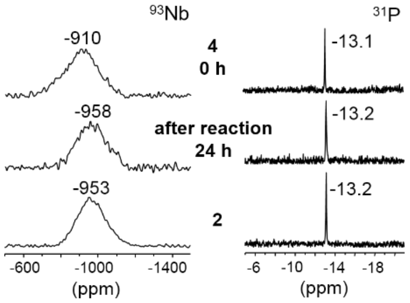


Figure 3. ^{93}Nb NMR and ^{31}P NMR spectra of **4** before and after the reaction with 5 equiv. MPS along with the corresponding spectra of **2**. Reaction conditions: [Nb-POM]/[MPS] ratio 1/5, MeCN, [**4**] 0.01 M, 60 °C.

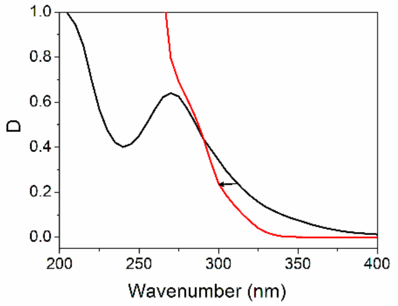
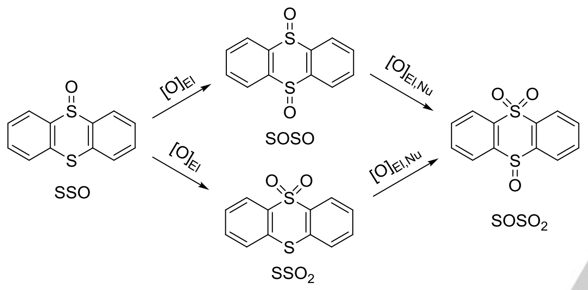


Figure 4. UV-vis spectra of **5** before (black line) and after addition of 5 equiv. of MPS (red line). Reaction conditions: [MPS] 0.0013 M, [**5**] 0.00026, MeCN, 30 °C, 5 min.

The reaction between **5** and MPS was monitored by UV-vis (Figure 4). Since the reaction is very fast, immediately after the addition of 5 equiv. of MPS to the solution of **5**, we observed disappearance of the characteristic absorption band attributed to $O_2 \rightarrow Nb$ ligand-to-metal charge transfer (310–350 nm).[6]

Oxidation of thianthrene 5-oxide

In 1984 Adam et al.[11] suggested the use of oxidation of thianthrene 5-oxide (SSO) as a mechanistic probe for the determination of the oxidant electronic character. The molecule of SSO contains electrophilic sulfoxide and nucleophilic sulfide sites. Therefore, an electrophilic oxidant would react with sulfide moiety to produce thianthrene 5,10-dioxide (SOSO), whereas a nucleophilic oxidant would react with sulfoxide site with the formation of thianthrene 5,5-dioxide (SSO_2). Both products could be further oxidized to thianthrene 5,5,10-trioxide ($SOSO_2$) via both mechanisms (Scheme 2).



Scheme 2. Oxidation of SSO.

The nucleophilicity of the oxidant can be estimated by calculating value of X_{Nu} parameter from equation X_{Nu} = (nucleophilic oxidation)/(total oxidation), where nucleophilic oxidation is a sum of SSO_2 and $SOSO_2$ yields and total oxidation is (SSO_2 + SOSO + $2SOSO_2$). It is widely accepted that $X_{Nu} \leq 0.3$ indicates electrophilic character of the oxidant while $X_{Nu} \geq 0.7$ is typical of nucleophilic ones. The results of stoichiometric oxidation of SSO in the presence of **3**, **4** and **5** are presented in Table 3. The value of X_{Nu} for three Nb-POM peroxo complexes differs significantly. Thus, protonated Lindqvist peroxocomplex **5** is the most electrophilic oxidant showing X_{Nu} 0.05 while Keggin peroxocomplex **4** with X_{Nu} 0.29 has moderate electrophilic properties. An intermediate value of X_{Nu} 0.55 was obtained for nonprotonated Lindqvist peroxocomplex **3**. Previously, Ballistreri et al.[12] observed similar results for a picolinate vanadium oxoperoxo complex, which is known as a typical radical oxidant. [7b, 13] Therefore, we also cannot exclude a contribution of one-electron oxidation in the case of **3**.

Table 3. Oxidation of thianthrene 5-oxide in the presence of Nb-POMs.[a]

POM	SSO conversion [%]	Yields [%][b]			X_{Nu}
		SSO_2	SOSO	$SOSO_2$	
3	15	6	4	5	0.55
4	14	2	9	3	0.29
5	19	0.3	18	0.7	0.05

[a] Reaction conditions:[SSO] 0.025 M, [Nb-POM] 0.005 M, MeCN 1 mL, 60 °C, 24 h. [b] Yield based on initial SSO.

Competitive oxidation of sulfide and sulfoxide

Another method for evaluation of the oxidant character is a competitive oxidation of a sulfide and a sulfoxide with different *p*-substituents in one run, under conditions when both substrates are in competition for the oxidant.[12] A considerable formation of either sulfoxide or sulfone indicates an electrophilic or nucleophilic character of the oxidant, respectively. We performed such competitive oxidation of Br-MPS and MPSO with three peroxocomplexes **3**, **4** and **5** (Table 4). In the presence of nonprotonated peroxocomplex **3**, a relatively high yield of sulfone with respect to sulfoxide was observed: the ratio of sulfoxide/sulfone was 1.4 (Table 4, entry 1). On the other hand, in the presence of **4** and especially **5**, the formation of sulfone was much less pronounced: the ratio of sulfoxide/sulfone attained the values of 6.4 and 100, respectively (Table 4, entries 2 and 3). Note that the reaction with **4** was performed at a higher temperature because of the low solubility of the peroxocomplex at 30 °C. Again**,** it is difficult to distinguish the type of the oxidation processin the case of **3**. On the other hand, the result acquired for the protonated Lindqvist peroxo complex **5** unambiguously supports strongly electrophilic character of the oxidant.

Table 4. Competitive oxidation of Br-MPS and MPSO with Nb-POMs.[a]

Entry	POM	Yields [%][c]		Br-MPSO/$MPSO_2$ ratio	Time [h]
		Br-MPSO	$MPSO_2$		
1	**3**[b]	5.5	4	1.4	24
2	**4**[c]	7.7	1.2	6.4	0.08
3	**5**[b]	11	0.1	110	0.08

[a] Reaction conditions: [Br-MPS] = [MPSO] 0.1 M, [Nb-POM] 0.0125 M, MeCN 1 mL, [b] 30 °C; [c] 60 °C. [d] Yield based on initial substrate.

Hammett correlations

The rate of the oxidation of aryl methyl sulfides with **3** revealed a complicated dependence on the nature of *p*-substituents in the aryl moiety. The correlation of $\log(W_X/W_H)$ with Hammett σ constants[14] showed acurved plot (Figure 5). More precisely, the curved plot consists of two intersecting linear correlations with opposite slopes: one correlation with $\rho = -0.48$ ($r = 0.989$) for electron-donating substituents ($\sigma < 0$) and the other correlation with $\rho = +0.42$ ($r = 0.720$) for electron-withdrawing substituents ($\sigma > 0$). Previously, Bonchio et al. obtained an analogous correlation in the oxidation of *p*-substituted aryl methyl sulfoxides with a Ti(IV)-(R,R,R)-tris(2-phenylethoxy)aminealkylperoxocomplex.[9c] They assumed that the reaction occurred by two parallel pathways: electrophilic and nucleophilic. The negative ρ indicates domination of electrophilic oxidative process for substrates with electron-donating substituents, while the positive ρ shows that the oxidation of substrates with electron-withdrawing substitution occurs mainly by the nucleophilic pathway. A similar curved Hammett plot was also obtained by Espenson et al. for oxidation of thiobenzophenone S-oxides with methyltrioxorhenium.[15] We also found that, for sulfides with electron-donating *p*-substituents, $\log(W_X/W_H)$ correlates better with σ than with σ^+ ($r = 0.966$). According to the literature, this is more consistent withthe oxygen transfer mechanism rather than with electron transfer one.[7d,e,g,i,l,8a-c]

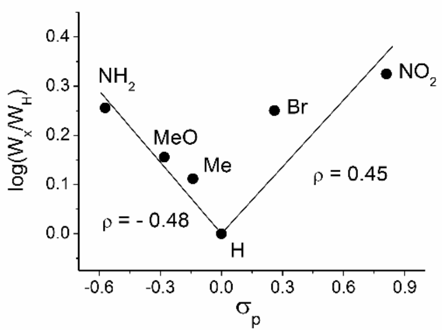


Figure 5. Hammett plot for the oxidation of *p*-substituted methyl phenyl sulfides with **3**. Reaction conditions: [X-MPS] 0.05 M, [**3**] 0.01 M, MeCN 1 mL, 60 °C.

The oxidation of *p*-substituted sulfides with **5** proceeds very fast (within 1-2 minutes), making impossible the determination of the initial reaction rates and investigation of Hammet correlations. However, we should mention that, for all the sulfide substrates studied, the corresponding sulfoxides were the sole oxidation product. This finding agrees well with our conclusion made on the basis of the other techniques about the strong electrophilic character of **5** and electrophilic oxygen transfer mechanism in the reaction with organic sulfides.

Conclusions

The Nb-substituted polyoxotungstates with Lindqvist and Keggin structures are effective catalysts in the H_2O_2-based oxidation of organic sulfides. Their peroxo complexes are able to oxidize sulfides under both turnoverand stoichiometric conditions. Nb-POM peroxocomplexes of the Lindqvist and Keggin structures reveal different electrophilic properties in the oxidation of S-compounds. While Keggin peroxocomplex **4** has medium electrophilic nature, Lindqvist peroxocomplex **3** reveals more complex oxidative properties, which can not be associated with one type of oxidation mechanism. The protonation greatly increases electrophilicity of **3**, which is manifested by significant increase in the thioether oxidation rate and sulfoxidation selectivity.

Experimental Section

Materials: Methyl phenyl sulfide (99%) and methyl phenyl sulfoxide (98%) were purchased from Acros, 4-bromothioanisole (98+%, Br-MPS) was obtained from Lancaster, thianthrene (97%) was purchased from Aldrich. Acetonitrile (HPLC–grade, Panreac) was dried and stored over activated 4 Å molecular sieves. The concentration of H_2O_2 (ca. 35 wt % in water) was determined iodometrically prior to use. All the other compounds were the best available reagent grade and used without further purification. Thianthrene 5-oxide was prepared from thianthrene following the literature protocol,[16] and its purity was confirmed by ^1H NMR.

Instrumentation: GC analyses were performed using a gas chromatograph Chromos GC-1000 equipped with a flame ionization detector and a quartz capillary column BPX5 (30 m × 0.25 mm). GC–MS analyses were carried out using an Agilent 7000B system with the triple-quadrupole mass-selective detector Agilent 7000 (HP-5ms quartz capillary column 30 m × 0.25 mm). HPLC measurements were performed using HPLC Agilent Technologies 1220 Infinity LC using ZORBAX Eclipse Plus C-18 column (4.6 × 150 mm, 5-Micron, H_2O-*i*PrOH = 40:60, 1mL/min, 25 °C). Aliquots of 2.5 µL of the reaction mixture were taken periodically by a syringe and diluted with*i*PrOH (100 µL) before analysis. ^1H, ^{31}P, ^{93}Nb, and ^{183}W NMR spectra were recorded at 400.130, 161.67, 97.94, and 16.67 MHz, respectively, on a Brüker AVANCE-400 spectrometer using high-resolution multinuclear probe head with 10 mm o.d. (3 mL solution volume) sample tubes. Chemical shifts for ^{31}P,^{93}Nb, and ^{183}W, δ, were determined relative to 85% H_3PO_4, $NbCl_5$, and Na_2WO_4, respectively. For convenience, secondary external standards were used: 0.2 M solution of $H_4PVMo_{11}O_{40}$ in water for ^{31}P (−3.70 ppm), 0.05 M $H_5SiW_{11}NbO_{40}$ (-975 ppm) for ^{93}Nb NMR, and 0.4 M $H_4SiW_{12}O_{40}$ for ^{183}W NMR (−103.6 ppm). 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 Cary–50 spectrophotometer using a 0.2 cm quartz cells.

Synthesis and characterization of POMs: The synthetic procedures for$(Bu_4N)_3[Nb(O)W_5O_{18}]$ (**1**), $(Bu_4N)_4[PW_{11}NbO_{40}]$ (**2**), $(Bu_4N)_3[Nb(O_2)W_5O_{18}]$ (**3**), $(Bu_4N)_2[HNb(O_2)W_5O_{18}]$ (**5**), and $(Bu_4N)_4[(NbW_5O_{18})_2O]$ (**6**) were reported elsewhere.[6] Characterization of all the compounds is provided in the Supporting Information, Table S1 (NMR data) and Table S2 (IR data).

$(Bu_4N)_4[PW_{11}Nb(O_2)O_{39}]$ (4): $H_3PW_{12}O_{40}\cdot 6H_2O$ (9 g, 3 mmol) was dissolved in 20 mL of water. Then 0.9 mL of 0.325 M H_3PO_4, 50 mL of hot aqueous solution of $Na_7HNb_6O_{19}\cdot 15H_2O$ (0.702 g, 0.5 mmol), and 1 mL of 30% H_2O_2 (11 mmol) were subsequently added and the reaction mixture was stirred upon heating during 1 h. TBA salt was precipitated by the addition of a solution of TBABr (4.5 g in 20 mL of water). The yellow residue was isolated by filtration, washed with THF, dried at 80-90 °C, and then recrystallized from MeCN and dried at air. Yield ca. 70 %. The number of TBA cations (4) was determined by ignition. The presence of 0.8 peroxo group per molecule of **4** was confirmed by titration with triphenylphosphine (PPh_3) followed by monitoring with ^{31}P NMR. IR (KBr, 1100-400 cm^{-1}): 1068, 965, 894, 812, 606, 590, 516. ^{31}P NMR (ppm, in MeCN): -13.1. ^{183}W NMR (ppm, in MeCN): -83, -90, -93, -101, -108.5, -110. ^{93}Nb NMR (ppm, in MeCN): -910.

General method for thioanisoles oxidation: All reactions were performed in thermostated glass vessels under vigorous stirring (500 rpm) in MeCN. Each experiment was reproduced at least two times. All products were identified by the comparison of GC retention time with those of the authentic samples as well as by GC-MS. Substrate conversion and product yields were determined by GC or HPLC using biphenyl as an internal standard for both methods.

Catalytic and stoichiometric oxidation of MPS in the presence of Nb-POMs: Catalytic reactions were initiated by addition of H_2O_2 (0.2 mmol) into the solution of MPS (0.2 M) and Nb-POM (0.004 M) in 1 mL of MeCN at 60 °C. In stoichiometric conditions, reactions were started by addition of 0.5 mL of a Nb-POM solution in MeCN (0.02 M) to 0.5 mL of MPS solution (0.1 M) to achieve concentrations [MPS] = 0.05 M and [Nb-

POM] = 0.01 M in 1 mL of MeCN at 30 °C. MPS conversion and product yields were determined by GC.

Kinetic study: The reactions were initiated by addition of H_2O_2 (0.02-0.2 M) into the solution of Br-MPS (0.02-0.2 M), catalyst **1** (0.001-0.01 M) and H_2O (0.18-1.8 M) in 1 mL of MeCN at 60 °C. The concentration of H_2O in the experiments to determine the reaction order in H_2O_2 was kept constant (0.7 M) by the addition of corresponding amounts of water. Br-MPS consumption was determined by HPLC. Initial rates were determined from the reaction profiles at low conversions.

Catalytic and stoichiometric oxidation of thianthrene 5-oxide in the presence of Nb-POMs: Catalytic reactions were initiated by addition of H_2O_2 (0.025 mmol) into the solution of thianthrene oxide (0.025 M) and Nb-POM (0.0005 M) in 1 mL of MeCN at 60 °C. Stoichiometric reactions were carried outat 60 °C by mixing 0.5 mL of the solution of Nb-POM (0.01 M) with 0.5 mL of the solution of thianthrene oxide (0.05 M) to achieve the following concentrations: [Nb-POM] = 0.005 M and [SSO] = 0.025 M. After 24 h, the reaction mixtures were cooled down to the room temperature and evaporated. $CHCl_3$ was added to the solid to dissolve reaction products. The insoluble catalyst was filtered off. $CHCl_3$ was evaporated once more and deuterated $CDCl_3$ was added to the residue for ^{1}H NMR analysis of the product composition. Thianthrene 5-oxide conversion and products yields were calculated from ^{1}H NMR spectra by integration of corresponding signals taking into consideration that total amount of all products is 100%.

Competitive study: To initiate the reaction, 0.5 mL of the solution of Nb-POM in MeCN (0.025 M) was added to 0.5 mL of the solution of Br-MPS (0.2 M) and MPSO (0.2 M) in MeCN at 60 °C. Concentrations of Nb-POM, Br-MPS, and MPSO in the reaction mixture were 0.0125 M, 0.1 and 0.1 M, respectively. Br-MPS and MPSO consumption and product yields were determined by GC.

Hammett correlation: The reaction was started by addition of 0.5 mL of $(Bu_4N)_3[Nb(O_2)W_5O_{18}]$ (**3**) solution in MeCN (0.02 M) to 0.5 mL of the solution of *p*-substituted sulfide (X-MPS) in MeCN (0.1 M) at 60 °C. Concentrations of Nb-POM and X-MPS in the reaction mixture were 0.01 M and 0.05 M, respectively. X-MPS consumption was quantified by HPLC. Initial rates were determined from the reaction profiles at low conversions.

Acknowledgments

The authors thank Dr. I. E. Soshnikov and Dr. R. I. Maksimovskaya for ^{1}H and ^{183}W NMR measurements, respetively; V. Yu. Evtushok for collecting IR spectra, and V. A. Utkin for product identification by GC–MS. This work was carried out in the framework of budget project No. AAAA-A17-117041710080-4 for Boreskov Institute of Catalysis and partially supported by the Russian Foundation for Basic Research (RFBR grant N 16-03-00827).

Keywords: sulfoxidation • niobium • polyoxometalate • Lindqvist structure • hydrogen peroxide

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