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Role of Water in Polyoxometalate-Catalyzed Oxidations in Nonaqueous Media. Scope, Kinetics, and Mechanism of Oxidation of Thioether Mustard (HD) Analogs by *tert*-Butyl Hydroperoxide Catalyzed by $H_5PV_2Mo_{10}O_{40}$

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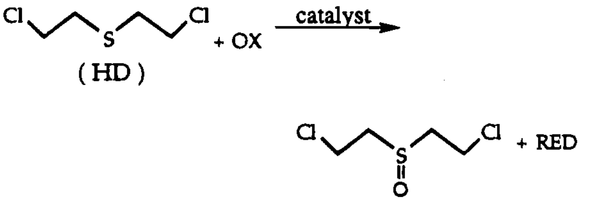
A range of heteropolyoxometalates catalyze the oxidation of thioether analogs of mustard (HD) to the corresponding sulfoxides by *tert*-butyl hydroperoxide (TBHP) rapidly at 25 °C, with selectivities as high as any seen in the literature for thioether oxidations. The strongly acidic complexes $H_3PW_{12}O_{40}$ and $H_3PMo_{12}O_{40}$ function primarily as acid catalysts for thioether oxidation by TBHP, producing sulfoxide with 98−99% selectivities (1−3% sulfone present) at modest conversions. Three lines of evidence involving the model compound, tetrahydrothiophene (THT), indicate that several vanadium-substituted heteropoly acids, including hydrated $H_5PV_2Mo_{10}O_{40}$ (**1**), are significantly more selective (>99.9%): (1) No sulfone ($THTO_2$) is detectable at the limits (1 part in 10^5) of gas chromatographic and gas chromatographic−mass spectrometric analyses, (2) THTO and $THTOH^+$ are both stable under the reaction conditions, and (3) $(THTOH)_4(H)(PV_2Mo_{10}O_{40})$, or **2**, identified by NMR, IR, UV−visible, and elemental analysis, is stable for a period of at least 1 month under the conditions of the title catalytic reactions (homogeneous acetonitrile, 25 °C). The rates of thioether oxidation to sulfoxide catalyzed by **1**, based on six aliphatic and aromatic thioethers, vary over a factor of more than 10^3 and do not correlate well with the thioether redox potentials. The data, including rates and selectivities of the reaction with and without TBHP, establish that these reactions proceed by initial thioether oxidation and polyoxometalate reduction followed by reduced polyoxometalate reoxidation by TBHP. This mechanism is in sharp contrast to the conventional mechanisms for metal complex mediated peroxide oxidations (electrophilic peroxide activation by the metal complex or radical processes). Two important and heretofore undocumented roles of H_2O are consistent with the rate studies of THT oxidation by **1** in the absence of TBHP. First, the reaction is strongly inhibited by water and the rate law is $v_0 = k[\mathrm{THT}][\mathbf{1}][H_2O]^{-1}$. In the absence of water, the rate becomes independent of THT substrate ($v_0 = k'[\mathbf{1}]$) and dehydration of the polyoxometalate may be rate limiting. All the data, including the activation parameters ($\Delta H^{\ddagger} = 8.06 \pm 0.64$ kcal mol^{-1} and $\Delta S^{\ddagger} = -29.7 \pm 0.18$ eu), are most consistent with outer sphere electron transfer for the key thioether oxidation step in the mechanism.

Introduction

Catalytic methods for the selective oxidation of the highly toxic agent bis(2-chloroethyl) sulfide, known as mustard or HD, eq 1, are needed.[1] The selectivity is crucial inasmuch as the



(1)

corresponding sulfoxide, bis(2-chloroethyl) sulfoxide, is relatively nontoxic while the corresponding sulfone is highly toxic.[2] There are many methods to oxidize thioethers,[3−14] and decontamination systems based on microemulsion technology,[12] phase transfer catalysis,[13] catalytic dehalogenation,[14] and coupled photochemical and thermal redox catalysis[15] have been reported. Few thioether oxidation methods are rapid and catalytic under ambient laboratory conditions. In addition, few are also adequately selective for effective HD decontamination via eq

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(1) Yang, Y.-C.; Baker, J. A.; Ward, J. R. Decontamination of Chemical Warfare Agents. *Chem. Rev.* **1992,** *92,* 1729−1743.

(2) Hirade, J.; Ninomiya, A. *J. Biochem.* **1950,** *37,* 19−34.

(3) (a) Henbest, H. B.; Khan, S. A. *J. Chem. Soc., Chem Commun.* **1968,** 1036. (b) Djerassi, C.; Engle, R. R. *J. Am. Chem. Soc.* **1953,** *75,* 3838.

(4) (a) Block, E. In *Chemistry of ethers, crown ethers, hydroxyl groups and their sulphur analogues,* Part 1; Patai, S, Ed.; John Wiley: New York, 1980; Chapter 13. (b) Oae, S. In *Organic Chemistry of Sulfur;* Oae, S., Ed.; Plenum: New York, 1977; Chapter 8. (c) Ranky, W. O.; Nelson, D. C. In *Organic Sulfur Compounds;* Kharasch, N., Ed.; Pergamon: New York, 1964; Vol. I, Chapter 17. (d) Ledlic, M. A.; Allum, K. G.; Howell, I. V.; Pitkethly, R. C. *J. Chem. Soc., Perkin Trans. 1* **1976,** 1734 and references cited in each.

(5) See for example: (a) Howard, J. A.; Korcek, S. *Can. J. Chem.* **1971,** *49,* 2178. (b) Correa, P. E.; Hardy, G.; Riley, D. P. *J. Org. Chem.* **1988,** *53,* 1695.

(6) (a) Kozhevnikov, I. V.; Simagina, V. I.; Varnakova, G. V.; Matveev, K. I. *Kinet. Catal. (Engl. Transl.)* **1979,** *20,* 416. (b) Tarabanko, V. E.; Sidel'nikov, V. N.; Kozhevnikov, I. V. *React. Kinet. Catal. Lett.* **1982,** *21,* 109.

(7) Riley, D. P. *Inorg. Chem.* **1983,** *22,* 1965.

(8) James, B. R.; Pacheco, A.; Rettig, S. J.; Ibers, J. A. *Inorg. Chem.* **1988,** *27,* 2414.

(9) Riley, D. P.; Smith, M. R.; Correa, P. E. *J. Am. Chem. Soc.* **1988,** *110,* 177.

(10) Roecker, L.; Dobson, J. C.; Vining, W. J.; Meyer, T. J. *Inorg. Chem.* **1987,** *26,* 779.

(11) (a) Curci, R.; Di Furia, F.; Modena, G. *J. Chem. Soc., Perkin Trans. 2* **1977,** 576. (b) Curci, R.; Di Furia, F.; Testi, R.; Modena, G. *J. Chem. Soc., Perkin Trans. 2* **1974,** 752. (c) DiFuria, F.; Modena, G. *Recl. Trav. Chim. Pays-Bas* **1979,** *98,* 181.

(12) (a) Menger, F. M.; Elrington, A. R. Rapid Deactivation of Mustard via Microemulsion Technology. *J. Am. Chem. Soc.* **1990,** *112,* 8201−8203. (b) Menger, F. M.; Elrington, A. R. Organic Reactivity in Microemulsion Systems. *J. Am. Chem. Soc.* **1991,** *113,* 9621−9624.

(13) Ramsden, J. H.; Drago, R. S.; Riley, R. *J. Am. Chem. Soc.* **1989,** *111,* 3958−3961.

0020-1669/94/1333-5015$04.50/0

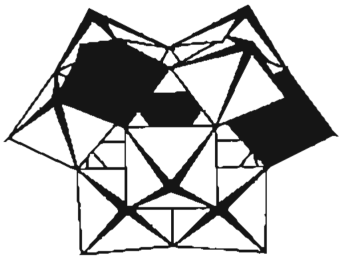

Figure 1. Polyhedral representation of the 1,6 isomer of $PV_2Mo_{10}O_{40}^{5-}$ (the dehydrated form of **1**). All literature investigations to date indicate that the 5 positional isomers have very similar reactivities and equilibrate in aqueous or acetonitrile solution. The 1,6 isomer is dominant in water.[29]

1. Unfortunately, production of sulfone, eq 3, by subsequent

$$R_2S + OX \rightarrow R_2SO + RED \qquad (2)$$

$$R_2SO + OX \rightarrow R_2SO_2 + RED \qquad (3)$$

$$R_2S + 2OX \rightarrow R_2SO_2 + 2RED \qquad (4)$$

oxidation of the initial sulfoxide product from eq 2 or, less frequently, by mechanisms not involving intermediate sulfoxides, eq 4, is almost always measurable. For a few processes the rate of eq 3 is greater than the rate of eq 2, and little sulfoxide can be produced.[3] Most thioether oxidations, including a variety of stoichiometric oxidations,[4] autoxidation,[4,5] metal catalyzed/mediated autoxidations,[6-9] and metal promoted oxygenations,[10,11] all exhibit finite rates for eq 3, and small amounts of sulfone are produced, particularly at high conversions of thioether substrate. The autoxidation of thioethers catalyzed by heteropoly acids,[6] Ru complexes,[7,8] and Ce(IV)[9] has been investigated fairly thoroughly. We report here thioether oxidations by the inexpensive oxidant *tert*-butyl hydroperoxide (TBHP)[16] catalyzed by the representative, readily accessible, and inexpensive heteropolyanions (heteropolyoxometalates) of the Keggin structural class (Figure 1). Some of these oxidations, those catalyzed by $H_5PV_2Mo_{10}O_{40}{\cdot}nH_2O$ (**1**·H_2O), proceed in 99.9+% selectivity even at high conversion of thioether substrate.

Polyoxometalate derivatives[17] are well documented to facilitate oxidations of a variety of substrates in one of five homogeneous modes. In mode 1, the polyoxometalate directly oxidizes the substrate and a terminal oxidant reoxidizes the reduced form of the polyoxometalate.[18-21] In mode 2, the polyoxometalate functions as a cocatalyst. A large class of such reactions is the three-component systems (Pd or Pt/polyoxometalate/O_2) analogous to the Wacker reaction where the polyoxometalate has replaced Cu.[18] In mode 3, a polyoxometalate derivative catalyzes oxo transfer oxidation (oxygenation) of the substrate.[22,23] In mode 4, the polyoxometalate is a photocatalyst. The excited state of the complex directly oxidizes the substrate, and reoxidation of the reduced complex takes places independently in one of several ways.[24] In mode 5, the cation of the polyanion activates or oxidizes the substrate.[25] The first two modes are the most common and lend themselves to a number of applications. The catalytic thioether oxidations reported here take place by mode 1. In conjunction with a thorough investigation of the scope and mechanism of the title reactions, we document for the first time a significant role of water in mode 1 polyoxometalate-based catalytic oxidations in nonaqueous media.

Experimental Section

Materials. All solvents were Burdick and Jackson glass-distilled grade. In reactions probing the effect of water, the tetrahydrothiophene and the acetonitrile were dried before use over 3-Å molecular sieves. The molecular sieves were activated under vacuum at 390 °C for 15 h. The source of TBHP in all experiments was a 90% aqueous solution from Aldrich (the only detectable impurities were 5% H_2O and 5% *tert*-butyl alcohol). Thioethers and their oxidation products, sulfoxides and sulfones, were purchased from Aldrich or Fluka. The purity (>98%), in all cases, was checked by gas chromatography. The *p*-toluenesulfonic acid monohydrate ($TsOH{\cdot}H_2O$, Aldrich) and $Li_2MoO_4{\cdot}2H_2O$ (Alfa, 98.5% purity) were commercial samples of the highest possible purity. The (acetylimino)tetramethylenesulfonium bromide was prepared and purified by literature procedures;[26] mp 66 °C (lit. mp 66–68 °C). The infrared and ^{1}H NMR spectra were also consistent with the product. The catalysts used in this study were prepared by following published procedures: α-$H_3PW_{12}O_{40}{\cdot}xH_2O$,[27] α-$H_3PMo_{12}O_{40}{\cdot}xH_2O$,[27] $H_{3+n}PV_nW_{12-n}O_{40}{\cdot}xH_2O$,[28,29] and $H_{3+n}PV_n$-

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(14) Sattari, D.; Hill, C. L. Catalytic Carbon-Halogen Bond Cleavage Chemistry by Redox-Active Polyoxometalates. *J. Am. Chem. Soc.* **1993**, *115*, 4649.

(15) Chambers, R. C.; Hill, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 8427.

(16) (a) Sharpless, K. B.; Verhoeven, T. R. *Aldrichimica Acta* **1979**, *12*, 63. (b) Hanson, R. M.; Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922.

(17) Recent reviews of polyoxometalates: (a) Pope, M. T.; Müller, A. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 34–48. (b) *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994.

(18) (a) Kozhevnikov, I. V.; Matveev, K. I. *Russ. Chem. Rev. (Engl. Transl.)* **1982**, *51*, 1075–1088. (b) Kozhevnikov, I. V.; Matveev, K. I. *Appl. Catal.* **1983**, *5*, 135–150. (c) Grate, J. H.; Hamm, D. R.; Mahajan, S. In *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*; Pope, M. T., Müller, A., Eds.; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1994; pp 281–305 and references cited therein.

(19) (a) Neumann, R.; Assael, I. *J. Chem. Soc., Chem. Commun.* **1988**, 1285–1287. (b) Neumann, R.; Lissel, M. *J. Org. Chem.* **1989**, *54*, 4607–4610. (c) Neumann, R.; Levin, M. *J. Org. Chem.* **1991**, *56*, 5707–5710. (d) Neumann, R.; Levin, M. *J. Am. Chem. Soc.* **1992**, *114*, 7278.

(20) (a) Ali, B. E.; Brégeault, J.-M.; Mercier, J.; Martin, J.; Martin, C.; Convert, O. *J. Chem. Soc., Chem. Commun.* **1989**, 825–826. (b) Ali, B. E.; Brégeault, J.-M.; Martin, J.; Martin, C. *New J. Chem.* **1989**, *13*, 173–175.

(21) Hill, C. L.; Duncan, D. C.; Harrup, M. K. *Comments Inorg. Chem.* **1993**, *14*, 367–384.

(22) Representative papers on oxygenation by such complexes: (a) Hill, C. L.; Brown , R. B., Jr. *J. Am. Chem. Soc.* **1986**, *108*, 536–538. (b) Mansuy, D.; Bartoli, J.-F.; Battioni, P.; Lyon, D. K.; Finke, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 7222–7226. (c) Ellis, P. E., Jr.; Lyons, J. E. Alkane Oxidation Process. U.S. Patent 4,898,989, Feb 6, 1990. (d) Neumann, R.; Abu-Gnim, C. J. *J. Am. Chem. Soc.* **1990**, *112*, 6025–6031. (e) Rong, C.; Pope, M. T. *J. Am. Chem. Soc.* **1992**, *114*, 2932–2938. (f) Schwegler, M.; Floor, M.; van Bekkum, H. *Tetrahedron Lett.* **1988**, *29*, 823–826. (g) Steckhan, E.; Kandzia, C. *Synlett* **1992**, 139–140. (h) Fedotov, M. A.; Il'inich, O. M.; Kuznetsova, L. I.; Semin, G. L.; Vetchinova, Y. S.; Zamaraev, K. I. *Catal. Lett.* **1990**, *6*, 417–422. (i) Khenkin, A. M.; Hill, C. L. *J. Am. Chem. Soc.* **1993**, *115*, 8178–8186.

(23) Review: Hill, C. L.; Kim, G.-S.; Prosser-McCartha, C. M.; Judd, D. *Mol. Eng.* **1993**, *3*, 263–275.

(24) Reviews: (a) Papaconstantinou, E. *Chem. Soc. Rev.* **1989**, *18*, 1. (b) Hill, C. L.; Prosser-McCartha, C. M. In *Photosensitization and Photocatalysis Using Inorganic and Organometallic Complexes*; Kalyanasundaram, K., Grätzel, M., Eds.; Kluwer Academic Publishers: Dordrecht, Netherlands, 1993; Chapter 10, pp 307–326.

(25) Siedle, A. R.; Gleason, W. B.; Newmark, R. A.; Skarjune, R. P.; Lyon, P. A.; Markell, C. G.; Hodgson, K. O.; Roe, A. L. *Inorg. Chem.* **1990**, *29*, 1667–1673.

(26) Kise, H.; Whitfield, G. F.; Swern, D. *J. Org. Chem.* **1972**, *37*, 1121.

(27) (a) Wu, H. *J. Biol. Chem.* **1920**, *43*, 189. (b) Souchay, P. *Ions Minéraux Condensés*; Masson et Cie: Paris, 1969; p 92.

(28) Domaille, P. J.; Watunya, G. *Inorg. Chem.* **1986**, *25*, 1239. See also: Domaille, P. J. *J. Am. Chem. Soc.* **1984**, *106*, 7677–87.

(29) The vanadomolybdophosphate catalysts containing two or three vanadium atoms, including **1**, are an equilibrating mixture of positional isomers in water and in acetonitrile. The speciation chemistry of this complex system in water was most definitively characterized in a very recent paper: Pettersson, L.; Andersson, I.; Selling, A.; Grate, J. H. *Inorg. Chem.* **1994**, *33*, 982–993.

$Mo_{12-n}O_{40}{\cdot}xH_2O$[29,30] ($n = 1-3$). The compounds were purified by several recrystallizations from water. The infrared, ^{31}P NMR, and UV–visible spectra of all the catalysts agreed with literature values.[27-30]

Instrumentation. Gas chromatographic analyses were performed using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a 5% phenyl methyl silicone capillary column. The electronic absorption spectra were recorded on a Hewlett-Packard 8451A diode array spectrophotometer. Infrared spectra were taken on a Nicolet 510M FTIR spectrometer. ^1H and ^{13}C NMR measurements were made using a 300-MHz General Electric QE-300 spectrometer, and ^{31}P NMR spectra were recorded on an IBM WP-200SY spectrometer. Electrochemical measurements were made on a Princeton Applied Research Model 173 potentiostat/galvanostat equipped with a Model 175 universal programmer and a Houston Instruments chart recorder. Temperature control for the Eyring plot was achieved with a metal-jacketed cuvette holder connected to a VWR 1155 refrigerated constant-temperature circulator.

Synthesis of the Tetrakis(hydroxysulfonium) Salt $(C_4H_8SOH^+)_4(H^+)(PV^V_2Mo^{VI}_{10}O_{40})(C_4H_8SO)_2$, 2. Tetrahydrothiophene oxide (THTO), 0.5 mL (~5.5 mmol), was added dropwise over a period of 5 min to 2.27 g (~1 mmol) of **1** dissolved in 50 mL of acetonitrile at room temperature. An orange precipitate formed readily. After 15 min of stirring, the complex was separated from the mixture by filtration using a medium glass frit. The product was then washed with three 2-mL portions of acetonitrile and three 3-mL portions of ether and finally dried in vacuo to give 1.90 g of **2** (yield ~75%). $\{^1H\}^{13}C$ NMR (~4 × 10^{-5} M in D_2O; δ in ppm): 24.51 (s, β-C, 2H), 52.78 (s, α-C, 2H). Literature values for $\{^1H\}^{13}C$ NMR of free THTO (δ in ppm): 25.4 (s, β-C, 2H), 54.3 (s, α-C, 2H).[31] ^1H NMR (~4 × 10^{-5} M in D_2O; δ in ppm): 2.83 (multiplet, methylene protons α to SO group, 4H), 1.95–2.14 (multiplets, methylene protons β to SO group, 4H). Infrared (cm^{-1}): 2982–2861 (w, broad), 1438 (w), 1396 (w), 1047 (m), 947 (s), 862 (s), 784 (s).

Anal. Calcd for $C_{24}H_{53}O_{46}PS_6V_2Mo_{10}$: C, 12.20; H, 2.27; S, 8.14; O, 31.14; P, 1.31; V, 4.31; Mo, 40.62. Found: C, 12.39; H, 2.14; S, 7.57; P, 1.27; V, 4.15; Mo, 40.34.

Comparison of Polyoxometalate Catalytic Activity. The oxidation of the thioether substrates by TBHP catalyzed by heteropoly acids was assessed by monitoring the organic reactants and products by gas chromatography as a function of time. In an exemplary reaction, 5.00 × 10^{-3} mmol of the heteropoly acid catalyst, 0.284 mmol of thioether (organic sulfide) in 4.8 mL of CH_3CN with 5 μL of *m*-dibromobenzene, a gas chromatography internal standard, were placed in 25-mL Schlenk flasks. The resulting solutions were taken through several gas/degas cycles. Finally, 0.284 mmol of TBHP under argon was added to the reaction mixture. Samples for GC analysis were withdrawn by syringes inserted through septum stoppers in the Schlenk flasks. Product analyses were executed immediately.

Evaluation of the products and rates of thioether oxidation by TBHP in the absence of the polyoxometalate catalysts was made by following protocols identical to those above except that no catalyst was present.

Determination of Rate Law for Oxidation of THT by 1. The simplicity of the products and the lack of competing or subsequent reactions facilitated the detailed kinetics studies in this work. The initial-rate method and ln–ln plots were employed to determine reaction orders (ln of the initial rate as a function of the ln of the reactant concentration). The initial rate was obtained by following the formation of the reduced form of the catalyst, **1** ($\lambda_{max} = 780$ nm and $\epsilon = 1430$ M^{-1} cm^{-1} in CH_3CN). For determination of the order with respect to THT, six vials each containing 0.0280 g of **1**, 40 μL of H_2O, and 4 mL of CH_3CN were allowed to sit overnight to ensure complete equilibration. Also, six vials each containing 6 mL of CH_3CN and varying amounts of THT from 25 to 200 μL were prepared. The reactions were conducted under argon using a 1 cm path length quartz cuvette with an affixed glass stopcock. Immediately prior to the experiment, both the catalyst and substrate solutions were degassed by repeating the vacuum/argon cycle three times. Next, 1 mL of the catalyst solution was injected through a rubber septum stopper into an argon-filled cuvette, and then the cuvette was placed in the UV–vis spectrometer. The reaction was initiated by injecting 1.5 mL of the substrate solution into the cuvette which thoroughly stirred the contents. The timer was started at the time of substrate injection. The absorbance was measured every 2 s for 30 s and then less frequently until it leveled off. The final concentrations of the reactants in the cuvette were as follows: **1**, 1.60 × 10^{-3} M; H_2O, 2.20 × 10^{-1} M, 0.40% by volume; THT, from 2.82 × 10^{-2} to 2.20 × 10^{-1} M).

For determination of the order with respect to **1**, H_2O, and THT as a function of H_2O, the same method was used as for THT above. Final concentrations in the cuvette for the order determination in **1** were as follows: **1**, 4.59 × 10^{-4}–1.61 × 10^{-3} M; H_2O, 2.20 × 10^{-1} M, 0.40% by volume; THT, 3.24 × 10^{-1} M. Final concentrations in the cuvette for the order determination in H_2O were as follows: **1**, 7.24 × 10^{-4} M; H_2O, (6.40 × 10^{-2} M to 5.56 M; and THT, 1.13 × 10^{-1} M. For the determination of the order with respect to THT as a function of H_2O added, the order was determined with 0, 0.2, 0.4, and 1% water added. The percent water added represents the final concentration of water in the cuvette.

Determination of Rate Constants. The rate constant for eq 7 was evaluated using the integrated first-order rate law

$$A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t) \qquad (5)$$

under pseudo-first-order conditions. The concentrations of THT, H_2O, and **1** were 3.24 × 10^{-1}, 2.20 × 10^{-1}, and 4.61 × 10^{-4} M, respectively. The following values were determined experimentally: $A_\infty = 0.337$ and $A_0 = 0.069$. The calculated rate constant from eq 5 was 3.29 s^{-1}; that from initial-rate methods was 3.65 s^{-1}. Kaleidagraph version 3.0.1 (Synergy Software, Reading, PA) was used to treat the data.

Eyring Plot. The same method was used as for the determination of order (previous section). Final concentrations in the cuvette were as follows: **1**, 8.86 × 10^{-4} M; H_2O, 2.20 × 10^{-1} M; and THT, 8.51 × 10^{-2} M. The temperature in the cuvette was controlled with a constant-temperature circulating bath. The substrate and catalyst solutions were brought to the desired temperature by suspension in the bath prior to reaction.

Electrochemical Measurements. The oxidation potentials of six thioether substrates were measured using cyclic voltammetry at ambient temperature in acetonitrile with 0.80 M tetrabutylammonium hexafluorophosphate as the supporting electrolyte with a 200 mV s^{-1} sweep rate, a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/0.01 M $AgNO_3$ reference electrode. The thioethers were 8 mM.

Results and Discussion

Polyoxometalate-Catalyzed Oxidation of Thioethers by *tert*-Butyl Hydroperoxide (TBHP). Scope and General Features. Although the oxidation of thioethers to the corresponding sulfoxides as well as oxidation of the sulfoxides to the corresponding sulfones by hydroperoxides is thermodynamically favorable, neither thioethers nor sulfoxides are oxidized rapidly by these oxidants at room temperature in the absence of catalysts. In contrast, vanadium(V)-substituted heteropolymolybdic and heteropolytungstic acids of formula $(H^+)_{3+n}[PV_nM_{12-n}O_{40}]$ ($n = 0-3$; M = W, Mo), including hydrated $H_5PV_2Mo_{10}O_{40}$ (**1**), complexes derived from the parent Keggin structure (T_d symmetry $[PM_{12}O_{40}]^{3-}$; M = Mo^{VI}, W^{VI}), catalyze the oxidation of thioethers by hydroperoxides to the corresponding sulfoxides (eq 6) rapidly, efficiently, in very high conversions and, most significantly, with virtually quantitative selectivity (Table 1). The selectivities seen with the vanadium-free Keggin complexes, including $H_3PMo_{12}O_{40}$, are high (96%) but far lower than that for **1**.

$$R_2S + ROOH \xrightarrow[\text{heteropoly acid (catalyst)}]{\text{vanadium-substituted}} R_2SO + ROH \qquad (6)$$

$$R = \text{alkyl or aryl group}$$

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(30) Tsigdinos, G. A.; Hallada, C. J. *Inorg. Chem.* **1968**, *7*, 437.

(31) Kalinowski, H. O.; Berger, S.; Braun, S. *^{13}C NMR Spectroscopy*; John Wiley: New York, 1988; p 359.

Table 1. Oxidation of Tetrahydrothiophene (THT) by *t*-BuOOH (TBHP) Catalyzed by Representative Heteropolyoxometalates and Acids[a]

catalyst	yield of sulfoxide,[b] %; turnovers	selectivity,[c] % for sulfone	selectivity,[c] % for sulfoxide
$H_6PV_3W_9O_{40}$	83; 47	...[d]	>99
$H_5PV_2Mo_{10}O_{40}$ (**1**)	70; 40	...	>99
1[e]	96; 54	...	>99
none	1.7; ...	...	99
$Q_{5-x}H_xPV_2Mo_{10}O_{40}$[f]	1.8; ...	...	99
p-TsOH[g]	20; 2.5	<1%	99
$H_3PW_{12}O_{40}$	24; 14	...	99
$H_3PMo_{12}O_{40}$	21; 12	2%	96
$Li_2MoO_4{\cdot}2H_2O$[h]	6.3; 1	<1%	99

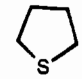
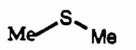
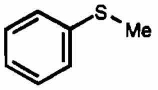
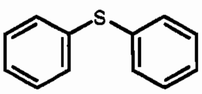
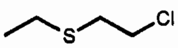
[a] Reaction conditions: both THT and TBHP (90% aqueous solution) were 56.8 mM in CH_3CN (4.98 mL); catalyst 1 mM unless otherwise indicated. In all cases, reaction temperature = 25 °C and reaction time = 1 h. [b] Yield with respect to initial *t*-BuOOH; turnovers = (mol of product)/(mol of catalyst). [c] [(mmol of product)/(mmol of thioether reactant)] × 100. [d] ... = below detection limit. [e] 5 equiv of $(n\text{-}Bu_4N)(HSO_4)$ added/equiv of **1**. [f] Q = $(n\text{-}Bu)_4N^+$. It is difficult to make pure Q_5. A mixed salt of a varying Q/H ratio is typically obtained. [g] *p*-Toluenesulfonic acid monohydrate (4.6 mM). [h] $Li_2MoO_4{\cdot}2H_2O$ (3.24 mM).

Three independent lines of evidence indicate an extraordinary sulfoxide selectivity for catalysis by **1**. First, when equivalent molar amounts or a slight excess of TBHP over THT is used, no sulfone whatsoever is produced with this catalyst. Gas chromatographic and gas chromatographic–mass spectrometric analyses that can detect at least one part in 10^5 indicate no sulfone. Second, control experiments establish that the sulfoxide (THTO) and the protonated sulfoxide (hydroxysulfonium ion = $THTOH^+$) are completely stable under the reaction conditions. Third, a precipitate forms in the reaction containing **1** and five points confirm it is the tetrakis(hydroxysulfonium) salt of starting vanadopolymolybdophosphate, namely, $(THTOH)_4(H)(PV_2Mo_{10}O_{40})$, or **2**: NMR, IR, and elemental analysis, independent synthesis from authentic **1** and THTO (see Experimental Section), and release of 4 equiv of free THTO upon treatment with 4 equiv of $n\text{-}Bu_4N^+OH^-$. That **2** is stable for a period of least 1 month at the temperature of the reactions in Table 1 (25 °C) indicates a ratio of reactivities, $k_{\text{thioether}}/k_{\text{protonated sulfoxide}}$, of at least 10^5, which is consistent with a sulfoxide selectivity in solution above 99.9%.

In contrast to the Keggin heteropoly acid derived vanadopolymolybdates and vanadopolytungstates, the tetra-*n*-alkylammonium forms of the same heteropoly compounds are ineffective as catalysts (note reactions 1–5, Table 1). The presence of strong Brønsted acids can catalyze THT oxidation by TBHP to some extent, as illustrated for example using three different acids, the conventional hydrophobic *p*-toluenesulfonic acid and the two Keggin heteropoly acids $\alpha\text{-}H_3PW_{12}O_{40}$ and $\alpha\text{-}H_3PMo_{12}O_{40}$ (reactions 6–8, Table 1). The addition of excess strong acids, however, can alter the kinetic selectivities of the oxidants, resulting in finite oxidation of sulfoxide to sulfone (in contrast to reactions 1–3, Table 1) and, ultimately, the degradation of the polyoxometalate catalysts. The similar levels of reaction of the three acidic reactions (reactions 6–8, Table 1) indicates that most of the THT oxidation activity in these reactions is due to acid-catalyzed activation and oxidation by TBHP, not oxidation by the polyoxometalate.

In line with the formulation of **2**, addition of an oxidatively resistant counteranion of moderate polarity, HSO_4^-, prevents the precipitation of **2** and leads to the most reactive and catalytic thioether oxidation system (reaction 3, Table 1). It is believed that the sulfoxide product preferentially binds to $(n\text{-}Bu)_4NHSO_4$ instead of the catalyst. As a result, more of the catalyst is in solution and available for reaction. The formation of a polyoxometalate Q salt ($Q_{5-x}H_xPV_2Mo_{10}O_{40}$), upon addition of $(n\text{-}Bu)_4NHSO_4$, cannot be ruled out. If this were occurring however, the activity would be expected to decrease as opposed to increasing as reflected by reaction 5 Table 1.

Table 2. Relative Initial-Rate Constants for Oxidation of Representative Thioethers and Their Corresponding Potentials[a]

sulfide	k_0(rel)	$E°$,[b] V
	1168	1.24
	209	1.31
	101	1.35
	3.43	1.08, 1.52
	20.6	1.23, 1.48, 1.82
	1[c]	1.48

[a] Reaction conditions: 25 °C, under argon, RSR (3.60×10^{-1} M), H_2O (2.20×10^{-1} M), and $H_5PV_2Mo_{10}O_{40}$ (2.02×10^{-3} M) in CH_3CN. [b] Voltammetry at a glassy carbon electrode with 200 mV/s sweep rate, reactant concentrations of 8 mM in acetonitrile with 0.80 M tetrabutylammonium hexafluorophosphate as supporting electrolyte, and measured at 25 °C versus a Ag/0.01 M $AgNO_3$ (in acetonitrile) reference electrode. [c] There was evidence that an impurity in the CEES (2-chloroethyl ethyl sulfide) was reoxidizing the catalyst, causing the rate as monitored by UV–vis to appear slower than it really was.

The relative rates of oxidation of six representative thioethers, a diaryl sulfide, $(C_6H_5)_2S$, one aryl alkyl sulfide, $(C_6H_5)(CH_3)S$, and four dialkyl sulfides, THT, $(CH_3)_2S$, $(CH_3CH_2)_2S$, and "half-mustard" (2-chloroethyl ethyl sulfide or CEES), by TBHP catalyzed by **1** are given in Table 2. The absolute rates for the reference (CEES) and THT reactions under the conditions in Table 2 are $v_0 = 1.24 \times 10^{-5}$ and 1.43×10^{-2} M s^{-1}, respectively. Also given in Table 2 are the potentials for each of these substrates measured in the same solvent (acetonitrile) at the same temperature. There is little correlation between the rates and the potentials of the substrates (Table 2). Two points that follow from this data warrant articulation. First, the potentials for electrochemical oxidation of substrates such as thioethers are rarely completely reversible and, as a consequence, the measured potentials may be significantly different from the true thermodynamic ones. The related key point here is that as all the thioethers were measured in this work under identical conditions, the relative potentials should be internally consistent. Second, it is clear that the lack of correlation is sufficiently great that factors other than just the potential, such as steric effects, play a significant role in the thioether oxidation process.

The reactions in Table 1, eq 6, take place by mode 1 described in the Introduction, that is, by initial thioether reduction of polyoxometalate (eq 7) and subsequent reoxidation of the reduced polyoxometalate by the terminal oxidant, TBHP in this case (eq 8). Oxidative titrations with Ce^{IV} and spectroscopic

$$R_2S + 2\underset{\mathbf{1}}{H_5PV_2Mo_{10}O_{40}{\cdot}H_2O} \rightarrow \underset{\mathbf{3}}{(R_2SOH)H_5(PV_2Mo_{10}O_{40})} + H_6PV_2Mo_{10}O_{40}{\cdot}H_2O \quad (7)$$

methods established the products and stoichiometries in eqs 7

$$2H_6PV_2Mo_{10}O_{40} + t\text{-BuOOH} \rightarrow 2H_5PV_2Mo_{10}O_{40} + t\text{-BuOH} + H_2O \quad (8)$$

and 8 by running each reaction separately. The heteropoly acids examined in these studies are hydrated. Only 1 equiv of these water molecules of hydration, that of **1**, is indicated in eq 7, as the other waters of hydration are not involved in the net transformation. In accord with previous work on the reduction of polyvanadomolybdic acids[17,18] and redox potentials, only the V^V ions and not the Mo^{VI} ions are reduced.

At least four points indicate the applicability of eqs 7 and 8. First, THT and other thioether substrates are stoichiometrically oxidized by **1** and other vanadium-substituted phosphomolybdic and phosphotungstic acids in the absence of the hydroperoxide, TBHP, or other oxidants (eq 7 but not eq 8) to give the same products as obtained under turnover conditions (TBHP present). Second, in the absence of TBHP, reoxidation of the reduced form of **1**, eq 8, is not operable, and no net catalytic turnover of **1** or the other polyoxometalates is observed. Third, the relative reactivities of thioethers for the same complex, **1**, under the same conditions vary greatly, indicating that both the thioether and the complex are involved in the slow step of the reaction (see section on the mechanism below) and little or no reaction takes place when only thioether substrate and TBHP are present. Fourth, subsequent anaerobic treatment of the products from stoichiometric oxidation (eq 7 but not eq 8) with TBHP does not change the products over the time scale dictated by conducting and analyzing the reactions. A final result is significant: when a molar excess of thioether is present over **1**, the monohydroxysulfonium salt, **3**, is formed exclusively. These facts explain the observation that under the stoichiometric anaerobic reaction conditions, eq 7, regardless of the mole ratio of THT to **1**, no precipitate forms in contrast to the case of catalytic reactions in the presence of TBHP described above (e.g., Table 1). In the stoichiometric reactions, insufficient sulfoxide is generated to form the relatively insoluble **2**.

Mechanism of Reduction of 1 by THT (Eq 7) and the Role of Water. The course of the catalytic reactions (Table 1) or the stoichiometric reactions (eq 7) shows conventional kinetics. That is, there is no induction period, autocatalysis, inhibition behavior, or other complex kinetics behavior. Figures 2S and 3S in the supplementary material show representative reactions involving THT as the substrate and **1** under catalytic and stoichiometric conditions, respectively.

Figures 2 and 3 show that the oxidation of THT by **1** (eq 7) leads to the experimental rate law in eq 9: the reaction is first order in THT, first order in **1**, and negative first order in H_2O.

$$V_0(\text{for eq 7}) = k[\text{THT}][\mathbf{1}][H_2O]^{-1} \quad (9)$$

The rate data indicate two unique features involving H_2O in the polyoxometalate-catalyzed reactions. The first is the $[H_2O]^{-1}$ rate dependence, and the second is the effect of $[H_2O]$ on the order with respect to the substrate THT. In the course of carefully checking the kinetics as a function of H_2O, it was discovered that the order with respect to THT appeared to be varying reproducibly with the H_2O content. A quantitative study of this phenomenon in the form of four order plots for THT at varying $[H_2O]$ indicates that the order in THT indeed varies with $[H_2O]$ from rigorously first order at or above 0.4% H_2O to significantly less than this and asymptotically approaches zero order at very low $[H_2O]$ (Figure 4). Unfortunately, the hydration of **1** and the hygroscopic nature of the solvent precluded any determinations below 15 mM H_2O.

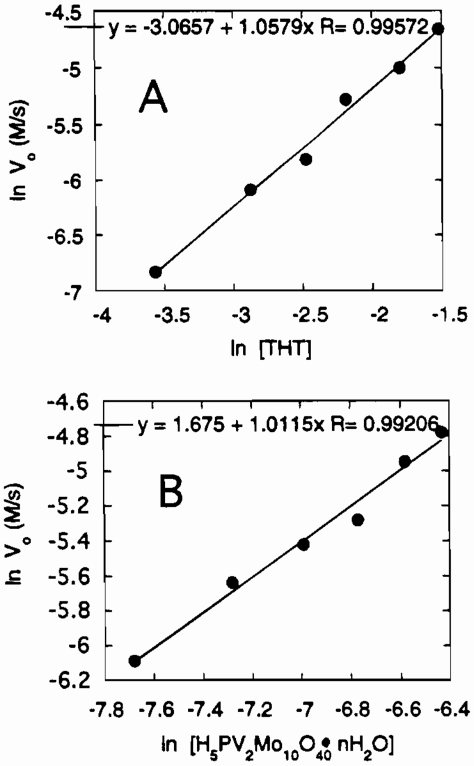


Figure 2. (A) ln−ln plot illustrating the initial rate of THT oxidation by $H_5PV_2Mo_{10}O_{40}$ (**1**) as a function of [THT]. $[H_5PV_2Mo_{10}O_{40}] = 1.60 \times 10^{-3}$ M, $[H_2O] = 2.20 \times 10^{-1}$ M. (B) ln−ln plot illustrating the initial rate of THT oxidation by **1** as a function of **1**. $[\text{THT}] = 3.24 \times 10^{-1}$ M, $[H_2O] = 2.20 \times 10^{-1}$ M. In both parts, the reactions were run under argon at 25 °C.

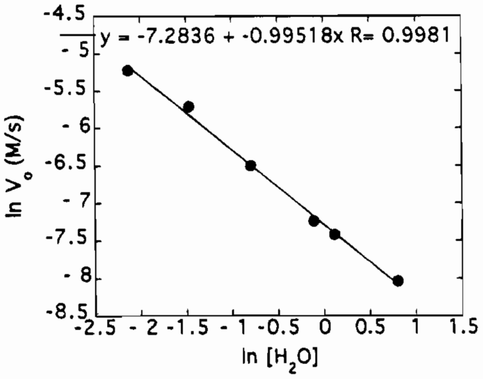


Figure 3. ln−ln plot illustrating the initial rate of THT oxidation by **1** as a function of $[H_2O]$. $[\mathbf{1}] = 7.24 \times 10^{-4}$ M, $[\text{THT}] = 1.13 \times 10^{-1}$ M; reaction run under argon at 25 °C.

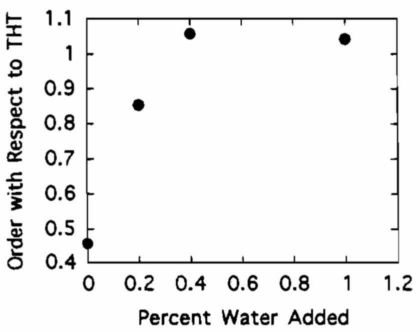


Figure 4. Plot of the order with respect to THT vs the percent water added for oxidation of THT by **1**.

A mechanism consistent with all the data is given in eqs 10−16. If $k_2[R_2S][\mathbf{1}\text{-}H_2O]$ is taken as the rate-limiting step and eq 10 is consequently a preequilibrium, then the derived rate law, applying a steady state approximation to the dehydrated and active form of **1**, expressed in terms of total catalyst ($\mathbf{1}_{\text{total}} = \mathbf{1}$

+ **1**-H_2O), is eq 17. At high [H_2O], [H_2O] ≫ [R_2S], and

$$\underset{\mathbf{1}}{H_5PV_2Mo_{10}O_{40}{\cdot}H_2O} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\mathbf{1}\text{-}H_2O}{H_5PV_2Mo_{10}O_{40}} + H_2O \quad (10)$$

$$R_2S + \mathbf{1}\text{-}H_2O \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} R_2S^{\bullet +} + \underset{(\mathbf{1}\text{-}H_2O)^-}{[H_5PV_2Mo_{10}O_{40}]^-} \quad (11)$$

$$R_2S^{\bullet +} + H_2O \rightleftharpoons R_2S^{\bullet}{-}OH + H^+ \quad (12)$$

$$H^+ + (\mathbf{1}\text{-}H_2O)^- \rightleftharpoons H_6PV_2Mo_{10}O_{40} \quad (13)$$

$$R_2S^{\bullet}{-}OH + \mathbf{1}\text{-}H_2O \rightleftharpoons R_2S^+{-}OH + (\mathbf{1}\text{-}H_2O)^- \quad (14)$$

$$R_2S^+{-}OH \rightleftharpoons R_2SO + H^+ \quad (15)$$

$$H^+ + (\mathbf{1}\text{-}H_2O)^- \rightleftharpoons H_6PV_2Mo_{10}O_{40} \quad (16)$$

$$V_0 = \frac{k_1k_2[R_2S][\mathbf{1}_{\text{total}}]}{k_1 + k_{-1}[H_2O] + k_2[R_2S]} \quad (17)$$

$$V_0 = k'[R_2S][\mathbf{1}_{\text{total}}][H_2O]^{-1} \quad (18)$$

$$V_0 = k_1[\mathbf{1}_{\text{total}}] \quad (19)$$

assuming $k_1 \ll k_{-1}[H_2O]$, eq 17 reduces to eq 18, which agrees with the observed rate law. At low [H_2O], [H_2O] ≪ [R_2S], and assuming $k_1 \ll k_2[R_2S]$, eq 17 reduces to eq 19, in which the reaction is zero order in THT. On the basis of eq 17, the order with respect to THT would then be expected to very from zero to first order as a function of water concentration. This has been experimentally demonstrated (Figure 4). Interestingly, the approach to zero order in THT could also be explained by a change in the rate-limiting step to k_1[**1**]. Rate-limiting dehydration of the polyoxometalate may play a significant role in polyoxometalate-catalyzed reactions in nonpolar media and at this point cannot be ruled out.

There are precedents for the steps subsequent to the rate-limiting one in the mechanism. Rapid capture of thioether cation radicals by H_2O, eq 12,[4a,9,32,33] and rapid oxidation of radicals less reducing than $R_2S^{\bullet}{-}OH$ by polyoxometalates, eq 14,[34] are both well documented. Thioether cation radicals are the most common initial products resulting from the oxidation of thioethers under both chemical and electrochemical[4,32,33,35] conditions, and they are the most likely initial products resulting from oxidation of thioethers by dehydrated **1** (eq 11). Although the thioether substrates, in principle, could be oxidized by abstraction of a hydrogen on a carbon atom α to sulfur by intermediate radicals, the reported behavior of thioethers in the presence of oxidizing radicals indicates that this process would be less likely than direct oxidation of the sulfur atom.[4,32] Furthermore, oxidation of thioethers by polyoxometalates under photochemical conditions is known to proceed by α-hydrogen atom abstraction and the products are those expected from reaction of such radicals; sulfoxide and sulfone are not formed.[15]

It is also possible that thioether cation radicals may trap small quantities of O_2 generated in situ under catalytic conditions by the well-known Haber–Weiss radical chain decomposition mechanism of alkyl hydroperoxides followed by alkylperoxy radical dimerization[37] or, less likely for these reactions, by polar heterolytic alkyl hydroperoxide decomposition mechanisms, eq 20. The chemistry of the initial product thioperoxy radicals, **4** in eq 20, including their chain-carrying role in thioether autoxidation reactions, has been documented.[9] The relative rates of reaction of H_2O and O_2 with thioether cation radicals have been implicated in at least one type of homogeneous liquid phase process, the metal-catalyzed autoxidation of thioethers investigated by Riley and co-workers. In the latter reactions, O_2 reacts more rapidly than H_2O.[9] It also possible, on the basis of the chemistry of iminosulfonium salts[36] and thioether cation radicals,[32] that, in the absence of any stronger nucleophiles, thioether cation radicals could be trapped by acetonitrile, eq 21. To assess the potential importance of the trapping of thioether cation radical intermediates by CH_3CN, the principal product resulting from this process, the (acetylimino)sulfonium cation, **5** (specifically the THT-derived cation, R_1R_2 in eq 21 = $-CH_2CH_2CH_2CH_2-$), was independently synthesized as its bromide salt and shown not to convert to the observed product (~100% sulfoxide) under the reaction conditions. This result rules out the intermediacy of freely diffusing **5**. On balance, the most likely trapping agent for intermediate thioether cation radicals, particularly in the early stages of reaction, is H_2O.

$$R_1R_2S^{\bullet +} + O_2 \rightleftharpoons \underset{\mathbf{4}}{R_1R_2S^+OO^{\bullet}} \xrightarrow[\text{radical chain chemistry}]{\text{subsequent}} \quad (20)$$

$$R_1R_2S^{\bullet +} + CH_3CN \rightleftharpoons R_1R_2S^{\bullet}{-}N{=}C^+{-}CH_3 \xrightleftharpoons{\text{oxidation and hydrolysis}} \underset{\mathbf{5}}{R_1R_2S^+{-}NH{-}CO{-}CH_3} + H^+ \quad (21)$$

A final experiment was conducted to garner information about the slow step in the water-containing reactions, $k_2[R_2S][(\mathbf{1}\text{-}H_2O)]$. The temperature dependence of the reaction was determined and the Eyring plot yielded the following activation parameters: $\Delta H^{\ddagger} = 8.06 \pm 0.64$ kcal mol^{-1} and $\Delta S^{\ddagger} = -29.7$

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(32) Shine, H. J. In *The Chemistry of the Sulphonium Group* Part 2; Patai, S., Ed.; John Wiley & Sons: New York, 1981; Chapter 14.

(33) Ledlic, M. A.; Allum, K. G.; Howell, J. V.; Pikethly, G. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1734.

(34) Oxidation of radicals by polyoxometalates was first reported by Papaconstantinou in pulse radiolysis studies involving highly reducing alcohol derived radicals and heteropoly acids in water (Papaconstantinou, E. *J. Chem. Soc., Faraday Trans.* **1982**, *78*, 2769. See also: Lerat, O.; Chauveau, F.; Hickel, B. *New J. Chem.* **1990**, *14*, 37). Studies of alkyl radical oxidation by polyoxometalates in conjunction with alkane functionalization was addressed in some detail more recently (Renneke, R. F.; Pasquali, M.; Hill, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 6585. Renneke, R. F.; Kadkhodayan, M.; Pasquali, M.; Hill, C. L. *J. Am. Chem. Soc.* **1991**, *113*, 8357).

(35) Magno, F.; Bontempelli, G. *J. Electroanal. Chem. Interfacial Electrochem.* **1972**, *36*, 389.

(36) Kise, H.; Whitfield, G. F.; Swern, D. *J. Org. Chem.* **1972**, *37*, 1121.

(37) The Haber–Weiss mechanism for the radical chain decomposition of alkyl hydroperoxides, eqs i and ii, plays a central role in metal-catalyzed homolytic oxidations of organic substrates by O_2 including industrial autoxidation reactions where the initial hydroperoxide products (ROOH) are largely decomposed by such a mechanism. The principal fate of the alkylperoxy radicals is dimerization, eq iii, evolving oxygen. For a review, see: Tolman, C. A.; Druliner, J. D.; Nappa, M. J.; Herron, N. In *Activation and Functionalization of Alkanes*; Hill, C. L., Ed.; Wiley: New York, 1989; Chapter 10.

$$M_{\text{red}} + ROOH \rightarrow M_{\text{ox}} + RO^{\bullet} + OH^- \quad \text{(i)}$$

$$M_{\text{ox}} + ROOH \rightarrow M_{\text{red}} + ROO^{\bullet} + H^+ \quad \text{(ii)}$$

M_{red} = reduced form of the transition metal complex

M_{ox} = its oxidized counterpart

$$2ROO^{\bullet} \rightarrow O_2 + 2RO^{\bullet} \quad \text{(iii)}$$

± 0.18 eu. These activation parameters were compared with those for representative reactions of the three most likely mechanisms for oxidation of THT to THTO by an oxometal complex such as **1**, namely inner and outer sphere electron transfer and oxo transfer. The activation parameters for THT + **1** are closest to those of outer sphere electron transfer.[19d,38,39] They are also close to those for oxo transfer oxidation of dimethyl sulfide by $[(bpy)_2(py)Ru(O)]^{2+}$.[10] As there is effectively no credible evidence yet for oxo transfer oxidation of organic substrates by d^0 polyoxometalates under mild homogeneous conditions, the collective data are most consistent with outer sphere electron transfer although significant preassociation and inner sphere character in the rate-limiting step cannot be ruled out.

All the data argue for a fundamentally novel mechanism for a metal-catalyzed peroxide oxidation. Nearly all other such oxidations involve electrophilic activation of the peroxide by the metal with subsequent attack by a metal−peroxo complex on the substrate or metal-induced or -modulated radical reactions, not direct thermal oxidation of substrate by the metal complex catalyst itself.

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Supplementary Material Available: Figures showing infrared spectra of tetramethylene sulfoxide (neat), 1.43% $(THTOH)_4HPV_2Mo_{10}O_{40}$ in KBr, and 0.60% $H_5PV_2Mo_{10}O_{40}$ in KBr, the time dependence of the oxidation of THT by TBHP catalyzed by **1**, and absorbance spectra illustrating the interaction of a 1 mM solution of **1** in 2 mL of acetonitrile with a 57-fold molar excess of THT under argon at 25 °C (3 pages). Ordering information is given on any current masthead page.

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[38] Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH Publishers, Inc.: New York, 1991; p 260 and references therein.

[39] Ayoko, G. *Inorg. Chim. Acta* **1990**, *170*, 89.