Ruthenium Tetroxide as a Phase Transfer Catalyst in Biphasic System and Its in situ Electrochemical Regeneration: Oxidation of Aromatic Primary Alcohol and Aldehydes

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The application of ruthenium tetroxide as a phase transfer catalyst in a biphasic system comprised of carbon tetrachloride and saturated aqueous sodium chloride at platinised titanium anode, for the regeneration of spent oxidant, for the oxidation of benzyl alcohol, benzaldehyde and *p*-anisaldehyde has been investigated.

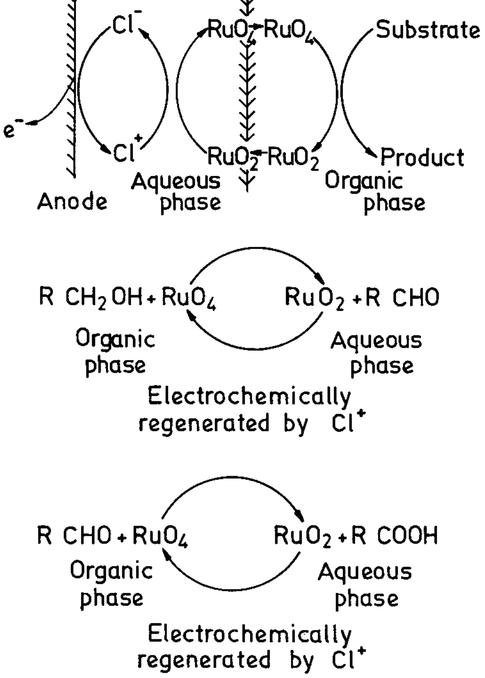
Ruthenium tetroxide (RuO_4) is a multipurpose oxidant because of its availability at various oxidation states of ruthenium such as II, III, IV, VI, VII and VIII. Redox reactions of ruthenium, like conversion of ruthenium(IV) to ruthenium(VIII) or vice versa, has made RuO_4 a highly versatile redox agent which can be electrochemically regenerated to be used continuously in a biphasic system.

Several papers have described the application of RuO_4 for the oxidation of organic compounds.[1-10] However, in the biphasic system, the use of RuO_4 and its electrochemical regeneration has not been investigated thoroughly. In synthetic organic chemistry, the oxidation of a primary alcohol to either a carbonyl compound[11-13] or to an acid is an important reaction and is generally carried out using either chromic acid or potassium permanganate.[14] In chromic acid oxidation, the disposal of the spent oxidant which invariably contains chromium(VI) creates pollution problems for its disposal. Though attempts have been made[15] to regenerate chromium(VI) from spent oxidant, the numbers of cycles to regenerate chromium(VI) are limited because of the formation of various oxidation states like Cr^4, Cr^{+5} etc. Whereas the acidic potassium permanganate cannot be regenerated electrochemically and the use of neutral potassium permanganate causes the problem of disposal of manganese(IV) oxide formed during the oxidation reaction, the alkaline potassium permanganate finds a limited use because of one electron transfer reaction which requires a large amount of oxidant. Oxidation of an organic substance in aqueous medium is often hampered by its insolubility in aqueous medium along with the side reaction of oxidation of electrolyte itself. In recent years the phase transfer catalysis technique has proved to be a boon to synthetic organic chemistry. One of the versatile reagents for oxidation reaction using phase transfer catalysis technique is RuO_4, in combination with carbon tetrachloride and aqueous sodium chloride as organic and aqueous phases. The RuO_4 which is soluble in the organic phase goes to ruthenium(IV) on reduction and gets transferred to the aqueous phase. In this aqueous phase on a suitable anode it is reoxidised to RuO_4 which immediately is transferred to the organic phase. We have explored this property of the $RuO_4 \rightleftarrows$ ruthenium(IV) system for the oxidation of benzyl alcohol to benzaldehyde, benzaldehyde to benzoic acid and *p*-anisaldehyde to *p*-anisic acid and in situ electrochemical regeneration of oxidant in a cyclic way as explained in the following Scheme.

Ruthenium tetroxide is soluble in organic solvents, whereas ruthenium dioxide, a reduced form of ruthenium tetroxide, is insoluble in organic phase but is soluble in aqueous phase and immediately gets transferred to aqueous phase, where it is reoxidised to ruthenium(VIII) which has a very poor solubility in aqueous phase and hence gets transferred to organic phase in which it has a high solubility. Accordingly as depicted in the Scheme, the present electrolysis process recycles in three reaction steps which involve (i) oxidation of the substrate by ruthenium tetroxide in the organic phase. (ii) regeneration of ruthenium tetroxide from ruthenium dioxide by the action of active chlorine species (Cl_2 or $[Cl^+]$)[16] in an aqueous phase; and (iii) electrooxidation of chloride ion to reactive chlorine species at an anode.

Ruthenium dioxide oxidation to RuO_4[17] is nearly quantitative under acidic or neutral conditions. However under alkaline condition, the reactive species are RuO_4^- and RuO_4^{2-}.[18-20] In the present work the pH of the system is almost neutral and hence oxidation is brought about by RuO_4 and not by RuO_4^- and RuO_4^{2-}.

Between pH 5.0 and 8.0, to ensure the stability of RuO_4 generated in the aqueous layer, a large proportion partitions into the carbon tetrachloride layer[7] where it is able to oxidise the substrate.



Scheme

Oxidation of benzyl alcohol to benzaldehyde is very selective in the pH range 6.0–7.0, whereas the lowering of the pH to 4.0 leads to further oxidation of benzaldehyde to benzoic acid, because, under these conditions, benzaldehyde probably forms a weak chelate with the catalyst to give benzoic acid.

In summary, electrochemically generated RuO_4 in the carbon tetrachloride layer is used to oxidize benzyl alcohol to benzaldehyde, benzaldehyde to benzoic acid and *p*-anisaldehyde to *p*-anisic acid in good yields.

All chemicals used in this study were of BDH grade. Triple distilled H_2O was used to prepare solutions. The regeneration of Ru(VIII) was carried out at a platinised Ti anode.

Electrolyses were carried out in an undivided double walled glass cell (250 mL capacity) fitted with a stirring bar, graphite cathode (1 × 10 × 0.1 cm) and platinised Ti anode (1 × 10 × 0.2 cm). The temperature of the electrolyte was maintained constant by circulating water from a water bath maintained at 25 ± 1 °C.

$RuCl_3$ (0.5 to 1.0 %) suspended in sat. NaCl (100 mL)/CCl_4 (50 mL) was electrolysed with vigorous stirring. The CCl_4 layer turned yellow with RuO_4.

FTIR spectrum was recorded on a Nicolet 20 DXB (frequency range of 4000–400 cm^{-1}) and ^1H FT NMR spectrum was recorded with a Bruker Pulse NMR spectrometer CXP (90.2 MHz).

Electrooxidation of Benzyl Alcohol to Benzaldehyde:
A mixture of CCl_4 (50 mL) and sat. NaCl solution (100 mL) was taken in an undivided glass cell (250 mL capacity). To this mixture 1 % aqueous solution of $RuCl_3$ (1 mL) and benzyl alcohol (1 mL, 1.05 g, 9.7 mmol) were added. The graphite cathode and platinised Ti anode were immersed in the upper aqueous layer of the biphase mixture. The mixture was stirred vigorously with a stirring bar. Current (1 Amp., 2.0 V, current density 125 $mA.cm^{-2}$) was passed for 6 h. The temperature of the system was maintained at 25 ± 1 °C. During the course of the reaction, the pH of the system varied from 6.0 to 7.0 but this change in pH value did not affect the course of the reaction or the yield of the product. Benzaldehyde produced was extracted with Et_2O and purified by distillation; yield: 841 mg (80 %); bp 179 °C/760 Torr (Lit.[21] bp 178–179 °C/760 Torr). It was characterised as its bisulphite adduct and semicarbazone derivative. Its FTIR, and ^1H FT NMR spectra were identical with an authentic sample.

Electrooxidation of Benzaldehyde to Benzoic Acid:
A mixture of CCl_4 (50 mL) and sat. NaCl solution (100 mL) was taken in an undivided glass cell (250 mL capacity). To this mixture, a 0.5 % aq solution of $RuCl_3$ (1 mL) and benzaldehyde (1 mL, 1.044 g, 9.8 mmol) were added. The graphite cathode and platinised Ti anode were immersed in the upper aqueous layer of the biphase mixture. The mixture was stirred vigorously with a stirring bar. Current (0.5 Amp., 4.0 V current density: 62.5 $mA.cm^{-2}$) was passed for 1 h. The temperature of the system was maintained at 25 ± 1 °C. During the course of the reaction the pH of the system varied from 4.0 to 6.5 but this change in pH value did not affect the course of the reaction or the yield of the product. The aqueous layer was separated and acidified with conc. HCl, to precipitate the organic acid formed by oxidation. The precipitate was recrystallised from boiling water; yield: 940 mg (90 %); mp 121 °C (Lit.[21] mp 122–123 °C). Its FTIR and ^1H FT NMR spectra were identical with an authentic sample.

Electrooxidation of *p*-Anisaldehyde to *p*-Anisic Acid
A mixture of CCl_4 (50 mL) and sat. NaCl solution (100 mL) was taken in an undivided glass cell (250 mL capacity). To this mixture a 0.5 % aq solution of $RuCl_3$ (1 mL) and *p*-anisaldehyde (1 mL, 1.12 g, 8.2 mmol) were added. The graphite cathode and platinised Ti anode were immersed in the upper aqueous layer of the biphase mixture. The mixture was stirred vigorously with a stirring bar. Current (0.25 Amp., 4.2 V current density: 31.3 $mA.cm^{-2}$) was passed for 1 h. The temperature of the system was maintained at 25 ± 1 °C. During the course of the reaction, the pH of the system varied from 5.0 to 7.0 but this change in pH value did no affect the course of the reaction and the yield. The aqueous layer was separated and acidified with conc. HCl, to precipitate the organic acid formed by oxidation. It was recrystallised from boiling water; yield: 1.05 g (90 %); mp 184 °C (Lit.[21] 182–185 °C). Its FTIR and ^1H FT NMR spectra were identical with an authentic sample.

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