Potassium Ruthenate: a Catalytic Oxidant for Organic Substrates

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Summary Potassium ruthenate ($K_2[RuO_4]$) can be used catalytically in the presence of persulphate ion, for oxidation of organic substrates under mild conditions.

BOTH osmium and ruthenium tetraoxides are valuable oxidants in organic chemistry, particularly when used in the presence of suitable oxidising agents so that their action becomes catalytic.[1] The related ruthenium(VI) ion, $[RuO_4]^{2-}$, is a potential two-electron oxidising agent, and has been used stoicheiometrically in alkaline solution to oxidise alcohols to ketones or acids and benzylamine to benzaldehyde.[2] It is, however, hazardous to prepare (oxidising fusion of $RuCl_3$[3] or alkaline reduction of RuO_4[4]) and both inconvenient and costly to use. The present procedure overcomes these difficulties by generating and using the reagent catalytically.

Solutions containing $[RuO_4]^{2-}$ can be readily prepared by reaction of ruthenium trichloride with aqueous persulphate,[5] and we find that the persulphate quickly regenerates $[RuO_4]^{2-}$ if the latter is reduced by organic substrates. Spectrophotometric measurements on such solutions show that all the ruthenium is present as $[RuO_4]^{2-}$, no $[RuO_4]^{-}$ or RuO_4 being detected. Results obtained using catalytic solutions (typically $1{\cdot}7 \times 10^{-4}$ M in $[RuO_4]^{2-}$, 3×10^{-2} M in potassium persulphate, and 2×10^{-1} M in potassium hydroxide for the oxidation of alcohols) are listed in the

Table. The oxidations were carried out at room temperature in air (the use of inert atmospheres had no apparent effect on the yields) with a substrate: $[RuO_4]^{2-}$ molar ratio of *ca.* 45 : 1. The reactions were complete within the times indicated. Although persulphate is known to oxidise alcohols and aldehydes in the presence of silver(I) ion,[6,7] we find that alkaline persulphate alone does not oxidise the substrates listed in the Table; the oxidations listed therein are, however, also effected by alkaline ruthenate in the absence of persulphate. It appears therefore that persulphate functions not only as a ready generator of $[RuO_4]^{2-}$, but also as a secondary oxidising agent for the catalytic oxidations of organic substrates by $[RuO_4]^{2-}$.

TABLE. Catalytic oxidations using $[RuO_4]^{2-}$ and potassium persulphate.

Compound	Product	Reaction time/h	Yield[a]/%
Benzyl alcohol	Benzoic acid	1·5	98
4-Nitrobenzyl alcohol	4-Nitrobenzoic acid	1	97
1,2,3,4-Tetrahydro-1-naphthol	α-Tetralone	2	84
Cyclohexanol	Cyclohexanone + adipic acid	2	64
Benzhydrol	Benzophenone	5	95
3-Chlorobenzaldehyde	3-Chlorobenzoic acid	2	99
trans-Cinnamyl alcohol	*trans*-Cinnamic acid	3	97
Cyclohex-3-enemethanol	Cyclohex-3-ene-1-carboxylic acid	6	86
Cyclopentanol	Cyclopentanone	2	71
Benzylamine	Benzonitrile	24	66
Butylamine	Butyric acid	24	34
Cyclohexene	No reaction	6	—
	Adipic acid[b]	96	20
Acetylenedicarboxylic acid	No reaction	5	—
t-Butyl alcohol	No reaction	5	—

[a] Yields of isolated, pure products. [b] Oxidation was carried out using $[RuO_4]^{2-}$ stoicheiometrically.

In addition to requiring only mild conditions, the reagent is highly specific. Primary and secondary alcohols and aldehydes are readily oxidised to the corresponding carboxylic acids and ketones. These oxidations are also successful on a larger scale with a greater catalytic turnover; thus, 4-nitrobenzaldehyde (53 g, 0·35 M) and benzyl alcohol (54 g, 0·5 M) are catalytically oxidised by $[RuO_4]^{2-}$ ($1{\cdot}4 \times 10^{-3}$ M) in 16 and 36 h to the corresponding acids in 92 and 81% yields, respectively. This suggests that general, full-scale oxidations of alcohols and aldehydes can be carried out by $[RuO_4]^{2-}$ using a much higher catalytic turnover. Reaction of $[RuO_4]^{2-}$ with tertiary alcohols (*e.g.*, t-butyl alcohol), alkenes, and alkynes is, however, very slow at room temperature. Thus acetylene dicarboxylic acid, though very water soluble, is unaffected by the reagent over a period of 5 h, while cyclohexene is slowly oxidised by $[RuO_4]^{2-}$ without persulphate over four days to give adipic acid in low yield. These properties make $[RuO_4]^{2-}$ particularly useful for the catalytic oxidation of unsaturated alcohols and aldehydes; thus, *trans*-cinnamyl alcohol and cyclohex-3-enemethanol are catalytically oxidised to the corresponding unsaturated carboxylic acids in high yield. This is in contrast to osmium and ruthenium tetraoxide which react readily with alkenes and alkynes.[1,8]

We find that by using lower substrate ratios (*ca.* 10 : 1), and a longer reaction time than normal (*ca.* 24 h), benzylamine is catalytically oxidised to benzonitrile as the main product. It seems likely that the mechanism of this reaction involves base abstraction of the α-protons, as has been proposed for the oxidation of benzylamine to benzonitrile by silver(II) picolinate under basic conditions.[9] Other primary amines, such as butylamine, are oxidised to carboxylic acids as the main products; the catalytic reagent, however, is found to oxidise imines (*e.g.*, $PhCH{=}NCH_2Ph$) and nitriles (*e.g.*, benzonitrile) only very slowly, the starting materials being recovered in high yield.

Since $[RuO_4]^{2-}$ is readily reduced by alcohols and aldehydes, reacting molar ratios of $[RuO_4]^{2-}$: substrate can be measured by titration of solutions of $[RuO_4]^{2-}$ without persulphate against these substrates. The concentration of $[RuO_4]^{2-}$ in solution was determined spectrophotometrically. It was found that $[RuO_4]^{2-}$ oxidises alcohols in a 2 : 1 $[RuO_4]^{2-}$: substrate ratio and aldehydes in a 1 : 1 $[RuO_4]^{2-}$: substrate ratio, thus confirming that $[RuO_4]^{2-}$ is indeed acting as a two-electron oxidant.

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