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Oxidation of primary alcohols to aldehydes with oxygen catalysed by tetra-*n*-propylammonium perruthenate

Masihul Hasan [a], Mehdi Musawir [a], Paul N. Davey [b], Ivan V. Kozhevnikov [a,*]

[a] *Department of Chemistry, The Leverhulme Centre for Innovative Catalysis, University of Liverpool, Liverpool L69 7ZD, UK*
[b] *Quest International, Ashford, Kent TN24 0LT, UK*

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Abstract

The liquid-phase oxidation of a series of saturated and unsaturated non-allylic alcohols to aldehydes with oxygen or air catalysed by tetra-*n*-propylammonium perruthenate (TPAP, represented as $[(n\text{-Pr})_4\text{N}]\text{RuO}_4$) at 80–110 °C is shown to proceed with selectivities of 72–91% at 55–80% alcohol conversion. The unsaturated alcohols, such as 9-decenol, 9-octadecenol and β-citronellol, give the corresponding unsaturated aldehydes without competing double bond attack. The time course of oxidation indicates a complex reaction mechanism. The results on oxidation of a test alcohol, *t*-Bu(Ph)CHOH, suggest that one-electron processes do not play an important role in the TPAP-catalysed aerobic oxidation of alcohols. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Primary alcohols; Oxidation; Unsaturated aldehydes

1. Introduction

The catalytic conversion of primary alcohols to aldehydes is essential for the preparation of fragrances and food additives as well as of many synthetic intermediates in organic chemistry [1]. Traditional methods for the synthesis of aldehydes generally involve the use of stoichiometric amounts of inorganic oxidants, such as Cr^{VI}, and generate large quantities of waste. Hence, search for effective catalytic systems that use environmentally benign and inexpensive oxidants such as oxygen (air) or hydrogen peroxide to convert alcohols to carbonyl compounds remains an important challenge.

Most examples of aerobic oxidation of alcohols involve the use of catalysts based on platinum group metals (PGMs). Supported platinum and palladium catalysts, often modified with bismuth or lead, have long been used for alcohol oxidation [2]. Among other PGMs, ruthenium compounds have attracted much interest. The ruthenium catalysts involve soluble complexes [3–7] or solid materials (e.g. RuO_2 [8] and Ru–Co–Al hydrotalcite [9]). Generally, these catalysts are sufficiently selective and tolerant to many other functional groups if they are present in the alcohol molecules. In particular, tetra-*n*-propylammonium perruthenate (TPAP, represented as $[(n\text{-Pr})_4\text{N}]\text{RuO}_4$), either in homogeneous systems [10,11] or as supported on an ion exchange resin [12] or MCM-41 molecular sieve [13], is a very efficient catalyst for the aerobic oxidation of a broad range of primary and secondary alcohols under mild conditions in non-aqueous media. Sensitive functional groups, such

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[*] Corresponding author. Tel.: +44-151-794-2938;
fax: +44-151-794-3589.
E-mail address: kozhev@liverpool.ac.uk (I.V. Kozhevnikov).

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as allylic, epoxy, lactone, indole, silyl ether, acetal, etc. are unaffected by TPAP [10,11,14]. Most work has so far been done on benzylic and allylic alcohols that are much easier to oxidise to the corresponding aldehydes than primary aliphatic alcohols. The mechanism of these reactions is unknown. Few mechanistic studies on the stoichiometric alcohol oxidation by oxo-complexes of Ru^{VI} and Ru^{VII} in aqueous solution have been published [14–16].

In this work, we have studied the liquid-phase oxidation of a series of “difficult” primary alcohols to aldehydes with oxygen (or air) as an oxidant catalysed by TPAP. The substrates include aliphatic alcohols as well as non-allylic unsaturated alcohols. It is shown that these alcohols can be oxidised to the corresponding aldehydes with good selectivities, without affecting the double bonds. A tentative reaction mechanism is proposed.

2. Experimental

2.1. Materials

1-Dodecanol, 9-decenol, 9-octadecenol, 3-methyl-5-phenylpentanol and authentic samples of the corresponding aldehydes were provided by Quest International. 1-Decanol, β-citronellol and the corresponding aldehydes, decanal and β-citronellal, as well as 2,2-dimethyl-1-phenyl-1-propanol and 2,2-dimethylpropiophenone were from Aldrich. All the alcohols were used as received without further purification. TPAP was kindly provided by Johnson Matthey. The solvents, toluene, fluorobenzene and 1,2-dichloroethane (DCE), were dried over a 4 Å molecular sieve.

2.2. Techniques

Product analysis was carried out on a 3800 Varian gas chromatograph equipped with a 25 m BP5 capillary column. The thermal gravimetric analysis (TGA) was performed on a Setaram TG-DSC 111 analyser.

2.3. Oxidation procedure

The oxidation of alcohols was carried out in a 50 ml round-bottom three-neck glass flask equipped with a reflux condenser, a magnetic stirrer and a gas inlet allowing to bubble a flow of oxygen or air (25 ml/min) into reaction mixture. *Because of the inherent unsafety of mixing oxygen with hot organics, appropriate precautions should be taken when carrying out this work, particularly if scaling it up*. Typically, a mixture of an alcohol (2.5 mmol), TPAP (0.125 mmol) and decane (a GC internal standard) in a solvent (10 ml) was charged in the reactor and saturated with oxygen at room temperature for 5 min while intensely stirred. Then the reactor was placed into the oil bath preheated to a certain temperature to start the reaction. Samples of the reaction mixture were taken out at appropriate time intervals to monitor the reaction by GC using a Varian 3800 gas chromatograph equipped with a BP5 capillary column (25 m). Decane was used as an internal standard. The product aldehydes were identified by GC–MS using the authentic samples of aldehydes.

3. Results and discussion

3.1. Reaction products

The oxidation of primary alcohols catalysed by TPAP occurs readily in liquid phase under oxygen at ambient pressure to form the corresponding aldehydes as major products (Eq. (1)). Tables 1 and 2 show the reaction yields (GC, non-isolated), conversions and selectivities.

$$RCH_2OH + \tfrac{1}{2}O_2 \overset{TPAP}{\rightarrow} RCHO + H_2O \qquad (1)$$

The oxidation of 1-dodecanol was studied in more detail to optimise the reaction variables such as alcohol/TPAP molar ratio, temperature, length of time, solvent and oxidant (O_2 or air). The results are given in Table 1. The reaction under O_2 proceeds smoothly in the temperature range of 65–110 °C, reaching 68–75% selectivity to dodecanal at 66–78% alcohol conversion in 2–3 h. At higher conversions, a small amount of dodecanoic acid (less than 5% selectivity) was observed (GC). During the reaction, the initially dark green solution of TPAP turns into a black suspension that appears to be RuO_2. The RuO_2 itself under these conditions showed some catalytic activity for the oxidation of 1-dodecanol. Toluene, acetonitrile, 1,2-dichloroethane (DCE) or fluorobenzene can all

Table 1
Oxidation of 1-dodecanol (ROH) to dodecanal catalysed by TPAP[a]

Solvent	ROH/TPAP (mol/mol)	Temperature (°C)	Time (min)	Yield (conversion) (%)[b]	Selectivity (%)
PhMe	20:1	65	210	50 (67)[c]	75
PhMe	20:1	65	240	45 (66)[d]	68
PhMe	20:1	80	120	46 (90)[d]	51
PhMe	10:1	80	50	50 (92)[d]	54
PhF	20:1	80	180	52 (81)	64
DCE[e]	20:1	80	240	38 (62)	61
MeCN	20:1	80	180	50	
PhMe	20:1	110	150	47 (82)	57
PhMe	20:1	110	150	44 (75)[f]	59
PhMe	20:1	110	110	56 (78)	72
PhMe	4:1	110	170	10 (49)[g]	20
PhMe	4:1	110	15	49 (91)	54
PhMe	4:1	110	300	5 (99)	5

[a] Typically, unless otherwise stated, a mixture of dodecanol (2.5 mmol), TPAP (0.125 mmol) and a solvent (10 ml) was treated with O_2 flow (25 ml/min) at a specified temperature.

[b] Values are GC yields of dodecanal and the values in parenthesis are conversions of 1-dodecanol by internal standard.

[c] Isolated yield, 10 mmol scale.

[d] 4 Å molecular sieve (1 g) added.

[e] 1,2-Dichloroethane.

[f] Air (25 ml/min) instead of O_2 as oxidant.

[g] Stoichiometric reaction under N_2; the yield was calculated assuming TPAP to be a four-electron oxidant.

be used as solvents, refluxed toluene being the best. The alcohol/TPAP molar ratio of 20:1 was found to be optimal, which is in agreement with the previous reports [10,14]. In the absence of TPAP, no alcohol oxidation was observed under the above conditions. In the absence of oxygen (under N_2), TPAP stoichiometrically oxidises alcohols to aldehydes (Table 1) [14]. To examine a possible effect of by-product water that is known to enhance the overoxidation of alcohols to acids [2], some oxidations were performed in the presence of a 4 Å molecular sieve similar to [10,14]. However, no significant effect was observed.

Table 2
Oxidation of alcohols to aldehydes catalysed by TPAP[a]

Alcohol	Solvent	Temperature (°C)	Time (min)	Aldehyde	Yield (conversion) (%)[b]	Selectivity (%)
1-Decanol	PhMe	110	65	Decanal	59 (67)[c]	88
1-Dodecanol	PhMe	110	110	Dodecanal	56 (78)	72
9-Decenol	PhMe	110	270	9-Decenal	54 (75)	72
9-Octadecenol	PhMe	110	180	9-Octadecenal	62 (80)	78
	PhMe	110	180		40 (62)[d]	65
	PhF	80	160		40 (63)	63
3-Methyl-5-phenylpentanol	PhMe	110	40	3-Methyl-5-phenylpentanal	62 (80)	78
β-Citronellol	DCE[e]	83	320	β-Citronellal	50 (55)	91
	DCE[e]	83	440		62 (75)	83

[a] Typically, unless otherwise stated, a mixture of alcohol (2.5 mmol), TPAP (0.125 mmol) and a solvent (10 ml) was treated with O_2 (25 ml/min) at a specified temperature.

[b] Values are GC yields of aldehydes and the values in parenthesis are alcohol conversions by internal standard.

[c] Decanol (10 mmol) and TPAP (0.50 mmol) in 10 ml of PhMe.

[d] Air (25 ml/min) instead of O_2 as oxidant.

[e] 1,2-Dichloroethane.

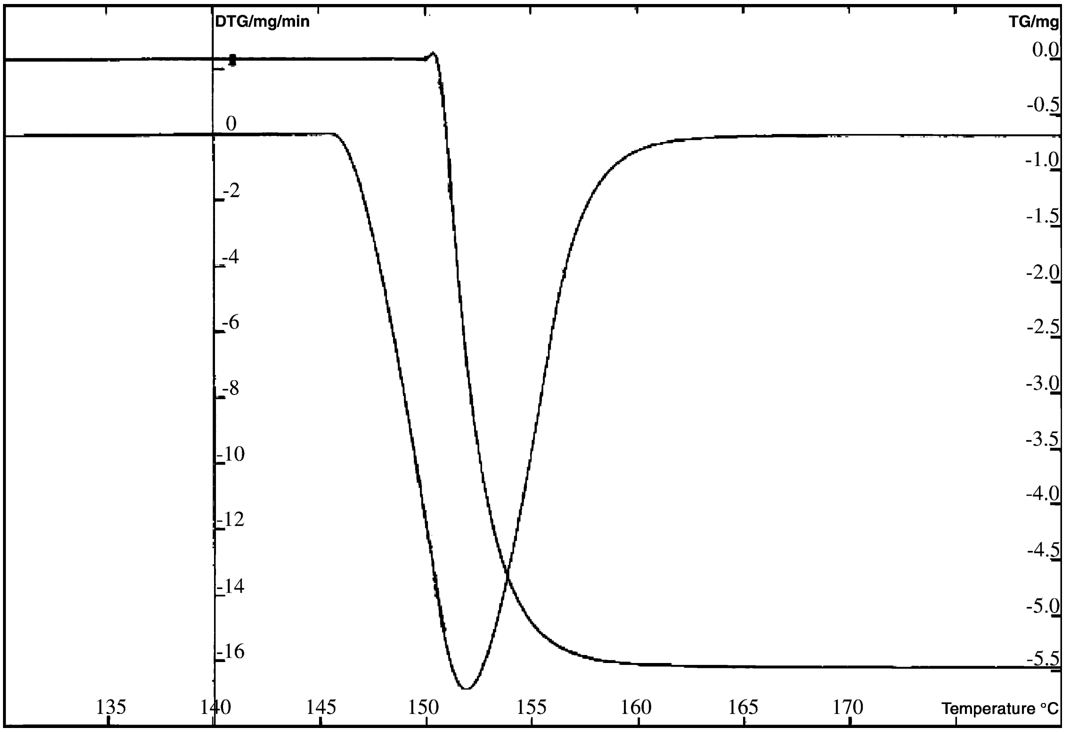
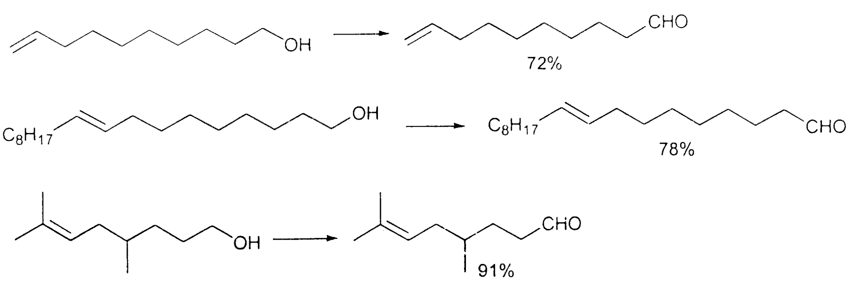


Fig. 1. TG/DTG analysis of TPAP.

Reaction (1) was also carried out with air as the oxidant instead of O_2. Air, by all means, is a more attractive and safe oxidant than pure oxygen. In this case, however, the oxidation was slower, providing a lower yield of aldehydes (Tables 1 and 2). On these bases, the following optimal reaction conditions that provided reproducible yields of aldehydes were chosen: 2.5 mmol/0.125 mmol alcohol/TPAP, 10 ml toluene, at reflux (110 °C) and 25 ml/min O_2 flow. From our TG analysis, solid TPAP is stable on air up to 151 °C (Fig. 1).

The results for other saturated and unsaturated non-allylic alcohols are summarised in Table 2. These oxidations proceed with 72–91% selectivity to aldehydes at 55–80% alcohol conversion. The reactivity of these alcohols is quite similar to that of 1-dodecanol, which is not unexpected. Importantly, in the case of unsaturated alcohols the double bond remains unaffected, in agreement with the previous reports [10,11]. Thus, the oxidation of 9-decenol, 9-octadecenol and β-citronellol gives the corresponding unsaturated aldehydes with good selectivities.



Attempt was made to identify by-products in the oxidation of dodecanol (10 mmol scale) in refluxed toluene (1 h). The products were isolated by filtering the reaction mixture through a Celite pad followed by purification by column chromatography on silica gel as described elsewhere [10]. It gave 57% dodecanal (isolated yield) at 67% alcohol conversion together with two "dimer" by-products (ca. 7%). One of them showed a strong carbonyl band in the IR spectrum and could be identified as ester. The other might be an aldol.

GC–MS analysis of the reaction mixture after the oxidation of 9-decenol (Table 2) revealed the following by-products: tripropylamine, propyl decenoate, two dimeric aldehydes (probably aldols) and traces of benzaldehyde. The first two apparently originated from TPAP, the last one from the oxidation of toluene.

Overall, the TPAP-catalysed oxidation of saturated or unsaturated primary alcohols gives the corresponding aldehydes with good selectivities. Some overoxidation to acids or esters occurs at higher conversions. The product aldehydes are stable under the reaction conditions in the absence of TPAP but slowly oxidise in its presence. It should be noted that the previous reports [10,11] claim that there is no overoxidation in the aerobic alcohol-to-aldehyde oxidation with TPAP. It appears to be the case with benzylic and allylic alcohols that give more stable aldehydes. But with non-activated primary alcohols, a relatively small amounts of acids and esters do form.

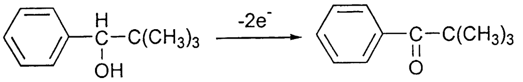
No catalyst reuse for the homogeneous aerobic oxidation of alcohols with TPAP has so far been reported (see, e.g. [10,11]). Our attempts to recycle the catalyst were not successful either.

3.2. Reaction mechanism

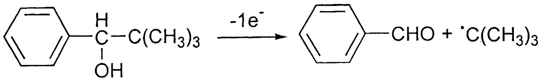
The mechanism of ruthenium-catalysed oxidation of organic compounds is complex and scarcely known. The complexity arises from the manifold of oxidation states of ruthenium ranging from -2 to $+8$ [17]. Complexes of $\mathrm{Ru^{VIII}}$, $\mathrm{Ru^{VII}}$, $\mathrm{Ru^{VI}}$, $\mathrm{Ru^{V}}$ and $\mathrm{Ru^{IV}}$ can all stoichiometrically oxidise alcohols to aldehydes or ketones [14]. This favours a redox stepwise mechanism for the TPAP-catalysed aerobic oxidation of alcohols, provided the reduced form of the ruthenium complex is reoxidisible in situ. Such a mechanism would include the oxidation of alcohol by a Ru^{n+} complex to form aldehyde and $\mathrm{Ru}^{(n-2)+}$, followed by the reoxidation of $\mathrm{Ru}^{(n-2)+}$ to Ru^{n+} with O_2. However, one cannot rule out a concerted mechanism, e.g. one including the oxidation of alcohol by O_2 in the coordination sphere of Ru^{n+}. The TPAP-catalysed oxidation of secondary alcohols by *N*-methylmorpholine-*N*-oxide has been shown to proceed through the formation of a complex between TPAP and alcohol [18].

The stoichiometric oxidation of alcohols by perruthenate $[\mathrm{RuO_4}]^-$ has been suggested to proceed via the intermediates with the α-C–$\mathrm{Ru^{VII}}$ bond [15]. Alternatively, an ester intermediate $[\mathrm{RCH_2{-}O{-}Ru(OH)O_3}]^-$ similar to that proposed for $\mathrm{Cr^{VI}}$ oxidation of alcohols [19] may be suggested. TPAP oxidises cyclobutanol to cyclobutanone in organic media in good yield (unlike the situation with $[\mathrm{RuO_4}]^-$ in aqueous solution [15]) suggesting that one-electron processes do not play an important role in the stoichiometric oxidation by TPAP [14]. The stoichiometric oxidation of isopropanol by TPAP in $\mathrm{CH_2Cl_2}$ has been found to be autocatalytic probably due to coordination of $[\mathrm{RuO_4}]^-$ with colloidal particles of the product $\mathrm{RuO_2}$ [16].

In this work, we used another test alcohol, *t*-Bu(Ph)CHOH, to probe the mechanism of catalytic reaction (1)—one-electron transfer versus two-electron transfer ([20] and references therein). With two-electron oxidants, e.g. $\mathrm{Pd^{II}}$ this alcohol gives cleanly a ketone, *t*-Bu(Ph)CO, with the same carbon backbone (Eq. (2)). With one-electron oxidants, e.g. $\mathrm{Ce^{4+}}$ or $\mathrm{S_2O_8}^{2-}$ the C–C bond cleaves to yield benzaldehyde and *t*-butyl radical as the primary products (Eq. (3)). $\mathrm{PdCl_2}$ has been reported to give *t*-Bu(Ph)CO with 100% selectivity, whereas with $\mathrm{Ce^{4+}}$, 94% PhCHO and 6% *t*-Bu(Ph)CO has been obtained [20].



(2)



(3)

The TPAP-catalysed oxidation of *t*-Bu(Ph)CHOH with O_2 (2.5 mmol alcohol, 0.25 mmol TPAP, 25 ml/min O_2, 10 ml toluene, at reflux, 0.5 h) was found to give *t*-Bu(Ph)CO with 88% selectivity at 94% conversion and only 3% benzaldehyde. Blank test showed that most of the benzaldehyde came from

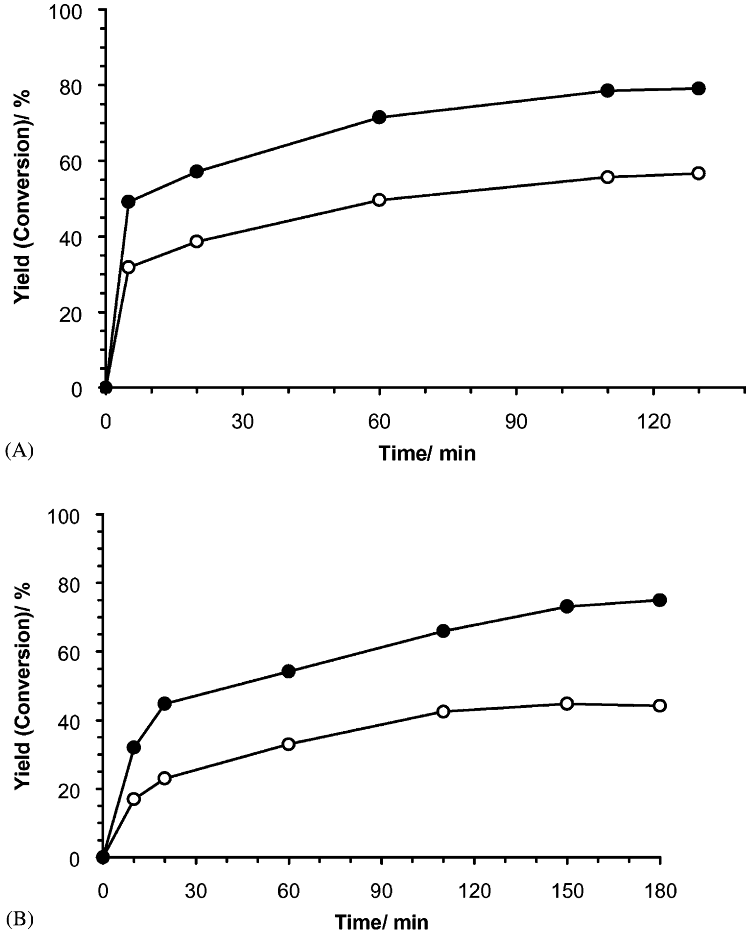


Fig. 2. Yield (○) and conversion (●) vs. time for the oxidation of 1-dodecanol (2.5 mmol) to dodecanal catalysed by TPAP (0.125 mmol) in refluxed toluene (10 ml) at 110 °C: (A) oxidation with O_2 (25 ml/min); (B) oxidation with air (25 ml/min).

the oxidation of toluene. This result suggests that one-electron processes do not play an important role in the TPAP-catalysed aerobic oxidation of alcohols.

It should be noted that TPAP is not soluble in neat toluene even at reflux, but readily dissolves in it in the presence of alcohol. This is indicative of the formation of complexes between TPAP and alcohol which might be reaction intermediates.

The time course for the TPAP-catalysed oxidation of alcohols (1-decanol, 1-dodecanol and β-citronellol) with O_2 or air is shown in Figs. 2 and 3. It is evident that all the reactions, regardless of the substrate and reaction conditions, follow a similar course. It includes a fast stage up to 40–50% conversion, followed by a slower stage, which indicates a complex mechanism. These two stages are likely to involve different active ruthenium species.

The first stage, apparently homogeneous, is suggested to involve anionic oxo-ruthenium species, such as $[RuO_4]^-$, $[RuO_4]^{2-}$, etc. stabilised by alcohol solvation. Hypothetically, the process can be viewed as follows:

$$Ru^{VII} + RCH_2OH \rightarrow Ru^{V} + RCHO \qquad (4)$$

$$Ru^{VII} + Ru^{V} \rightarrow 2\,Ru^{VI} \qquad (5)$$

$$Ru^{VI} + RCH_2OH \rightarrow Ru^{IV} + RCHO \qquad (6)$$

$$Ru^{IV} + O_2 \rightarrow Ru^{VI} \qquad (7)$$

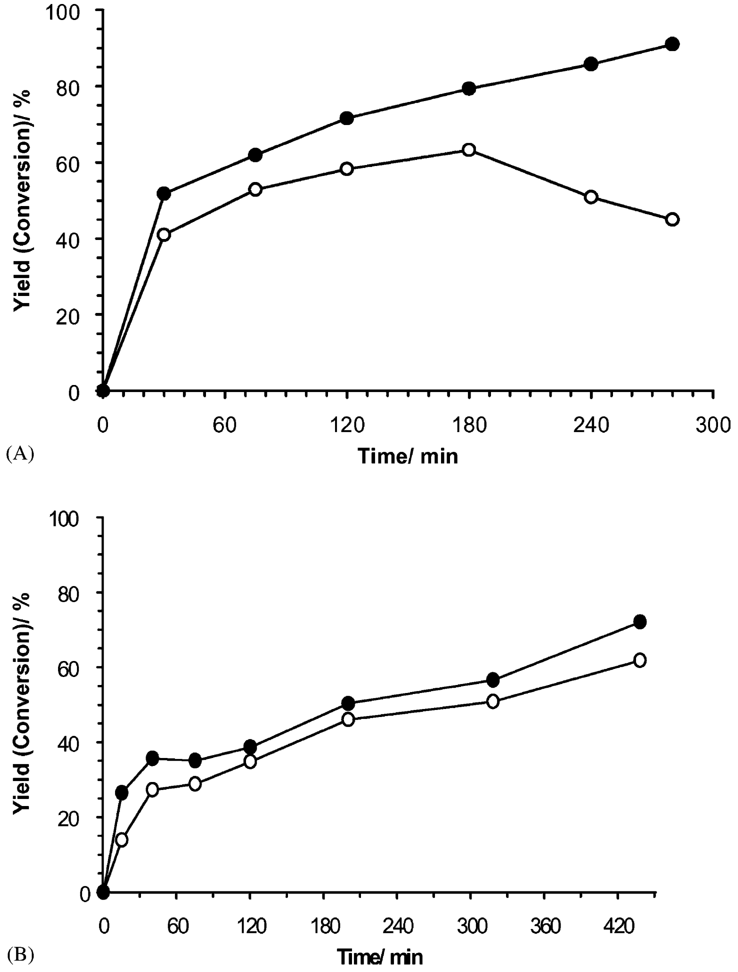
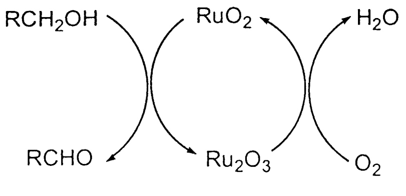


Fig. 3. Yield (○) and conversion (●) vs. time for the oxidation of alcohol (2.5 mmol) with O_2 (25 ml/min) catalysed by TPAP (0.125 mmol): (A) oxidation of 1-decanol to decanal in refluxed toluene (10 ml) at 110 °C; (B) oxidation of β-citronellol to β-citronellal in refluxed 1,2-dichloroethane (10 ml) at 83 °C.

Steps (4)–(6) have been suggested for the stoichiometric oxidation of alcohols by perruthenate [14,15].

The second stage comes in at a higher alcohol conversion when the anionic oxo-ruthenium species are no longer stable in solution. In this stage, the process appears to be heterogeneously catalysed by RuO_2. The ruthenium dioxide effects both stoichiometric and catalytic (with O_2) oxidation of alcohols in liquid phase [8], but the mechanism is unknown. This reaction may proceed via a Mars–van Krevelen type redox mechanism (Scheme 1).

Alternatively, a Langmuir–Hinshelwood type mechanism may be operative whereby the alcohol is oxidised with oxygen chemisorbed on the surface of RuO_2. It has been reported [21] that hydrated RuO_2



Scheme 1.

possesses a large surface area (200 m^2/g) and carries a certain amount of chemisorbed oxygen.

4. Conclusion

This work demonstrates that TPAP is a very efficient catalyst for selective oxidation of primary saturated and unsaturated non-allylic alcohols to the corresponding aldehydes with oxygen. The reaction occurs in liquid phase at 80–110 °C with the selectivity of 72–91% to aldehydes at 55–80% alcohol conversion. A small amount of acids or esters is also formed at higher conversions. The unsaturated alcohols oxidise cleanly without competing double bond attack. Although less efficient, air can also be used as the oxidant. The mechanism of this reaction is complex; this aspect needs further investigation.

Acknowledgements

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References

[1] R.A. Sheldon, I.W.C.E. Arends, A. Dijksman, Catal. Today 57 (2000) 157.
[2] T. Mallat, A. Baiker, Catal. Today 19 (1994) 247.
[3] T. Naota, H. Takaya, S.I. Murahashi, Chem. Rev. 98 (1998) 2599.
[4] M. Matsumoto, S. Ito, Chem. Commun. (1981) 907.
[5] C. Bilgrien, S. Davis, R.S. Drago, J. Am. Chem. Soc. 109 (1987) 3786.
[6] J.E. Bäckvall, R.L. Chowdhury, U. Karlsson, Chem. Commun. (1991) 473.
[7] A. Dijksman, I.W.C.E. Arends, R.A. Sheldon, Chem. Commun. (1999) 1591.
[8] M. Matsumoto, N. Watanabe, J. Org. Chem. 49 (1984) 3435.
[9] T. Matsushita, K. Ebitani, K. Kaneda, Chem. Commun. (1999) 265.
[10] I.E. Marko, P.R. Giles, M. Tsukasaki, I. Chelle-Regnaut, C.J. Urch, S.M. Brown, J. Am. Chem. Soc. 119 (1997) 12661.
[11] R. Lenz, S.V. Ley, J. Chem. Soc., Perkin Trans. 1 (1997) 3291.
[12] B. Hinzen, R. Lenz, S.V. Ley, Synthesis-Stuttgart (1998) 977.
[13] A. Beloch, B.F.G. Johnson, S.V. Ley, A.J. Priece, D.S. Shephard, A.W. Thomas, Chem. Commun. (1999) 1907.
[14] W.P. Griffith, Chem. Soc. Rev. (1992) 179.
[15] D.G. Lee, L.N. Congson, Can. J. Chem. 68 (1990) 1774.
[16] D.G. Lee, Z. Wang, W.D. Chandler, J. Org. Chem. 57 (1992) 3276.
[17] F.A. Cotton, G. Wilkinson, Advanced Inorganic Chemistry, 5th Edition, Wiley, New York, 1988, pp. 871–900.
[18] K.J. Tony, V. Mahadevan, J. Rajaram, C.S. Swamy, React. Kinet. Catal. Lett. 62 (1997) 105.
[19] K.B. Wiberg (Ed.), Oxidation in Organic Chemistry, Part A, Academic Press, New York, 1965.
[20] I.V. Kozhevnikov, V.E. Tarabanko, K.I. Matveev, Kinet. Katal. 22 (1981) 619.
[21] J.M. Fletcher, W.E. Gardner, B.F. Greenfield, M.J. Holdoway, M.H. Rand, J. Chem. Soc. A (1968) 653.