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Redox Catalysis Involving Substrate Photooxidation with Catalyst Regeneration by Substrate Reduction. Simultaneous Oxidative C-H Bond Cleavage and Reductive C-S Bond Cleavage in Thioethers Catalyzed by $W_{10}O_{32}^{4-}$

R. Carlisle Chambers and Craig L. Hill*

Contribution from the Department of Chemistry, Emory University, Atlanta, Georgia 30322.

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Abstract: Several experiments examining the photooxidation of thioethers by polyoxotungstates have established that the less oxidizing photochemically active complex $W_{10}O_{32}^{4-}$ but not the more oxidizing photochemically active heteropolytungstates such as α-$PW_{12}O_{40}^{3-}$ can be used to effect both substrate photooxidation and reduction in the same reaction. Under anaerobic conditions in solution at ambient temperature, the excited state of $W_{10}O_{32}^{4-}$ reacts with thioethers in high selectivity by α-hydrogen abstraction to form the α-carbon radicals. Neither photooxidation by electron transfer to generate the thioether cation radicals nor production of the conventional oxygenated products, sulfoxide and sulfone, is seen in these reactions. The principal reduced form of the catalyst, $W_{10}O_{32}^{6-}$, reduces thioethers to effect C-S bond cleavage; thus, the net observed products in anaerobic photooxidation of these substrates catalyzed by $W_{10}O_{32}^{4-}$ are the dimers resulting from coupling of the α-carbon radicals and C-S bond cleavage products including the hydrocarbon resulting from complete desulfurization of the thioether. The only important processes exhibited by the excited state, $W_{10}O_{32}^{4-*}$, under conditions where background photooxidation of CH_3CN solvent is not significant ([thioether] > 25 mM) are attack on thioether substrate, k, and unimolecular radiationless decay, k_{rd}. The rate law for production of the readily monitored inorganic product, $W_{10}O_{32}^{6-}$ (rate = $k\phi I[R_2S]/k[R_2S] + k_{rd}$), is consistent with the kinetically competent excited state, $W_{10}O_{32}^{4-*}$, being produced by absorption of one photon of near-UV light and rate-limiting attack of this species on thioether. Under aerobic conditions, $W_{10}O_{32}^{4-}$ catalyzes the complete oxidative conversion of thioethers principally to sulfoxides and sulfones by a complicated process that involves, in part, radical-chain autoxidation. Sulfoxides readily quench the photoredox-active excited state of $W_{10}O_{32}^{4-}$ ($k_q\tau$ = 9.4 M^{-1}).

Introduction

The photoinduced redox chemistry of some classes of early-transition-metal-based polyoxometalate complexes has attracted attention recently for several reasons: (1) this chemistry can be used to produce unusual products from saturated hydrocarbons and other organic substrates,[1,2] (2) it has direct application in photomicrolithography,[3] and (3) it has potential use in catalytic photochemical decontamination of a broad spectrum of toxic materials.[4] Three *general* attributes that render this large class of d^0 inorganic complexes of interest are their reasonable accessibility,[5] solubility in a range of media,[5] and low toxicity.[6]

The general processes involved in d^0 polyoxometalate-based photoinduced redox phenomena, (illustrated in eqs 1-6) and some

$$P + h\nu \rightarrow P^* \tag{1}$$

$$P^* + SH_2 \rightarrow P_{red} + S + 2H^+ \tag{2}$$

$$P_{red} + 2H^+ \rightarrow P + H_2 \tag{3}$$

net reaction from eqs 1-3:

$$SH_2 + h\nu \xrightarrow{P} S + H_2 \tag{4}$$

$$P_{red} + 2\ H^+ + \tfrac{1}{2}O_2 \rightarrow P + H_2O \tag{5}$$

net reaction from eqs 1, 2, and 5:

$$SH_2 + \tfrac{1}{2}O_3 + h\nu \xrightarrow{P} S + H_2O \tag{6}$$

$$P_{red} + SH_2 \rightarrow P + SH_2 \text{ redn products} \tag{7}$$

of the detailed features of these processes are now fairly well understood[1,2] (P = oxidized resting state of polyoxometalate catalyst; P_{red} = reduced form of catalyst; SH_2 = organic substrate = alcohols, amides, ethers, hydrocarbons, others; and S = oxidized organic product). Equations 1-6 do not necessarily represent elementary processes, and in general, they do not imply mechanism as written. One logical extension of this chemistry involves reoxidation of the photogenerated reduced polyoxometalates, P_{red} in eqs 2, 3, or 5, by a useful substrate reduction process (eq 7). Such catalytic cycles involving both direct oxidation and reduction of substrate by distinct redox forms of the catalyst are rare.[7] We report here a prototypic process combining photooxidation of substrate by the oxidized form of a catalyst with thermal reduction of the substrate by the resulting reduced form of the catalyst. The

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(7) Coupled oxidation and reduction cycles in metal-mediated oxidations of organic substrates by sacrificial or terminal oxidants are well-known, including the metal-mediated Haber-Weiss radical-chain decomposition of the initial alkyl hydroperoxides in hydrocarbon autoxidation. In these cases, however, attack by the redox catalyst directly on the substrate is not seen. Rather, direct attack by the catalyst on the oxidant is observed. See, for example: Sheldon, R. A.; Kochi, J. K. *Metal-Catalyzed Oxidations of Organic Compounds*; Academic Press: New York, 1981.

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catalyst in this case is the isopolytungstate $W_{10}O_{32}^{4-}$, and the substrates are thioethers (organic sulfides). The development of facile methods for the modification or degradation of toxic thioethers remains an important goal.[8] This study examines several reactions involving photooxidation of thioethers by various polyoxotungstates and establishes the presence of products and multiple processes in these thioether photooxidation/thermal reduction processes that are highly unusual given the extensive literature on oxidation or reduction of these organic compounds by other reagents and methods.[9-11] These experiments confirm the multiple roles played by the redox catalyst, $W_{10}O_{32}^{4-}$

Experimental Section

Materials. The solvents were obtained, purified, and manipulated as described earlier.[1,2d] The thioether substrates tetrahydrothiophene (THT), 2-chloroethyl ethyl sulfide (half mustard), diphenyl sulfide, methyl phenyl sulfide, dimethyl sulfide, and butyl sulfide were all Aldrich reagent grade and were used without further purification. Bis(chloromethyl) sulfide (BCMS) was obtained from TCI and was used without further purification. The sulfoxide and sulfone of 2-chloroethyl ethyl sulfide were prepared by *tert*-butylhydroperoxide oxidation catalyzed by $H_5PV_2Mo_{10}O_{40}$.[12] The sulfoxides and sulfones derived from the other thioether substrates were obtained from Aldrich, except for methyl phenyl sulfone (Fluka), diphenyl sulfoxide (Eastman Kodak), diphenyl sulfone (Eastman Kodak), and dimethyl sulfoxide (Fisher). Benzenethiol (Aldrich), diphenyl disulfide (Aldrich), and benzene (Burdick and Jackson) were used without further purification. Pivalonitrile (Lancaster) was used as an internal standard in all reactions. The polyoxometalate complexes α-$H_3PW_{12}O_{40}$,[13] $Q_3PW_{12}O_{40}$,[13] $Q_4W_{10}O_{32}$,[14] and $Na_4W_{10}O_{32}$[1e] (where Q = $(n\text{-}C_4H_9)_4N^+$) were prepared and purified by use of literature procedures. Zero-grade oxygen (parts per million impurities of H_2O, CO_2, and hydrocarbons) and argon were both obtained from Linde Corp. ^1H NMR samples were run in $CDCl_3$ (Aldrich); chemical shifts reported relative to TMS.

Methods. In a typical reaction, 5.0 mL of an acetonitrile solution (10 mM in thioether, 0.2 mM in polyoxometalate, and 9 mM in internal standard) was placed in a 30-mL Pyrex Schlenk flask fitted with a Teflon stopper. After thorough degassing, the irradiation was begun with either a 550-W medium-pressure Hg lamp (for reactions >10 h) or a 1000-W ozone-free Xe arc lamp (for reactions <10 h). During irradiation, the reactions were vigorously stirred with a Teflon-covered stir bar and maintained at a constant temperature of 20 °C with a thermostated circulating water bath. Anaerobic reactions were maintained under ~1 atm of Ar. Aerobic reactions were conducted by adding 20 cm^{-3} of O_2 (zero grade) (800 equiv relative to polyoxometalate) to the flask prior to irradiation.

Product analyses were conducted with a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector and a 25 m × 0.2 mm 5% phenyl methyl silicone capillary column. Nitrogen was used as the carrier gas, and products were recorded on a Hewlett-Packard 3390A integrator. Products were identified and quantified by coinjection with authentic samples. ^1H NMR samples were prepared in 5 mm × 4.2 mm (i.d.) tubes (Wilmad) and analyzed on a QE-300 instrument from General Electric.

Separation of organic products was carried out by HPLC. A Rainin instrument equipped with a HP/HPX drive module, a 5-mL Rainin Rabbit pump head, a Waters μ-Porasil analytical column (3.9 mm i.d. × 30 cm), and a Knauer Model 87 variable-wavelength detector was used. Separatations were performed isocratically with pentane by use of a 200-μL sample-injection loop.

Kinetic Measurements of Reduced Decatungstate and BCMS. Kinetic experiments involving $Q_4W_{10}O_{32}$ and BCMS in CH_3CN were carried out with a 2.0-mm path length quartz cylindrical Schlenk cuvette. The techniques for anaerobic sample preparation were the same as those described previously. The kinetics measurements involved monitoring the initial rate of formation of the two-electron-reduced species, $W_{10}O_{32}^{6-}$ (λ_{max} = 630 nm; ϵ = 12 500 cm^{-1} M^{-1} in CH_3CN),[1d] in the absorption spectrum. A microprocessor-controlled Hewlett-Packard 8451A multidiode array UV–visible instrument was used in these experiments. The rate dependence on light intensity was determined by use of neutral-density filters to decrease irradiance intensity. In several thioether photooxidation reactions, substantial quantities of the reduced decatungstate species were generated by photooxidation of the CH_3CN solvent. Solvent oxidation was much less pronounced for the reactions containing $Q_4W_{10}O_{32}$ than for those containing $Na_4W_{10}O_{32}$. All rate data were corrected for background solvent photooxidation processes.

The rate of reduced decatungstate reoxidation by diphenyl sulfide was monitored by the loss of the reduced complex with absorption spectroscopy (decay of the distinctive absorption maxima at 630 nm of the $W_{10}O_{32}^{6-}$ reactant) and by the generation of C–S organic cleavage products with gas chromatography (GC). These reduced polyoxometalate reoxidations by aryl thioethers are more than 1 order of magnitude slower than the photooxidation process generating the reduced polyoxometalates; thus, the former processes interfere minimally with kinetics measurements on the latter processes. Reoxidation of reduced polyoxometalates by some aliphatic thioethers such as THT is no faster than reoxidation by H_2 evolution and does not interfere with the kinetics whatsoever.

Preparation and Characterization of 1,2-Bis(methylthio)ethane (1). Reactions containing 25 mM $Q_4W_{10}O_{32}$ and 100 mM dimethyl sulfide in 25 mL of acetonitrile were prepared anaerobically and irradiated with the 550-W Hg vapor lamp for ~60 h as described previously. The products of four such reactions were combined and condensed to ~2 mL by passing N_2 over the solution. The organic products were then extracted into pentane and condensed to ~1 mL. Analysis of the reaction mixture before and after every step by GC showed that at all times only one major product (~90% of total products) was present and that this product was not lost as a result of evaporation or other processes. Analysis of the pentane solution indicated that unreacted dimethyl sulfide was almost completely removed during the condensation steps. The residue after removal of the pentane was dissolved in $CDCl_3$. ^1H NMR (300 MHz, $CDCl_3$) δ 2.147 (s, 6 H), 2.723 (s, 4 H); ^{13}C NMR (75.480 MHz, $CDCl_3$) δ 15.54, 33.76. Product peak assignment was made by comparison with dimethyl sulfide and 1,4-dithiacyclohexane. Dimethyl sulfide: ^1H NMR (300 MHz, $CDCl_3$) δ 2.119 (s); ^{13}C NMR (75.480 MHz, $CDCl_3$) δ 18.01. 1,4-Dithiacyclohexane: ^1H (300 MHz, $CDCl_3$) δ 2.899 (s); ^{13}C NMR (75.480 MHz, $CDCl_3$) δ 29.16. Mass spectral analysis: *m/z* 122 (100), 75 (48.6), 61 (98.7). Identification was based on fragmentation patterns and abundances of M + 2 peaks.

Preparation and Characterization of 1,1-Bis(chloromethylthio)methane (2). Reactions containing 25 mM $Q_4W_{10}O_{32}$ and 100 mM BCMS in 25 mL of acetonitrile were prepared anaerobically and irradiated with the 550-W Hg vapor lamp for ~60 h as described previously. The products of four such reactions were combined and condensed to ~2 mL by passing N_2 over the solution. The organic products were extracted into pentane, and the resulting solution was condensed to ~1 mL. Analysis of the reaction mixture before and after every step by GC showed that at all times no products were lost as a result of evaporation or other processes. Only one major product (~85% of total products) was present.

Separation of the pentane solution and isolation of the major product was carried out by HPLC (UV-vis detector set at λ = 240 nm). Only one product peak was observed. The product fraction was stripped down by evaporation as described previously and the residue dissolved in $CDCl_3$. Analysis of the product fraction before and after evaporation by GC indicated a purity ~95%. NMR analysis: ^1H NMR (300 MHz, $CDCl_3$) δ 4.091 (s, 2 H), 4.814 (s, 4 H); ^{13}C NMR (75.480 MHz, $CDCl_3$) δ 32.59, 46.671. Product peak assignment was made by comparison with BCMS and 1,3-dithiacyclohexane. BCMS: ^1H NMR (300 MHz, $CDCl_3$) δ 4.875 (s); ^{13}C NMR (75.480 MHz, $CDCl_3$) δ 45.75. 1,3-Dithiacyclohexane: ^1H NMR (300 MHz, $CDCl_3$) δ 2.078 (quintet, *J* = 5, 2 H), 2.830 (t, *J* = 5.5, 4 H), 3.784 (s, 2 H); ^{13}C NMR (75.480

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Table I. Anaerobic Oxidation of Thioethers by Polyoxometalates[a]

reaction	thioether (mM)	polyoxometalate (mM)	time (h)	% dec R_2S[b]
1	THT (10)	$Na_4W_{10}O_{32}$ (0.2)	14	30
2	THT (25)	$Na_4W_{10}O_{32}$ (0.4)	16	51
3	THT (25)	$Q_4W_{10}O_{32}$ (0.4)	16	35
4	PhSPh (10)	$Na_4W_{10}O_{32}$ (0.2)	14	44
5	$EtS(CH_2)_2Cl$ (10)	$Na_4W_{10}O_{32}$ (0.2)	14	66
6	$PhSCH_3$ (10)	$Na_4W_{10}O_{32}$ (0.2)	14	46
7	BuSBu (10)	$Na_4W_{10}O_{32}$ (0.2)	14	42

[a] Reactions were run in 5 mL of CH_3CN in 30-mL Schlenk flasks. Reactions were irradiated with a 550-W Hg vapor lamp (see Experimental Section). [b] $(1 - [R_2S]_t/[R_2S]_0) \times 100$, where $[R_2S]_t$ = quantity of thioether at elapsed time of reaction indicated.

MHz, $CDCl_3$) δ 26.59, 29.93, 31.96. Mass spectral analysis: m/z 176 (37.0), 95 (100). Identification was based on fragmentation patterns and abundances of M + 2 peaks.

Results

The photooxidation of thioethers by polyoxotungstates was carried out under both anaerobic and aerobic conditions. Reactions conducted under anaerobic conditions facilitated detailed product distribution and kinetics studies and established the unusual products and roles of the polyoxotungstate catalyst, $W_{10}O_{32}^{4-}$, in these reactions. The reactions conducted under aerobic conditions defined the potential scope and utility of polyoxometalate-catalyzed oxidative functionalization and/or degradatiion of thioethers.

Anaerobic Oxidation of Thioethers. Irradiation of acetonitrile solutions of thioethers and polyoxotungstates under an inert atmosphere results in oxidative degradation of the thioether (Table 1). The reactions catalyzed by $W_{10}O_{32}^{4-}$ were chosen for close experimental scrutiny for two reasons: they are faster than the corresponding reactions containing α-$H_3PW_{12}O_{40}$, and the chromophores of both the oxidized and reduced forms of the former complex are more amenable to spectral monitoring than those of the latter. The decatungstate-derived products in these reactions were the one- and two-electron-reduced complexes, $W_{10}O_{32}^{5-}$ and $W_{10}O_{32}^{6-}$, formed in a ~1:4 mole ratio, respectively. $W_{10}O_{32}^{5-}$ was reduced to $W_{10}O_{32}^{6-}$ under the reaction conditions. The rate of reoxidation of both $W_{10}O_{32}^{5-}$ and $W_{10}O_{32}^{6-}$ by hydrogen evolution (eq 3) was more than 2 orders of magnitude slower than the rate of their production (eqs 1 and 2). Unlike nearly all thioether oxidations by oxometal species,[9] no oxygenated organic products (i.e., sulfoxide or sulfone) were detected in any of these anaerobic processes despite the presence of reduced oxygen in the form of a few equivalents of water likely present and the oxo groups of the complex $W_{10}O_{32}^{4-}$ itself.[15] The product distributions depend on the thioether substrate to some extent, but in most cases products of C–S bond cleavage were observed. In the case of diphenyl sulfide, the major identifiable product was thiophenol. A small amount of diphenyl disulfide was also observed. The thiol and disulfide collectively accounted for ~60% of the thioether consumed. The disulfide is quite unstable under the reaction conditions and goes on to form thiol. The ultimate yield of benzene is ~95% based on the consumed thioether defining a fairly efficient overall thioether desulfurization process. Irradiation of $W_{10}O_{32}^{4-}$ in the presence of thioanisole yields thiophenol as the major product.

Inasmuch as C–S bond cleavage is well documented to be the principal mode of photochemical decomposition of thioethers in the absence of other photochemically active species,[16] we sought to determine to what extent this process might be occurring in polyoxotungstate-based anaerobic oxidative thioether degradation reactions. The direct formation of n,π* or π,π* thioether excited states in the polyoxotungstate-containing reactions is unlikely on the basis of the relative absorbances of the thioether and the $W_{10}O_{32}^{4-}$ under the reaction conditions (1 and 99%, respectively). This was confirmed experimentally when even direct irradiation of an exemplary aliphatic thioether, tetrahydrothiophene (THT), over a period of 16 h with the same experimental apparatus produced no detectable chemistry, while the most strongly absorbing aryl thioether, diphenyl sulfide, produced only small quantities of products.[17]

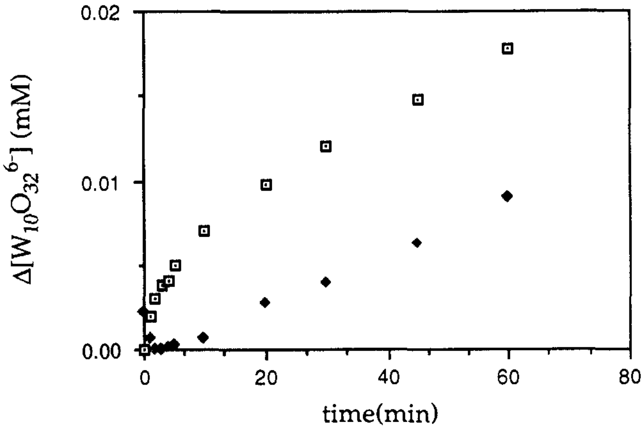

Figure 1. Rate of reoxidation of $W_{10}O_{32}^{6-}$ with (□) and without (◆) 21.5 mM diphenyl sulfide added to the reaction. The y axis represents $[W_{10}O_{32}^{6-}]_{init} - [W_{10}O_{32}^{6-}]_t$ where the latter term is the absorbance of this species at time t. $[W_{10}O_{32}^{6-}] = 6.0 \times 10^{-5}$ M in acetonitrile; T = 25 ± 2 °C.

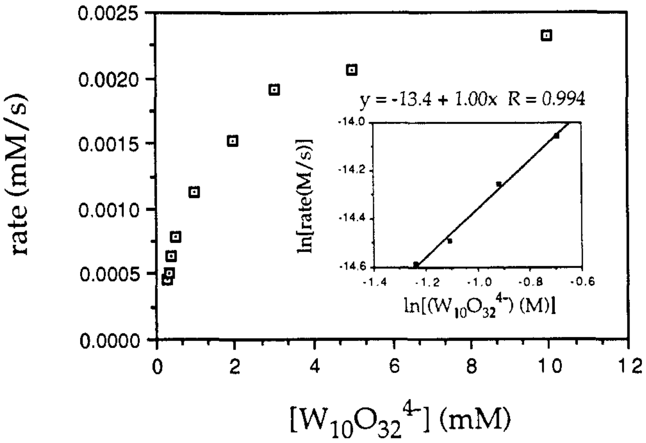

Figure 2. Dependence of the initial rate of BCMS photooxidation by $W_{10}O_{32}^{4-}$ on the concentration of $W_{10}O_{32}^{4-}$. Rate determined by the initial-rate method as a function of $[W_{10}O_{32}^{4-}]$. Inset: ln–ln plot in the low-concentration and optically dilute regime; equation just above figure is a least-squares equation approximating the data. [BCMS] = 0.1 M; T = 25 ± 2 °C; 3.0 mL of solution in a 2.0-cm cylindrical quartz Schlenk cuvette was irradiated under an inert atmosphere (see Experimental Section).

Since carbon–sulfur bond cleavage is a dominant mode of reaction exhibited by thioethers upon reduction by a variety of agents,[9,18] we examined the reactions of thioethers in the presence of the fully reduced dectungstate, $W_{10}O_{32}^{6-}$. Diaryl thioethers such as diphenyl sulfide were reduced thermally at slow rates by

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[15] Although there is no experimental precedence for oxo transfer from a d^0 polyoxometalate to an organic substrate, such as two-electron process is possible with some substrates in principle.

[16] Review (photochemical C–S bond cleavage): Von Sonntag, C.; Schuchmann, H.-P. In *The Chemistry of Ethers, Crown Ethers, Hydroxyl Groups and Their Sulphur Analogues*; Patai, S., Ed.; Wiley: New York, 1980, Part 2, Chapter 22. The excited states of some transition-metal complexes such as $Pt_2(P_2O_5H_2)_4^{2-}$ can reductively cleave C–S bonds: Che, C.-M.; Kwong, H.-L.; Cho, K.-C. *Inorg. Chem.* **1988**, *27*, 3692.

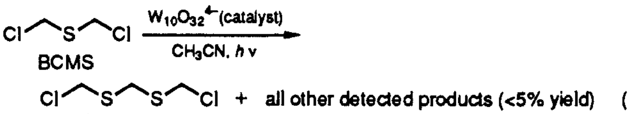
[17] More likely, but still unlikely given the minimally overlapping chromophores of the diphenyl sulfide absorption and $W_{10}O_{32}^{4-}$ emission and the energies of the pertinent excited states, would be indirect production of the diphenyl sulfide excited states photosensitized by the complex.

[18] (a) Takahashi, T.; Hashiguchi, S.; Kasuga, K.; Tsuji, J. *J. Am. Chem. Soc.* **1978**, *100*, 7424. (b) Harison, C. R.: Hodge, P. *J. Chem. Soc., Perkin Trans. 1* **1976**, 1772. (c) Chan, M.-C.; Cheng, K.-M.; Li, M. K.; Luh, T.-Y. *J. Chem. Soc., Chem. Comm.* **1985**, 1610. (d) Brown, H. C.; Weissman, P. M.; Yoon, N. M. *J. Am. Chem. Soc.* **1966**, *88*, 1458. (e) Gassman, P. G.; Drewes, H. R. *J. Am. Chem. Soc.* **1978**, *100*, 7600.

this complex. There is a substantial increase in the rate of reoxidation of $W_{10}O_{32}^{6-}$ over the background reoxidation rate associated with hydrogen evolution when this thioether is added to the reaction containing this reduced complex (Figure 1).

Examination of product distributions generated upon oxidation of other substrates with more informative products than those generated by diphenyl sulfide, namely those generated from dimethyl sulfide and bis(chloromethyl) sulfide (BCMS), indicated that processes other than those involving the thioether excited states were operable. Photochemical oxidation of dimethyl sulfide by $W_{10}O_{32}^{4-}$ under anaerobic conditions led to a most unusual result. The principal product, representing ~90% of the total organic products, was 1,2-bis(methylthio)ethane (**1**), the product resulting from the coupling of two of the parent moieties at the methyl carbon atoms (eq 8). Mass spectral analysis of the reaction mixture also indicated two products with m/z 182 (M^+) and fragmentation patterns that corresponded to further C–C bond formation. Complete identification of these subsequent products was not attempted. Photochemical oxidation of BCMS under the same conditions generated 1,1-bis(chloromethylthio)methane (**2**), a product implicating C–S bond cleavage, as by far the major product, eq 9.

(8)



(9)

The different reactivity of the Na^+ versus the $(n\text{-}C_4H_9)_4N^+$ (Q) salts of decatungstate is noteworthy given the likelihood that both salts are quite dissociated in the acetonitrile solvent. The origin for this difference is not yet apparent. Clearly, the rates are different in part because the Q cation itself is photooxidized, producing reduced polyoxometalate. More significantly, however, the intermediates (including radicals) in this process could interfere with the fundamental photochemistry by acting as scavengers of key intermediates in the main reaction or possibly affecting the excited state.

With knowledge of the stability of the reduced decatungstate complexes and various oxidized thioether-derived products in hand, we could examine in some detail the rate behavior of an exemplary anaerobic system, the photooxidation of BCMS by $W_{10}O_{32}^{4-}$ in acetonitrile solution at 25 °C. For this system it was established that the rate of reoxidation of the reduced polyoxometalate species monitored in the rate studies ($W_{10}O_{32}^{6-}$) by this particular substrate (BCMS) was sufficiently slower (at least 2 orders of magnitude) than the rate of the forward reaction that the former did not interfere with rate measurements on the latter. Under optically dilute conditions, this reaction proved to be first order in $W_{10}O_{32}^{4-}$ and approximately first order in light intensity (Figures 2 and 3, respectively). The order of the reaction with respect to BCMS substrate was difficult to quantify, as the rate of background oxidation of acetonitrile was a problem in the low-concentration regime; this background reaction accounted for 50% of the production of $W_{10}O_{32}^{6-}$ when [BCMS] < 25 mM. At high [BCMS], the reaction became zero order in [BCMS].

Control reactions established that neither sulfoxide nor sulfone is highly reactive toward the excited state of $W_{10}O_{32}^{4-}$. No detectable $W_{10}O_{32}^{6-}$ is generated when sulfide is replaced by either sulfoxide or sulfone under the usual photochemical reaction conditions (see the Experimental Section or Table I).[19] Both the sulfoxide and sulfone derived from THT proved to be, at a minimum, 2 orders of magnitude less reactive than this thioether. The major role of sulfoxide appears to be that of a quencher of the photoredox-active excited states of the polyoxotungstate. The presence of a typical sulfoxide, DMSO, decreased the net quantum efficiencies for the photooxidation of an exemplary thioether (BCMS) and photoreduction of $W_{10}O_{32}^{4-}$. A Stern–Volmer analysis (Figure 4) yielded a value for the $k_q\tau$ of 9.4 M^{-1}, where k_q is the bimolecular rate constant for quenching of the excited state and τ is the lifetime of the excited state. For this plot, I and I_0 are for $W_{10}O_{32}^{6-}$. This plot holds for the case where $k[R_2S] \ll \sum k_d$, where k = the rate of substrate oxidation by the excited state and $\sum k_d$ = sum of the rates of all the excited-state decay processes (see Discussion). Under these conditions the Stern–Volmer equation simplifies to $I_0/I = 1 + k_q/\sum k_d = 1 + k_q\tau[Q]$, where the quencher, Q, is DMSO. If we estimate the value of τ to be 20 ps, then an approximate value for k_q is 5×10^{11} M^{-1} s^{-1}.[20]

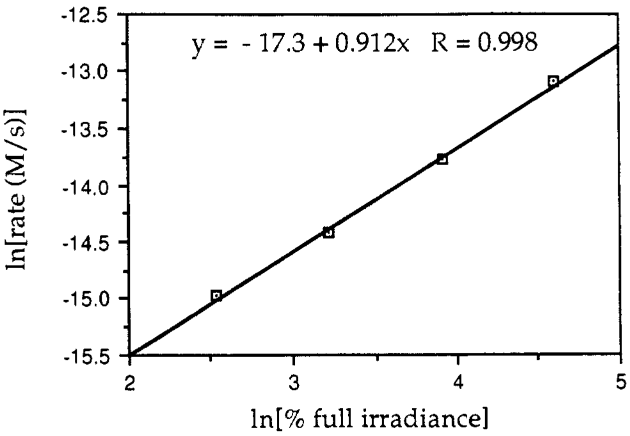


Figure 3. Dependence of the initial rate of BCMS photooxidation by $W_{10}O_{32}^{4-}$ on light intensity (percent full irradiance of light source). Values obtained at 630 nm under optically dense conditions ($[W_{10}O_{32}^{4-}]$ = 5 mM; [BCMS] = 0.1 M; T = 25 ± 2 °C) by use of UV neutral-density transmittance filters (50%, 25.1%, 12.6%). 3.0 mL of solution in a 2.0-cm cylindrical quartz Schlenk cuvette was irradiated under an inert atmosphere (see Experimental Section).

Aerobic Oxidation of Thioethers. The photochemical oxidative degradation of six representative thioethers, THT, 2-chloroethyl ethyl sulfide, methyl phenyl sulfide, diphenyl sulfide, dibutyl sulfide, and dimethyl sulfide, by the exemplary heteropolytungstate $\alpha\text{-}H_3PW_{12}O_{40}$ or the isopolytungstate decatungstate, $W_{10}O_{32}^{4-}$, in the presence of 1 atm of air was examined in aqueous and in acetonitrile media. Some oxidative degradation was seen in all reactions examined. The oxidation of thioethers takes place readily in water, the medium most likely to be used in decontamination, as well as in acetonitrile. Oxidative degradation proceeds readily in aqueous media even when the thioethers are immiscible. Inasmuch as product distribution and other studies could be readily carried out in acetonitrile, this solvent was used in all subsequent experiments. Representative reactions conducted in acetonitrile are summarized in Table II.

All thioethers examined with the exception of diphenyl sulfide were quantitatively oxidized to other products by $W_{10}O_{32}^{4-}$ after

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[19] (a) Hill, C. L.; Bouchard, D. A. *J. Am. Chem. Soc.* **1985**, *107*, 5148. (b) Combs, L. A.; Cassidy, B. Unpublished results.

[20] The lifetime of the weakly emissive excited state of $W_{10}O_{32}^{4-*}$ in solution generated upon excitation by a frequency-tripled YAG laser system (355 nm) has been measured in two different laboratories to be approximately 21 ps (Kozik, M.; Winkler, J.; Hilinski, E. F.; Tate, K.; Duncan, D.; Hill, C. L. Unpublished work). However, the only solvents that are compatible with all the photochemistry here, water and acetonitrile, quench the excited state. A quantitative comparison between the value for diffusion-limited processes in these solutions under these conditions ($k_{diff} \sim 1 \times 10^{10}$ M^{-1} s^{-1}) and the calculated value of k_q from the Stern–Volmer plot ($k_q \sim 5 \times 10^{11}$ M^{-1} s^{-1}) cannot be made. In addition to the large uncertainty in the value of τ and hence k_q, there is some error in the experimental determination of the values for both rate constants, k_{diff} and k_q, under these conditions. Although we feel that it is unlikely, it is possible that these values (k_{diff} and k_q) may be within experimental error of each other. If k_q proves to be larger than k_{diff} when the value of τ and other variables are better known, then the quenching and likely the principal photoredox processes and internal conversion of the polyoxotungstate excited state take place within a solvent pair that behaves like a single entity kinetically.

Table II. Polyoxometalate-Initiated Aerobic Oxidation of Thioethers[a]

reaction	thioether (mM)	initiator (mM)	time (h)	product yields[b] % R_2SO	product yields[b] % R_2SO_2	% dec R_2S[c]
1	THT (10)	$Na_4W_{10}O_{32}$ (0.2)	14	(0) [0]	(3.7) [27]	100
2	THT (25)	$Na_4W_{10}O_{32}$ (0.4)	16	(0) [0]	(4.5) [11]	100
3	THT (10)	$Na_4W_{10}O_{32}$ (0.4)	1	(0.3) [3.0]	(0.6) [6.1]	>95
4	THT (10)	$Na_4W_{10}O_{32}$ (0.4)	0.5	(4.3) [15]	(0) [0]	54
5	THT (25)	$Q_4W_{10}O_{32}$ (0.4)	16	(0) [0]	(3.0) [12]	~50
6	THT (25)	$H_3PW_{12}O_{40}$ (0.4)	16	(7.5) [29]	(1.1) [4.6]	55
7	PhSPh (10)	$Na_4W_{10}O_{32}$ (0.4)	14	(6.1) [55]	(0.84) [7.5]	62
8	$EtS(CH_2)_2Cl$ (10)	$Na_4W_{10}O_{32}$ (0.4)	14	(0) [0]	(~2.5) [~23]	100
9	$PhSCH_3$ (10)	$Na_4W_{10}O_{32}$ (0.4)	14	(0) [0]	(4.2) [41]	100
10	BuSBu (10)	$Na_4W_{10}O_{32}$ (0.4)	14	(0) [0]	(0) [0]	100
11	MeSMe (11)	$Q_4W_{10}O_{32}$ (0.4)	16	(0) [0]	(6.1) [56]	*d*

[a] Reactions were run in 5 mL of CH_3CN in 30-mL Schlenk flasks. Reactions were irradiated with a 550-W Hg vapor lamp (see Experimental Section). Reactions 3 and 4 irradiated with 1000-W Xe lamp. [b] Product yields reported as concentration (mM) of product and conversion [%] based on initial substrate concentration. [c] $(1 - [R_2S]_t/[R_2S]_0) \times 100$, where $[R_2S]_t$ = quantity of thioether at elapsed time of reaction indicated. [d] Me_2S percent conversion not quantifiable by gas chromatography analysis.

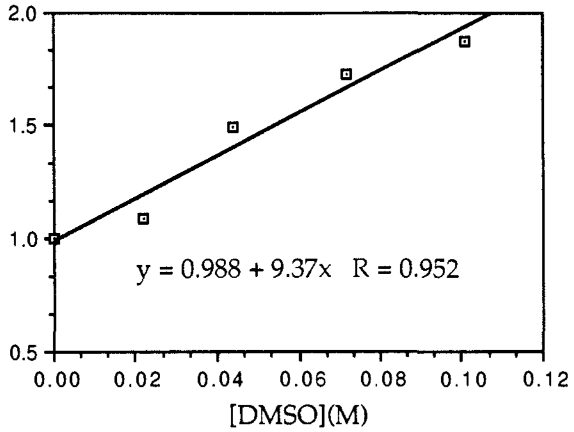

Figure 4. Stern–Volmer plot of the quenching of BCMS photooxidation by $W_{10}O_{32}^{4-}$ by an exemplary sulfoxide, dimethyl sulfoxide (DMSO), under optically dense conditions ($[W_{10}O_{32}^{4-}]$ = 5 mM; [BCMS] = 0.1 M; $T = 25 \pm 2$ °C). I and I_0 are for $W_{10}O_{32}^{6-}$. This plot holds for the case where $k[R_2S] \ll k_{rd}$ (see text).

an irradiation time of 16 h. Products resulting from desulfurization of the substrate were not detected by GC. This is in dramatic contrast to the related reactions run under anaerobic conditions, which in some cases generate sulfur-free organic products in nearly quantitative yield on the basis of the substrate thioether consumed (vide supra). The selectivity for production of any one product in these aerobic reactions is not high. Sulfoxide, a predominant initial product, is consumed rapidly under the reaction conditions producing sulfone and other products. Only in the case of diphenyl sulfide did the amount of detected oxidized product match the amount of reacted substrate. Diphenyl sulfoxide accounted for 89% of the organic products.

The isopolytungstate $W_{10}O_{32}^{4-}$ is substantially more reactive than the heteropolytungstate α-$H_3PW_{12}O_{40}$. This result parallels those from studies in which these and other polyoxometalates were used as initiators for radical-chain autoxidation of hydrocarbons[1c] and unrelated studies where these complexes were used as catalysts for the anaerobic photochemical dehydrogenation of alkane substrates.[1a,b,d] The quantum yields for polyoxometalate reduction and thioether oxidation are higher for $W_{10}O_{32}^{4-}$ than for α-$H_3PW_{12}O_{40}$ (typically 0.2 versus 0.1 throughout the low-energy d^0 charge-transfer absorption envelope of these species, $\lambda > 280$ nm), and the former complex absorbs substantially more light.[1c,10,14] The isopolytungstate $W_{10}O_{32}^{4-}$ has a $\lambda_{max} = 324 \pm 2$ nm (ϵ = 13 000 M^{-1} cm^{-1}), while the heteropolytungstate α-$PW_{12}O_{40}^{3-}$ absorbs considerably less than that at this wavelength and generally less throughout the region transparent to the Pyrex reaction vessels used in these experiments ($\lambda > 280$ nm cutoff). The reactivity of $W_{10}O_{32}^{4-*}$ not only for the thioether substrates but also for the acetonitrile solvent is dependent on the cation. The sodium salt of the complex is more reactive than the tetra-*n*-butylammonium salt.

The reactions are catalytic in polyoxotungstate. The reduced polyoxotungstates are reoxidized readily by the O_2 present under the reaction conditions. The rates of reoxidation of the reduced complexes (eq 5) are faster than the rates of their generation (eqs 1 and 2); thus, the blue color of the reduced complexes is not observable under conditions of steady-state photolysis. For all the catalytic aerobic thioether oxidative degradations, including th reactions summarized in Table II, control reactions without either polyoxometalate or light showed negligible degradation of the thioethers. Small amounts of sulfoxide (THTO) and sulfone ($THTO_2$) were observed when THT was photooxidzed in the absence of polyoxotungstate for times longer (4 h) than those used in the polyoxometalate-containing reactions, however.

Inasmuch as the thioether-derived oxidation products are not stable under the reaction conditions and a number of sumultaneously operating substrate-oxidizing species are likely present during these aerobic reactions including organoperoxy radicals and other chain-propagating intermediates in autoxidation, we were not surprised to find that rate measurements under aerobic conditions proved to be marginally reproducible and indicated very complicated kinetic behavior.

Discussion

Photoredox-active isopoly- and heteropolytungstates catalyze the oxidation of thioethers, R_2S, under both aerobic and anaerobic conditions upon irradiation with near-UV light. The photochemical anaerobic oxidation of thioethers catalyzed by decatungstate, $W_{10}O_{32}^{4-}$, generates dimers, $(R_2S[-H])_2$, resulting from coupling of thioether α-carbon radicals, $R_2S[-H]^\bullet$; thiols, RSH, resulting from C–S bond cleavage; and hydrocarbons, RH. A minimal mechanism that explains these products and the observed rate behavior is summarized in eqs 10–19. Production of the

$$W_{10}O_{32}^{4-} + h\nu \xrightarrow{\phi I} W_{10}O_{32}^{4-*} \tag{10}$$

$$W_{10}O_{32}^{4-*} \xrightarrow{k_{rd}} W_{10}O_{32}^{4-} \tag{11}$$

$$W_{10}O_{32}^{4-*} + R_2S \xrightarrow[\text{r.d.s.}]{k} W_{10}O_{32}^{5-} + R_2S[-H]^\bullet + H^+ \tag{12}$$

$$2R_2S[-H]^\bullet \rightarrow (R_2S[-H])_2 \tag{13}$$

$$2W_{10}O_{32}^{5-} \rightarrow W_{10}O_{32}^{4-} + W_{10}O_{32}^{6-} \tag{14}$$

$$W_{10}O_{32}^{6-} + R_2S \rightarrow W_{10}O_{32}^{5-} + R_2S^{\bullet-} \tag{15}$$

$$R_2S^{\bullet-} \rightarrow RS^- + R^\bullet \tag{16}$$

$$R^\bullet + RSH \rightarrow RH + RS^\bullet \tag{17}$$

$$RS^- + W_{10}O_{32}^{4-} \rightarrow RS^\bullet + W_{10}O_{32}^{5-} \tag{18}$$

$$2RS^\bullet \rightarrow RSSR \tag{19}$$

charge-transfer excited state that is kinetically competent to oxidize substrate thioether (eq 10) is a one-photon process based on the rate data. ϕ is the quantum efficiency for production of this state, and I is the rate of light absorption by $W_{10}O_{32}^{4-}$. The predominant role of substrate attack probably involves generation of the thioether α-carbon radical (eq 12) rather than electron transfer to form the thioether cation radical. The principal products observed are those that would result from radical coupling at these carbon atoms (eq 13). It is hard to rationalize formation of this type of product by the documented mechanisms of thioether oxidation in other systems, and to the best of our knowledge this type of coupling product has never been reported as the dominant species produced in any thioether oxidation process. Although deprotonation of thioether cation radicals to generate thioether α-carbon radicals has been proposed in both anodic electrooxidation[21] and chemical oxidation[9,22] of thioethers, radical coupling products are not seen in these literature reports, as subsequent oxidation or other reactions of the intermediate radicals are faster than bimolecular radical coupling. The rates of radical oxidation by polyoxotungstates can range from nearly diffusion limited to substantially less than this; oxidation of radicals by $W_{10}O_{32}^{4-}$ in these reactions is probably slow.[1d,e,23-25]

The principal argument against electron transfer to generate the thioether cation radical being the *dominant* substrate activation process in the overall mechanism is that thioether cation radicals in the presence of some water are known to undergo nucleophilic addition to form sulfoxide.[10] As stated in the Results, however, we see no oxygenated products, including sulfoxide, when the anaerobic thioether oxidation reactions are run in the presence of some water. We cannot preclude within the limits of the current experimental resolution, of course, that cation radicals are not being formed at all. They may well be involved in minor side processes.

The most likely mode for production of the observed reduction product, the two-electron-reduced complex, $W_{10}O_{32}^{6-}$, is by disproportionation (eq 14). This process is more likely than thermal reduction of $W_{10}O_{32}^{5-}$ by intermediate radicals or by reduction of $W_{10}O_{32}^{5-}{*}$.[1d,26]

The dominant mode of C–S bond cleavage in these reactions is undoubtedly reductive in nature. Unlike thioether cation radicals, sulfonium salts, and probably thioether α-carbon radicals, thioether anion radicals, the most often postulated intermediates in a range of thioether reduction processes, and the likely intermediates in the reactions reported here (eq 15), are documented to decompose principally by C–S bond cleavage (eq 16).[9,21] Furthermore, we have presented experimental evidence that $W_{10}O_{32}^{6-}$ can be directly reoxidized thermally under anaerobic conditions by thioethers and that the thioether products in these reactions are hydrocarbons, RH (eq 17), and thiols, RSH (eq 16).[27] There are protons available from the initial photooxidation reactions (eq 12) to generate thiols from the thiolate anions. The carbon-centered radicals generated in eq 16 should be susceptible to redox processes involving decatungstate species, to atom-transfer quenching (hydrogen abstraction) from thiol intermediates or other organic hydrogen donors, or to coupling. Thiyl rdicals, RS$^{\bullet}$, formed either by hydrogen abstraction from thiols (eq 17) or by oxidation of thiolate anions (eq 18) generated in reductive C–S cleavage (eq 16) couple to produce the observed disulfide products (eq 19). Thiyl radicals generally do not fragment.[28] Fragmentation of a sulfide cation radical has been proposed for a photoassisted TiO_2 reaction; however, no experimental evidence was given to support this claim.[29]

Cleavage of the C–S bond in thioethers to thiols has been accomplished by acid catalysis.[30] This type of reaction most likely proceeds by protonation of the sulfide, which then fragments, generating the thiol. While the protonated forms of some polyoxometalates have very low pK_a values, this type of specific acid catalysis would be minimal with the neutral salt forms of the polyoxotungstates used in the reactions reported here.

Formation of **2** (eq 9) undoubtedly involves C–S bond cleavage. The most likely mechanism for formation of this high-yield product involves coupling of the [(chloromethyl)thio]methyl radical ($^{\bullet}CH_2SCH_2Cl$) with the (chloromethyl)thiyl radical ($^{\bullet}SCH_2Cl$). The presence of both these speices as freely diffusing radicals is defensible. Recently, systems based on photoredox-active polyoxometalates such as decatungstate have been developed that efficiently dehalogenate a range of halocarbons including primary chlorides in solution upon irradiation.[31] The principal reactions operable here involve the generation of substantial quantities of freely diffusing alkyl radical intermediates. Primary alkyl radicals from dechlorination are doubtless generated in eq 9. These could then couple with thiyl radicals that arise by oxidation of the thiolate anion (eqs 15, 16, and 18).

Direct abstraction of hydrogen atoms in thioethers is not unknown.[28] However, almost all reactions involving C–H cleavage in these compounds involve deprotonation and α-carbanion formation. The use of α-metalated (prinicpally lithiated) thioethers remains a synthetically useful tool for C–C bond formation. The relative reactivities of C–H bonds α to various functional groups toward radicals have been examined. The α-C–H bonds in thioethers are typically 6 times as reactive toward the phenyl radical as the corresponding C–H bonds in alkanes and roughly twice as reactive as those in the related ethers.[28,32] Abstraction rates for the hydrogens on the α-carbons in sulfoxides and sulfones are roughly 20 and 5 times slower, respectively, than those for the corresponding hydrogens in thioethers.[28]

The rate data under anaerobic conditions establish that the substrate-activation process in the mechanism, most likely eq 12 as discussed previously, is rate limiting. A minimal rate law that explains the orders with respect to the reactants and saturation kinetics in R_2S is given in eq 20 (ϕ and I were defined in eq 10

$$\text{rate} = +\mathrm{d}[W_{10}O_{32}^{6-}]/\mathrm{d}t = k\phi I[R_2S]/k[R_2S] + k_{rd} \qquad (20)$$

and in the previous text). Only two processes seriously compete for the excited state: oxidation of the substrate, k, and radiationless decay, k_{rd}. The quantum yields for emission are orders of magnitude lower than those for k or k_{rd}.[20] It is clear from the lack of curvature in the plot of rate versus $[W_{10}O_{32}^{4-}]$ at high $[W_{10}O_{32}^{4-}]$ that radiationless decay is principally first order in $W_{10}O_{32}^{4-}$.

Finally, the addition of O_2 to polyoxotungstate-catalyzed thioether oxidation reactions enhances the oxidative removal of thioether but greatly complicates the chemistry. Both the extensive background autoxidation chemistry of thioethers[11b,c,33] and ex-

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(21) (a) Shono, T. In ref 9, Chapter 8. (b) Cottrell, P. T.; Mann, C. K. *J. Electrochem. Soc.* **1969**, *116*, 1499.

(22) Perhaps the most the up-to-date and thorough discussions of the chemistry of thioether cation radicals can be found in the following: (a) Asmus, K.-D. In *Radioprotectors and Anticarcinogens*; Nygaard, O. F.; Simic, M. G., Eds.; Academic Press: New York, 1983; pp 23–42. (b) Mönig, J.; Goslich, R.; Asmus, K.-D. *Ber. Bunsen-Ges. Phys. Chem.* **1986**, *90*, 115. (c) Asmus, K.-D.; Lal, M.; Mönig, J.; Schöneich, C. In *Oxygen Radicals in Biology and Medicine*; Simic, M. G., Taylor, K. A., Ward, J. F., von Sonntag, C., Eds.; Plenum: New York, 1988, pp 67–73.

(23) (a) Papaconstantinou, E. *J. Chem. Soc., Faraday Trans.* **1982**, *78*, 2769. (b) Lerat, O.; Chauveau, F.; Hickel, B. *New J. Chem.* **1990**, *14*, 37.

(24) Prosser-McCartha, C. M.; Hill, C. L. *J. Am. Chem. Soc.* **1990**, *112*, 3671.

(25) Indirect support for eqs 12 and 13 is that the excited states of some polyoxotungstates not only effect the cleavage of unactivated C–H bonds to form radicals[1] but lead to the activation of C–H bonds in molecules bearing activating functional groups at positions that are remote from the activating groups: Hill, C. L.; Renneke, R. F.; Combs, L. A. *New. J. Chem.* **1989**, *13*, 701.

(26) Yamase, T.; Usami, T. *J. Chem. Soc., Dalton Trans.* **1988**, 183.

(27) Other thioether-derived intermediates have been postulated to exist in various thioether reduction processes including thioether dianions and thiol dianion radicals; however, there appears to be little hard evidence for such species. See: Farnia, G.; Severin, G.; Capobiano, G.; Vianello, E. *J. Chem. Soc., Perkin Trans.* **1978**, *2*, 1.

(28) Block, E. *Reactions of Organosulfur Compounds*; Academic Press: New York, 1978.

(29) Davidson, R. S.; Pratt, J. E. *Tetrahedron Lett.* **1983**, *24*, 5903.

(30) Hiskey, R. G.; Rao, V. R.; Rhoades, W. G. In *Protective Groups in Organic Chemistry*; McOmie, W., Ed.; Plenum: New York, 1973.

(31) (a) Sattari, D.; Hill, C. L. *J. Chem. Soc., Chem. Commun.* **1990**, 634. (b) Sattari, D.; Hill, C. L. Unpublished work.

(32) Russell, G. A. In *Free Radicals*; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 299.

perimental evidence from our laboratory on thioether oxidations establishes this fact. The following points can be made: (1) Although superoxide is undoubtedly generated via reduction of O_2 by $W_{10}O_{32}^{5-}$ or $W_{10}O_{32}^{6-}$,[2] its known rates of reaction with both thioethers and the principal initial product, sulfoxide, are sufficiently low that the latter processes are unlikely to contribute significantly to the chemistry.[34] Disproportionation or capture by electrophiles is a more likely fate of superoxide. (2) Both singlet oxygen, a species known to react with thioethers,[35] and thioether-dioxygen complexes also not likely to play a major role in the chemistry. There is no evidence that polyoxometalates upon excitation with the light used in these studies ($\lambda > 280$ nm) can photosensitize the production of significant quantities of singlet oxygen, and the known absorption spectrum of thioether-dioxygen complexes are such that direct excitation of such species would not compete with the strongly absorbing $W_{10}O_{32}^{4-}$ chromophore. (3) One main role of O_2 in $W_{10}O_{32}^{4-}$-catalyzed oxidative degradation of thioethers under aerobic conditions is doubtless its participation in radical-chain autoxidation at sulfur, a process whose catalysis by metal ions and basic kinetic features have been fairly well investigated.[11b,c]

Conclusions

A unique catalytic redox system is presented that combines reduction of the excited state of the oxidized form of the catalyst by substrate with reoxidation of the resulting reduced form of the catalyst by another molecule of substrate. The catalyst is the isopolytungstate $W_{10}O_{32}^{4-}$, a complex that has fairly negative ground-state redox potentials (-1.3 and -1.8V vs Ag/Ag^+),[1e,14] yet whose oxidized form has a highly oxidized and kinetically competent charge-transfer excited state.

The principal oxidative process involves abstraction of the hydrogens α to the sulfur atoms of the thioether substrates, while the principal reductive process involves reduction of these substrates by the two-electron-reduced form of the catalyst, $W_{10}O_{32}^{6-}$, generating the thioether anion radical. The latter than undergoes principally C-S bond cleavage.

The unusual dual oxidation and reduction processes lead to products almost never seen in reactions of thioethers with stoichiometric oxidants. High yields of dimeric products resulting from coupling at the α-carbon atoms are seen in some systems, while high yields of hydrocarbons from complete desulfurization of the substrates are seen with the aromatic thioethers.

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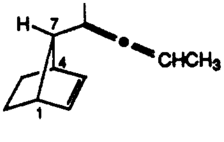
Stereoselective Thermal Rearrangement of *syn*-7-(1,2-Butadienyl)-1-methylbicyclo[2.2.1]hept-2-ene [*syn*-7-(3-Methylallenyl)-1-methylnorbornene][†]

James A. Duncan,* Robert T. Hendricks, and Katy S. Kwong

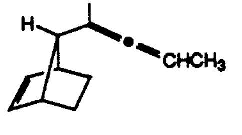
Contribution from the Department of Chemistry, Lewis and Clark College, Portland, Oregon 97219. *Received November 13, 1989. Revised Manuscript Received July 9, 1990*

Abstract: The synthesis and separate thermal rearrangements of (±)-(1*R**,4*S**,7*S**)-7-[(*R**)-1,2-butadienyl]-1-methylbicyclo[2.2.1]hept-2-ene (**8a**) and (±)-(1*R**,4*S**,7*S**)-7-[(*S**)-1,2-butadienyl]-1-methylbicyclo[2.2.1]hept-2-ene (**8b**) are described. Both **8a** and **8b** are shown to rearrange to (±)-*cis*-1-ethylidene-3a,4,5,7a-tetrahydro-6-methylindene (**9**) and (±)-*cis*-1-ethylindene-3a,4,5,7a-tetrahydro-3a-methylindene (**10**) with greater than 90% stereoselectivity. Epimer **8a** gives predominantly (*E*)-**9** and (*Z*)-**10**, whereas **8b** gives predominantly (*Z*)-**9** and (*E*)-**10**, results consistent with either a six-electron [σ2s + π2s + π2s] Cope or eight-electron [σ2s + π2s + (π2s + π2a)] augmented Cope process. Stereochemical assignments (**8a** vs **8b**, (*E*)-**9** vs (*Z*)-**9**, and (*E*)-**10** vs (*Z*)-**10**) are based upon experiments in nuclear Overhauser effect (NOE) difference spectroscopy.

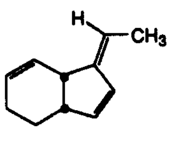
Earlier we reported[1] that (±)-*syn*-7-(1,2-butadienyl)bicyclo[2.2.1]hept-2-ene (**1a**) undergoes a thermal rearrangement above 160 °C to give racemic trienes (*E*)-**2** and (*Z*)-**2** as the only products, whereas the anti epimer **1b** was found to be thermally stable. We contrasted our results with those obtained with similar vinyl compounds,[2] which tend to indicate that thermal reorganization of the 1,5-diene moiety in **1a** by an ordinary orbital symmetry controlled[3] [σ2s + π2s + π2s] concerted boat-like Cope rearrangement process might be sterically retarded. For example, it was reported[2b] that at 250 °C (±)-*syn*-7-ethenyl-*anti*-7-methoxynorbornane (**3a**) and its anti, syn epimer **3b** rearrange to the same formal Cope product, 1-methoxy-3a,6,7,7a-tetrahydroindene (**4**). 2-Methoxybicyclo[3.2.2]nona-2,6-diene (**5**), a formal [1,3] sigmatropic shift product, was also formed in each case. These results were interpreted in terms of biradical processes initiated by the cleavage of the 1,7-bond in **3a** or **3b**. The methoxy substituents, which are known to stabilize radical centers, undoubtably play a role in favoring the biradical process in these cases. In fact



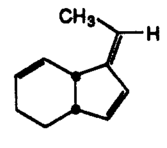
1a



1b



(*E*)-**2**



(*Z*)-**2**

[†] Taken in part from the 1986 Undergraduate Thesis of R.T.H. and the 1987 Undergraduate Thesis of K.S.K.

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