

Ruthenium and Osmium Oxo Complexes as Organic Oxidants

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Recent advances in the application of ruthenium tetroxide, lower-valent oxo ruthenates and osmium tetroxide are summarised here, with particular reference to uses or potential uses of these materials in the fine chemicals industry.

Ruthenium and osmium are unequalled in the entire Periodic Table in that they can sustain, in a handful of complexes, the VIII oxidation state; no other elements exhibit octavalency. In most of these complexes, and also in many other complexes of these two elements in the VII, VI, V and IV oxidation states, the strongly σ - and π -donating oxo ligand O^{2-} has a dominant role. A number of oxo complexes involving these higher oxidation states have been used in homogeneous organic oxidations, and this paper will concentrate, for the most part, on recent advances in these areas.

Being a second-row transition element, ruthenium will hold its outer d electrons more tightly than will osmium, so that, for a given complex in a given oxidation state, the ruthenium complex will tend to be more oxidising than its osmium counterpart. Thus, for example, ruthenium tetroxide is a more powerful oxidant than osmium tetroxide, and the per-ruthenate ion $[RuO_4]^-$ is more oxidising than $[OsO_4]^-$. The range of ruthenium-based oxidants for organic chemistry is consequently greater than for osmium, though osmium tetroxide is unrivalled in its degree of efficiency and selectivity in some types of reaction.

Ruthenium

Ruthenium Tetroxide

This is the best known and most commonly used ruthenium oxidant. Ruthenium, the last of the six platinum metals to be isolated, was discovered by Karl Karlovich Klaus

(1796–1864) in 1844 (1); but he did not isolate the highly oxidising and consequently rather unstable ruthenium tetroxide until 1860 (2). This was long recognised to be a powerful oxidant, but it was not until 1953 that a systematic survey was made of its reactions with organic substrates (3). There are now two comprehensive reviews on the use of ruthenium tetroxide as an organic oxidant (4, 5).

Ruthenium tetroxide is a pale yellow material with a high vapour pressure at room temperatures; it melts at 25°C and its density is 3.28 g/cm³. Its solubility in water is fairly low, only 1.7 per cent at 0°C and 2.1 per cent at 50°C, but it is very soluble in those organic solvents with which it does not react, such as carbon tetrachloride and cyclohexane. It is tetrahedral in the gas, liquid, solid and solution phases.

Because of its high vapour pressure, vigour of oxidation and toxicity, ruthenium tetroxide is hardly ever used on its own. However it is very easily generated in an aqueous solution from $RuCl_3 \cdot nH_2O$, or $RuO_2 \cdot nH_2O$ (a better starting material), with excess aqueous sodium periodate (4), sodium hypochlorite (bleach) (4) or sodium bromate (6). In the presence of these co-oxidants it functions as a catalytic oxidant, ruthenium tetroxide being regenerated after reaction with the organic substrate by the co-oxidant, so that the actual quantity of ruthenium needed is very small. Oxidations are effected either in aqueous solution or in a biphasic system, the non-aqueous phase usually being carbon tetrachloride. Excess ruthenium

tetroxide can be removed with 2-propanol, which is oxidised by it to acetone (4, 7, 8).

Although ruthenium tetroxide is generally considered to be a vigorous and rather non-selective oxidant it is its very vigour, its ability to function at room temperature and the relative ease with which it can be prepared in a catalytic form which make it attractive for some oxidations. It will oxidise alkenes, alkynes, alcohols, aromatic rings and ethers, cleaving double bonds and some aromatic rings. It is, perhaps, most commonly used by organic chemists for the oxidations of secondary hydroxyl groups in carbohydrates to ketones, such as, for example, the oxidative formation of a ulose derivative, which is shown below in Scheme 1 (4, 9), and for the oxidation of steroidal alcohols to ketones, either for the oxidation of hydroxyl groups to keto functions as in the oxidation of cholestan-3 β ,6 β -diol-3-acetate to cholestan-3 β -ol-6-one-3-acetate, Scheme 2, or for the cleavage of aromatic rings in such systems (4,8).

It has additional useful applications. It will cleave some aromatic rings; for example, it oxidises naphthalene to phthalic acid and cyclohexanebenzene to cyclohexane-carboxylic acid (4,5).

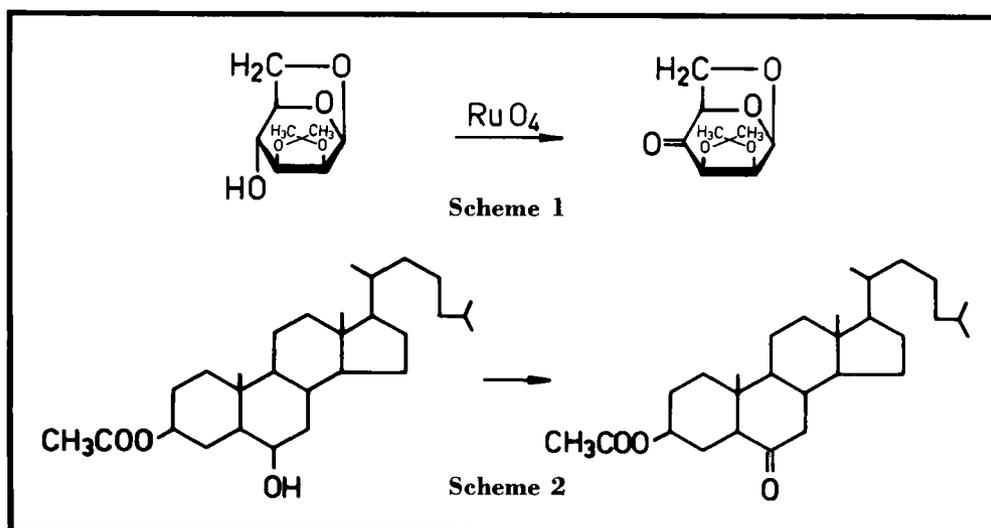
The use of ruthenium tetroxide in pollution control has been covered in this Journal

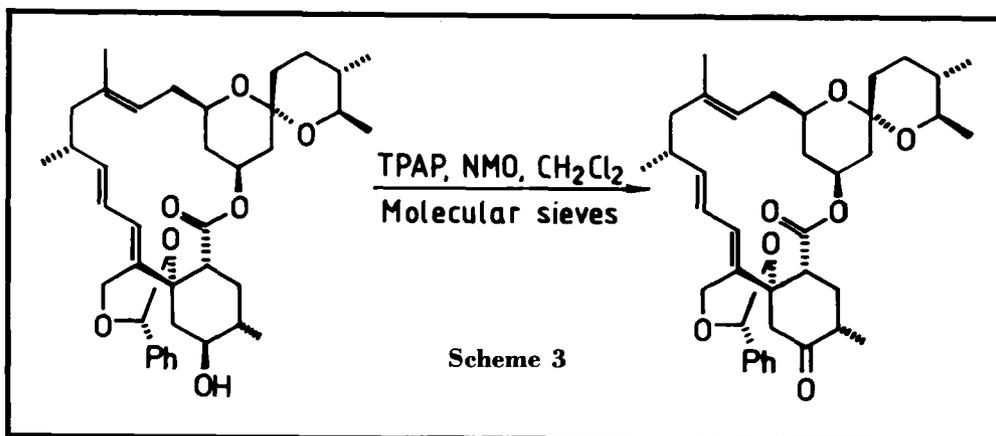
previously (10) and so will be mentioned here only briefly. The possibility of using catalytic ruthenium tetroxide-hypochlorite catalytic mixtures to destroy dioxins has been demonstrated (11), as has its capacity to destroy oxidatively other industrial pollutants such as organosulphur reagents and polychlorinated biphenyls (PCBs) (12, 13).

Oxoruthenium Complexes as Selective Oxidants

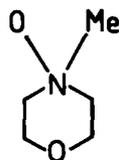
Ruthenium (VII). Despite the uses to which ruthenium tetroxide has been put it cannot be described as a delicate reagent; its virtues lie in its powerful oxidising ability. By using oxoruthenium complexes in which the metal is in a lower oxidation state, however, gentler oxidations can be accomplished, and much research has been done in this area in recent years. There is great need in the fine organic chemicals industry, for example pharmaceutical manufacture, for oxidants which are regioselective and/or stereoselective, and thus able to bring about the oxidation of a specific group without affecting other sensitive groups.

The perruthenate ion $[\text{RuO}_4]^-$ has long been known, and is a rare example of heptavalent ruthenium. In aqueous base it does indeed function as a milder oxidant than ruthenium tetroxide, converting primary





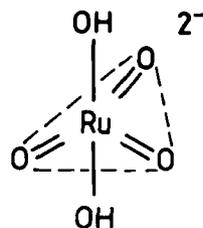
alcohols to carboxylic acids and secondary alcohols to ketones (14, 15). It cleaves double bonds in such alcohols, in addition to oxidising them, and is not catalytic in its action. However, the addition of tetra-*n*-butylammonium hydroxide ($(\text{C}_4\text{H}_9)_4\text{N}\text{OH}$) to the aqueous $[\text{RuO}_4]^-$ ion gives $(\text{C}_4\text{H}_9)_4\text{N}[\text{RuO}_4]$, which is readily soluble in a wide range of solvents, and will oxidise primary alcohols to aldehydes, and secondary alcohols to ketones without attacking double or allylic bonds (16). This salt, which we have called "TBAP", and its tetra-*n*-propylammonium analogue $(\text{C}_3\text{H}_7)_4\text{N}[\text{RuO}_4]$ ("TPAP"), can more easily be made by passing a current of air through a mixture of $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ in aqueous sodium periodate and carrying the ruthenium tetroxide so formed into an aqueous basic solution of tetra-*n*-propyl- or tetra-*n*-butylammonium hydroxide (17, 18). The deep green TPAP or TBAP precipitates, TPAP in higher yield than TBAP. These can readily be dissolved in dichloromethane or acetonitrile and will function catalytically if *N*-methylmorpholine-*N*-oxide (NMO) is used in excess as a co-oxidant (17).



A wide range of selective oxidations has been

performed by TPAP in particular; when used in acetonitrile with powdered molecular sieves, to remove water formed during reaction. It will oxidise alcohols without affecting such otherwise sensitive linkages as epoxides, lactones, indoles, silyl ethers, acetals and tetrahydropyranyl functions. A recent example of its use in the synthesis of a natural product is one stage (Scheme 3) in the preparation of the anti-parasitic reagent Milbemycin β_1 (19).

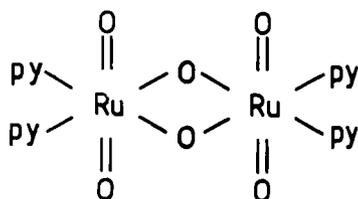
Ruthenium(VI). The ruthenate ion $\text{trans}[\text{RuO}_3(\text{OH})_2]^{2-}$ has an unusual trigonal bipyramidal structure, below (20), and can be



generated very simply from $\text{RuCl}_2 \cdot n\text{H}_2\text{O}$ or $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ in base with excess persulphate. The ruthenate ion then functions as a two-electron oxidant, oxidising primary alcohols to carboxylic acids and secondary alcohols to ketones, itself being reduced to ruthenium dioxide (21). The excess persulphate then functions as a co-oxidant re-oxidising the ruthenium dioxide back to $\text{trans}[\text{RuO}_3(\text{OH})_2]^{2-}$ so that the system is catalytic just like $\text{RuO}_4/\text{IO}_4^-$. As might be expected, it is a much gentler oxidant than ruthenium tetroxide, although less so than

TPAP. Nevertheless allylic alcohols are partially cleaved by it (15). It has recently been observed that in some systems this reagent will oxidise nitro to keto groups (22), a reaction which should be investigated further. The species $\text{trans}[\text{RuO}_2(\text{HIO}_6)_2]^{6-}$ is also very like ruthenate in its action towards alcohols, but unusual in that it is an overall six electron oxidant with both the ruthenium(VI) centre and the two iodine(VII) ligands each functioning as two electron oxidants. This complex is made from $\text{RuO}_2 \cdot n\text{H}_2\text{O}$ and periodate in base, the latter preventing further oxidation to ruthenium tetroxide, and is catalytic with periodate (IO_4^-) as co-oxidant (23).

The dimeric species $\text{Ru}_2\text{O}_6\text{py}_4$, made from ruthenium tetroxide and pyridine (py), is soluble in dichloromethane and acetonitrile and is an overall eight electron oxidant (four electrons per metal atom):



It behaves rather like TPAP, oxidising primary alcohols to aldehydes and secondary alcohols to ketones. It is catalytic in the presence of NMO but is also catalysed by oxygen at room temperatures, albeit with modest turnovers (24). A number of other ruthenium(VI) oxidants have been studied; for example, $\text{trans}[\text{RuO}_2(\text{porph})]$, where porph is tetramesityl-porphyrin, will effect aerobically catalysed epoxidations of alkenes (25), while a variety of macrocyclic complexes of the form $\text{trans}[\text{RuO}_2(\text{R-TMC})]^{2+}$ will oxidise alcohols and epoxidise alkenes (R-TMC = macrocyclic tetra-aza nitrogen donor ligands) (26).

Osmium

Osmium Tetroxide

This was the first form in which osmium was isolated in 1803 by the English chemist Smithson Tennant (1761–1815) (27).

Like ruthenium tetroxide, osmium tetroxide is a pale yellow solid with a substantial vapour pressure at room temperature. It melts at 40.6°C , boils at 121.2°C and has a density of 4.906 g/cm^3 . Its solubility in water is 7.2 per cent at 25°C , but it is much more soluble in inert organic solvents. Because it is a much milder oxidant than ruthenium tetroxide it is in some ways easier to use, although, like the latter, it is often used catalytically in conjunction with co-oxidants such as chlorate, tert-butylhydroperoxide, NMO, hypochlorite, hydrogen peroxide, chloramine-T and N-chloro-N-argenticarbamates, either in a single or a biphasic system.

The author wrote a short article on osmium tetroxide and its applications in *Platinum Metals Review* some years ago, (28), and there are two recent and comprehensive reviews on osmium tetroxide as an oxidant (29, 30). It is of course milder than ruthenium tetroxide, but will cause the oxidation of a number of organic substrates. Its pre-eminent use is, however, for the stereoselective cis-hydroxylation of alkenes to vicinal diols, that is, glycols. As an oxidant it has unparalleled efficiency and smoothness of reaction for this process. An exciting recent development, of great interest and application to the fine organic chemicals and pharmaceuticals industries, is the production of optically active glycols by the asymmetric catalytic osmylation of alkenes. The procedure was first employed by Sharpless who used the acetates of quinidine and hydroquinidine as chiral amines weakly bound to the osmium tetroxide. Curiously, pyridine and other tertiary amines, which are often used to accelerate the osmium tetroxide-alkene reaction, have an inhibitory effect on asymmetric osmylation. The use of NMO as a co-oxidant renders the reaction catalytic and extremely efficient; very little osmium tetroxide is required (31).

Footnote

Because of their high volatilities at room temperature and the toxicity of their vapours, both ruthenium tetroxide and osmium tetroxide should be handled with great care in well-ventilated fume cupboards. Solutions containing these materials in catalytic quantities are, however, far less hazardous.

References

- 1 K. Klaus, *Uch. Zap. Kazanskaya Univ.*, 1844, **III**, 15
- 2 K. Klaus, *J. Prakt. Chem.*, 1860, **79**, 43
- 3 C. Djerassi and R. Engle, *J. Am. Chem. Soc.*, 1953, **75**, 3838
- 4 D. G. Lee and M. van der Engh in "Oxidation in Organic Chemistry", Vol. B, ed. W. S. Trahanowsky, Academic Press, New York 1973, p. 177
- 5 J. L. Courtney in "Organic Syntheses by Oxidation with Metal Compounds", ed. W. J. Meijs and C. R. H. I. de Jonge, Plenum, New York, 1986, p. 445
- 6 S. Giddings and A. Mills, *J. Org. Chem.*, 1988, **53**, 1103
- 7 J. C. Sheehan and R. W. Tulis, *J. Org. Chem.*, 1974, **39**, 2264
- 8 H. Nakata, *Tetrahedron*, 1963, **19**, 1959
- 9 R. F. Butterworth and S. Hannessian, *Synthesis*, 1971, 70
- 10 E. S. Gore, *Platinum Metals Rev.*, 1983, **27**, (3), 111; see also *ibid.*, 1988, **32**, (4), 186
- 11 D. C. Ayres, *Nature*, 1981, **290**, 323
- 12 C. S. Creaser, A. R. Fernandes and D. C. Ayres, *Chem. Ind.*, 1988, (15), 499
- 13 D. C. Ayres, C. S. Creaser and D. P. Levy in "Chlorinated Dioxins and Dibenzofurans in the Total Environment II", ed. L. K. Keith, C. Rappe and C. Choudhary, Butterworths, London, 1985, p. 37
- 14 Y. Nakano and T. A. Foglia, *J. Am. Oil Chem. Soc.*, 1982, **59**, 163
- 15 G. Green, W. P. Griffith, D. M. Hollinshead and S. V. Ley, *J. Chem. Soc., Perkin I*, 1984, 681
- 16 A. C. Dengel, R. A. Hudson and W. P. Griffith, *Trans. Met. Chem.*, 1985, **10**, 98
- 17 W. P. Griffith, S. V. Ley, G. P. Whitcombe and A. D. White, *J. Chem. Soc., Chem. Commun.*, 1987, 1625
- 18 A. C. Dengel, A. M. El-Hendawy and W. P. Griffith, *Trans. Met. Chem.*, 1989, **14**, 230
- 19 N. J. Anthony, A. Armstrong, S. V. Ley and A. Madin, *Tetrahedron Lett.*, 1989, **30**, 3209
- 20 M. O. Elout, W. G. Haijie and M. J. A. Maaskant, *Inorg. Chem.*, 1988, **27**, 610
- 21 M. Schröder and W. P. Griffith, *J. Chem. Soc., Chem. Commun.*, 1979, 58
- 22 E. J. Corey and A. G. Myers, *J. Am. Chem. Soc.*, 1985, **107**, 5574
- 23 A. M. El-Hendawy, W. P. Griffith, C. A. O'Mahoney and D. J. Williams, *J. Chem. Soc., Dalton Trans.*, 1988, 1983
- 24 A. M. El-Hendawy, W. P. Griffith, M. N. Moussa and F. I. Taha, *J. Chem. Soc., Dalton Trans.* 1989, 901; A. C. Dengel, A. M. El-Hendawy and W. P. Griffith, *ibid.*, submitted for publication
- 25 J. T. Groves and K.-H. Ahn, *Inorg. Chem.*, 1987, **26**, 3831; J. T. Groves and R. Quinn, *J. Am. Chem. Soc.*, 1985, **107**, 5790
- 26 C. M. Che, T. F. Lai and K. Y. Wong, *Inorg. Chem.*, 1987, **26**, 2289
- 27 Smithson Tennant, *Phil. Trans.*, 1804, **94**, 411
- 28 W. P. Griffith, *Platinum Metals Rev.*, 1974, **18**, (3), 94
- 29 M. Schröder, *Chem. Rev.*, 1980, **80**, 187
- 30 H. S. Singh in Ref. 5, p. 633
- 31 J. S. M. Wei, I. Marko, J. S. Svendsen, M. G. Finn, E. N. Jacobsen and K. B. Sharpless, *J. Am. Chem. Soc.*, 1989, **111**, 1123; E. N. Jacobsen, I. Marko, W. S. Mungall, G. Schröder and K. B. Sharpless, *ibid.*, 1988, **110**, 1968

Palladium Impedes Radionuclide Pick-Up in Steel

The γ -emitting isotope, ^{60}Co , is known to be the primary offender in causing radioactivity of reactor structural steels. This radionuclide readily incorporates into the various oxides that form on the out-of-core steel surfaces of nuclear reactors operating in coolant environments, at temperatures of approximately 280°C. Thus to lessen the build up of radiation in these structural materials there is a need to eliminate or reduce the incorporation of ^{60}Co .

Some extremely encouraging experimental results from North America have recently been reported following the exposure of various pre-treated austenitic 304 steels to simulated boiling water reactor and pressurised water reactor primary coolant conditions (1, 2). Two metallic films and nineteen pre-oxidation treatments were evaluated for their efficacy in reducing ^{60}Co contamination. Of these treatments, the

deposition of palladium by an electroless technique proved to be particularly effective. Palladium, about 0.6 μm thick, deposited from a standard electroless plating bath closely followed the contours of the steel, and generally filled in major defects on the surface. This layer reduced the corrosion of the stainless steel and so impeded radionuclide pick-up.

Although amorphous nickel-phosphorus films performed reasonably well, it is pointed out that such a system has less attractive characteristics, due to the potential release of the γ -emitting ^{58}Co isotope from radioactivated nickel.

References

- 1 H. Ocken, B. G. Pound and D. H. Lister, *Thin Solid Films*, 1989, **171**, (2), 313-322
- 2 H. Ocken, C. C. Lin and D. H. Lister, *Thin Solid Films*, 1989, **171**, (2), 323-334