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Selective Oxidation of Thioether Mustard (HD) Analogs by *tert*-Butylhydroperoxide Catalyzed by $H_5PV_2Mo_{10}O_{40}$ Supported on Porous Carbon Materials

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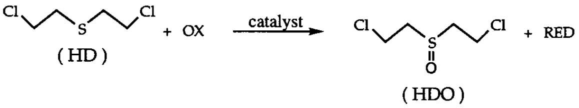
The polyoxometalate $H_5PV_2Mo_{10}O_{40}$ (1) supported on porous carbons forms selective and recoverable heterogeneous catalysts for the rapid room temperature oxidation of thioether mustard (HD) analogs. Both selectivities (95 to 99% for sulfoxide) and rates (∼20%) vary with the carbon support at parity of all other parameters. A 99% selectivity for the sulfoxide product, even at 75% conversion of the thioether substrate, is seen for the most selective system, 10 wt% 1 on Rohm and Haas Ambersorb (1/Ambersorb). Washing for 125 h in the solvent for catalysis, toluene, results in no significant loss in catalytic activity and a recovery and reusability study at high turnover also indicates that the catalysts are very stable. The polyoxometalate/carbon catalysts can be reactivated between uses by heating to ∼80°C. The oxidation of tetrahydrothiophene (THT) to THTO by *tert*-butylhydroperoxide (TBHP) catalyzed by 1/Ambersorb is first order in substrate and oxidant and proportional to the concentration of active sites on the 1/Ambersorb. The activation parameters for the process are $\Delta H^{\ddagger} = 11.4 \pm 0.05$ kcal/mol and $\Delta S^{\ddagger} = -38.8 \pm 0.22$ cal/K mol.

INTRODUCTION

The impetus for this research is twofold: First, to investigate the effect of immobilization on conventional inorganic support materials of polyoxometalates that are effective and selective homogeneous catalysts (1–4) and second, to develop effective catalysts for the selective oxidation of the highly toxic bis(2-chloroethyl)sulfide, also known as mustard or HD. Methods are needed for use not only in destroying stockpiles of mustard in a controlled fashion, but also by soldiers who may encounter mustard in the field (5). One goal of this research is to formulate a supported selective catalyst for mustard oxidation that can be used in self decontaminating protective gear. Selectivity is crucial in this endeavor. It is known that the corresponding sulfoxide, bis(2-chloroethyl)sulfoxide (HDO), is relatively nontoxic, whereas, the corresponding sulfone is highly toxic (6).



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Heteropoly compounds have been used extensively as unsupported solid acid catalysts in such processes as Friedel-Crafts alkylation and acylation (7), esterification and hydrolysis (8), and selective oxidation of alkanes (9) to name a few. Due to their enhanced redox properties, compounds containing Mo and V are used commercially for the synthesis of methacrylic acid from methacrolein and isobutyric acid (10).

Soluble and catalytically active heteropoly compounds (4) have also been supported on inorganic materials to improve catalyst stability. For the oxidation of methanol it was found that the $H_{3+n}PV_nMo_{12-n}O_{40}$ acid catalysts supported on $K_3PMo_{12}O_{40}$ generally showed higher activity than the unsupported catalysts (11). Studies of heteropoly compounds supported on silica (7, 8, 12), titanium dioxide (anatase) (12), and ion exchange resin (13) have also been reported. Unpublished results in our laboratories have indicated that organic supports such as chitosan (nontoxic, robust, and biodegradable) and other polysaccharides are sometimes unsatisfactory supports for polyoxometalate oxidation catalysts as these supports inhibit some catalytic reactions (14).

In 1981 Izumi and Urabe found that heteropoly acids (HPAs) could be entrapped in activated carbon and that the heteropoly compounds did not leach out as they sometimes did for other supports (15). Izumi studied the liquid phase etherification of butanol with *tert*-butyl alcohol and the vapor phase esterification of acetic acid with ethanol. In both cases he found the polyoxometalate to be tightly bound to the carbon. Izumi *et al.* also did a study comparing several supports including silica, alumina, titania, and carbon for the alkylation of benzene, esterification of acetic acid with ethanol, and dehydrogenation of 2-propanol (12). The supported heteropoly acids were found to exhibit even better

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selectivity than some zeolite catalysts. Neumann and Levin reported the selective oxidation of alcohols and amines catalyzed by 10 wt% $Na_5PV_2Mo_{10}O_{40}$ on activated carbon with a focus on the organic transformations (16), and Fujibayashi *et al.* recently reported a new mixed addenda heteropolyoxometalate, $(NH_4)_5H_4PV_6Mo_6O_{40}$, supported on active carbon that exhibited catalytic activity for the aerobic oxidation of phenols, hydroquinones, and benzyl alcohol (17).

It has recently been reported that $H_5PV_2Mo_{10}O_{40}$ (**1**) homogeneously catalyzes the oxidation of the HD analog tetrahydrothiophene (THT) by TBHP rapidly at room temperature with exceptional (>99.9%) selectivity by virtue of a highly unusual mechanism for peroxide based catalytic oxidations (18). We report here the first thioether oxidation chemistry by carbon supported polyoxometalates and, more significantly, the first detailed mechanism studies of these heterogeneous systems.

EXPERIMENTAL SECTION

Materials. Ambersorb-572 (henceforth referred to as Ambersorb), Calgon, and Maxsorb are finely divided forms of carbon available from the Rohm and Haas Company, the Calgon Corporation, and the Kansai Coke and Chemicals Co. Ltd., respectively. The surface areas of Ambersorb, Calgon, and Maxsorb are 1100, 1200, and 3100 m^2/g, respectively. The relative pore volumes which can be estimated from BET of Ambersorb, Calgon, and Maxsorb are 0.19, 0.72, and 1.8 ml/g, respectively. The Ambersorb was ground up before use to make aliquot withdrawal from the reaction mixture easier. This would increase the external particle area but has only a minor effect on the total pore volume (19). The $H_5PV_2Mo_{10}O_{40}$ catalyst was prepared and purified by literature procedures (20). All other reactants, solvents, internal standards, and products were obtained from Aldrich and the purities (>98%) were checked by gas chromatography. The terminal oxidant, *tert*-butylhydroperoxide, was purchased as a solution in decane (4.52 *M*) to prevent solubility problems.

Instrumentation. Reactions were monitored on a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a 5% phenyl methyl silicone capillary column. For the Eyring plot the temperature was controlled using a DATAPLATE digital hot plate/stirrer (720 series).

Synthesis of carbon supported $H_5PV_2Mo_{10}O_{40}$ catalysts. The carbons (2 g) were stirred in 10-ml of a 2% solution of **1** (i.e., 2 g of 1 in 100 ml of water) for 16 h to form 10 wt% **1** on carbon. The **1** impregnated carbons were filtered off and air dried. Analysis of the supernatant by UV–vis showed no polyoxometalate, indicating quantitative adsorption by the carbon.

Comparison of catalysts and determination of the rate law for the catalytic oxidation of THT by TBHP. In all reactions the toluene, TBHP, and carbon-supported catalysts were placed in a 10-ml round bottom flask sealed with a Suba Seal septum stopper and taken through 3 degas/gas cycles with argon. Next, 10 μl of degassed internal standard (trimethylacetonitrile or isooctane) was added. Injection of the degassed thioether substrate through the septum stopper initiated the reaction. The reactions were stirred at 700 rpm at ambient temperature. Aliquots were extracted at various times and analyzed by gas chromatography. The reaction aliquots were filtered with Rainin Nylon-66 syringe filter units (45-micrometer porosity) to remove carbon particles before analysis. The TBHP was quenched by addition to one equivalent of tetrabutylammonium borohydride in 100 μl of chloroform. Several other quenching agents, including methyltriphenylphosphonium iodide, tetrapentylammonium iodide, and hydrazine, were tried but were unsatisfactory. Tetrabutylammonium borohydride was found to effectively prevent any background reaction without reducing the sulfoxide product. Conversion was determined by following the loss of thioether (Tables 1 and 2). The rate law was determined by monitoring the formation of sulfoxide product (tetrahydrothiophene oxide). See tables and figure captions for exact concentration information in each experiment.

TABLE 1

Selective Catalytic Oxidation of an HD Analog, Tetrahydrothiophene (THT), by *t*-BuOOH (TBHP) Catalyzed by $H_5PV_2Mo_{10}O_{40}$ (1) Supported on Various Forms of Porous Carbon[a]

Rxn. no.	Catalyst[b]	(% Conversion; turnovers)[c]	% Selectivity[d]	Temperature (°C)
1	**1**/Ambersorb	(75, 46)	99	25
2	**1**/Calgon	(68, 41)	97	25
3	**1**/Maxsorb	(87, 56)	95	25
4	Ambersorb[e]	(2, NA[f])	NA	25
5	None	(3, NA[f])	NA	25
6	**1**/Ambersorb	(16, 13)	>99	0
7	**1**/Ambersorb	(98, 64)	83	60
8	**1**/Ambersorb[g]	(81, 49)	98	25
9	**1**/Ambersorb[h]	(79, 48)	99	25

[a] Reaction conditions: [THT] = 50.5 m*M*, [TBHP] = 91.1 m*M*, Catalyst = 0.1000 g with each carbon being 10 wt% **1**, 10 μl trimethylacetonitrile (internal standard), 25°C, in 7.00 ml of toluene with stir rate of 700 rpm under Ar for 125 min.

[b] See experimental section. The Ambersorb was ground up before use to facilitate the withdrawal by syringe of reaction aliquots.

[c] Conversion = $(([THT]_o - [THT])/[THT]_o) \times 100$ and turnovers = mol of sulfide derived product(s)/mol of **1** on the carbon (21).

[d] Selectivity = (mol of sulfoxide product/total mol of all sulfide derived products) × 100.

[e] No $H_5PV_2Mo_{10}O_{40}$.

[f] Not applicable because no polyoxometalate, **1**, is present.

[g] 0.4% H_2O present.

[h] 1% H_2O present.

TABLE 2

Oxidation of Representative Thioethers by *t*-BuOOH (TBHP) Catalyzed by $H_5PV_2Mo_{10}O_{40}$ (1) Supported on Carbon[a]

Thioether	Catalyst	% Conversion[b]
Tetrahydrothiophene (THT)	**1**/Ambersorb	77
Thioanisole	**1**/Ambersorb	41
2-Chloroethyl ethyl sulfide	**1**/Ambersorb	38
Diphenyl sulfide	**1**/Ambersorb	15

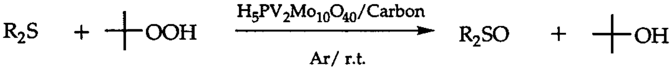
[a] Reaction conditions: [Thioether] = 50.5 m*M*, [TBHP] = 91.1 m*M*, Catalyst = 0.1000 g (**1**)/Ambersorb, 10 μl isooctane (internal standard), 25°C, solvent (volume) = toluene (7.00 ml), stir rate = 700 rpm, atmosphere = Ar, reaction time = 125 min.

[b] % Conversion = $(([\mathrm{THT}]_o - [\mathrm{THT}])/[\mathrm{THT}]_o) \times 100$.

Eyring plot. The rate was monitored by following the formation of the sulfoxide product by gas chromatography. The reactions were run as described in the previous section. The temperature was varied while all other parameters were held constant. The reaction conditions were 0.7865 *M* THT, 0.1581 *M* TBHP, 0.02 grams of catalyst (at 5.18×10^{-5} mol $H_5PV_2Mo_{10}O_{40}$/g carbon), 0.0084 *M* isooctane (internal standard), 700 rpm stir rate, argon atmosphere, and toluene solvent. The temperature was varied from 0 to 60°C.

RESULTS AND DISCUSSION

Catalytic efficiencies and selectivities. The carbon supported free acid polyoxometalate catalyzes the rapid and selective oxidation of thioether HD analogs by the stoichiometry given in Eq. [2].



[2]

Under a typical set of reaction conditions (3.24 *M* THT, 0.130 *M* TBHP, 0.0500 g of **1**/Ambersorb, and 25°C), the rate is 3.15×10^{-5} *M* sec^{-1}. Given that the carbons are 10 wt% **1**, there would be 2.59×10^{-6} mol of **1** in this reaction (taking into account the 11 waters of hydration, the molecular weight of **1** is 1927.81). Dividing the rate by the number of polyoxometalate ions would give a minimum turnover frequency of 12.2 if we assume all of the polyoxometalate ions to be accessible. Conversions and selectivities are given in Table 1 (21). Entries 1–3 of Table 1 demonstrate the catalytic nature of the **1**/carbon in comparison to entry 4, which contained carbon without supported catalyst, and entry 5, which contained no carbon or catalyst. Although Ambersorb-572 has been reported to have some oxidizing capacity (22), entry 4 shows that it does not contribute to the reactivity of this system. **1**/Maxsorb was the fastest catalyst, while **1**/Ambersorb was the most selective. The temperature dependence of the selectivity and rate is illustrated by entries 6 and 7 of Table 1. The activation parameters ($\Delta H^{\ddagger} = 11.4 \pm 0.05$ kcal/mol and $\Delta S^{\ddagger} = -38.8 \pm 0.22$ cal/K mol) were obtained from an Eyring plot ($R = 0.9985$ for a 5 point fit, see Fig. 1). It is difficult to draw any conclusions about the mechanism based on the activation parameters because the reaction is heterogeneous and the kinetics are complex (*vide infra*).

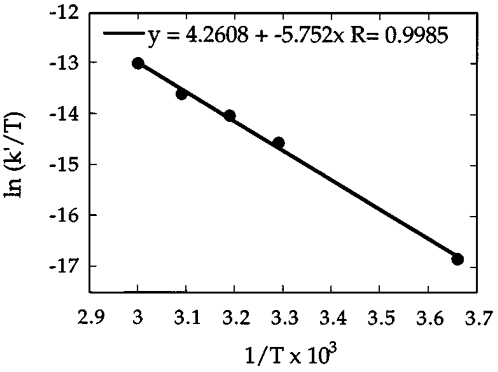


FIG. 1. Eyring plot: 0.7865 *M* THT, 0.1581 *M* TBHP, 0.0200 g of **1**/Ambersorb (at 5.18×10^{-5} mol of **1**/g of carbon), argon atmosphere, ambient temperature, 700 rpm stir rate, toluene solvent. Typically one divides the rate by the molar concentration of all reactants of calculate $k\prime$, which is plotted as ln $k\prime/T$ on the *y* axis. In this case, the moles of catalyst has been incorporated into the rate constant as it is a heterogeneous material without a formal concentration.

Stability of the catalyst. Toluene was chosen as the solvent because polar solvents such as CH_3CN were found to dissolve the free acid catalyst. A washing study was performed to determine stability of the catalyst in the toluene solvent. Two THT oxidations by TBHP were conducted. In one the **1**/Ambersorb catalyst was washed in toluene for 123.5 h and then dried at 76°C for 17 h before use. In the other, the **1**/Ambersorb catalyst was used as synthesized. The good agreement between the two reaction profiles (Fig. 2) suggests that there is little or no damage to the catalyst from the solvent.

The overall stability and reusability of the catalyst was assessed by reclaiming the catalyst after reaction and reusing it several times. The catalyst was filtered off and heated to 79–80°C for 18–22 h in a vacuum oven between each reaction. Figure 3 illustrates the percentage conversion as a function of time for each use with the cumulative number of turnovers indicated (for example, the turnover number for the third use also includes the turnovers of the first and second use).

The difference in the slopes of the reactions at early times is a consequence of the time between heating the catalyst and using it. The catalyst was not heated at all before the first use. Before the fourth use the catalyst was heated and used immediately after it cooled down. The second and third times the catalyst was used it was heated as described

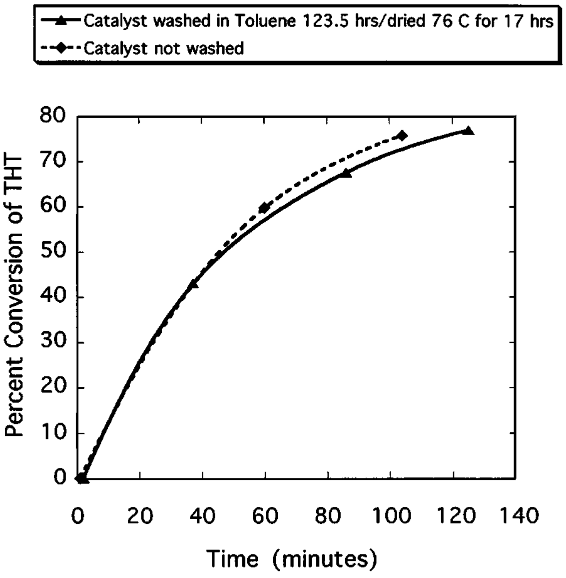


FIG. 2. Washing experiment: 50.5 m*M* THT, 91.1 m*M* TBHP, 0.1000 g of **1**/Ambersorb (at 5.18×10^{-5} mol of **1**/g of carbon), argon atmosphere, ambient temperature, 700 rpm stir rate, toluene solvent. ▲, The catalyst was washed in toluene for 123.5 h and dried at 76°C for 17 h. ◆, The catalyst was not washed in toluene before use.

but allowed to sit for several days on the bench before use. Entries 8 and 9 in Table 1 show that adding water at these concentrations has a minimal effect on the rate of reaction. Figure 3, however, shows that activation of the catalyst by dehydration in a vacuum oven increases the rate. Control experiments showed that the reaction rates were ~2.5 × faster when the catalyst was heated before use. Two likely explanations for the inhibiting effect of water at low concentrations of water are blocking of the catalyst sites by water molecules and/or repulsion of the organic substrate due to the increased hydrophilicity of the carbon. Figure 3 clearly demonstrates that in addition to being fast and selective, these polyoxometalate/carbon catalysts are also recoverable and reusable.

The catalytic oxidation of four representative thioether substrates are compared in Table 2. Several factors likely come into play regarding the relative reactivities of these substrates including steric effects and the hydrophobicity of the carbon support. One would expect, based on steric and electronic effects, that the electron rich and cyclic substrate THT would be much faster than diphenyl sulfide (cf. entries 1 and 4). In THT, the alkyl groups are effectively pinned back yielding greater access to the S atom than in acyclic aliphatic thioethers. The Ambersorb carbon used in this study was of a hydrophilic nature which would also explain, in part, why diphenyl sulfide is slower than THT. The order of reactivity is also consistent with an electron transfer mechanism whether preequilibrium association of the substrate with catalyst is significant or not.

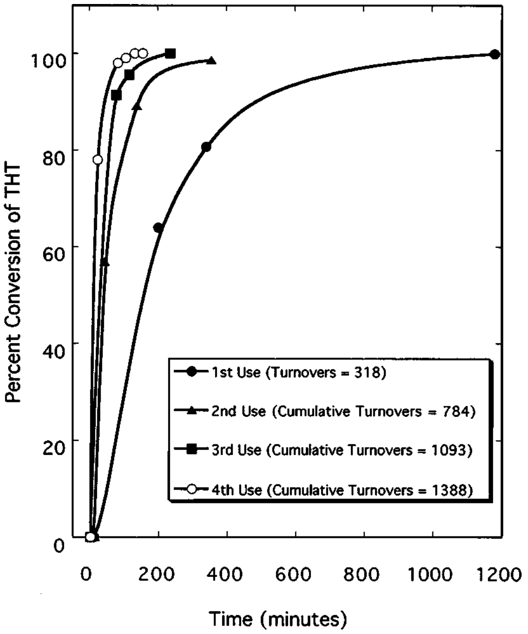


FIG. 3. Stability study: THT (152 m*M*), TBHP (226 m*M*), **1**/Ambersorb (0.1500 g; 5.18×10^{-5} mol of **1**/g of Ambersorb), argon atmosphere, ambient temperature, 700 rpm stir rate, toluene solvent. Turnover number is corrected for any changes in moles of catalyst as a result of mechanical loss of carbon with each recovery.

Mechanism of the catalytic oxidation of THT by TBHP catalyzed by $H_5PV_2Mo_{10}O_{40}$*/Ambersorb.* The simplicity of this reaction (Eq. [2]) and the lack of side reactions enabled us to perform detailed kinetic studies. Figures 4, 5, and 6 show that the oxidation of THT by TBHP catalyzed by **1**/Ambersorb (Eq. [2]) leads to the experimental rate law given by Eq. [3]. The catalyst concentration in Fig. 6 is expressed in moles rather than molarity as the catalyst is not in solution. In the following equations [**1**/Ambersorb]

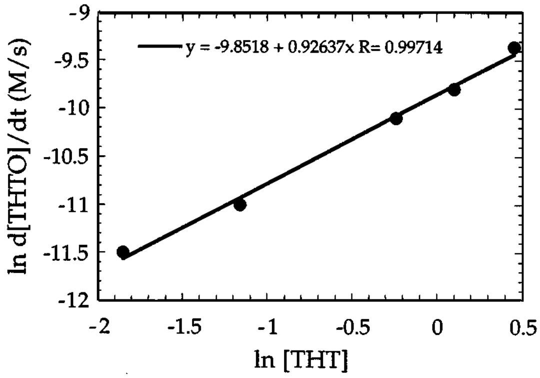


FIG. 4. ln–ln plot illustrating the rate of THTO formation from the oxidation of THT by TBHP catalyzed by **1**/Ambersorb as a function of [THT]. [THT] varied from 0.1573 to 1.57 *M*, [TBHP] = 0.1254 *M*, and 0.0500 g of **1**/Ambersorb (at 5.18×10^{-5} mol of **1**/g of Ambersorb) were used.

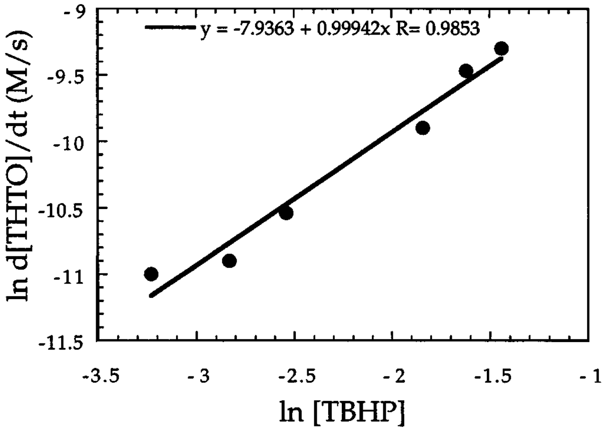


FIG. 5. ln–ln plot illustrating the rate of THTO formation from the oxidation of THT by TBHP catalyzed by **1**/Ambersorb as a function of [TBHP]. [TBHP] varied from 3.95×10^{-2} to 2.37×10^{-1} *M*, [THT] = 0.7865 *M*, and 0.0200 g of **1**/Ambersorb (at 5.18×10^{-5} mol of **1**/g of Ambersorb) were used.

represents the moles of **1** present on the carbon (21). While assessment of the order of a reaction in a heterogeneous component using such van't Hoff ln–ln plots (ln rate as a function of ln [supported **1**] here) is often not meaningful and can in some cases be misleading, the quality of the data argue for its inclusion and consideration.

$$d[\text{THTO}]/dt = k[\text{THT}][\text{TBHP}][\mathbf{1}/\text{Ambersorb}] \qquad [3]$$

A mechanism consistent with the data is given in Eqs. [4]–[7], starting with an equilibrium preassociation of the heterogeneous catalyst (POM in Eq. [4]) and the substrate to form $[\text{HPOM} \cdot \text{THT}]^+$. It is not clear what species provides the proton in Eq. [4]. It could be associated with the POM or waters of hydration. Applying a steady state approximation to $[\text{HPOM} \cdot \text{THT}]^+$, with $k_2[\text{HPOM} \cdot \text{THT}]^+[\text{TBHP}]$ as the product generating step, leads to the derived rate law in Eq. [8]. The catalyst concentration has been expressed in terms of total catalyst ($\text{POM}_{\text{total}} = \text{POM} + [\text{HPOM} \cdot \text{THT}]^+$).

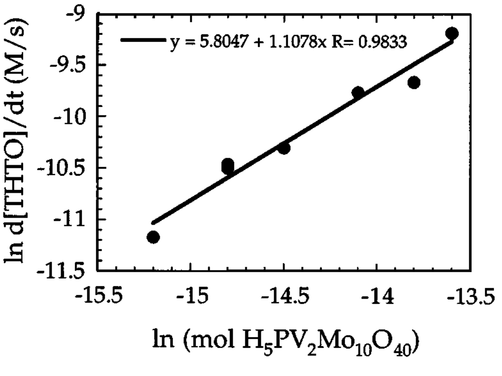


FIG. 6. ln–ln plot illustrating the rate of THTO formation from the oxidation of THT by TBHP catalyzed by **1**/Ambersorb as a function of the moles of $H_5PV_2Mo_{10}O_{40}$ present on carbon. $H_5PV_2Mo_{10}O_{40}$ varied from 2.59×10^{-7} to 1.3×10^{-6} mol, [TBHP] = 0.1254 *M*, [THT] = 0.7865 *M*.

Based on Eq. [8], this mechanism would predict that the order of TBHP should approach zero as $k_2[\text{TBHP}] \gg k_1[\text{THT}][\text{H}^+] + k_{-1}$. The order of THT should also approach zero as $k_1[\text{THT}][\text{H}^+] \gg k_{-1} + k_2[\text{TBHP}]$. It was observed experimentally that the ln $d[\text{THTO}]/dt$ vs ln[TBHP] plot leveled off at very high concentrations of TBHP, indicating a change from first order to zero order. In the case of THT, it appeared that the plot began to decrease at high THT concentrations rather than leveling off. This is likely the expected leveling off with a superimposed solvent effect. At the lowest concentration, THT represents only 1.43% of the total volume. At the highest concentration, however, it represents 29% of the total volume thus a bulk solvent effect is expected. Equation [8] predicts a proton dependence and such a dependence is seen in this chemistry, but difficulties in quantifying proton activity in nonaqueous solvents prohibited the generation of a meaningful van't Hoff ln–ln plot.

$$\text{THT} + \underset{\text{(POM)}}{\mathbf{1}/\text{Ambersorb}} + \text{H}^+ \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} [\text{HPOM·THT}]^+ \qquad [4]$$

$$[\text{HPOM·THT}]^+ + \mathbf{+}\text{OOH} \xrightarrow{k_2} \text{POM} + \mathbf{+}\text{O·} + \text{H}_2\text{O} + \text{·THT}^+ \qquad [5]$$

$$\text{·THT}^+ + \text{H}_2\text{O} \longrightarrow \text{THTOH·} + \text{H}^+ \qquad [6]$$

$$\text{THTOH·} + \mathbf{+}\text{O·} \longrightarrow \text{THTO} + \mathbf{+}\text{OH} \qquad [7]$$

$$d[\text{THTO}]/dt = \frac{k_1k_2[\text{THT}][\text{TBHP}]\text{H}^+][\text{POM}_{\text{total}}]}{k_1[\text{THT}][\text{H}^+] + k_{-1} + k_2[\text{TBHP}]} \qquad [8]$$

There are precedents for the steps following the rate determining one, Eq. [5]. Thioether cation radicals are the most common initial products resulting from the oxidation of thioethers (23, 24). Additionally, rapid capture of thioether cation radicals by H_2O, Eq. [6] (23, 24), and hydrogen atom abstraction by alkoxy radicals, Eq. [7] (25), are both well documented and fast processes.

In summary, carbon supported **1** has several desirable catalytic properties including fast selective oxidation of thioethers and excellent recoverability and reusability. The kinetics indicate that the reaction goes via a straightforward mechanism which involves direct oxidation of the thioether by **1**/Ambersorb and subsequent reoxidation of the reduced form of the immobilized polyoxometalate by TBHP. The positive physical and catalytic properties indicate that these **1**/carbon systems combine the selectivity and tunability advantages of homogeneous polyoxometalate catalytic systems with the stability and utility (lower cost and ease of recovery) advantages of heterogeneous catalytic systems.

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