

The Oxidation of Alcohols to Aldehydes or Ketones

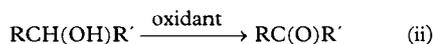
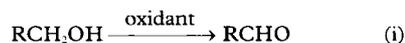
HIGH OXIDATION STATE RUTHENIUM COMPOUNDS AS CATALYSTS

By Holger B. Friedrich

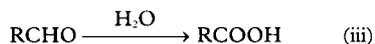
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The oxidations of alcohols to aldehydes and ketones are vital reactions in synthetic organic chemistry, and high selectivity and mild conditions are important prerequisites for ease of product work-up and lower cost. Currently, many of the best oxidants for these conversions contain high valent ruthenium, with ruthenium acting as a catalyst for these reactions. It is important to have detailed knowledge and understanding of the mechanisms of the oxidation reactions and the factors that influence them, as only by completely understanding how these processes work will it be possible to design better or optimal catalysts. In this paper, the more viable oxidants currently available are reported and some investigations into the mechanisms of the reactions and factors affecting them are discussed.

As the catalytic conversions of primary alcohols into aldehydes and of secondary alcohols into ketones are essential for the preparation of many key synthetic intermediates in organic chemistry, there is currently much activity being undertaken in the search for catalytic systems which can perform these operations.



In particular, the reaction shown in Equation (i) does not usually stop at the formation of the aldehyde and over-oxidation to the carboxylic acid often occurs.



Historically, various oxidative systems have been available for these reactions, including chromium(VI) oxo compounds, copper chromites (often used industrially for bulk preparations), vanadium pentoxide, PtO_2 , $\text{RuCl}_4/\text{Cu}(\text{II})$ (1, 2) and the Swern oxidation (3). However, there are various drawbacks to using these reagents; for instance, they are either rather aggressive, need relatively high or low temperatures, give unwanted and difficult to

remove by-products, are difficult to separate from the product after the reaction is over, require acidic conditions which limit the choice of substrate, or, they do not give complete conversions in all applications. Thus, there is clearly a need to prepare milder and more selective oxidants with higher rates of conversion. Several oxidative systems which at least partially fit the above criteria have recently been reported, and many of these contain or are based on ruthenium.

The chemistry of high-oxidation-state ruthenium is less well developed than that of, for example, osmium (4) or rhenium (5). Specifically, reaction mechanisms and the factors which influence the performance of various oxidants are poorly understood. It is clear, however, that several of the high valent oxo ruthenium compounds made so far are active in transforming both primary alcohols into aldehydes and secondary alcohols into ketones. While many compounds will cause these transformations, few do so catalytically and this may be ruthenium's strength. Many of the known ruthenium-containing oxidants are also tolerant of other sensitive functional groups in organic molecules. It would be desirable to have a very

selective catalytic oxidant, which would not attack other potentially reactive groups, such as double bonds, halides, epoxides, esters, amides, or protecting groups, such as silyl or benzoate, amongst many others. Ideally, this catalytic oxidant would also operate at room temperature in an environmentally friendly solvent system (such as water) and use "green" co-oxidants such as oxygen (O₂) or hydrogen peroxide (H₂O₂). This ideal catalytic oxidant should also be easy to recycle. Designing such systems remains a challenge, although significant progress is being made. Other factors which influence the acceptance of new catalysts include the ease of operation and the ease of (synthetically or commercially) producing the catalyst.

Ruthenium Oxide Catalyst Systems

The only known well-defined stable ruthenium(VIII) compound is ruthenium tetroxide, RuO₄, which is frequently far too vigorous an oxidant, as it attacks many functional groups, such as double bonds, and often forms carboxylic acids. Consequently, research has focused on ruthenium compounds in slightly lower oxidation states.

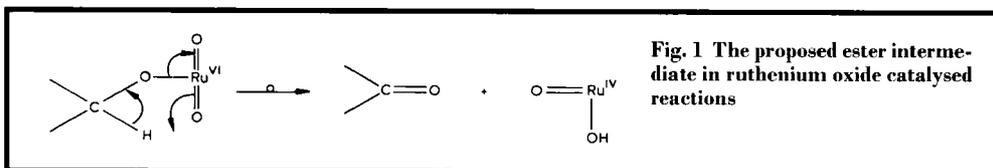
"Catalytic" systems reported in the literature with reasonably high selectivities, conversions (depending on substrates) and turnovers (measured as moles of product per mole of catalyst), are [Ru₂O₆(py)₄]·3.5H₂O (py = pyridine), *trans*-[4-^tBu-Hpy][RuO₂Cl₂(4-^tBu-py)] (Hpy is a protonated pyridine), [LPh₃][RuO₂Cl₂] (L = P, As) and *trans*-[RuO₂(py)₄][BF₄]₂, all having 4-methylmorpholine N-oxide, MNO, as co-oxidant (6–8). These compounds are obtained in moderate yield, and the first two are made by utilising RuO₄ as a gas, and require appropriate manipulative and experimental skills. The dinuclear compound also appears to have a limited "shelf-life".

A series of compounds, which appear to have considerable potential as viable catalytic oxidants are the compounds *cis*-[PPh₃]₂[RuO₂Cl₂(OCOR)] (R = Me, Et, Pr, CHF₂), (9). The *cis*-oxo arrangement is unusual because of the considerable electronic stabilisation associated with the *trans*-dioxo, *d*², configuration

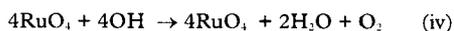
(10). The acetic acid derivative was shown to be a good catalytic oxidant with MNO as co-oxidant. No effects were observed on varying the length of the alkyl chain (R). It was felt that this system was worth further investigation and high yield routes to the compounds, where R = Me, CF₃, C₆H₅, C₆F₅ and C₃H₁₁, were developed, which avoided the need to use RuO₄ gas. The compounds were found to be stable and catalytically active with a wide range of co-oxidants (H₂O₂, NaOCl, ^tBuOOH {tertiary-butyl hydroperoxide}) with MNO and tetrabutylammonium periodate being the best, amongst others. Fluorinated compounds often display very different properties to their protonated analogues, probably because fluorine and hydrogen, although being of similar size, have very different electronegativities. However, we found that apart from significantly affecting the synthetic yields of the oxidants, no effect on the oxidations was observed.

The most well-known ruthenium oxide catalyst, tetrapropylammonium perruthenate (TPAP) and its sister tetrabutylammonium perruthenate (TBAP) are effective in many selective organic transformations of the type summarised in Equations (i) and (ii) using MNO as the co-oxidant. A comprehensive review has recently been published (11). TPAP is also almost the only ruthenium oxidation catalyst to have been studied kinetically. The reaction of TPAP with propan-2-ol was found to be autocatalytic, possibly due to the formation of colloidal RuO₂ which may form RuO₄·nRuO₂ (12). TPAP is a three-electron oxidant overall, but it is believed that the alcohol oxidation step is of the two-electron type. The fact that TPAP will oxidise cyclobutanol to cyclobutanone suggests that a one-electron oxidation process is not involved, since a one-electron oxidant would cleave cyclobutanol to acyclic products (13).

Other reported ruthenium(VI) oxidants will usually convert primary alcohols into acids, although internal alcohols will still be converted into ketones. Compounds reported to effect these transformations are K[RuO₄] and [RuO₄]²⁻ (really *trans*-[RuO₃(OH)₂]²⁻) (7, 14, 15). The yields range from moderate to good, depending



on the substrate. Conversions are carried out in basic aqueous media, as ruthenate and per-ruthenate are unstable at lower pH. This limits the reagents to substrates which are stable at high pH. The reactions are rendered catalytic by using $K_2S_2O_8$ (persulfate) or BrO_3^- (bromate) as the co-oxidant. Similar results are attained in the same media using $trans-[RuO_2(HIO_6)_2]^0$ as catalyst, with $NaIO_4$ as the co-oxidant (16). Even ruthenium tetroxide, RuO_4 , has been reported as oxidising secondary alcohols to ketones (1, 17). However, both RuO_4 and sodium ruthenate are known to attack double bonds, although sodium ruthenate will do so only if high temperatures or longer reaction times are employed (18, 19). Since RuO_4 is unstable at $pH > 8$, the active species in those reactions reported to involve RuO_4 and $NaOCl$ is probably RuO_4^- , see Equation (iv) (20).



At high pH (>12) though, ruthenate is the dominant species:

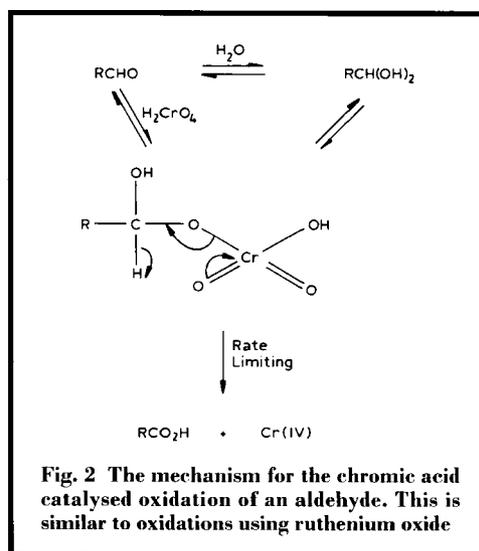


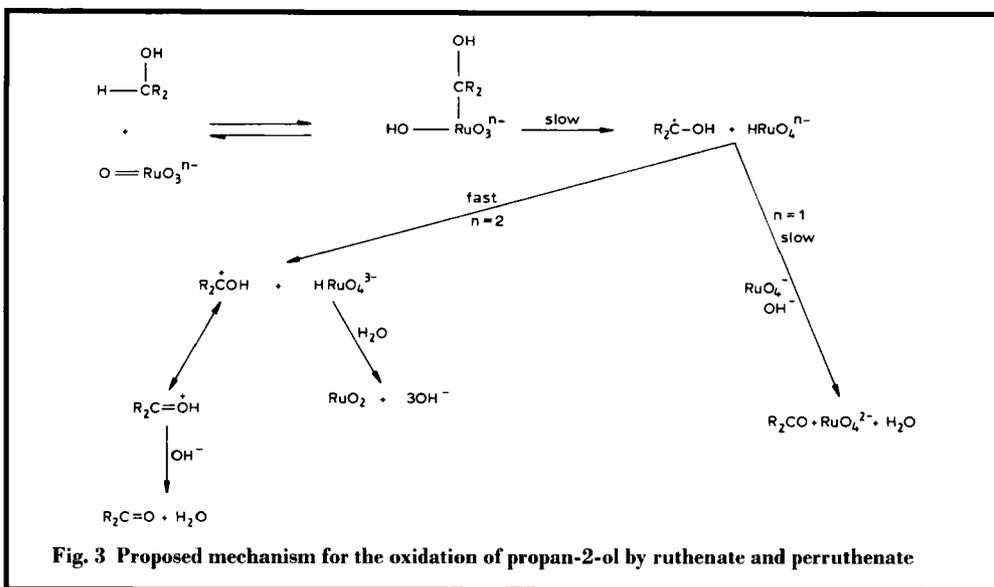
The compound $[RuO_2(\text{tetramesitylporphyrinato})]$ has been reported to oxidise alkyl alcohols to ketones, although its primary application is as an alkane oxidant (21).

Strictly speaking, few of the above mentioned ruthenium catalysts are true catalysts, since if the "catalytic" reactions are carried out with too little co-oxidant, the ruthenium compound remains in a reduced state. A catalyst should be unchanged after a reaction. Instead, the ruthenium oxo compounds are really primary oxidants, that is, they directly oxidise the substrate. The co-oxidant is the secondary oxidant – which regenerates the primary oxidant. A few of the commonly used secondary oxidants do react directly with alcohols (for example, MNO with

primary alcohols), but the conversions are generally low.

Alcohol oxidations with transition metal oxo reagents probably mainly involve the same basic transformation as shown in Figure 1, involving an ester intermediate. For all of the catalytic oxidants mentioned above, primary alcohols react more rapidly than secondary alcohols, probably due to steric hindrance of secondary alcohols. It is generally thought that the reagents, reported above, which effectively catalyse the reaction in Equation (i), do so because of the presence of molecular sieves in the reaction medium. The molecular sieves efficiently remove water (formed in the reaction and present as water of crystallisation of MNO). It is known that an aldehyde hydrate is necessary for the reaction in Equation (iii) to occur. The mechanism for the oxidation by chromic acid of an aldehyde is shown in Figure 2 (22) and ruthenium oxide oxidations are presumed to be similar. Some preliminary results from our



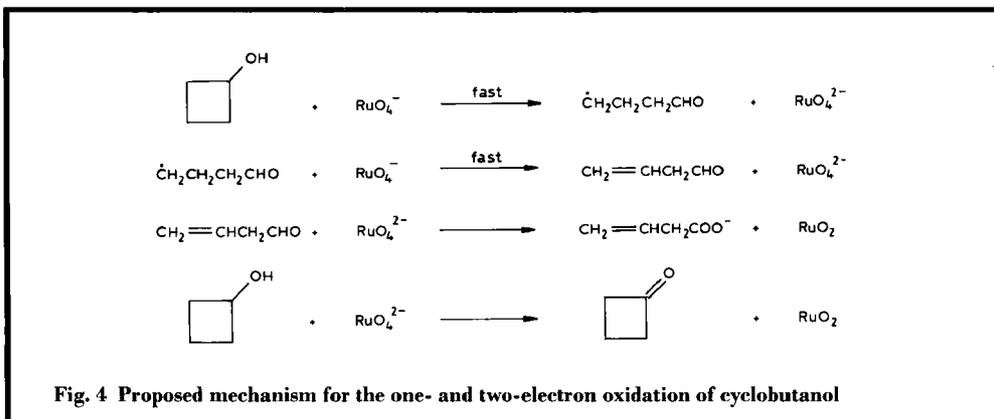


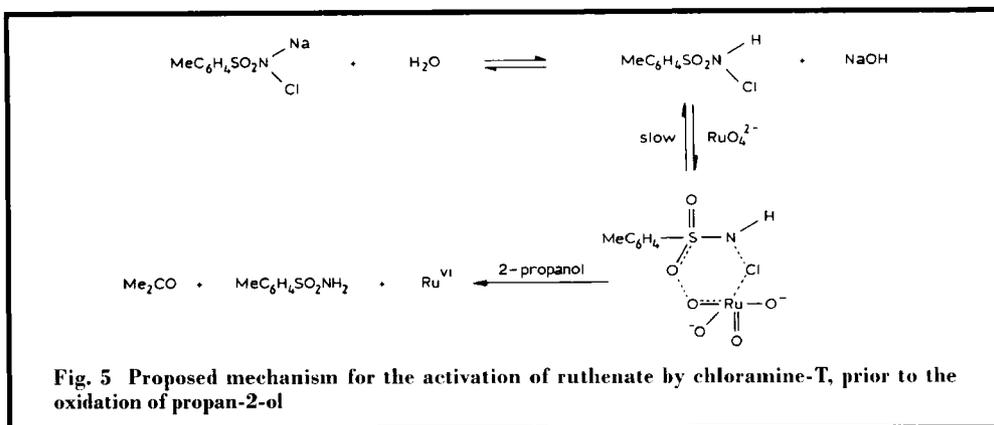
laboratory, however, imply that the presence of water in the reaction medium does not necessarily mean that the reaction in Equation (iii) will proceed.

The stoichiometric oxidations of propan-2-ol with the sodium salts of ruthenate and perruthenate have been investigated kinetically and mechanistically (23). Both reactions are believed to proceed via free radical-like transition states, although the subsequent steps differ. For both ruthenate and perruthenate, an ester intermediate, as shown in Figure 1, is thought to be unlikely and instead it is assumed that the

ruthenium salts add to an α -C-H bond of the alcohol. The proposed mechanism is shown in Figure 3. Since HRuO_4^{2-} is very reactive, it is believed that a single electron transfer would occur very rapidly, before the radical could diffuse out of the solvent cage. For the stoichiometric oxidation of propan-2-ol with perruthenate, as shown in Figure 3, it is thought likely that because the HRuO_4^{3-} ion is less reactive, the product would move out of the solvent cage before further reaction. These proposed mechanisms fit theoretical predictions (24).

The reactions of $[\text{RuO}_4]^-$ and $[\text{RuO}_4]^{2-}$ with





cyclobutanol suggest that the latter is a two-electron and the former, unlike TPAP, is a one-electron oxidant, see Figure 4 (25).

The mechanisms of the catalytic oxidations of propan-2-ol using $[\text{RuO}_4]^{2-}$ with a variety of co-oxidants have also been investigated. For the co-oxidants hexacyanoferrate(III), diperiodatocuprate(III) and periodate, the data imply that a complex is formed, as for the stoichiometric oxidation, Figure 3. The role of the co-oxidant is only to regenerate Ru(VI). The exception is when the co-oxidant is chloramine-T. In this case, the co-oxidant appears to react directly with the Ru(VI) ion, see Figure 5. This active complex then reacts rapidly with propan-2-ol to form acetone (26). It seems very likely, however, that these mechanisms are only valid in aqueous base and the mechanisms are probably different in non-aqueous media, as shown, for example, by the different reaction products obtained in the oxidation of cyclobutanol with TPAP and basic perruthenate.

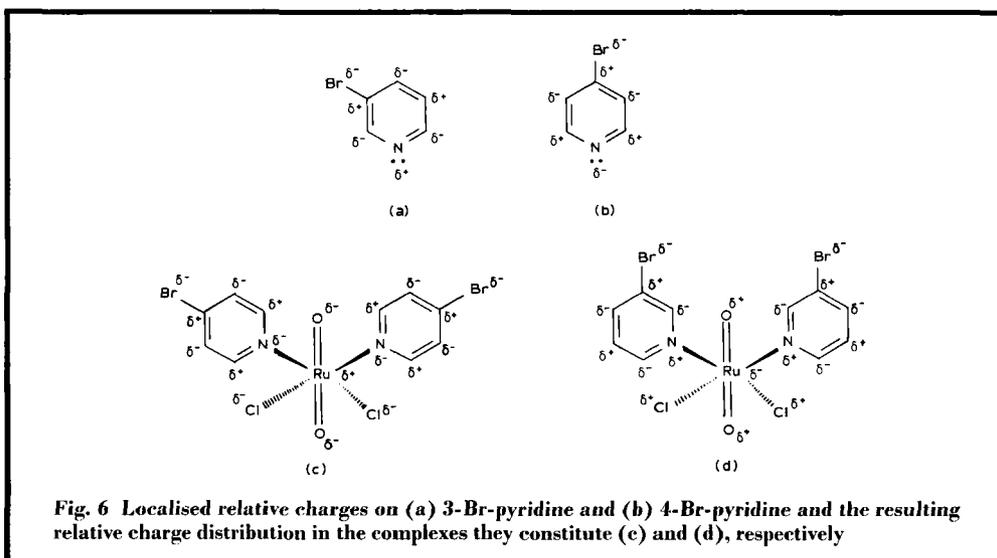
The disadvantages of many of the catalysts that catalyse the reaction in Equation (i) and also of several which efficiently catalyse the reaction in Equation (ii) are that they require CH_2Cl_2 or CH_3CN as solvents (which are not "green") and that they require MNO as co-oxidant. However, the MNO co-oxidant is expensive, an irritant to the eyes, the respiratory system and the skin, and its final product, 4-methyl morpholine, is corrosive and causes burns to the skin, the eyes and mucous layers in the nasal

tract. Apart from this, even the best known catalysts do not give quantitative or almost-quantitative transformations in all apparently suitable systems and, as such, there is a great need to develop more effective and more selective catalysts with higher turnovers.

In general, the activity of catalysts is affected by the steric bulk (for instance, cone angles) of the attached groups and the electron density on the metal. The significant effect of the groups attached to the Ru(VI) centre is demonstrated by the examples of Ru(VI)O₂ moieties bonded to porphyrins or to other bulky tetradentate ligands: many of these compounds are effective catalysts for the epoxidation of olefins (27). None of the other ruthenium(VI) oxo catalysts, referred to above, can perform this reaction. However, even Ru(VI)O₂ compounds, with bulky bidentate ligands, can catalyse epoxidation reactions (28).

Towards Commercial Catalysts

As part of a project to develop commercially viable catalysts for the oxidation of alcohols, we are interested in determining how various substituents affect the chemistry of ruthenium(VI) oxo compounds. One potential route would involve the synthesis of organometallic ruthenium(VI) oxo compounds. The possibility of being able to vary and fine-tune a wide range of alkyl or aryl substituents should offer much information on these systems and facilitate the design of highly specific catalysts. However, only a few



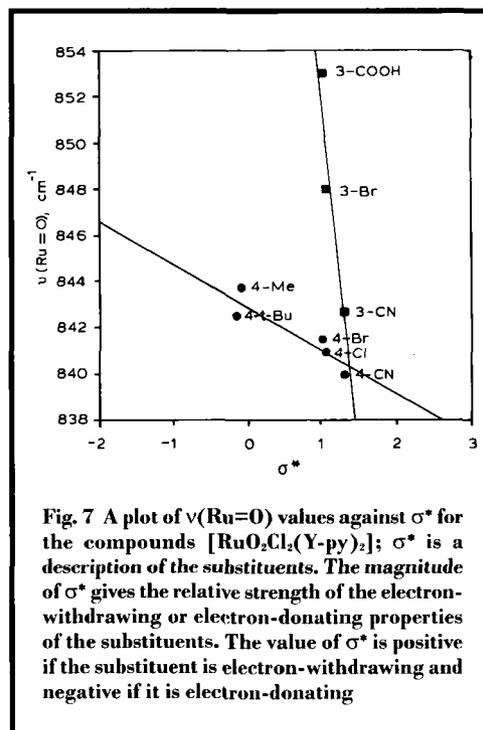
mono-oxo ruthenium(VI) organometallic compounds are known (29) and ruthenium(VI) organometallic di-oxo compounds have so far proved to be totally elusive.

Alternatively, one can study the effects of substituents in inorganic ruthenium oxo compounds. This latter approach has the advantage that routes to discreet, fully characterisable compounds of this type are already available.

The first system to be considered consisted of compounds of the type $[\text{RuO}_2\text{Cl}_2(\text{Y-py})_2]$ ($\text{Y} = \text{H}, 4\text{-}^i\text{Bu}, 3\text{-CN}, 4\text{-CN}, 2\text{-Br}, 3\text{-Br}, 4\text{-Br}, 4\text{-Cl}, 4\text{-Me}, 4\text{-C}(\text{O})\text{C}_6\text{H}_5, 3\text{-COOH}, 4\text{-COOH}$). This series was chosen because we thought that substituents on a flat aromatic ring, for which Hammett substituent constants were available, should show easily quantifiable electronic effects on the ruthenium centre. The first examples of compounds in this series ($\text{Y} = \text{H}, 4\text{-}^i\text{Bu}, 4\text{-Cl}$) were prepared by Griffith and co-workers (6) and the rest by us (30). As can be seen from Figure 6, substitution at either the 3- or 4-position of the pyridine ring should have a significant effect on the charge on the pyridine nitrogen and consequently on the net charge on the ruthenium centre.

Similarly, the nature of the substituent Y (either electron pushing or electron withdrawing) should affect the charge on the pyridine nitrogen and

hence on the ruthenium centre. These effects should be revealed by changes in the $\text{Ru}=\text{O}$ stretching vibrations. This is confirmed by examining the IR spectra of these compounds.



Stoichiometric and *Catalytic Oxidations of 1-Hexanol to Hexanal by (Y)O ₂ Cl ₂ Ru with a Range of Co-catalysts, over a 24-hour period						
Substituted pyridine (Y)	Stoichiometric oxidations	Co-catalysts, % conversion				Characteristic $\nu(\text{Ru}=\text{O})$, cm ⁻¹
		*H ₂ O ₂	*NaOCl	* ^t BuOOH	*MNO	
(4- ^t Bu-py) ₂	39	15	13	12	22	842.4(vs)
(3-CN-py) ₂	34	8	9	9	14	842.7(m)
(4-CN-py) ₂	38	10	11	10	16	840(vs); 831(s)
(2-Br-py) ₂	84	15	47	39	54	826(s)
(3-Br-py) ₂	63	45	85	55	97	848(vs); 817.7(s)
(4-Br-py) ₂	59	36	64	51	99	841.1(vs)
(4-Cl-py) ₂	50	-	65	-	96	840.5(vs)
(3-Cl-py) ₂	-	-	45	-	65	849.5(m)
(py) ₂	50	-	-	-	-	837.5(vs)
bipy	63	13	17	15	23	839(vs)
phen	7	6	6	5	16	845.5(vs)
(4-Me-py) ₂	-	-	-	-	-	843.7(vs); 830.9(s)
(4-C(O)C ₆ H ₅ -py) ₂	31	-	-	-	-	840.8(s)
(3-COOH-py) ₂	-	-	-	-	-	853(s)
(4-COOH-py) ₂	-	-	-	-	-	841.5(m)

All runs were repeated at least three times and are reproducible. m – medium, s – strong, vs = very strong

Excluding the compound where Y = H, the $\nu(\text{Ru}=\text{O})$ stretches correlate linearly with the Hammett, σ , and Taft, σ^* , values, see Figure 7, and Pauling type electronegativity (X) values of the Y substituents. Since these values are due to an inductive effect, one would expect the inductive effect to increase with decreasing distance between the substituent, Y, and the ruthenium centre. This is observed, with the slope of the graph for the 3-substituted compounds being much steeper than for the 4-substituted compounds.

Thus, these complexes are stoichiometric and “catalytic” oxidants for the conversion of alcohols to aldehydes, with the substituents, Y, clearly affecting the performance of the compounds. The Table shows values for stoichiometric oxidations of 1-hexanol to hexanal by (Y)O₂Cl₂Ru with a range of co-catalysts.

A sequence was observed of the oxidising ability for the stoichiometric oxidations: phen < 4-Me-py < benzoyl-py < 3-CN-py < 4-CN-py < 4-^tBu-py < 4-Cl-py ≈ py < 3-Br-py ≈ 4-Br-py < bipy. An almost identical sequence was

observed for the “catalytic” oxidations, using H₂O₂, hypochlorite (OCl) or *t*-butyl hydroperoxide ((CH₃)₃COOH) as the co-oxidants. Although the Y substituents clearly affect the $\nu(\text{Ru}=\text{O})$ values and hence the strength of the Ru=O bond and the electron density on the metal, no correlation between oxidising ability and substituent constants for Y is observed. This implies that electron density on the metal has no significant effect on these compounds as oxidants.

In addition, electronic effects do not appear to play a role in the performance of the Ru(VI) salts, [PPh₃]₂[RuO₂Cl₂(OCOR)], as reported above. While most of the above compounds are mediocre oxidants, the performance of [RuO₂Cl₂(4-Br-py)₂] is exceptional and so is that of [RuO₂Cl₂(3-Br-py)₂], to a lesser extent. Both of these are far superior oxidants to any of the other compounds in this series. The 4-Br-pyridine derivative gives especially high rates of conversion with reasonable turnovers. We are at present investigating this clear ligand effect.

A study of the compounds [RuO₂Cl₂L] (L =

bipyridyl, 1,10-phenanthroline) indicates that the rigidity of the ligands may also play a role, as the bipyridyl compound is a reasonable oxidant, whereas the phenanthroline compound is a very poor oxidant, as shown in the Table.

One of the great disadvantages of many homogeneous catalytic systems is the problem of separating the product from the catalyst. For this reason heterogeneous catalysts remain very popular, as the catalyst can simply be filtered off and reused.

One way of attempting to combine the advantages of homogeneous and heterogeneous catalysts is by bonding soluble catalysts to insoluble supports, although these have yet to attain a large scale industrial breakthrough (31). We have supported ruthenate on poly-(4-vinylpyridine) and on zeolite-Y. Both these supported catalysts appear to be very selective in the oxidations referred to in Equations (i) and (ii), with a wide range of co-oxidants at room temperature (32). The catalysts can be filtered off and reused. We are currently investigating both the structures and the versatility of these catalysts. We believe that the ruthenate may be bonded to the polymer, as is the OsO_4 /poly-(4-vinylpyridine) system for oxidising alkenes to diols, rather than just being supported (33).

A ruthenium hydrotalcite heterogeneous competitor has recently been reported (34). This catalyst is reported to oxidise primary and secondary alcohols into aldehydes and ketones, respectively, in high yields with high selectivity. This catalyst appears to be easily prepared and the oxidations take place at 60°C in toluene, using molecular oxygen as co-oxidant. It would appear that a heteronuclear interaction between ruthenium and cobalt is responsible for the high activity, with ruthenium probably being oxidised

to a +6 oxidation state within the Brucite, $\text{Mg}(\text{OH})_2$, layer.

The use of oxygen as co-oxidant, as in the system mentioned above, is very advantageous from an environmental point of view. We have carried out extensive studies on various co-oxidants for the catalysts $[\text{RuO}_2\text{Cl}_2(\text{Y-py})_2]$, $[\text{PPh}_3]_3[\text{RuO}_2\text{Cl}_2(\text{OCOR})]$ and polymer or zeolite “supported” ruthenate. While these systems are active for a wide range of co-oxidants, consistently, highest conversions for these systems and many of those reported above, are usually obtained using MNO , although tetrabutyl-ammonium periodate appears to be an excellent co-oxidant for the immobilised systems and also for the oxidation of primary alcohols with the salts $[\text{PPh}_3]_3[\text{RuO}_2\text{Cl}_2(\text{OCOR})]$ ($\text{R} = \text{CF}_3$, C_6H_5 , and C_6F_5).

Concluding Remarks

Thus, it would seem that high oxidation state ruthenium catalysts are amongst the best mild oxidants for the oxidation of alcohols, with little or no over-oxidation products being obtained. Our information remains limited on the mechanism of the reactions and on which factors, besides having ruthenium in a high oxidation state, influence the efficiency of these compounds. Our best hope of discovering what influences the oxidation chemistry of ruthenium will come from using homogeneous catalytic systems, although environmental and economic concerns may ultimately favour supported, heterogeneous or genuinely two-phase catalytic systems.

Acknowledgement

Thanks to the Alexander von Humboldt Foundation, NMT Electrodes, Western Platinum Refineries, the University of Natal and the Foundation for Research Development for their support; also to Vikash Gokul.

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Ruthenium in Living Radical Polymerisation

Living radical polymerisation has become an important technique in precision polymer synthesis for the construction of new polymers with tailor-made structural complexities. In order to assemble structurally well-defined polymers, in terms of molecular weights and molecular weight distributions, their polymerisation must be controlled. However, the control of the reactivity of the propagating chain ends was difficult, until the recent discovery of living (controlled) radical polymerisation. Due to its unique tolerance to water, radical polymerisation can be performed as suspension, dispersion and emulsion processes.

Most of these living radical polymerisations are based on transition metal catalysis (via reversible activation of a carbon-halogen terminal) or nitroxide-mediated processes.

Recently, workers at Kyoto University, Japan, have examined the living radical suspension polymerisation of methyl methacrylate (MMA) in water and alcohols using $\text{RuCl}_2(\text{PPh}_3)_2$, catalyst/activator and an organic halide initiator, such as PhCOCHCl_2 or CCl_2Br , in the

presence and absence of aluminium(III) isopropoxide, $\text{Al}(\text{Oi-Pr})_3$, at 80°C (T. Nishikawa, M. Kamigaito and M. Sawamoto, *Macromolecules*, 1999, **32**, (7), 2204–2209).

With ruthenium(II)-initiation, living radical suspension polymerisation of MMA proceeded to give poly(MMA) with controlled high molecular weights (\bar{M}_n) and narrow molecular weight distributions ($\bar{M}_w/\bar{M}_n = 1.1$ to 1.3). In water, the $\text{PhCOCHCl}_2/\text{RuCl}_2(\text{PPh}_3)_2$ initiating system gave poly(MMA) of $\bar{M}_n \sim 10^5$ and $\bar{M}_w/\bar{M}_n \sim 1.1$, even in the absence of $\text{Al}(\text{Oi-Pr})_3$.

Polymerisations were faster in water than in organic solvents, such as toluene. The radical mechanism of the polymerisation was confirmed and the high stabilities of the dormant carbon-halogen terminal and of the ruthenium catalyst in water and alcohols were demonstrated. Ruthenium complexes are known to be weakly oxophilic and sometimes water tolerant.

This living radical suspension polymerisation may also be used with other metal complexes or monomers and be applicable to the precision synthesis of block and random copolymers.