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Oxygen transfer reactions. 2. A comparison of the reactions of ruthenium tetroxide, chromyl chloride, and permanganate with thianthrene 5-oxide¹

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Products obtained from the oxidation of thianthrene 5-oxide, SSO, have been used to compare oxygen transfer mechanisms for three high-valent transition metals. Oxidation of SSO by benzyltriethylammonium permanganate in methylene chloride gives the corresponding sulfone, thianthrene 5,5-dioxide (SSO₂), as the exclusive product. Oxidation of SSO by ruthenium tetroxide also gives SSO₂ as the predominant product along with minor amounts of the disulfoxide, thianthrene 5,10-dioxide (SOSO). However, the converse is observed when chromyl chloride is used as the oxidant; SOSO is the major product. It is suggested that oxygen transfers from permanganate and ruthenium tetroxide are initiated by complexation between the central metal atom and the oxygen end of the S=O dipole, while oxidation by chromyl chloride is likely initiated by an alternative mechanism, possibly a single electron transfer.

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On a utilisé les produits obtenus lors de l'oxydation du thianthrène 5-oxyde, SSO, pour comparer les mécanismes de transfert d'oxygène de trois métaux de transition de valence élevée. L'oxydation du SSO par le permanganate de benzyltriéthylammonium dans le chlorure de méthylène conduit à la sulfone correspondante, le thianthrène 5,5-dioxyde (SSO₂), comme seul produit. L'oxydation du SSO par le tétroxyde de ruthénium fournit aussi le SSO₂ comme produit prépondérant aux côtés de quantités mineures du disulfoxyde, le thianthrène 5,10-dioxyde (SOSO). Toutefois, on a observé l'inverse lors d'oxydations avec le chlorure de chromyle; le SOSO est alors le produit majeur. On suggère que les transferts d'oxygène à partir du permanganate et du tétroxyde de ruthénium sont initiés par une complexation de l'atome métallique central et le portion oxygénée du dipôle S=O alors que l'oxydation par le chlorure de chromyle est vraisemblablement initiée par un autre mécanisme, possiblement un transfert unique d'électron.

[Traduit par la rédaction]

Introduction

Oxygen tranfers from transition metals to nonmetals are useful for organic synthesis (1) and essential for human life (2). The latter reactions usually involve porphyrin-complexed transition metals such as those found in hemoglobin (3) whereas the oxidants commonly used in organic synthesis are often highvalent transition metals with oxygen or halogen ligands (4). Although the oxidants may exist as neutral molecules, oxyanions, or complexes, most contain a common structural element, the metal-oxo bond, M=O (5). Despite the importance of these reactions, a detailed understanding of the way in which oxygen is transferred has not been achieved (4, 5).

Many oxygen transfers employed in organic synthesis are accompanied by significant bond transformation in the reductant. For example, the oxidation of alkanes to ketones by iron(V) compounds involves the cleavage of two carbonhydrogen bonds as well as an oxygen transfer (6), while the asymmetric dihydroxylation of terminal alkenes by osmium tetroxide involves the cleavage of a carbon-carbon π -bond as well as the formation of two C—O and two H—O bonds (7). However, when the reductants are sulfides ($L_nMO + R_2S \rightarrow$ $L_nM + R_2SO$) direct transfers not involving the cleavage or formation of other bonds occur (8, 9). Because these reactions are free of complications associated with the cleavage and (or) formation of other bonds, they provide a good vehicle for the study of oxygen transfers.

In this paper we wish to compare results that were obtained from a study of oxygen transfers to thianthrene 5-oxide (SSO) by ruthenium tetroxide, chromyl chloride, and permanganate ion. Thianthrene 5-oxide was chosen as the reductant because it contains sulfur atoms in two different oxidation states and can be used to quantify the selectivity of various reagents with respect to the oxidation of sulfides and sulfoxides (10-12). Oxidation of **SSO** by an oxidant with a high selectivity for sulfoxides results in formation of the corresponding sulfone, **SSO**₂, while the disulfoxide, **SOSO**, is obtained when the oxidant is selective for sulfides. Further oxidation of either of these two products results in the formation of thianthrene 5,5,10-trioxide, **SOSO**₂, as illustrated in Scheme 1.

The parameter, X_{SO} , defined in eq. 1, has been used as a quantitative measure of an oxidant's selectivity for sulfoxide oxidation (10–12). Under conditions where little or no **SOSO₂** is produced, X_{SO} is simply the mole fraction of **SSO₂** in the product.

[1]
$$X_{\text{SO}} = \frac{N_{\text{SO}_2} + N_{\text{SOSO}_2}}{N_{\text{SO}_2} + N_{\text{SOSO}} + 2N_{\text{SOSO}_2}}$$

The two sulfurs present in thianthrene 5-oxide are expected to have substantially different electron densities as illustrated by the resonance structures for **SSO** depicted in eq. [2]. Because of this, the magnitude of X_{SO} has been interpreted theoretically to be an indication of the electronic nature of oxygen transfer reagents. Those oxidants that preferentially oxidize sulfoxide sulfur and thereby produce X_{SO} values close to unity are considered to be nucleophiles; i.e., they react more readily with an electron-deficient sulfur. Conversely, those oxidants that selectively oxidize the sulfide sulfur, and produce small X_{SO} values, are considered to be electrophiles. X_{SO} has thus been used as a scale of nucleophilicity or electrophilicity to guide mechanistic predictions, although complexation prior to

¹For part 1 see ref 8.

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SOSO

SCHEME 1. The oxidation of thianthrene 5-oxide.

oxygen transfer can reduce the effectiveness of its application in this way (10).



Experimental

Materials Thianthrene 5-oxide, SSO, was prepared according to the procedure reported by Gilman and Swayampati (13): Thianthrene, SS, (5.0 g, 23 mmol) was stirred and refluxed in 81 mL of glacial acetic acid. Dilute HNO3 (2.9 mL of conc. HNO3 plus 6.3 mL of water) was added dropwise. The solution turned yellow and a brown gas, presumably N2O4, was released. After refluxing for an additional 15 min, the solution was poured into 300 mL of ice water. The white solid that precipitated was suction filtered, washed with water, and vacuum dried. Purification by flash chromatography followed by recrystallization from cyclohexane gave white, needle-like crystals, mp 148.5-149.5°C (lit. (14) mp 143.0–143.5°C). ¹H NMR (CDCl₃) δ : 7.35 (td, J = 7.5 and 2, 2H), 7.50 (td, J = 7.5 and 1.5, 2H), 7.55 (dd, J = 7.5 and 2, 2H), 7.90 (dd, J = 7.0 and 2, 2H). Anal. calcd. for $C_{12}H_8S_2O$: C 62.04, H 3.47; found: C 61.98, H 3.20. GC-MS analysis of this product indicated that it contained 1.4% unoxidized thianthrene that could not be removed by column chromatography or repeated recrystallization.

Benzyltriethylammonium permanganate was prepared by adding a saturated aqueous solution of KMnO₄ (4.16 g, 0.0264 mol) dropwise to a stirred solution of benzyltriethylammonium chloride (6.00 g, 0.0264 mol) in 100 mL of water (15). The dark purple precipitate that formed was collected under suction and vacuum dried over phosphorus pentoxide. It was recrystallized by dissolving in a minimum of hot methylene chloride, adding an equal amount of carbon tetrachloride, and cooling, mp 125–127.5°C (lit. (15) mp 114°C (dec.)). ¹H NMR (CDCl₃) δ : 1.6 (t, *J* = 7, 9H), 3.5 (q, *J* = 7, 6H), 4.7 (s, 2H), 7.6 (m, 5H). The UV–VIS spectrum exhibited four peaks between 500 and 575 nm that are characteristic of permanganate ion (16).

Ruthenium tetroxide was prepared by oxidation of ruthenium dioxide hydrate (0.4 g) with NaIO₄ (3.2 g, 0.015 mol) in a stirred heterogeneous solution of water (50 mL) and carbon tetrachloride (50 mL) at 0°C for 30 min (17). The carbon tetrachloride layer, now bright yellow, was separated and stored at 5°C over a few crystals of NaIO₄. Concentration was determined spectrophotometrically using known extinction coefficients (18).

Chromyl chloride was obtained commercially (Alfa Inorganics) and used without further purification.

Methylene chloride, the solvent used in these reactions, was carefully distilled from solid $KMnO_4$ before use.

Oxidations

Benzyltriethylammonium permanganate (0.1-0.2 g), dissolved in methylene chloride (50-100 mL), was added dropwise to a stirred solution of **SSO** (0.20 g, 0.86 mmol) in methylene chloride (20 mL). When the reaction was complete, MnO₂ was removed by suction filtration through a short column of alumina or silica and the products were eluted with acetone. The solvents were removed by rotary evaporation and the products vacuum dried (1 Torr (= 133.3 Pa)).

Ruthenium tetroxide (0.2–0.5 mmol) dissolved in carbon tetrachloride was added dropwise to a stirred solution of **SSO** (0.20 g, 0.86 mmol) in methylene chloride (20 mL). When the reaction was complete, RuO_2 was removed by suction filtration through 5 mm of Celite and the Celite washed with acetone to remove all products. After removal of the solvents by rotary evaporation, the products were vacuum dried.

Chromyl chloride (0.15-0.51 mmol), dissolved in methylene chloride (40 mL), was added dropwise to a stirred solution of **SSO** (0.20 g, 0.86 mmol) in methylene chloride (20 mL). The final solution was reddish-brown. 2-Propanol (3 mL) was added to reduce any excess oxidant. The solution was filtered through a short column of silcia gel (0.5 cm TLC grade silica and 3 cm 200-400 mesh silica gel) to remove the brown color. The column was eluted with acetone to recover all products. The solution was concentrated to about 40 mL and added to a similar volume of dilute aqueous NaCl. The products were extracted with $2 \times 30 \text{ mL}$ of CH₂Cl₂. Insoluble material at the interface was not collected because TLC showed it to contain no products. The extracts were filtered through silica once more to remove residual brown coloration and rotary evaporated to dryness.

Characterization of products

Thin-layer chromatography using 20:80 = 2-propanol:petroleum ether as the mobile phase indicated from four to six compounds present in the product mixture obtained from each reaction. These were separated using dry flash chromatography and characterized by gas chromatography (mass selective detector) and ¹H NMR (200 mHz). Thianthrene, **SS**: $R_f = 0.87$. ¹H NMR (CDCl₃) δ : 7.15 (dd, J = 6 and 3, 4H), 7.40 (dd, J = 6 and 3, 4H). Thianthrene 5-oxide, **SSO**: $R_f = 0.71$. ¹H NMR (CDCl₃) δ : 7.36 (td, J = 7.5 and 2, 2H), 7.50 (td, J = 7.5 and

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TABLE 1. Products obtained from the oxidation of thianthrene 5-oxide by benzyltriethylammonium permanganate (QMnO₄)

$\overline{\text{QMnO}_4 \text{ (mmol)}^a}$	Products	$\overline{A (\text{cm}^2)^b}$	Conc. (M)	Mass (mmol)	X _{so}
0.618	SSO	1.92	2.1×10^{-4}	5.3×10^{-1}	1.0
	sosó	0	0	0	
	SOSO ₂	0	0	0	
0.289	SSO ₂	1.89	2.06×10^{-4}	5.16×10^{-3}	1.0
	sosô	0	0	0	
	SOSO ₂	0	0	0	
0.351	SSO ₂	>2 ^C	$>2.2 \times 10^{-4}$	$>5.5 \times 10^{-3}$	1.0
	sosô	0	0	0	
	SOSO ₂	0	0	0	

^aQMnO₄ was reacted with 0.86 mmol of SSO. The products were collected and dried, and a portion dissolved in sufficient solvent (60% hexane, 15% 2-propanol, 25% methylene chloride) to give a concentration appropriate for HPLC analysis.

Peak area

The concentration, made deliberately high to search for trace amounts of SOSO and SOSO, gave a peak that went off scale.

$RuO_4 (mmol)^a$	Products	$A (cm^2)^b$	Conc. (M)	Mass (mmol)	X_{so}
0.257	SSO ₂ SOSO SOSO ₂	2.90 1.80 1.16	3.35×10^{-4} 5.12×10^{-5} 5.91×10^{-5}	8.37×10^{-3} 1.28×10^{-3} 1.48×10^{-3}	0.78
0.259	SSO ₂ SOSO SOSO ₂	4.23 2.75 1.71	5.04×10^{-4} 7.99×10^{-5} 9.12×10^{-5}	1.26×10^{-2} 2.00×10^{-3} 2.28×10^{-3}	0.78
0.514	SSO ₂ SOSO SOSO ₂	1.67 0.96 0.65	1.8×10^{-4} 2.6×10^{-5} 3.0×10^{-5}	8.9×10^{-3} 1.3×10^{-3} 1.5×10^{-3}	0.79

TABLE 2. Products obtained from the oxidation of thianthrene 5-oxide by ruthenium tetroxide

^aRuO₄ was reacted with 0.86 mmol of SSO. The products were collected and dried, and a portion dissolved in sufficient solvent (60% hexane, 15% 2-propanol, 25% methylene chloride) to give a concentration appropriate for HPLC analysis. ^bPeak area.

1.5, 2H), 7.58 (dd, J = 7.5 and 1.5, 2H), 7.89 (dd, J = 7.0 and 2.0, 2H) Thianthrene 5,5-dioxide, SSO₂: $R_f = 0.59$. ¹H NMR (CDCl₃) δ : 7.45 (m, 4H), 7.60 (td, J = 6.5 and 2.5, 2H), 8.15 (dd, J = 6.0 and 2.0). Thianthrene 5,5,10-trioxide, **SOSO**₂: $R_{\rm f} = 0.43$. ¹H NMR (CDCl₃) δ : 7.70 (m, 4H), 8.07 (dd, J = 7.5 and 1.5, 4H). Thianthrene 5,10-dioxide, **SOSO**: $R_f = 0.13$. ¹H NMR (CDCl₃) δ : 7.60 (dd, J = 6.0 and 2.0, 4H), 8.03 (dd, J = 6.0 and 2.0, 4H). Thianthrene 5,5,10,10-tetroxide, **SO₂SO₂:** $R_f = 0.$ ¹H NMR (DMSO- d_6) δ : 8.05 (dd, J = 6.0 and 2.5, 4H), 8.33 (dd, J = 6.0 and 2.0, 4H).

Disproportionation of thianthrene 5-oxide

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As noted above, thianthrene 5-oxide used in these experiments contained 1.4% thianthrene, SS, that could not be removed by column chromatography or repeated recrystallization. When oxidized by permanganate or chromyl chloride, the amount of SS present in the product decreased, presumably because it had been oxidized to SSO. When the oxidant was ruthenium tetroxide, however, the amount of SS in the product was always greater than 1.4%. This additional SS appears to have come from the disproportionation of SSO (to SS and SOSO or SSO₂). A similar reaction was observed to occur when a solution of RuO₂ and SSO was stirred for a few hours. No reaction was observed, however, when SSO was stirred with MnO_2 .

Results

The products were analyzed by HPLC. Chromatograms were obtained using a Dionex Series 4000i liquid chromatograph fitted with an Alltech, Econosphere, 250-mm silica (5 μm) column and a Perkin Elmer UV detector operated at 258 nm. Integration was performed manually. The flow rate was 2.0 mL/min and the solvent protocol was 80% hexane, 20% 2propanol (1.0-3.5 min), gradient (3.5-7.0 min), 35% hexane, 65% 2-propanol (3.5-10.5 min). Injection was started at 1.0 min and stopped at 1.5 min.

Using pure compounds, standard curves of concentration vs. peak area were prepared for SS, SSO, SOSO, SSO₂, SOSO₂, and SO_2SO_2 under these conditions. The results obtained from triplicate experiments with each oxidant are summarized in Tables 1–3. The estimated uncertainties are $\pm 2\%$ in individual concentration measurements and $\pm 10\%$ in the X_{SO} values.

Discussion

The results summarized in Tables 1-3 clearly indicate that there is a substantial difference in selectivity for the three highvalent transition metal oxidants under consideration, with permanganate showing the greatest selectivity for oxygen transfer to a sulfoxide sulfur. This result is consistent with the work of Ogura et al. (19) who found that methyl (methylthio)methyl sulfoxide, 1, was oxidized by permanganate to methyl (methylthio)methyl sulfone, 2, in 97% yield. It also explains why monosulfones, and not disulfoxides, are the usual products

chloride								
$CrO_2Cl_2 (mmol)^a$	Products	$A (cm^2)^b$	Conc. (M)	Mass (mmol)	X _{so}			
0.245	SSO ₂ SOSO SOSO ₂	0.56 5.30 0.95	$3.73 \times 10^{-5} 2.11 \times 10^{-4} 4.73 \times 10^{-5}$	$ \begin{array}{r} 1.86 \times 10^{-3} \\ 1.05 \times 10^{-2} \\ 2.36 \times 10^{-3} \end{array} $	0.25			
0.484	SSO ₂ SOSO SOSO ₂	0.57 8.30 0.80	$\begin{array}{c} 3.85 \times 10^{-5} \\ 3.30 \times 10^{-4} \\ 3.84 \times 10^{-5} \end{array}$	9.63×10^{-4} 8.25×10^{-3} 9.58×10^{-4}	0.17			
0.646	SSO ₂	0.57	3.85×10^{-5}	9.63×10^{-4}	0.15			

TABLE 3. Products obtained from the oxidation of thianthrene 5-oxide by chromyl chloride

 o CrO₂Cl₂ was reacted with 0.86 mmol of SSO. The products were collected and dried, and a portion dissolved in sufficient solvent (60% hexane, 15% 2-propanol, 25% methylene chloride)

10.05

0.80

 4.00×10^{-4}

 3.84×10^{-5}

to give a concentration appropriate for HPLC analysis. "Peak area.

SOSO

SOSO



SCHEME 2. The oxidation of a sulfoxide by permanganate.

obtained from the oxidation of *gem*-disulfides by permanganate (20).



From a comparison with other permanganate oxidations, it seems likely that oxygen transfer is preceded by complexation between the oxidant and the reductant (21). It is known that the manganese atom in permanganate is approximately dipositive with the oxygen atoms bearing corresponding negative charges as depicted in structure 3 (22). It therefore seems likely, on the basis of electrostatic considerations, that complex formation would involve interaction between the manganese atom and the oxygen end of the sulfoxide dipole as in Scheme 2. Oxygen transfer could then occur as indicated. The product, manganate(V) ion, also suggested as an intermediate in other permanganate oxidations (23), would likely be reduced very rapidly to manganese(IV) by electron capture from the solvent.



 9.99×10^{-3}

 9.58×10^{-4}

SCHEME 3. The oxidation of a sulfide by RuO_4 .

A similar mechanism would account for the oxidation of SSO to SSO_2 by ruthenium tetroxide. However, the observation of some SOSO in the products of this reaction indicates that the sulfide sulfur is also oxidized by RuO_4 , although at a substantially slower rate. Such an oxidation may be initiated by electron transfer to give perruthenate and a radical cation as in Scheme 3. Since the medium is nonpolar, it is unlikely, as envisaged in Scheme 3, that these ions would diffuse out of the solvent cage prior to oxygen transfer.

It is also possible that the small amount of **SOSO** observed in the product when **SSO** is oxidized by RuO_4 could be due to the reactions of RuO_3 , which is a by-product of these reactions.

The observation that transfer of oxygen to the sulfide sulfur is the main reaction when **SSO** is oxidized by chromyl chloride indicates that an alternative reaction mechanism must pertain. By analogy with the preceding discussion, a single electron transfer mechanism may be considered as a possibility for the reactions of this oxidant. This suggestion is also consistent with other known chemical properties of chromyl chloride. Recent results, described by Cook and Mayer (24), provide strong evidence for the intermediacy of cyclohexyl radicals during the oxidation of cyclohexane by chromyl chloride, and free radical intermediates have also been suggested for the Etard reaction (Cl₂CrO₂ + ArCH₃), which ultimately yields arylaldehydes (25).

A tentative mechanism involving electron transfer as the initial reaction has been outlined in Scheme 4.

The difference between chromyl chloride and other transition metal oxides or oxyanions may be associated with different modes of polarization of the M=O and M--Cl bonds. Polarization of the metal oxo bond (M==O \leftrightarrow M-O⁻) places a greater positive charge on the metal while the converse would be true for metal-chlorine bonds (M--Cl: \leftrightarrow M==Cl) (26). Permanganate could therefore be considered as a resonance hybrid of the



chromyl chloride and the other two oxidants considered in this study. For this reason the extensive experimental and theoretical information currently available for chromyl chloride oxidations (24, 27) may not be directly applicable to an understanding of other high-valent transition metal oxidants.

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structures depicted in eq. [4] (22), while the corresponding structures for chromyl chloride would be those in eq. [5]. A reduction of the positive charge on chromium as compared to manganese, suggested by these resonance structures, and the presence of an electron-deficient chlorine ligand could promote an electrostatic interaction between the ligand and the nonbonding electrons of sulfur that would initiate an alternative reaction such as a single electron transfer.

In any event it is clear from these results that there is a fundamental difference between the oxygen transfer reactions of

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