J. CHEM. SOC., CHEM. COMMUN., 1986 1097

The Novel Cerium(IV)-catalysed Molecular Oxygen Oxidation of Thioethers to Sulphoxides

Dennis P. Riley*[†] and Paul E. Correa

The Procter & Gamble Company, Miami Valley Laboratories, P.O. Box 39175, Cincinnati, Ohio 45247, U.S.A.

Thioethers can be oxidized with catalytic amounts of Ce^{IV} salts rapidly and selectively to sulphoxides using molecular oxygen (P_{O_2} = 5—15 bar) as the oxidant.

Thioethers are subject to a very slow (1—3 days) autoxidation which occurs under high O_2 pressures (70 bar), at elevated temperatures (>90 °C), and in polar solvents to yield sulphoxides selectively.[1] We report here that the addition of a catalytic amount of Ce^{IV} salt accelerates these autoxidations by at least a factor of 10^3, even at lower pressures and temperatures, affording a synthetically useful reaction.[‡]

The mechanism of the high-pressure uncatalysed autoxidation involves an initial unfavourable electron transfer to oxygen [equation 1(a)], followed by oxygenation of the sulphur-based radical cation (1) (equation 2).

$$SR_2 + Ox^{n+} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{(\mathbf{1})}{R_2\overset{+}{S}\cdot} + Ox^{(n-1)+} \qquad (1)$$

$$(a)\ Ox = O_2 \qquad (b)\ Ox = Ce^{IV}$$

$$\underset{(\mathbf{1})}{R_2\overset{+}{S}\cdot} + O_2 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \underset{(\mathbf{2})}{R_2\overset{+}{S}OO\cdot} \qquad (2)$$

The oxygenated radical (2) can either oxidize another molecule of substrate (chain-propagating) or react with superoxide to yield the zwitterionic species (3) (equation 3), which are known to yield sulphoxide by reaction with additional thioether (equation 3).[3]

$$\underset{(\mathbf{3})}{R_2\overset{+}{S}OO^-} + SR_2 \xrightarrow{k_4} 2R_2S{\rightarrow}O \qquad (3)$$

Since the initial electron transfer (equation 1) is rate-determining, we began a search for other one-electron oxidants that could initiate this cation-radical oxygen oxidation. Many different oxidants were tried, but Ce^{IV} salts are unique in promoting this chemistry. This is due, at least in part, to the fact that Ce^{IV} better satisfies the thermodynamic requirements for oxidation of a thioether,[§] thus facilitating electron transfer to yield the radical cation (1) [equation 1(b)].

All of the Ce^{IV} reactions of aryl and alkyl thioethers are selective to sulphoxide and exhibit a pseudo first-order thioether concentration dependence under constant oxygen pressure (15 bar) and a first-order dependence in total added cerium(IV) concentration. For the same reaction, addition of Ce^{III} under 15 bar O_2 pressure retards the observed reaction rate with an observed [Ce^{III}] order of −0.7. The oxygen pressure dependence in these reactions for all classes of thioethers is zero-order over the pressure ranges studied (2—100 bar O_2),[¶] indicating that oxygen is not involved in the rate-determining initial electron transfer step.

Since superoxide would not be generated in this system, the recombination pathway ($R_2S\cdot^+$ + $O_2\cdot^-$) is not available. Consequently, the reaction could proceed *via* a true catalytic pathway in which the oxygenated radical cation (1) must oxidize Ce^{III} to Ce^{IV} with production of the zwitterion (3) (equation 4). This reaction may also proceed as a chain reaction in which the role of Ce^{IV} is as an initiator only. To distinguish between these two pathways attempts were made to initiate chain chemistry with irreversible one-electron oxidizing systems such as $S_2O_8^{2-}/Ag^+$[||] and constant current coulometry under high oxygen pressure (P_{O_2} > 50 bar). In all cases only *stoicheiometric* reactions occur. The observed first-order substrate dependence and zero-order oxygen dependence of this Ce^{IV}-based chemistry also indicates that a chain mechanism is not operative.

$$\underset{(\mathbf{2})}{R_2\overset{+}{S}OO\cdot} + Ce^{III} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \underset{(\mathbf{3})}{R_2\overset{+}{S}OO^-} + Ce^{IV} \qquad (4)$$

The stoicheiometric reaction was carried out using 10% $^{18}OH_2$ in acetonitrile as solvent with decyl methyl sulphide under 200 psig oxygen pressure at 70 °C and $S_2O_8^{2-}/Ag^+$ to generate the radical cation (1), $R_2S\cdot^+$.[||] The reaction proceeds rapidly to yield the desired sulphoxide, which by g.c.–mass spectroscopy contains less than 1% ^{18}O incorporation. Thus, $^3O_2$ acts as the trapping agent of the sulphur radical cation and is the source of the sulphoxide oxygen.

An integrated rate expression based on the catalytic scheme of equations 1(b)—4 has been derived assuming a steady-state treatment for the concentration of (1), (2), and (3) (equation 5). If the term $k_2k_3[O_2] \gg k_{-1}k_{-2} + k_1k_3[Ce^{III}]$ then equation (5) simplifies to equation (6) which agrees with experimental observations. Equation (5) suggests that as the [Ce^{III}] increases an inhibition would be expected, as observed.

[†] *Present address:* Monsanto Co., 800 N. Lindbergh Boulevard, St. Louis, Missouri 63167, U.S.A.

[‡] In a typical reaction with 5% ceric ammonium nitrate added at 100 °C under 200 psig oxygen pressure, thioanisole (0.16 M) is completely oxidized in acetonitrile to the sulphoxide in 1.5 h. A Griffen–Worden apparatus was used as described in ref. 2.

[§] Cyclic voltammograms were obtained in dry acetonitrile with 0.1 M tetrabutylammonium tetrafluoroborate using a glassy carbon electrode and a Ag/AgCl reference electrode. Irreversible oxidation waves were observed. Peak potentials are for thioanisole 1.50 V, diphenyl sulphide 1.75 V, decyl methyl sulphide 1.85 V, tetrahydrothiophene 1.68 V. Reversible oxidation of Ce^{III} is observed at 1.13 V.

[¶] The selectivity for sulphoxide is maximized at O_2 pressures equal to or greater than 15 bar.

[||] The $S_2O_8^{2-}/Ag^+$ system has been used by numerous workers (ref. 4) for the irreversible generation of radical cations. This prevents complication of the result by back reactions. This chemistry is not as clean as the Ce^{IV}-catalysed system since considerable sulphone is produced (up to 30%) owing to oxidation of the sulphoxide by the potent oxidant $SO_4\cdot^-$.

$$V = \frac{2k_1k_2k_3[SR_2][Ce^{IV}][O_2]}{k_{-1}k_{-2} + k_{-1}k_3[Ce^{III}] + k_2k_3[O_2]} \quad (5)$$

$$V = 2\,k_1[SR_2][Ce^{IV}], \text{ where } [Ce^{IV}] \sim [Ce]_t \quad (6)$$

Finally, this mechanistic picture implies that both oxygen atoms of O_2 are utilized in the product. The stoicheiometry was confirmed in separate O_2 uptake studies of the Ce^{IV} catalysed oxidation of both decyl methyl sulphide and thioanisole at T = 80 °C and P_{O_2} = 15 bar.

Received, 20th January 1986; Com. 087

References

1 D. P. Riley and P. E. Correa, *J. Org. Chem.*, 1985, **50**, 1787.
2 D. P. Riley and R. E. Shumate, *J. Chem. Ed.*, 1984, **61**, 923.
3 C. S. Foote and J. W. Peters, *J. Am. Chem. Soc.*, 1971, **93**, 3795.
4 F. Minisci, A. Citterio and C. Giordano, *Acc. Chem. Res.*, 1983, **16**, 27.