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Ruthenium (II) - catalyzed oxidation of alcohols by persulfate

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(Received June 22, 1992; accepted September 14, 1992)

Abstract

Alcohols are oxidized to carbonylic compounds by aqueous persulfate in the presence of catalytic amounts (0.2%) of ruthenium trichloride and of a choice of ruthenium(II) complexes. Secondary alcohols are quantitatively converted to ketones, whereas primary alcohols can be converted to aldehydes with good selectivities. A kinetic investigation suggests a concerted mechanism for the bi-electronic oxygen transfer.

Key words: alcohols; oxidation; persulphate; ruthenium

Introduction

The preparation of carbonyl compounds by the oxidation of alcohols is of great value in organic synthesis. Although many standard procedures are available for this purpose, there is a constant need to develop new, mild, versatile and selective systems to avoid the use of reagents containing heavy metals, such as lead dioxide, silver carbonate, manganese oxide and chromates. Catalytic alternatives to well-established methods are therefore attractive and many transition metal complexes have been tested as catalysts in conjunction with a variety of oxidants.

Ruthenium tetroxide, which is a very reactive oxidizing agent, is able to accomplish a number of effective stoichiometric oxidations, including those of primary and secondary alcohols [1,2], and these reactions can be made catalytic in the presence of a wide variety of secondary oxidants, such as halogenated compounds [3,4], oxygen [5–7], iodosobenzene [8,9], amine-N-oxides [10–14], tert-butyl hydroperoxide [10,15], unsaturated organic compounds [16], hydrogen peroxide [17] and bromate [18,19]; ruthenium-oxo complexes have also been tested in the electrocatalytic oxidation of alcohols [20–23]. The standard procedure for the ruthenium-catalyzed oxidations is based on the use of commercial ruthenium trichloride as the catalyst (up to 4%), and of sodium

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periodate [24] or periodic acid [25] as the stoichiometric oxidants, in a biphasic carbon tetrachloride-water system containing significant quantities of acetonitrile, which probably prevents formation of metallic ruthenium and therefore inactivation of the catalyst [24]. It is therefore of some interest to ascertain the possible effectiveness of the oxidation of alcohols with ruthenium (II) complexes containing ligands of a good coordinating capacity for the lower oxidation states, in the presence of hypochlorite and persulfate, two important oxidants, recently introduced for the metal-catalyzed epoxidation of olefins [26].

Whereas we recently reconsidered the hypochlorite reaction in the presence of ruthenium (II) complexes [27,28], in this paper we report on the oxidation of primary and secondary alcohols using KHSO₅ as oxidant in a waterdichloromethane (or dichloroethane) double phase. The catalysts examined are either commercial ruthenium trichloride and a representative choice of ruthenium (II) complexes containing phosphorus, sulfur or oxygen donors, i.e. *cis*-[RuCl₂(Me₂SO₄], [RuCl(DPP)₂]PF₆ (DPP=1,3-bis (diphenylphosphino)propane); K₅[Ru(H₂O)PW₁₁O₃₉]; and [Ru(H₂O)₂(Me₂SO)₄](BF₄)₂. Most of the above complexes have already been shown to be effective catalysts in oxygen-atom transfers to alkenes [29–31] and alkanes and ethers [32–36]. The closely related osmium (II) derivative [OsCl(DPP)₂]PF₆ was also tested, but gave negligible yields in all the cases examined.

Experimental

Materials

Commercial products were used for gas-chromatographic standardization. The five-coordinate $[MCl(DPP)_2]PF_6$ complexes (M=Ru [37], Os [38]) were prepared by refluxing ethanolic suspensions of the corresponding *trans*- $[MCl_2(DPP)_2]$ derivatives in the presence of excess NH_4PF_6 . *cis*- $[RuCl_2\{(CH_3)_2SO\}_4]$ was prepared by standard procedures [39].

Preparation of cis- $[Ru(H_2O)_2\{(CH_3)_2SO\}_4](BF_4)_2$

Ethanol solutions of cis-[RuCl₂{(CH₃)₂SO}₄] are refluxed ca. 1 h with excess AgBF₄ under nitrogen; the crude yellow precipitate is repeatedly recrystallized from water-ethanol (yield 60%). Elemental analyses (C, H, Ru) within 0.5% of calculated values.

Preparation of $K_5[Ru(H_2O)PW_{11}O_{39}] \cdot 15 H_2O$

Equimolar amounts of $K_7[PW_{11}O_{39}] \cdot 15 H_2O$ and $cis \cdot [Ru(H_2O)_2 \{(CH_3)_2SO\}_4\}]BF_4)_2$ are dissolved in water and briefly heated under nitrogen.

A red product separates upon addition of methanol, which is recrystallized from water-methanol (yield 85%). Elemental analyses (K, P, Ru, W) within 0.5% of calculated values; ³¹P NMR (D_2O): 10.4 ppm.

Procedure for the catalytic oxidations

A dichloromethane or 1,2-dichloroethane solution (1 ml) containing 1 mmol of the substrate and a gas-chromatographic standard (n-decane or 2octanone, 0.005 mmol) were stirred magnetically in a 2-ml vial together with 1 ml of an aqueous solution of commercial Oxone (Aldrich) corresponding to a 0.5 M concentration of active oxygen as KHSO₅, as determined by iodometric titrations; the metal catalysts (0.002 mmol) were dissolved either in the organic or in the aqueous phases, depending upon the solubilities. The reactions were carried out at 22°C in the absence of phase transfer agents and were not affected by the presence of air. Reaction rates were determined for early stages of the reaction (up to 50 turnovers) and were reproducible to within 15%. Organic analyses were performed on aliquots withdrawn with a hypodermic microsyringe on a DANI 3800 gas chromatograph equipped with FID, using 30 m SE-30 or polypropylene glycol ester capillary columns (0.25 mm i.d.). The identity of each product was confirmed by comparison of the fragmentation pattern in the mass spectra obtained with a VG 16F mass spectrometer operating in the electron ionization mode at 70 eV.

Results and discussion

All our investigations involve a system in which the reaction takes place at room temperature in two phases consisting of an acidic (pH ca. 2) aqueous solution of oxone 0.5 mol/l in KHSO₅, and an organic phase (dichloromethane or 1,2-dichloroethane) containing an excess of the substrate (1 M). The catalysts, 0.2% (mol) with respect to the substrate, were dissolved either in the organic ($[RuCl(DPP)_2]PF_6$ or $[RuCl_2(Me_2SO)_4]$) or in the aqueous phase $([Ru(H_2O)_2(Me_2SO)_4](BF_4)_2, K_5[Ru(H_2O)PW_{11}O_{39}] and RuCl_3), depend$ ing upon their solubility: it should be noted that none of the substrates examined undergoes oxidation with persulfate in the absence of the catalysts. Typical conversion rates, yields to the oxidant and product distributions are shown in Tables 1 and 2 for 1-octanol, 1-butanol, benzylic alcohol, 2-octanol and cyclooctanol. Yields to the oxidant are generally high with most of the ruthenium(II) complexes examined, and also the initial rates are generally maintained for extended periods of time (over 1000 cycles have been observed without loss of activity), despite evidence of the formation of negligible amounts of metallic ruthenium at the end of the reactions. Quantitative yields were never achieved in the ruthenium trichloride-catalyzed oxidations, probably due to its extensive reduction to metallic ruthenium in the absence of coordinating agents, or coordinating solvents [24], or even phase transfer agents [17].

Oxidation of secondary alcohols selectively yields the corresponding ke-

TABLE 1

Catalyst	Cyclooctanol		1-Octanol		
	Rate ^b	Yield ^c	Rate ^b	Yield⁴	Selectivity
$[RuCl_2(Me_2SO)_4]$	36	85%	14	85% ^f	68%
RuCl ₃ ·3 H ₂ O	40	65%	18	65%	80%
$[Ru(H_{2}O)_{2}(Me_{2}SO)_{4}](BF_{4})_{2}$	10	$55\%^{f}$	16	70%	85%
$K_{5}[Ru(H_{2}O)PW_{11}O_{20}] \cdot 15 H_{2}O$	5	$35\%^{f}$	15	$70\%^{f}$	48%
$[\operatorname{RuCl}(\operatorname{DPP})_2]\operatorname{PF}_6$	34	99%	13	80% ^f	92%

Persulfate oxidation of cyclooctanol and 1-octanol by ruthenium catalysts*

^aReaction conditions: catalyst, 2×10^{-6} mol; substrate, 10^{-3} mol; KHSO₅, 5×10^{-4} mol, in 2 ml of CH₂Cl₂: H₂O (1:1); 22°C.

^bInitial rate, turnovers per hour.

°Yields to the oxidant, after 24 h (selectivity in cyclooctanone: over 99%).

^dYields to the oxidant, after 24 h (one or two equivalents of oxidant are calculated for the formation of octanal or octanoic acid, respectively).

*Selectivity in octanal, after 24 h.

^fStill running.

TABLE 2

Persulfate oxidation of	primary and seconda	ry alcohols catalyzed	by [RuCl(DPP) ₂]F	γF ₆ ª
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Substrate	Rate ^b	Yield ^c	Selectivity ^d	
2-octanol	11	60%°	99%	-
cyclooctanol	34	99 %	99%	
1-octanol	13	80%°	92%	
1-butanol ^f	20	92%	91%	
benzylic alcohol	12	g	g	

^aReaction conditions: catalyst, 2×10^{-6} mol, substrate, 10^{-3} mol, KHSO₅, 5×10^{-4} mol in 2 ml of CH₂Cl₂: H₂O (1:1); 22°C.

^bInitial rate, turnovers per hour.

^eYields to the oxidant, after 24 h (one or two equivalents of oxidant are calculated for the formation of the carbonylic derivatives or the carboxylic acids, respectively).

^dSelectivity in aldehydes or ketones, after 24 h.

Still running.

^f1,2-Dichloroethane, instead of CH₂Cl₂.

^gParallel oxidative fission of the aromatic nucleus.

tones, whereas tertiary alcohols are unreactive, implying that a hydrogen atom on the α -carbon of the alcohol is necessary for the reaction to occur. Primary aliphatic alcohols give rise to the corresponding aldehydes together with varying amounts of carboxylic acids (the amounts of the carboxylic acids could be directly measured in the organic phase, owing to the presence of a strongly acidic aqueous phase). The nature of the metal catalyst has important consequences on selectivities, but at the moment it is difficult to determine a ration-

ale for this. Whereas the powerful oxidant RuO_4 is reported to produce almost quantitative amounts of carboxylic acids from primary alcohols [1,2] and most of the ruthenium (II), and in particular $K_5[Ru(H_2O)PW_{11}O_{39}]$, showed poor selectivities for aldehyde formation over carboxylic acid, satisfactorily high selectivities (over 90%) in aldehydes were observed with the $[RuCl(DPP)_2]PF_6$ catalyst, provided that an excess substrate with respect to the oxidant was used (Fig. 1). It should be noted that, in the same reaction conditions, ready oxidation of aldehydes (octanal, benzaldehyde) to the corresponding carboxylic acids occurs only in the presence of the metal catalyst, whereas persulfate alone turned out to be completely unreactive. Benzylic alcohol is also rapidly oxidized to benzaldehyde and to benzoic acid: in this case, however, a parallel oxidation takes place, leading to significant oxidative fission of the aromatic nucleus to carbon dioxide and water, with a rapid consumption of large quantities of the oxidant. This makes a comparison of the results difficult. Oxidative fission of aromatic nuclei is a typical feature of ruthenium trichloride-catalyzed oxidations and has already been observed in early reports [1,2,27,28].

Oxidation of cyclobutanol provides a useful and widely reported test for distinguishing between different reaction mechanisms for the oxidation of alcohols: bi-electronic transfer agents are expected to afford cyclobutanone selectively [40], while with mono-electronic transfer agents, such as chromium(IV), cerium(IV), manganese(III) and vanadium(V), bond cleavage occurs and non-cyclic products are predominantly obtained [41]. The present persulfate-ruthenium(II) systems always lead to the formation of cyclobutanone, together with minor amounts of γ -butyrolactone (up to 20%), but without any evidence of non-cyclic products. Since independent experiments proved that the lactone arises from the (metal-catalyzed?) persulfate oxidation of



Fig. 1. Time course for the persulfate oxidation of 1-octanol in the presence of: (a) $K_5[Ru(H_2O)PW_{11}O_{39}]$; (b) $[RuCl(DPP)_2]PF_6$. Octanal formation (\Box), octanoic acid formation (\blacksquare), oxidant consumption (\triangle). Reaction conditions: KHSO₅, 0.5 M in water; 1-octanol, 1 M in CH₂Cl₂; catalysts, 0.2% mol; 22°C.

cyclobutanone itself, the outcome of cyclobutanol oxidation should indicate the occurrence of a two-electron transfer, although two sequential mono-electronic transfers cannot be ruled out, since ring opening can occur only if the resulting mono-electronic intermediate can diffuse apart, before a second electron transfer occurs.

Experimental time courses for the oxidation of variously deuterated forms of 1-butanol to butanal by KHSO₅ and $[RuCl(DPP)_2]PF_6$ are reported in Fig. 2. Clearly worth noting are the virtual absence of a deuterium kinetic isotopic effect (D-KIE), the small k_H/k_D values observed having their origin mainly in the deuteration of the C–H bond. The absence of D-KIE for OH-deuteration suggests that proton transfer from the hydroxyl group of the alcohol is unimportant in the activation step. On the other hand, intervention of $[Ru-O-CHR_2]$ intermediates is unlikely in light of the fact that dehydrogenation of ruthenium alkoxides usually requires remarkably high temperatures [42]. The kinetic analysis, based on the measurement of the amount of carbonylic products formed for the oxidation of a secondary (cyclooctanol) and a primary alcohol (1-butanol), indicated a linear dependence of the reaction rates on the concentration of the ruthenium(II) catalysts, whereas the reaction order in the substrates varies between 0 and 1 (Fig. 3), zero order being approached at very low concentration (down to 0.1 M) by 1-butanol.

It should be noted that most bi-electronic transfers on putative oxo-ruthenium(IV) derivatives, where the hydrido abstraction is generally the slow step (Eqn. 2), are commonly characterized by first order kinetic dependences in both the metal and the alcohol and by large primary D-KIEs on the α carbon [43].



Fig. 2. Deuterium isotope kinetic effects for the oxidation of 1-butanol variously deuterated; $CD_3(CD_2)_3OD$ (\Box), $CH_3(CH_2)_3OD$ (\bigcirc), $CH_3(CH_2)_3OH$ (\blacksquare). Reaction conditions: KHSO₅, 0.5 M, in D₂O; 1-butanol, 1 M, and catalyst, [RuCl(DPP)₂]PF₆, 2 mM, in 1,2-C₂H₄Cl₂; 22°C.



Fig. 3. Initial rate dependence upon substrate concentration for the oxidations of cyclooctanol (\Box) and 1-butanol (\blacksquare). Reaction conditions: KHSO₅, 0.5 M, in water; catalyst, [RuCl(DPP)₂]PF₆, 2 mM, and substrates in either CH₂Cl₂ (cyclooctanol) or 1,2-C₂H₄Cl₂ (1-butanol); 22°C.

$$[\operatorname{Ru}^{\mathrm{II}}] + [O] \to [\operatorname{Ru}^{\mathrm{IV}} = O]$$
(1)

 $[Ru^{IV}=R_2CHOH \rightarrow [Ru^{II}-OH] + R_2C(^+)OH \text{ (generally slow)}$ (2)

$$[Ru^{II}-OH] + R_2C(^+)OH] \rightarrow [Ru^{II}-H_2O] + R_2C=O \text{ (generally fast)}$$
(3)

A zero-order dependence in the substrates, associated with small D-KIEs, may suggest that the rate determining step does not involve the substrates and simply consists in the formation of the oxo-metal species (Eqn. 1). In this case, however, one must also expect that the overall oxidation rates are completely independent of the nature of the substrate itself: instead, the present catalytic systems exhibit different rates, not only for the oxidation of different alcohols (Table 1), but also for the oxygenation of other substrates, like alkanes and ethers [32–36]. In order to explain the kinetic behavior a tight binding of the substrate prior to the rate determining step may be suggested and, owing to the lack of evidence for the coordination of alcohols to the starting complexes of ruthenium(II), an interaction with the oxo-ruthenium species formed *in situ* is likely to occur (Eqn. 4).

$$[Ru^{IV}=O] + R_2 CHOH \rightarrow [Ru^{IV}=O(R_2 CHOH)]$$
(4)

At least two alternative mechanisms can be suggested to take account of the absence of significant KIEs during the oxidation, although no direct evidence has been obtained for either of them. The first consists of a two-step mechanism, involving a slow electron transfer followed by a fast proton transfer; but a concerted oxygen insertion into a C-H bond of the alcohol may also be proposed. A clear distinction between carbon-hydrogen insertion ('perpendicular approach') and hydrido-abstraction ('linear approach') pathways (Fig. 4) is not possible on the basis of direct evidence, yet small KIEs (near to 1) are expected for concerted mechanisms [46,47].



Fig 4. Possible reaction intermediates for a perpendicular approach (coordination-assisted) (a) and a linear approach (b).

It has indeed been recently suggested [45] that one important factor in favour of a concerted mechanism in the oxidation of sp^3 CH moieties by oxometal reagents could be the presence of metal-coordinating groups in the α -position, since the formation of relatively stable adducts between the metal and, say, the hydroxyl group of alcohols, should, at least for steric reasons, hamper the perpendicular approach (Fig. 4).

Acknowledgements

The authors thank Mr. A. Ravazzolo, C.N.R., for helpful technical assistance and C.N.R., Progetto Finalizzato Chimica Fine and Centro di Studio Stabilità e Reattività dei Composti di Coordinazione of Padova, and the Ministry of Universities of Italy for financial support.

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