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Selective Molecular Oxygen Oxidation of Thioethers to Sulfoxides Catalyzed by Ce(IV)

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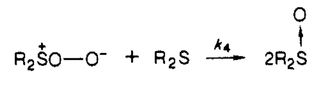
Abstract: The selective molecular oxygen conversion of thioethers to sulfoxides is catalyzed by ceric ammonium nitrate (CAN) with rate enhancements that are at least three orders of magnitude greater than the uncatalyzed autoxidation of thioethers. Mechanistic studies (including spectroscopic, labeling, uptake, mixed reactant, and autocatalysis studies) of this novel reaction reveal that both atoms of dioxygen are incorporated into product sulfoxide, that a novel oxygen-driven Ce(IV)/Ce(III) redox cycle gives rise to the catalysis, and that molecular oxygen efficiently traps a sulfur-centered radial cation of the thioether (produced by Ce(IV) oxidation of thioether) to yield the oxygenated radical cation $R_2S^+OO^•$, which, it is proposed, reoxidizes Ce(III) to Ce(IV). The zwitterionic $R_2S^+OO^-$ intermediate (persulfoxide) reacts with thioether to yield two sulfoxide product molecules.

The ability to selectively convert a particular molecule via an oxidation utilizing the abundant and cheap oxidant oxygen often represents a desirable low-cost method for upgrading the value of a raw material. The goal of much of our research in recent years has been directed toward the utilization of oxygen as a cheap and selective oxidant. During our research into better methods of selectively oxidizing waste thioethers (e.g., Me_2S) to their more valuable sulfoxides, we discovered that thioethers are subject to a novel autoxidation process that under high oxygen concentrations, elevated temps., and polar solvents yields almost exclusively the sulfoxide product.[1] The mechanism of this unusual autoxidation most likely involves an initial unfavorable electron transfer step (eq 1), followed by triplet oxygen (in high concentration) trapping of the resultant radical cation (eq 2).[2] Back-donation of an electron from superoxide to the oxygenated radical cation yields the zwitterionic species (eq 3) whose chemistry is known to yield sulfoxide upon exposure to additional thioether (eq 4).[3]

$$R_2S + {}^3O_2 \rightarrow R_2\overset{+}{S}{}^{\bullet} + O_2^{\bullet -} \qquad (1)$$

$$R_2\overset{+}{S}{}^{\bullet} + {}^3O_2 \rightarrow R_2\overset{+}{S}OO^{\bullet} \qquad (2)$$

$$R_2\overset{+}{S}O{-}O^{\bullet} + O_2^{\bullet -} \longrightarrow R_2\overset{+}{S}O{-}O^{-} + O_2 \qquad (3)$$



$$R_2\overset{+}{S}O{-}O^{-} + R_2S \xrightarrow{k_4} 2R_2\overset{\overset{O}{\uparrow}}{S} \qquad (4)$$

Given that the initial unfavorable electron-transfer step is rate-determining in this slow autoxidation reaction, we believed that the use of a suitable one-electron oxidant would possibly be capable of catalyzing or initiating the desired oxygen oxidation of R_2S to sulfoxide. We have communicated our preliminary successful attempts to catalyze this reaction using Ce(IV),[4] and in this paper we present additional examples and mechanistic studies of the novel Ce(IV)-catalyzed molecular oxygen oxidation of thioethers to sulfoxides.

Experimental Section

All of the thioethers used in these studies were purchased from Aldrich Chemical Co. and distilled before use. Sulfoxide standards were prepared by standard procedures with H_2O_2,[5] and $(NH_4)_2Ce(NO_3)_6$ and $Ce(NO_3)_3{\cdot}6H_2O$ and purchased from Alfa-Ventron. HPLC grade acetonitrile was distilled before use and distilled, de-ionized water was used in all cases.

Electronic spectra were monitored by using matched quartz cells in a Hitachi 110A UV-VIS spectrophotometer over the range 200–500 nm. All high-pressure catalytic runs used an apparatus analogous to that reported previously.[6] In general reactions were carried out with a reaction volume of 10 mL in an all glass/Teflon reactor. This small volume also minimized the potential risks inherent in running reactions with oxygen in an explosive regime. *Caution* must be exercised in such studies. In our system the reactor head-space (or gas) volume was kept very small; thus, only a small amount of O_2 is present in the reactor at any time. This reduces the possibility of extensive deflagration. Gas uptake measurements were made by utilizing a pressurized external calibrated steel tube connected directly to the reactor. Pressure drop in this calibrated external tube could be correlated to moles of O_2 consumed during the reaction. Reactions were monitored by gas chromatography on a Varian Model 3400 GC with a flame ionization detector and analyzed on a 15 M OV101 capillary column. Yields were determined by utilizing dodecane as an internal standard and by comparison to calibrated solutions. Electrochemical studies were performed on a Bioanalytical Systems CV-1B cyclic voltammograph, and voltammograms were recorded on a Houston Instruments 100 XY recorder. All cyclics were recorded in dry methylene chloride with 0.5 M tetra-*n*-butylammonium tetrafluoroborate

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[‡] The Proctor and Gamble Company.

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Table I. Examples of Ce(IV)-Promoted Oxygen Oxidations of Thioethers

substrate (concn, M)	solvent	temp (°C)	P_{O_2} (bar)	time (hrs)	% conv	products (as % of conv)
thioanisole (0.16)	CH_3CN	100	14	1	97	sulfoxide (88)
diphenyl sulfide (0.11)	CH_3CN	100	14	3.5	37	sulfoxide (64)
tetrahydrothiophene (0.23)	CH_3CN	60	14	0.5	88	sulfoxide (83)
pentamethylene sulfide (0.20)	CH_3CN	60	14	5.0	98	sulfoxide (85)
decyl methyl sulfide[b] (0.20)	70% CH_3CN[b]	70	14	5.5	21	sulfoxide (81)

[a] All runs contain ceric ammonium nitrate at a concentration of 5% of substrate and all runs unoptimized. [b] H_2O required to prevent cerium precipitation.

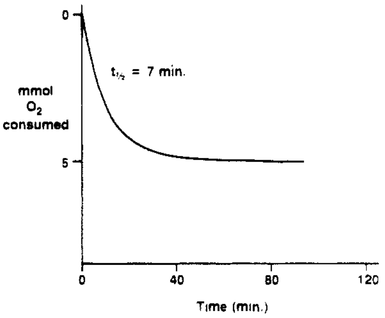


Figure 1. The $(NH_4)_2Ce(NO_3)_6$-catalyzed molecular oxygen oxidation of tetrahydrothiophene at 75 °C, 125 psi O_2 pressure, in 9:1 CH_3CN/H_2O (10.0 mL) with $[SR_2]$ = 1.0 M and sub/cat = 60.

as a supporting electrolyte. A single two-electrode cell was used which contained a glassy-carbon working electrode and a Pt reference electrode utilizing the Fe(II,III) couple of ferrocene as an internal standard (all potentials are corrected to SHE).

Results and Discussion

In our attempts to catalyze the oxygen oxidation of thioethers to sulfoxides via a one-electron scheme described in eq 1–4, a variety of one-electron oxidants were utilized (including NO^+, $Fe(bpy)_3^{3+}$, $Ru(bpy)_3^{3+}$, $Ag^+/K_2S_2O_8$, $Mo(CN)_8^{3-}$, $KBrO_3$, electrochemical cell, etc.) under conditions of high O_2 concentration (≥0.1 M). In no case was any catalytic (nonstoichiometric) chemistry observed. In contrast, we observe that Ce(IV) salts in catalytic amounts, especially $(NH_4)_2Ce(NO_3)_6$, give a very large rate enhancement to the selective O_2 oxidation of thioethers. In Table I are listed a few examples of unoptimized Ce(IV)-promoted oxygen oxidations. For comparison under similar conditions (100 °C, 1000 psi O_2 pressure) thioethers require several days to autoxidize completely to sulfoxides. Clearly, Ce(IV) has a profound and unique effect on the rates of O_2 oxidation in this chemistry.

In general with all the thioethers that we have investigated in detail (thioanisole, decylmethyl sulfide, tetrahydrothiophene, pentamethylene sulfide, and hexamethylene sulfide), we observe first-order thioether substrate kinetics at O_2 pressures above 30 psi (the lowest O_2 pressure we have studied). In Figure 1 is shown a typical reaction profile in which the uptake of oxygen is monitored as a function of time. The reaction proceeds rapidly to completion with a half-life of 7 min under the conditions noted. Analyses of reaction samples demonstrate two significant points: (i) the stoichiometry is such that for each mole of O_2 consumed 2 mol of sulfoxide are generated, and (ii) the reaction is very selective; i.e., the reaction proceeds to >98% thioether conversion with >95% selectivity to the sulfoxide (with up to 2% sulfone being observed near the time of 100% conversion) when optimized for temperature and pressure. The dependence of this reaction on the $[O_2]$ (or pressure) has been investigated over the range 30–1000 psi and found to be zero-order. These cerium-catalyzed (or initiated) reactions display first-order substrate kinetics. Not only are linear plots of log [thioether] versus time obtained, but the initial rates of thioether conversion versus $[\text{thioether}]_{\text{initial}}$ are linear (Figures 2 and 3). The cerium dependence on the reaction rates with several thioether substrates has also been studied, and we have observed that both the initial rates and the observed rate constants for thioether loss are first-order in [Ce(IV)] added. In Figure 4 is shown a plot of one such study for thioanisole. Not only are the reactions first-order in total Ce, but we observe a non-zero intercept to the observed reaction rates. This is consistent with the presence of the slow catalyst-free autoxidation reaction discussed above. Initial addition of Ce(III) (as $Ce(NO_3)_3{\cdot}6H_2O$) to the reaction has a very large inhibitory effect on the reaction, but addition of Ce(III) as the perchlorate salt has little inhibitory effect on the thioanisole oxidation rate. We assume this is due to the added nitrate coordinating with Ce(IV) and inhibiting the interaction of SR_2 with Ce(IV). In fact, control experiments with added $Ga(NO_3)_3$ and $LiNO_3$ exhibit the same suppressing effect.

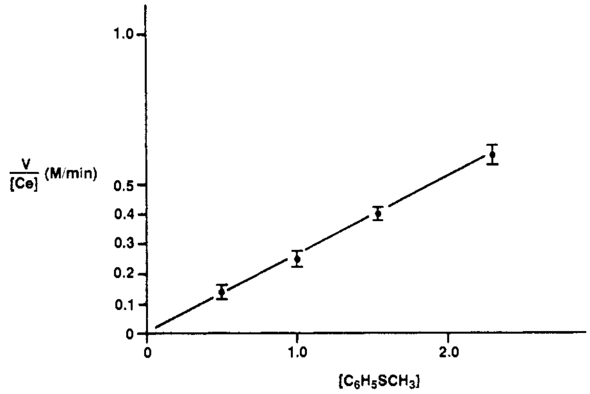


Figure 2. The plot of the initial rate (V/[Ce]) of the oxidation of thioanisole with O_2 (125 psi) catalyzed by $Ce(NH_4)_2(NO_3)_6$ ([Ce] = 0.0258 M) in dry acetonitrile at 70 °C as a function of $[C_6H_5SCH_3]$.

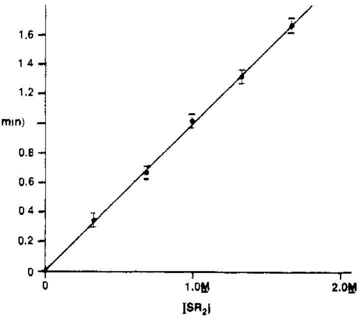


Figure 3. The plot of the initial rate of oxidation of tetrahydrothiophene with O_2 (125 psi) and with $Ce(NH_4)_2(NO_3)_6$ ([Ce] = 0.017 M) as catalyst in 9:1 CH_3CN/H_2O at 75 °C as a function of $[SR_2]$.

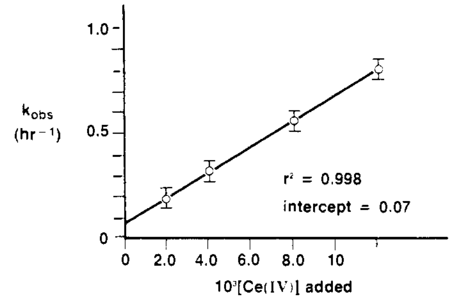


Figure 4. The plot of the $[(NH_4)_2Ce(NO_3)_6]$ dependence on the observed first-order rate constants for the O_2 (200 psi) oxidation of thioanisole (0.5 M) in acetonitrile at 70 °C.

All of the kinetic results are consistent with a rate-determining step in the Ce(IV)-promoted oxidations in which the thioether

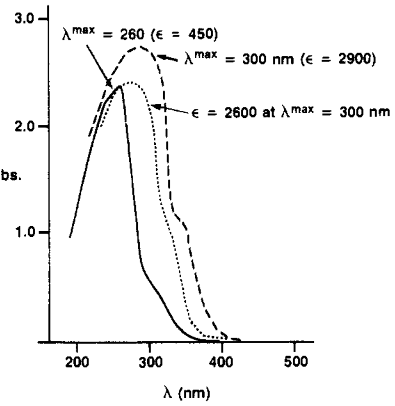


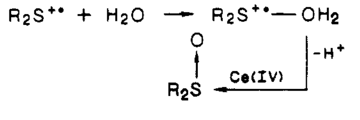
Figure 5. The electronic spectra of various cerium species in 9:1 CH_3CN/H_2O: (—) $Ce(NO_3)_3{\cdot}6H_2O$, 5.6 × 10^{-3} M; (---) $(NH_4)_2Ce(NO_3)_6$, 9.0 × 10^{-4} M; and (···) an actual reaction aliquot diluted to 1.0 × 10^{-3} M in Ce.

is oxidized to its radical cation by Ce(IV) (eq 5).[7] The observed zero-order $[O_2]$ dependence is consistent with this since Ce(IV)

$$R_2S + Ce^{IV} \xrightarrow{k_1} R_2\overset{+}{S}{}^{\bullet} + Ce^{III} \tag{5}$$

is a much better oxidant than O_2. In separate studies, we monitored the reaction of Ce(IV) with 100-fold excesses of various thioethers at 25 °C under N_2 and found that this oxidation is actually slow, with half-lives on the order of 1–2 h typically. Thus, at elevated temperatures, the observed rates are consistent with this assignment of the rate-determining step. The absence of an observed Ce(III) inhibition reveals that the reverse of this first step is insignificant in this system; thus, k_{-1} is likely negligible. Further insight into the nature of the cerium in this system was obtained spectrophotometrically by removing aliquots from the reactor and diluting them into cold acetonitrile. Their electronic spectra were then determined in the region 200–500 nm. In Figure 5 are shown examples of Ce(IV), Ce(III), and an actual experimental run aliquot diluted to 1.0 × 10^{-3} M in Ce. The spectrum of the experimental sample clearly appears to be dominated by the lower energy absorbance with the extinction coefficient ~2500 characteristic of Ce(IV). In separate additions, spectra of both Ce(III) and Ce(IV) (in short times) were found to be relatively insensitive to the presence of other donors, such as thioethers or sulfoxide. Thus, in these systems, the spectral fingerprint is consistent with Ce(IV), so that $[Ce(IV)] \cong [Ce]_{total}$.

Since it is known that Ce(IV) will promote the stoichiometric oxidation of thioethers to sulfoxides by a hydration mechanism,[7,8] we attempted to ascertain if indeed O_2 or H_2O is the trapping



(6)

reactant in our systems via labeling studies with 99.9% ^{18}O-labeled H_2O. Unfortunately, in the Ce(IV)-promoted system no conclusive incorporation information could be obtained by GC–mass spectra. This resulted from the fact that Ce(IV) was shown to promote the sulfoxide oxygen/water oxygen exchange reaction at elevated temperatures. To circumvent this problem and to demonstrate that O_2 is a suitable trapping agent of a thioether radical cation, reactions were carried out under 200 psi O_2 pressure using thioanisole and decyl methyl sulfide at 70 °C in an acetonitrile solvent mixture containing 10% $^{18}OH_2$ and a stoichiometric amount of $S_2O_8^{2-}/Ag^+$ to generate the radical cation $R_2S^{\bullet+}$.[9] The reaction proceeds rapidly to yield the desired sulfoxide, which by GC–mass spectroscopy contains less than 1% ^{18}O incorporation for decyl methyl sulfoxide and 18% ^{18}O incorporation for thioanisole. This reveals that $^3O_2$ is a competent trapping agent for the thioether sulfur radical cation (the proposed intermediate of eq 2) and that O_2 is apparently a much more effective trapping agent than H_2O. Further, in our studies we were often limited by solubility of cerium salts in dry acetonitrile, but with thioanisole homogeneous solutions in dry acetonitrile are obtained. Thus, in this system, at least, the hydration pathway cannot be operative, since there is no water available.

In separate studies with other oxidants, including constant current coulometry under O_2 pressures (up to 1000 psi), no indication of radical cation chain chemistry was observed,[10,11] only stoichiometric thioether oxidation. The Ce(IV,III) system is unique in promoting the non-stoichiometric chemistry, but cerium must be providing more than an initial potent oxidant to generate the sulfur radical cation. In fact, in absence of any nonstoichiometric initiated radical cation chain reactions with other potent oxidants, it is likely that the cerium systems must be truly catalytic. To accomplish this Ce(IV) must be regenerated from Ce(III) in these systems; thus, a potential oxidizing intermediate must be generated. We propose that an oxygenated sulfur radical cation is likely to be such an intermediate, in analogy to carbon systems.[10–13] Thus, we believe that the catalytic cycle is completed with the reoxidation of Ce(III) by the oxygenated sulfur radical cation (eq 7). Since Ce(IV) and Ce(III) both have a high affinity

$$R_2\overset{+}{S}OO^{\bullet} + Ce^{III} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} R_2\overset{+}{S}OO^{-} + Ce^{IV} \tag{7}$$

for oxygen donors, such an inner-sphere coordination-driven electron-transfer step could be favorable. The generation of sulfoxide could then be accomplished by the known rapid reaction of thioether with the persulfoxide (of eq 7), as depicted above in eq 4.

The temperature dependence of this reaction (60–100 °C) was studied for decyl methyl sulfide oxidations in 9:1 CH_3CN/H_2O under 200 psi O_2. The activation energy for this cerium-catalyzed reaction was 10.6 kcal. The uncatalyzed autoxidation under the same conditions exhibits a much larger activation energy, 24 kcal, thus, consistent with our proposed mechanistic role for Ce in these systems.

An integrated rate expression based on the mechanistic scheme contained in eq 5, 6, 7, and 4 has been derived assuming a steady-state treatment for the concentration of the $R_2S^{\bullet+}$, $R_2S^+OO^{\bullet}$, and $R_2S^+OO^-$ intermediates (eq 8). If the term

$$V = \frac{2k_1k_2k_3[SR_2][Ce(IV)][O_2]}{k_{-1}k_{-2} + k_{-1}k_3[Ce(III)] + k_2k_3[O_2]} \tag{8}$$

$k_2k_3[O_2] >> k_{-1}k_{-2} + k_{-1}k_3[Ce(III)]$, then eq 8 reduces to eq 9.

$$V = 2k_1[SR_2][Ce(IV)], \text{ where } [Ce(IV)] \simeq [Ce]_t \tag{9}$$

The assumption that $k_2k_3[O_2]$ is larger than the other terms of the denominator of eq 8 is realistic since these reactions are carried out at $[O_2] \geq 0.1$ M and $[Ce]_t \leq 0.02$ M. In addition, k_{-1} is likely very small as noted above from the lack of a Ce(III) effect. This mechanistic picture is also consistent both with the zero-order oxygen dependence and with the O_2 uptake data, which confirms the overall stoichiometry and that O_2 and not H_2O is the source of the oxygen of the sulfoxide in these systems. Equation 9 is also in accord with spectroscopic data if $[Ce(IV)] \simeq [Ce]_t$, which reveal that most of the cerium is present as Ce(IV) in this catalytic reaction.

Another important prediction that the mechanistic scheme proposed here allows us to make is that owing to the background radical cation autoxidation these reactions should be autocatalytic

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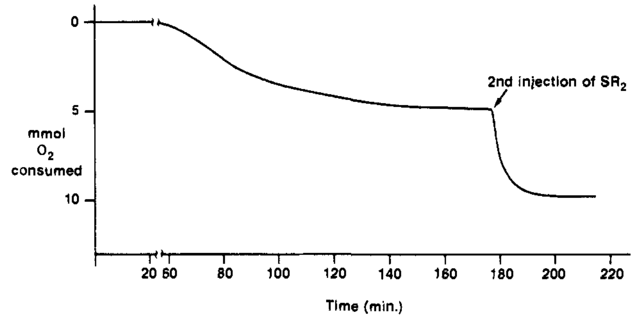


Figure 6. The autoxidation of tetrahydrothiophene ($[SR_2] = 1.0$ M) in the presence of $Ce(NO_3)_3 \cdot 6H_2O$ ($[Ce(III)] = 0.05$ M) in 9:1 CH_3CN/H_2O under 125 psi O_2 with $sub_t/cat = 100$.

Table II. The Ce(IV)-Catalyzed Oxygen Oxidation of Cyclic Thioethers at 60 °C in CH_3CN under 200 psi O_2 Pressure[a]

$-(CH_2)-_nS$ $n^{a,b}$	k_{obsd} (cat.) (h^{-1})	$E_{1/2}$ (V)[c]	selectivity at 90% conv	k_{obsd} (uncatalyzed)[d] (h^{-1})
4	8.9	1.68	93	0.27
5	0.11	1.76	89	0.11
6	0.12	1.80	88	0.18

[a] $[SR_2] = 0.2$ M. [b] $[(NH_4)_2Ce(NO_3)_6] = 1.0 \times 10^{-3}$ M. [c] Irreversible. [d] $T = 115$ °C and $P_{O_2} = 200$ psi.

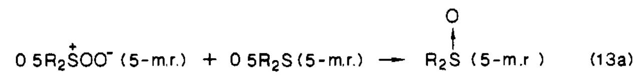
in Ce(III) with no added Ce(IV). Since the same oxygenated radical cation intermediate $R_2S^+{-}O{-}O^\bullet$ is expected to be present in both the noncatalytic and Ce-catalyzed regimes, this intermediate should be formed in the absence of Ce(IV) and slowly convert Ce(III) to Ce(IV) leading to autocatalysis. In Figure 6 is shown an example of such an experiment. We observe the slow conversion of thioether to sulfoxide. As the reaction approaches completion (monitored by O_2 uptake) an additional 10 mmol of thioether was added to the reactor. At this point the reaction proceeded rapidly at the same rate as if Ce(IV) had been used. These results further support the mechanistic view presented here and also demonstrate a principle we have shown in separate experiments, namely, the active catalyst species is generated and maintained in these systems allowing recycle of the active catalyst.

One intriguing aspect of these Ce(IV)-catalyzed oxidations was the observed effect of ring size in a series of cyclic thioethers on the observed rates of reaction. In Table II are listed some examples of cyclic thioether oxidations. The five-membered-ring thioether oxidizes in these systems much more rapidly than the 6- or 7-membered-ring system. While this may be due at least in part to the fact that tetrahydrothiophene is about 0.05 V easier to oxidize than the other thioethers, it is not clear at this point if other factors (e.g., steric) affecting the interaction with Ce(IV) may be operative. Nevertheless, these results suggest that if a high-energy intermediate, such as the persulfoxide cation, $R_2S^+OO^-$, is present, it should not be able to discriminate between different ring size thioethers when it reacts with thioether to generate two molecules of sulfoxide (eq 4). Thus, a mixed thioether reaction should reveal the validity of this step in the reaction sequence. In Figure 7, we show an example of such a Ce(IV)-catalyzed mixed thioether oxygen oxidation. Using a 1:1 ratio of tetrahydrothiophene and pentamethylene sulfide, we find that the initial rate is very fast (comparable to tetrahydrothiophene alone) but that the rate decreases faster than a first-order decay. In addition at the ~25% conversion point an aliquot of the reaction revealed by GC that a significant amount of pentamethylene sulfoxide is present. The ratio of $-(CH_2)_4SO$ and $-(CH_2)_5SO$ equaled 2.8. This number is actually very close to the value of three which the mechanism proposed here predicts at an early stage in the reaction. Early in the reaction most of the $R_2S^{\bullet+}$ generated will arise from the 5-membered-ring thioether, assuming (as we have observed) that oxidation of thioether by Ce(IV) is rate-determining. The sequence of reactions is shown here and can be seen to lead to 3 mol of 5-membered-ring sulfoxide and 1 mol of 6-membered-ring sulfoxide per every initiation by Ce(IV) (eq 10–13, where m.r. = membered ring). Since eq 13a and 13b

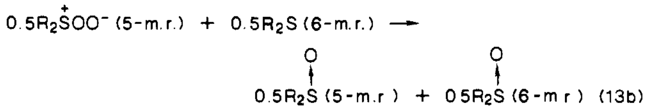
$$R_2S\ (5\text{-m.r.}) + Ce(IV) \rightarrow R_2\overset{+}{S}{}^{\bullet}(5\text{-m.r.}) + Ce^{III} \tag{10}$$

$$R_2\overset{+}{S}{}^{\bullet}\ (5\text{-m.r.}) + {}^3O_2 \rightarrow R_2\overset{+}{S}OO^{\bullet}\ (5\text{-m.r.}) \tag{11}$$

$$R_2\overset{+}{S}OO^{\bullet}\ (5\text{-m.r.}) + Ce^{III} \rightarrow R_2\overset{+}{S}OO^{-}\ (5\text{-m.r.}) + Ce^{IV} \tag{12}$$



$$0.5R_2\overset{+}{S}OO^-\ (5\text{-m.r.}) + 0.5R_2S\,(5\text{-m.r.}) \rightarrow R_2\overset{\overset{\displaystyle O}{\uparrow}}{S}\ (5\text{-m.r.}) \tag{13a}$$



$$0.5R_2\overset{+}{S}OO^-\ (5\text{-m.r.}) + 0.5R_2S\,(6\text{-m.r.}) \rightarrow 0.5R_2\overset{\overset{\displaystyle O}{\uparrow}}{S}\ (5\text{-m.r.}) + 0.5R_2\overset{\overset{\displaystyle O}{\uparrow}}{S}\ (6\text{-m.r.}) \tag{13b}$$

and 13b are equally probable early in the reaction, the ratio of 5-membered-ring to 6-membered-ring sulfoxides produced is 3. Our observation of a 2.8 to 1 ratio is in excellent agreement with this theory and supports the intermediacy of such a high-energy intermediate as $R_2S^+OO^-$.

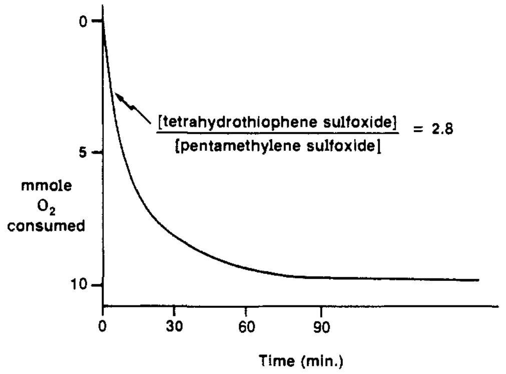


Figure 7. The $(NH_4)_2Ce(NO_3)_6$-catalyzed molecular oxygen oxidation of tetrahydrothiophene (1.0 M) plus pentamethylene sulfide (1.0 M) in 9:1 CH_3CN/H_2O under 125 psi O_2 with $sub_t/cat = 100$.

Conclusions

We have demonstrated Ce(IV) catalyzes the molecular oxygen oxidation of thioethers selectively to sulfoxides. The proposed mechanism involves the oxygenation of a thioether radical cation to produce a very potent oxidizing intermediate which reoxidizes Ce(III) to Ce(IV) and generates the known persulfoxide intermediate. This reaction represents the first example of a selective Ce(IV) catalyzed oxygen oxidation, and it is unique because it does not require the need for a co-reductant to activate the dioxygen molecule. Both atoms of O_2 are incorporated into the product sulfoxides; thus, in effect, this system represents a highly active and selective catalytic dioxygenase model.

Note Added in Proof. One of the referees has suggested that since electrochemical initiation does not start oxidation chains, then $R_2S^+OO^\bullet$ but be a weaker oxidant than $R_2S^{\bullet+}$. Further, Ce(III) must be a unique reductant capable of reducing $R_2S^+OO^\bullet$ irreversibly to the true oxidant $R_2S^+OO^-$. That $R_2S^+OO^\bullet$ is a weaker oxidant than $R_2S^{\bullet+}$ and that $R_2S^+OO^\bullet$ may lose O_2 faster than it gets reduced by the reduced forms of other oxidants capable of generating $R_2S^{\bullet+}$ from R_2S accounts for why no catalysis occurs in the electrochemical system or with any other oxidants, except cerium. Although the reasons for the uniqueness of cerium are not clear, it certainly could lie in the appropriateness of the Ce(IV)/Ce(III) redox couple and in the oxophilicity of Ce.