Inorg. Chem. **2002**, *41*, 1954–1957

Oxygen Transfer Reactions. 4. Reaction of High Valent Oxoruthenium Compounds with Sulfides

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Received August 3, 2001

The oxidation of methoxy substituted benzyl phenyl sulfides can be used to distinguish between oxidants that react by single electron transfer (followed by oxygen rebound) and those which react by direct oxygen atom transfer in a two-electron process. Transfer of a single electron results in the formation of an intermediate radical cation, which can undergo C–S bond cleavage and deprotonation reactions leading to the formation of methoxy substituted benzyl derivatives, methoxy substituted benzaldehydes, and diphenyl disulfide. The oxidation of 4-methoxybenzyl phenyl sulfide and 3,4,5-trimethoxybenzyl phenyl sulfide by oxidants known to participate in single electron transfers (Ce^{4+}, Mn^{3+}, and Cr^{6+}) results in the formation of the corresponding benzaldehydes, benzyl alcohols, benzyl acetates, and benzyl nitrates in variable yields. However, the only products obtained from the oxidation of the same compounds with RuO_4, RuO_4^-, and RuO_4^{2-} are sulfoxides and sulfones. Therefore, it is concluded that the oxidation of sulfides by oxoruthenium compounds likely proceeds by a concerted mechanism.

Introduction

Oxoruthenium complexes can be used as catalytic or stoichiometric oxidants for the conversion of sulfides into sulfoxides or sulfones. For example, porphyrin complexes of dioxoruthenium(VI) cations are effective catalysts for the oxidation of sulfides by dioxygen[1−4] or other oxygen donors such as lutidine *N*-oxide.[5−7] Oxoruthenium(IV) complexes may also be used as catalysts for the conversion of sulfides to sulfoxides[8,9] and as stoichiometric oxidants for similar purposes.[10−14] Ruthenium oxo species with no ancillary ligands, tetraoxoruthenium(VIII),[15,16] sodium tetraoxoruthenate(VII),[17] and tetrapropylammonium tetraoxoruthenate-(VII),[18] have also been used as both stoichiometric and catalytic oxidants.[19]

The overall reaction in each of these processes is the transfer of an oxygen atom from ruthenium to sulfur as summarized in eq 1.

$$RSR' + RuO_4^{n-} \rightarrow RSOR' + RuO_3^{n-} \qquad (1)$$

Such reactions could be the result of a direct oxygen atom transfer from ruthenium to sulfur in a synchronized process, or, alternatively, the reactions could be initiated by a single electron transfer (SET) from sulfur to ruthenium followed by recombination of the sulfur radical cation and the reduced ruthenium complex to give an "oxygen rebound" mechanism.[20] Under certain conditions, it is possible to divert the radical cations formed in SET processes to give different products, primarily aldehydes.[21−23]

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10.1021/ic0108336 CCC: $22.00
Published on Web 03/14/2002

This paper describes experiments designed to determine if oxoruthenium compounds react with organic sulfides by direct oxygen transfer or by an electron transfer initiated mechanism.

Experimental Section

Preparation of Oxidants and Reductants. Ruthenium tetroxide (RuO_4) was prepared by oxidation of hydrated ruthenium dioxide with sodium periodate as previously described.[24] Sodium ruthenate (Na_2RuO_4) was prepared in situ by treatment of ruthenium tetroxide with sodium hydroxide.[25] Potassium perruthenate ($KRuO_4$), tetrapropylammonium perruthenate ($(CH_3CH_2CH_2CH_2)_4NRuO_4$), ceric ammonium nitrate ($(NH_4)_2Ce(NO_3)_6$), manganese(III) fluoride (MnF_3), potassium chromate (K_2CrO_4), and benzyl phenyl sulfide were obtained commercially (Aldrich) and used without further purification.

4-Methoxybenzyl phenyl sulfide was prepared from the reaction of 4-methoxybenzyl chloride with thiophenol using a modification of a procedure described by Hilhorst et al.:[26] 4-Methoxybenzyl chloride (0.64 g, 4.10 mmol) was added to a mixture of thiophenol (1.32 g, 12.0 mmol) and K_2CO_3 (2.00 g, 14.5 mmol) in acetone (20 mL). The mixture was stirred under reflux for 5 h and filtered and the residue washed with CH_2Cl_2 (20 mL). The filtrate and washings were combined and concentrated. The resulting solid was purified by column chromatography (SiO_2; eluant 4/1 hexanes/CH_2Cl_2) to give a colorless solid (0.79 g, 3.4 mmol, 83%). The spectroscopic properties of this compound were identical to those described in the literature.[26]

^{1}H NMR (200 MHz, $CDCl_3$) δ 3.80 (s, 3H, OCH_3), 4.10 (s, 2H, $ArCH_2S$), 6.84 (d, 2H, $J = 8.5$ Hz, ArH), 7.10−7.40 (m, 7H, ArH).

^{13}C NMR (50 MHz, $CDCl_3$) δ 38.3, 55.2, 113.8, 126.2, 128.8, 129.3, 129.6, 129.9, 136.5, 158.7.

3,4,5-Trimethoxybenzyl phenyl sulfide was prepared, as described in the literature,[22] from the reaction of 3,4,5-trimethoxybenzyl alcohol with thiophenol as follows: *p*-Toluenesulfonic acid (0.10 g) was added to a stirred solution of 3,4,5-trimethoxybenzyl alcohol (1.02 g, 5.15 mmol) and thiophenol (1.07 g, 9.73 mmol) in benzene (20 mL). The resulting mixture was stirred under reflux for 1 h and concentrated to give a yellow oil. Purification by column chromatography (SiO_2; eluant 4/1 hexanes/CH_2Cl_2) gave a colorless solid (1.24 g, 4.28 mmol, 83%).

^{1}H NMR (200 MHz, $CDCl_3$) δ 3.78 (s, 6H, OCH_3), 3.83 (s, 3H, OCH_3), 4.02 (s, 2H, $ArCH_2S$), 6.48 (s, 2H, ArH), 7.38−7.16 (m, 5H, PhH).

^{13}C NMR (50 MHz, $CDCl_3$) δ 39.5, 55.8, 60.6, 105.5, 126.4, 128.7, 130.1, 132.9, 136.0, 136.8, 152.9.

Typical Oxidation Procedure. Oxidant (0.11 mmol) was added to a stirred solution of sulfide (0.10 mmol) in acetonitrile (2 mL). Progress of the reaction was monitored by TLC. When all of the oxidant had been reduced or all of the sulfide oxidized, the solution was diluted by addition of methylene chloride (25 mL) and washed with concentrated NaCl solution (5 mL) and water (5 mL). The organic layer was dried over anhydrous magnesium sulfate and concentrated. The residue was analyzed by TLC, ^{1}H NMR, and ^{13}C NMR.

Calculation of Product Ratios. Because extensive workup procedures could alter the composition of the product mixture, various methods for analyzing the crude product were investigated. Of the approaches considered, it was found that use of ^{1}H NMR integrals provided the most reliable measurements of the relative amounts of each product present. When artificially prepared product mixtures were used, the ^{1}H NMR integrals reproduced the known product ratios within ±3%. For all products, except aldehydes, the signals from the benzylic hydrogens were in regions where the integrals could be accurately measured; for aldehydes, the integral for the hydrogen attached to the carbonyl was used. The product ratios were then calculated by taking the integral for a particular product over the sum of the integrals for all of the other products, the aldehyde integrals being doubled. The ^{1}H NMR signals used are found at the following chemical shifts: benzyl phenyl sulfide ($\delta = 4.22$), benzyl phenyl sulfoxide ($\delta = 3.94-4.18$), benzyl phenyl sulfone ($\delta = 4.31$), benzaldehyde ($\delta = 10.03$), 4-methoxybenzyl phenyl sulfide ($\delta = 4.10$), 4-methoxybenzyl phenyl sulfoxide ($\delta = 3.87-4.08$), 4-methoxybenzyl phenyl sulfone ($\delta = 4.24$), 4-methoxybenzyl nitrate ($\delta = 5.35$), 4-methoxybenzyl acetate ($\delta = 5.04$), 4-methoxybenzyl alcohol ($\delta = 4.48$), 4-methoxybenzaldehyde ($\delta = 9.90$), 3,4,5-trimethoxybenzyl phenyl sulfide ($\delta = 4.02$), 3,4,5-trimethoxybenzyl phenyl sulfoxide ($\delta = 3.86-4.08$), 3,4,5-trimethoxybenzyl phenyl sulfone ($\delta = 4.23$), 3,4,5-trimethoxybenzyl nitrate ($\delta = 5.29$), and 3,4,5-trimethoxybenzaldehyde ($\delta = 9.86$).[27] All spectra were recorded on a Bruker AC-200 spectrometer using $CDCl_3$ as the solvent.

Diphenyl disulfide was also produced as a coproduct in many of the reactions. Although its presence could easily be detected using TLC (SiO_2; eluant 2/1 hexanes/ethyl acetate, $R_f = 0.68$), its ^{1}H NMR signals were not sufficiently distinct from those of other aromatic compounds present to be used quantitatively.

Results and Discussion

The products produced when oxidation is initiated by a single electron transfer (SET) may be illustrated by the use of reagents such as cerium(IV) ammonium nitrate,[28] manganese(III) fluoride,[29] and hydrogen chromate.[30] The oxidation of benzyl phenyl sulfides by these reagents results in the formation of substantial amounts of aldehydes and benzyl

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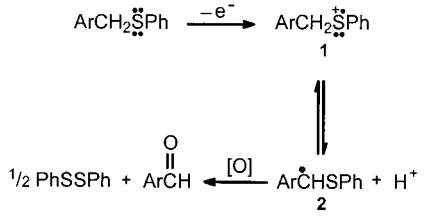
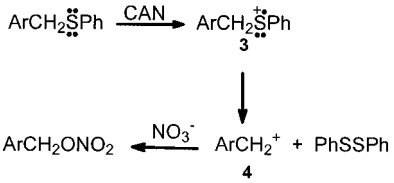
Scheme 1. Single Electron Transfer Followed by Proton Loss

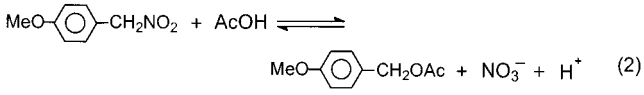


Scheme 2. Oxidation of 4-Methoxybenzyl Phenylsulfide ($ArCH_2SPh$) by Cerium(IV) Ammonium Nitrate (CAN)



derivatives ($ArCH_2OH$, $ArCH_2ONO_2$, and $ArCH_2OAc$), particularly when the benzyl ring is substituted with methoxyls. For example, the oxidation of benzyl phenyl sulfide by cerium(IV) ammonium nitrate (CAN) gives significant amounts of benzaldehyde (10−20%) in addition to sulfoxide. (Exact product ratios are given in Table 1 of the Supporting Information.) This product (i.e., benzaldehyde) is presumably formed by a mechanism in which electron transfer is followed by proton loss and further oxidation as in Scheme 1. It is known from previous work that the free radical, **2**, is very easily oxidized to an aldehyde and diphenyl disulfide.[21]

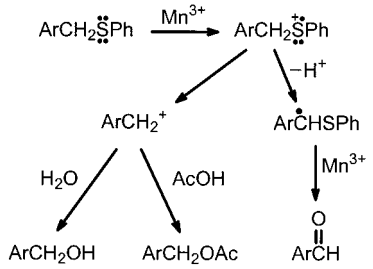
The major product obtained when 4-methoxybenzyl phenyl sulfide is oxidized by CAN in acetonitrile is 4-methoxybenzyl nitrate (∼70%). This product would be produced by a reaction in which the 4-methoxybenzyl phenyl sulfide radical cation, **3**, undergoes C−S bond cleavage to give a 4-methoxybenzyl carbocation, **4**, as in Scheme 2. The presence of a methoxyl substituent would promote C−S cleavage by its ability to stabilize the transition state leading to the carbocation, **4**. When acetic acid is added to the solvent, the final product is primarily 4-methoxybenzyl acetate (∼70%). A study of the distribution of products over time indicated that 4-methoxybenzyl nitrate, the initial product, is slowly converted into 4-methoxybenzyl acetate in a transesterification reaction when acetic acid is present (eq 2). Thus, the initially formed 4-methoxybenzyl nitrate is converted into 4-methoxybenzyl acetate when acetic acid is present and the reaction time is sufficiently long.



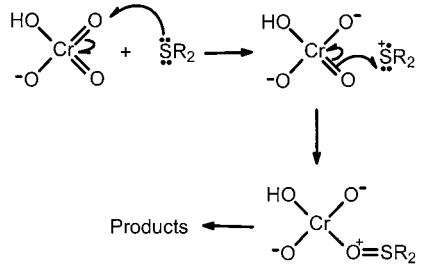
(2)

When 3,4,5-trimethoxybenzyl phenyl sulfide is oxidized by CAN in acetonitrile, the only products obtained are 3,4,5-trimethoxybenzaldehyde and diphenyl disulfide. These products are likely formed exclusively because the electron withdrawing effect of the three methoxyls on the aromatic ring increases the acidity of the benzylic hydrogens of the radical cation, **1**, and makes it prone to proton loss as in Scheme 1. Further oxidation of the resulting free radical, **2**, would give the observed products.

Scheme 3. Oxidation of 4-Methoxybenzyl Phenyl Sulfide ($ArCH_2SPh$) by Manganese(III) Fluoride



Scheme 4. Reaction of Hydrogen Chromate with Sulfides by an Oxygen Rebound Mechanism



In addition to the corresponding sulfoxide and sulfone, a significant amount of benzaldehyde (∼40%) is formed when benzyl phenyl sulfide is oxidized by manganese(III) fluoride in a 10:1 mixture of acetonitrile and acetic acid. When 4-methoxybenzyl phenyl sulfide is oxidized under the same conditions, the primary product is 4-methoxybenzyl acetate (∼70%). When acetic acid is replaced by water in the solvent, 4-methoxybenzyl alcohol (∼40%) is formed in addition to 4-methoxybenzaldehyde. These reactions are summarized in Scheme 3.

Chromium(VI), which is also believed to react with sulfides by initial electron transfer,[31] gives measurable amounts of the corresponding aldehydes on reaction with 4-methoxybenzyl phenyl sulfide and 3,4,5-trimethoxybenzyl phenyl sulfide (4 and 22%, respectively). However, the observation that the major product in both reactions is the corresponding sulfoxide suggests that oxygen rebound is sufficiently rapid to compete with C−S bond cleavage and deprotonation reactions. It appears that the structure of $HCrO_4^-$ may permit it to react by oxygen rebound before diffusing out of the solvent cage in a reaction somewhat like the one depicted in Scheme 4. An efficient oxygen rebound step would necessarily decrease products from C−S cleavage and deprotonation reactions.

When methoxy substituted benzyl phenyl sulfides are oxidized by oxoruthenium compounds, the products are, with one minor exception, sulfoxides and sulfones (Table 2 of the Supporting Information). A small amount of aldehyde (∼2%) that is observed among the products from the oxidation of 3,4,5-trimethoxybenzyl phenyl sulfide by ru-

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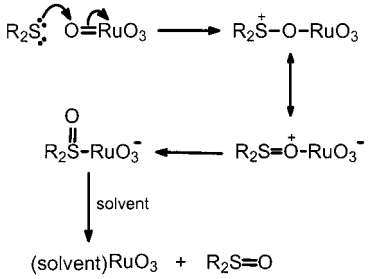
Scheme 5. Possible Mechanism for the Reaction between Oxoruthenium Compounds and Sulfides



thenium tetroxide may come from a side reaction. For example, previous studies have shown that ruthenium tetroxide readily reacts with aromatic rings.[32]

The virtual absence of cleavage products suggests that oxoruthenium compounds react with sulfides by an oxygen transfer mechanism which could be initiated by ligation, as previously suggested.[33] Alternatively, it is possible that the products of these reactions may be formed by a direct reaction of the sulfide sulfur with an oxo oxygen, as proposed in Scheme 5. This process, which results in an oxygen transfer without formation of discrete intermediate radicals or cations, is known to pertain when nonlabile oxoruthenium complexes react with sulfides. For example, Meyer et al. have shown that the oxidation of dimethyl sulfide by $[(bpy)_2(py)Ru(O)]^{2+}$ is initiated by formation of a bond between sulfur and oxygen as envisaged in Scheme 5.[11] Although nucleophilic attack on an electron rich oxygen[34] may seem like an improbable mechanism, it can be noted that the process results in a concurrent reduction of ruthenium and could, therefore, be considered to be a remote attack on the metal.

It is also possible that oxoruthenium reactions are initiated by single electron transfers followed by very rapid oxygen rebound steps. However, there is no reason to expect that these oxidants should undergo oxygen rebound any more rapidly than other reagents. Furthermore, theoretical calculations suggest that the SOMO of the radical cation formed by electron loss from 3,4,5-trimethoxybenzyl phenyl sulfide is primarily associated with the ring,[23] thereby decreasing the possibility of an oxygen rebound reaction that would result in oxidation at sulfur. Consequently, oxygen transfer from oxoruthenium oxidants appears to be a concerted process without involvement of intermediate radical cations.

Although both oxoruthenium and oxochromium compounds have similar chemical properties and can be used interchangeably for many synthetic procedures,[36] it is of interest to note that the mechanisms of their reactions seem to be different. It appears from this work that oxidations by oxochromium compounds are initiated by electron transfer, while oxoruthenium oxidations are concerted. Because the oxidation of proteins and lipids by one-electron processes has been associated with the onset of several diseases,[37] this observation is consistent with the belief that the carcinogenic properties of oxochromium compounds may be associated with their tendency to engage in free radical oxidations.[38] To the best of our knowledge, oxoruthenium compounds are not carcinogens;[39] in fact, ruthenium compounds are often used in cancer therapies.[40] This lack of carcinogenic properties may be a consequence of their mode of reaction, which does not involve the formation of free radicals.

Summary

Typical one electron oxidants such as cerium(IV) ammonium nitrate and manganese(III) fluoride react with methoxy substituted benzyl phenyl sulfides to give radical cation intermediates that can react by an oxygen rebound mechanism to give sulfoxides and sulfones and by cleavage or deprotonation reactions that result in the formation of benzyl derivatives, aldehydes, and diphenyl disulfide. Reaction of the same compounds with oxoruthenium oxidants gives only sulfoxides and sulfones, with one minor exception. It is therefore concluded that oxygen transfers from oxoruthenium compounds occur in a concerted fashion that does not involve the formation of intermediate radical cations. When hydrogen chromate reacts with methoxy substituted benzyl phenyl sulfides, measurable amounts of cleavage products are obtained. It, therefore, appears as if its reactions are initiated, at least in part, by single electron transfers. This latter observation may account for the carcinogenic properties of chromates.

Acknowledgment. The authors are pleased to acknowledge financial assistance from the Natural Sciences and Engineering Research Council of Canada (NSERC).

Supporting Information Available: Tables of product ratios for the oxidation of benzyl phenyl sulfide, 4-methoxybenzyl phenyl sulfide, and 3,4,5-trimethoxybenzyl phenyl sulfide by CAN, MnF_3, $NaHCrO_4$, RuO_4, $KRuO_4$, Pr_4NRuO_4, and Na_2RuO_4. This material is available free of charge via the Internet at http://pubs.acs.org.

IC0108336

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