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Ruthenium-catalysed homogeneous oxidation processes

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Abstract - The mechanism of the ruthenium catalysed oxidation of alcohols in alkaline aqueous solutions has been elucidated by kinetics and electrochemical studies. The active oxidising species is ruthenium tetroxide, RuO_4. This chemistry can be applied to the oxidative destruction of organochlorine substances such as hexachlorobenzene, polychlorinated biphenyls, and organochlorine pesticides. Complete oxidation to carbonate and chloride occurs. In alkaline solution hypochlorite is a convenient oxidant. Even though bleach is relatively inexpensive, the economics of the process are in part determined by the stoichiometry. To reduce costs oxidation by oxygen is desirable. This can be accomplished electrocatalytically.

RUTHENIUM CATALYSED OXIDATIONS

Originally RuO_4 was employed in organic chemistry as a stoichiometric reagent. Difficulties in handling the substance soon led, however, to its use as a catalyst. It is a versatile oxidant and has been used with a wide range of substrates which includes alcohols, aldehydes, ketones, ethers, amines, phosphines, arenes, alkenes and alkynes (ref. 1 and 2). A variety of terminal oxidants have been employed under different conditions. These include not only powerful oxidising agents such as persulfate, periodate, chlorine, and hypochlorite but also weaker oxidants such as oxygen and ferricyanide. The redox potentials of ruthenium in alkaline aqueous solution are given in Eq. 1 (ref. 3).

$$RuO_4 \xrightarrow[1.00\ v]{} RuO_4^- \xrightarrow[0.59\ v]{} RuO_4^{2-} \xrightarrow[\sim 0.2\ v]{} RuO_2(aq) \qquad (1)$$

These indicate that a weak oxidant such as ferricyanide cannot oxidise ruthenium to RuO_4. Kinetics (ref. 4-6) and electrochemical (ref.7) studies of the ruthenium catalysed oxidation of alcohols reveal, however, that RuO_4 is the active catalytic oxidant, even when ferricyanide is used as the consumed oxidising agent. The RuO_4 is formed by disproportionation of RuO_4^-, Eq. 2:

$$2\ RuO_4^- \rightleftharpoons RuO_4 + RuO_4^{2-} \qquad (2)$$

This equilibrium is driven to the right by the rapid consumption of RuO_4 in reaction with the substrate, Eq. 3:

$$RuO_4 + RR'CHOH \longrightarrow RuO_4^{2-} + RR'C{=}O \qquad (3)$$

The catalytic cycle is completed by the oxidation of ruthenate, RuO_4^{2-}, to perruthenate, RuO_4^-. With ferricyanide as the oxidant this reaction does not proceed to completion (Eq. 4).

$$RuO_4^{2-} + Fe(CN)_6^{3-} \rightleftharpoons RuO_4^- + Fe(CN)_6^{4-} \qquad (4)$$

For the oxidation of cyclohexanol either reaction (3) or (4) can be made rate-determining by the appropriate adjustment of conditions. The observed rate law is given by Eq. (5):

$$-\frac{d[Fe^{III}]}{dt} = [Ru]\left[\frac{2k_3k_4[ROH][Fe^{III}]}{2k_3[ROH] + k_4[Fe^{III}]}\right] \qquad (5)$$

Ruthenate can also disproportionate in a pH dependent reaction (Eq. 6) to perruthenate and ruthenium(IV):

$$3\ RuO_4^{2-} + 2\ H_2O \rightleftharpoons RuO_4^- + RuO_2(aq) + 4\ OH^- \qquad (6)$$

This disproportionation reaction is inhibited by high hydroxide concentrations. Hence the oxidation reaction is conducted in alkaline solutions.

OXIDATION OF ORGANOCHLORINES

Many organochlorine molecules are persistent environmental poisons. Although their manufacture has virtually ceased and they have been largely withdrawn from sale, there are substantial stocks both in use and in storage which require proper disposal. High-temperature incineration has been, until recently, the only method accepted for disposal of the largest class of these compounds, the polychlorinated biphenyls (PCB's). There has been significant opposition in some communities, however, to the siting of high-temperature incinerators.

Ruthenium compounds are known to catalyse the oxidation of dioxins (ref. 8), which are oxygen containing organochlorines. Recently, the reaction of ruthenium tetroxide with polychlorinated biphenyls (PCB's) was reported (ref. 9). Work at The University of Sydney has led to a mild treatment for the complete oxidative destruction of hexachlorobenzene (HCB), PCB's and organochlorine pesticides, termed the SYDOX process (ref. 10).

Chemical oxidation is equivalent to low-temperature incineration. The products of complete oxidation are carbon dioxide and hydrochloric acid, or, in alkaline solution, carbonate and chloride. There are no organic products for further treatment, although concern remains about incomplete oxidation, in both the chemical oxidation and the high-temperature incineration reactions. No chemical oxidation processes appear to have been commercialised. A variety of reactions have been described. These include electrochemical oxidation by superoxide ion (refs. 11 and 12) and electrochemical oxidation catalysed by Ag(II) (ref. 13), as well as the oxidation by chlorine or hypochlorite catalysed by ruthenium compounds (ref. 9).

The economics of any catalytic oxidation process are in part determined by the stoichiometry. For example, for oxidation in alkaline solution hypochlorite is a convenient oxidant. Even though bleach is relatively inexpensive, complete oxidation of a mole of hexachlorobenzene requires 9 moles of Cl_2 and 30 moles of NaOH. On a weight basis one tonne of C_6Cl_6 requires about 2 tonnes of Cl_2 and 4 tonnes of NaOH.

$$C_6Cl_6 + 9\ Cl_2 + 30\ NaOH \longrightarrow 6\ NaHCO_3 + 24\ NaCl + 12\ H_2O \qquad (8)$$

Table 1. Cost of a kilo-Faraday of oxidant (ref. 14).

Oxidant:	O_2	Cl_2	Br_2	I_2	H_2O_2	BaO_2	$Na_2S_2O_8$	MnO_2	$KMnO_4$	CrO_3	$K_2Cr_2O_7$
Cost(US$):	2	8	88	4800	30	56	160	14	83	88	120

Table 1 presents the relative costs of a kilomole of oxidising equivalents, i.e. the cost of a kilo-Faraday. Clearly, to reduce costs oxidation by oxygen is desirable. This eliminates the cost of the chlorine and also generates some of the base required:

$$O_2 + 2H_2O + 4\ e^- \longrightarrow 4\ OH^- \qquad (7)$$

Oxygen in alkaline solution, however, is too weak an oxidant to regenerate the active RuO_4 catalytic species. One solution is to conduct the two reactions separately in an electrocatalytic process. With a small applied voltage the ruthenium catalyst can be reoxidised at the anode and the electrocatalytic oxidation of organochlorines accomplished.

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