

A comparative study of the ruthenium(VI)dioxocarboxylato salts, $[\text{PPh}_4][\text{RuO}_2(\text{OCOR})\text{Cl}_2]$ ($\text{R} = \text{CH}_3, \text{CF}_3, \text{C}_6\text{H}_5, \text{C}_6\text{F}_5, \text{C}_5\text{H}_{11}$), in the oxidation of alcohols

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Abstract

The compounds $[\text{PPh}_4][\text{Ru}(\text{O})_2(\text{OCOR})\text{Cl}_2]$ ($\text{R} = \text{CH}_3$ **1a**, CF_3 **1b**, C_6H_5 **1c**, C_6F_5 **1d**, C_5H_{11} **1e**) were prepared and fully characterised. The fluorinated compounds **1b** and **1d** were obtained in significantly higher yields than their protonated analogues **1a** and **1c** and compound **1b** was found to be a clearly superior stoichiometric oxidant to compound **1a**. The compounds **1a–1e** were examined as catalytic oxidants for the oxidation of 1- and 2-hexanol, to hexanal and 2-hexanone respectively, with the co-oxidants H_2O_2 , NaOCl , *t*-BuOOH, *N*-methylmorpholine-*N*-oxide, Me_3NO , O_2 , $\text{C}_6\text{H}_5\text{IO}$ and Bu_4NIO_4 . Compounds **1c** and **1d** were further studied in the catalytic oxidation of a wide range of alcohols (using *N*-methylmorpholine-*N*-oxide and Bu_4NIO_4 as co-oxidants) and found to give the corresponding aldehydes or ketones very selectively, with no attack on sensitive linkages or functional groups and no over-oxidation products. Compounds **1c** and **1d** were also supported on poly(4-vinylpyridine) to give active catalysts. © 2007 Elsevier B.V. All rights reserved.

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1. Introduction

A number of reports of ruthenium(II) and ruthenium(III) carboxylato compounds can be found in the literature and they mostly exist as dimers or trimers [1]. Reports on monomeric ruthenium monocarboxylate compounds are, however, not common and very few ruthenium oxo carboxylates, where ruthenium is in a high oxidation state, are known. Perier et al. prepared the complexes $\text{trans-}[\text{RuO}_2(\text{py})_2(\text{OCOR})_2]$ ($\text{R} = \text{CH}_3, \text{CH}_3\text{CH}_2, \text{CH}_3\text{CH}_2\text{CH}_2, (\text{CH}_3)_2\text{CH}_2, \text{C}_6\text{H}_5$) and reported the crystal structure of the acetato derivative [2,3]. These compounds were shown to be unselective oxidants of organic substrates. Griffith and Jolliffe have reported the compounds $[\text{Ru}(\text{O})_2(\text{OCOR})\text{Cl}_2]^-$ ($\text{R} = \text{CH}_3, \text{CH}_3\text{CH}_2, \text{CH}_3\text{CH}_2\text{CH}_2, \text{CHF}_2$) and found these to be effective two electron oxidants in catalysing the oxidation of alcohols to aldehydes or ketones, sulphides to sulfoxides and triphenylphosphine to triphenylphosphine oxide, using *N*-methylmorpholine-*N*-oxide (NMO) as co-oxidant [4]. The crystal structure of the acetato

compound was reported, and showed a distorted octahedral structure with the acetato and *cis*-dioxo ligands in one plane [5].

We now report on the synthesis and comparative properties of the series of compounds $[\text{PPh}_4][\text{Ru}(\text{O})_2(\text{OCOR})\text{Cl}_2]$ ($\text{R} = \text{CH}_3$ **1a**, CF_3 **1b**, C_6H_5 **1c**, C_6F_5 **1d**, C_5H_{11} **1e**), where compounds **1b–1e** are new. We were particularly interested in comparing the fluorinated compounds **1b** and **1d** with the protonated compounds **1a** and **1c**. The oxidation chemistry of these compounds with respect to alcohols was examined in detail, since high valent ruthenium compounds have been shown to be very effective for this kind of chemistry [6–8].

2. Experimental

2.1. Techniques

IR spectra were recorded on a Nicolet 5DX FT (4000–400 cm^{-1}) and a Pye Unicam SP3-300 (4000–200 cm^{-1}) spectrophotometer as KBr disks. Gas-chromatographic analyses were carried out on either a Pye Unicam GCD, a Fisons GC 8000 or a Perkin-Elmer Autosystem XL chromatograph, all fitted with flame ionisation detectors.

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All stoichiometric and catalytic oxidations were carried out in Schlenk tubes, under N₂ (to prevent any possible oxidation by air) in the dark (to prevent free radical oxidation reactions initiated by UV radiation). Reactions were monitored by GC, using either packed or capillary columns. Internal standards used were *iso*-butylmethacrylate (Acros), 2-ethoxyethyl acetate or *n*-hexane (Lab Scan Analytical Services) and were chosen to achieve base-line separation on the GC traces. All conversion (yield) percentages represent the average of at least three runs.

2.2. Materials

The co-oxidants H₂O₂ (30% (m/v), Saarchem), NaOCl (15% (m/v), Associated Chemical Enterprises), *t*-BuOOH (70% (m/v), Aldrich), Me₃NO (Aldrich), O₂, *N*-methylmorpholine-*N*-oxide (Aldrich), and tetrabutylammonium periodate (Acros) were used as supplied. Iodosyl benzene was prepared according to a literature procedure and stored under N₂ in the fridge [9]. Tetraphenylphosphonium chloride (98%, Merck), glacial acetic acid, trifluoroacetic acid, benzoic acid, pentafluorobenzoic acid (all Aldrich, 99%) and hexanoic acid (Acros, 98%) were used as supplied. The substrates 1-hexene, 1-hexanol (both Acros Organics), 2-hexanol (Aldrich), cinnamyl alcohol (Acros Organics), cinnamyl chloride (Aldrich), geraniol (Acros Organics), crotyl alcohol (Aldrich), cyclohexanol (BDH Chemicals), furfuryl alcohol (H&W Fine Chemicals) and 4-nitrobenzylalcohol (Acros) were obtained commercially. Authentic standards of each product, hexanal (Aldrich), 2-hexanone (Aldrich), cinnamyl aldehyde (Acros Organics), croton aldehyde (Acros Organics), cyclohexanone (Kleber Chemicals), furfuraldehyde (BDH Chemicals), citral (BDH Chemicals) and 4-nitrobenzaldehyde (Aldrich) were also obtained commercially.

RuO₄ was prepared from RuCl₃ (1.54 g, 5.88 mmol) and sodium metaperiodate (5.50 g, 25.7 mmol) in water (40 mL) and extracted in CCl₄ (40 mL) as reported previously [10,11] and stored in a separating funnel. A solution of sodium metaperiodate (1.0 g) in water (10 mL) was layered above the RuO₄ in CCl₄ solution, which allowed this solution be stored for many weeks without degradation.

2.3. Catalyst preparation

2.3.1. Preparation of the compounds **1a–1e**

These compounds were prepared by a simplification of the literature procedure for **1a** [4]. Thus, Ph₄PCl (2.8 mmol) was

dissolved in CH₃CN (15 mL) at 0 °C whilst stirring. The RuO₄ solution (10 mL, 1.4 mmol) was added carefully at this temperature before sealing the flask and stirring overnight in the ice-bath. The resulting green solution was concentrated under reduced pressure (using a Teflon membrane vacuum pump) until precipitation occurred. The precipitate was filtered off, washed with drops of cold water and dried over silica gel under vacuum. Further concentration of the filtrate gave a second crop of sample, which was worked up as before. After drying, the dark green products were stored in a desiccator in the fridge. Yields are reported in Table 1. Elemental analyses, found (calculated): **1a** C, 51.31 (51.84) H, 3.70 (3.85); **1c** C, 56.24 (56.04) H, 3.64 (3.79); **1d** C, 50.39 (49.35) H, 2.72 (2.67).

Compounds **1a**, **1b** and **1d** could also be prepared at room temperature though in substantially reduced yields. Compounds **1c** and **1e** did not form at room temperature.

2.3.2. Preparation of compounds **2c** and **2d**

Poly(4-vinylpyridine) (1 g) was stirred with CH₂Cl₂ (5 mL) and compounds **1c** or **1d** added (100 mg). Stirring was continued for 5 h, after which the solvent was removed under reduced pressure and the product dried for 5 h under vacuum. The dark green supported catalysts were stored under N₂. Selected bands of infrared spectra (cm⁻¹)—**2c**: 3023(w) ν(C–H)-pyridine ring, 2925(m) ν(CH₂)-vinyl chain, 1598(s) ν(C=C)-pyridine ring, 1414(s) ν(C=N)-pyridine ring, 822(s) ν_{asym}(C–H)-vinyl chain, 682(m) ν(C–H)-aromatic ring, 1107(m) ν(C–O)-carboxylate, 875(w) ν_{sym}(Ru=O); **2d**: 3028(w) ν(C–H)-pyridine ring, 2924(m) ν(CH₂)-vinyl chain, 1596(s) ν(C=C)-pyridine ring, 1414(s) ν(C=N)-pyridine ring, 821(s) ν_{asym}(C–H)-vinyl chain, 684(m) ν(C–H)-aromatic ring, 1104(m) ν(C–O)-carboxylate, 879(w) ν_{sym}(Ru=O).

2.4. Oxidation reactions

2.4.1. Stoichiometric oxidation of 1- and 2-hexanol with **1a** and **1b**

Molecular sieves 4 Å (180 mg), CH₂Cl₂ (6 mL), hexanol (0.5 mmol), the internal standard (0.5 mmol) and the oxidant (**1a** or **1b**, 0.5 mmol) were added under N₂ to a Schlenk tube. The solution was stirred under N₂ at room temperature and the reaction monitored by GC.

2.4.2. Homogeneous catalytic oxidations

Molecular sieves 4 Å (180 mg), CH₂Cl₂ (6 mL), the alcohol (0.5 mmol), the internal standard (0.5 mmol), the co-oxidant

Table 1
Summary of the analytical results for the complexes (**1a–1e**)

Dioxoruthenium(VI) complexes	Yield (%)	Melting point ^a (°C)	Infrared spectra, selected bands (cm ⁻¹) ^b
[PPh ₄][RuO ₂ (OCOCH ₃)Cl ₂] (1a)	26	132	886(w) ν _{sym} (Ru=O); 864(vs) ν _{asym} (Ru=O); 1508(s) ν _{asym} (O–C–O); 334(s) ν(Ru–Cl)
[PPh ₄][RuO ₂ (OCOCF ₃)Cl ₂] (1b)	51	125	881(s) ν _{sym} (Ru=O); 862(m) ν _{asym} (Ru=O); 1516(m) ν _{asym} (O–C–O); 335(s) ν(Ru–Cl)
[PPh ₄][RuO ₂ (OCOC ₆ H ₅)Cl ₂] (1c)	28	104	884(w) ν _{sym} (Ru=O); 859(s) ν _{asym} (Ru=O); 1538(m) ν _{asym} (O–C–O); 322(s) ν(Ru–Cl)
[PPh ₄][RuO ₂ (OCOC ₆ F ₅)Cl ₂] (1d)	81	95	880(m) ν _{sym} (Ru=O); 855(w) ν _{asym} (Ru=O); 1519(s) ν _{asym} (O–C–O); 318(s) ν(Ru–Cl)
[PPh ₄][RuO ₂ (OCOC ₅ H ₁₁)Cl ₂] (1e)	43	106	882(w) ν _{sym} (Ru=O); 859(m) ν _{asym} (Ru=O); 1504(w) ν _{asym} (O–C–O); 320(s) ν(Ru–Cl)

^a Decomposed.

^b vs: very strong, s: strong, m: medium, and w: weak.

(0.75 mmol) and the catalyst (20 mg) were added under N₂ to a Schlenk tube. The solution was stirred under N₂ at room temperature and the reaction monitored by GC.

Turnover limits were investigated by doubling the alcohol and co-oxidant amounts (to 1 and 0.5 mmol, respectively, and halving the amount of catalyst (10 mg).

2.4.3. Oxidation of cyclohexanol with **2c** and **2d**

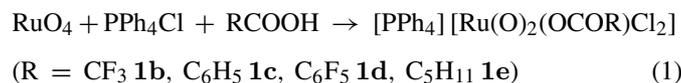
The procedure was as in Section 2.4.2, except that 200 mg of supported catalyst was used. Although no detailed leach tests were carried out, as these were outside the scope of this investigation, the solvent remained clear and colourless throughout the reactions. Since the catalysts are dark green in colour, no visual sign of leaching was thus observed.

2.4.4. Product isolation

These were carried out on scaled up reactions. Thus, e.g. for cyclohexanol, molecular sieves 4 Å (360 mg), CH₂Cl₂ (6 mL), cyclohexanol (9.7 mmol), NMO (14.6 mmol) and the catalyst (389 mg) were added under N₂ to a Schlenk tube. The solution was stirred under N₂ at room temperature and the reaction monitored by GC. After 72 h, the reaction mixture was filtered to remove the molecular sieves. The green filtrate was passed through a silica gel column, initially eluting with hexane, and finally flushing the column with CH₂Cl₂. The clear fractions were combined, the product isolated by distillation and characterised by ¹H and ¹³C NMR.

3. Results and discussion

The compounds **1a–1e** were prepared by the addition of a solution of RuO₄ to a solution of PPh₄Cl and the respective carboxylic acid in acetonitrile at 0 °C (Eq. (1)):



It was noticed that the fluorinated compounds, **1b** and **1d**, were obtained in a much higher yield (two- to three-fold) than their respective hydrogenated analogues, **1a** and **1c** (Table 1). This may be due to the different relative charge distributions within the compounds caused by the significant differences in the electronegativities of the fluorine and hydrogen atoms (which have approximately the same size) that constitute part of the ligands in these compounds (Fig. 1). Also apparent is that the fluorinated compounds decompose at slightly lower temperatures than their hydrogenated analogues.

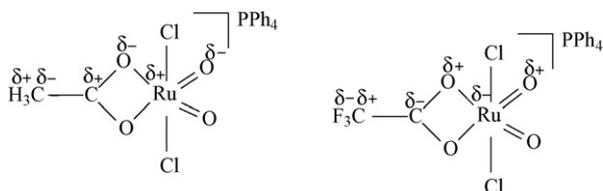


Fig. 1. Relative charge distributions for compounds **1a** and **1b**.

Table 1 also shows infrared data for the compounds **1**. The characteristic $\nu_{\text{sym}}(\text{Ru}=\text{O})$ stretch is seen in the range 880–886 cm⁻¹ and the $\nu_{\text{asym}}(\text{Ru}=\text{O})$ stretch is seen in the range 855–864 cm⁻¹ for all the compounds. The $\nu_{\text{sym}}(\text{Ru}=\text{O})$ stretches in the fluorinated compounds **1b** and **1d** are relatively stronger than those of their hydrogenated analogues and the converse is true for the $\nu_{\text{asym}}(\text{Ru}=\text{O})$ stretches. Again, this may be related to the different charge distributions as discussed previously. Further infrared bands are difficult to discern beneath bands due to [PPh₄]⁺, however, by comparing the infrared spectrum of the salt [PPh₄]Cl with those of the compounds **1**, distinct peaks can be identified apart from the peaks due to [PPh₄]Cl. Thus, slightly broad peaks between 1500 and 1540 cm⁻¹ can clearly be assigned to the carboxylate group (*i.e.* $\nu_{\text{asym}}(\text{O}-\text{C}-\text{O})$) [2–5,12,13]. The bands between 315 and 334 cm⁻¹ are assigned to Ru–Cl stretches. Noticeable is that the ruthenium-oxo and ruthenium-chloride stretches of the fluorinated compounds **1b** and **1d** are at lower wave numbers than their hydrogenated equivalents.

Compounds **1a** and **1b** were investigated as stoichiometric oxidants for the oxidation of 1-hexanol to hexanal. Both compounds showed a fairly rapid initial reaction rate, with **1a** showing a 61% conversion and **1b** an 81% conversion after 30 min. Compound **1a** had converted 69% of the hexanol to hexanal after 24 h, whilst **1b** had converted 91% in 3 h. Clearly the fluorinated compound is the better stoichiometric oxidant. This observation matches expectations in that the IR data implies weaker Ru=O bonds in the fluorinated compound.

The compounds **1a–1e** were then investigated as catalysts for the oxidation of 1-hexanol and 2-hexanol to give hexanal and 2-hexanone, respectively. Their reaction with 1-hexene was also investigated. Reactions were monitored over 24 h and a wide range of co-oxidants, namely H₂O₂, NaOCl, *t*-BuOOH, Me₃NO, O₂, *N*-methylmorpholine-*N*-oxide (NMO), iodosyl benzene (PhIO) and tetrabutylammonium periodate (Bu₄NIO₄) was examined. The results are shown in Tables 2 and 3. Since a fixed mass of catalyst (20 mg) was used for each reaction, the catalytic turnovers are included in parentheses to allow molar comparisons. The reaction of the above co-oxidants with 1-hexanol, 2-hexanol and 1-hexene was also investigated in the absence of the catalysts to determine to what degree the co-oxidants acted as stoichiometric oxidants. These results are also shown in Tables 2 and 3. Thus, H₂O₂, Me₃NO and O₂ did not oxidise 1-hexanol on their own, NaOCl showed a very low conversion, *t*-BuOOH, NMO and PhIO gave approximately the same conversion of 15, 18 and 20%, respectively, after 24 h, whilst Bu₄NIO₄ was found to be rather reactive with a 65% alcohol conversion. All the co-oxidants, except Me₃NO and Bu₄NIO₄, showed no oxidative activity with the secondary alcohol 2-hexanol. Conversions for the latter two were low.

None of the co-oxidants or any of the catalysts **1a–1e** showed any activity with respect to 1-hexene. This suggests that the catalysts do not attack double bonds.

Apart from O₂, all the co-oxidants examined were active for the above reactions. No specific trend in reactivity could be observed among the catalysts **1a–1e**. The effectiveness of the co-oxidants appears to be catalyst specific and the rela-

Table 2
Percentage conversion (yield) of 1-hexanol to hexanal by the compounds **1a–1e** with various co-oxidants

Complex	Reaction time	H ₂ O ₂ ^a	NaOCl	<i>t</i> -BuOOH	NMO	Me ₃ NO	O ₂	C ₆ H ₅ IO	Bu ₄ NIO ₄
1a	30 min	53 (8)	64 (10)	59 (9)	100 (15)	28 (4)	0	51 (8)	76 (11)
	24 h	56 (8)	83 (13)	64 (10)	100 (15)	60 (9)	0	67 (10)	100 (15)
1b	30 min	55 (9)	74 (13)	37 (6)	87 (13)	47 (8)	8 (1)	70 (12)	96 (16)
	24 h	51 (9)	91 (15)	79 (13)	89 (13)	60 (10)	10 (2)	70 (12)	100 (17)
1c	30 min	60 (10)	72 (12)	60 (10)	100 (17)	20 (3)	0	90 (15)	100 (17)
	24 h	73 (12)	77 (13)	66 (11)	100 (17)	81 (14)	9 (2)	100 (17)	100 (17)
1d	30 min	30 (6)	52 (10)	62 (12)	83 (16)	34 (7)	0	44 (8)	100 (19)
	24 h	36 (7)	71 (14)	67 (13)	97 (18)	58 (11)	5 (1)	62 (12)	100 (19)
1e	30 min	40 (7)	75 (13)	45 (8)	93 (16)	26 (4)	0	52 (9)	100 (17)
	24 h	53 (9)	80 (14)	49 (8)	96 (16)	62 (11)	29 (5)	76 (13)	100 (17)
None	30 min	0	0	0	0	0	0	0	54
	3 h	0	1	10	6	0	0	0	54
	24 h	0	4	18	15	0	0	20	65

^a Turnovers are shown in parentheses.

Table 3
Percentage conversion (yield) of 2-hexanol to 2-hexanone by the compounds **1a–1e** with various co-oxidants

Complex	Reaction time	H ₂ O ₂ ^a	NaOCl	<i>t</i> -BuOOH	NMO	Me ₃ NO	O ₂	C ₆ H ₅ IO	Bu ₄ NIO ₄
1a	30 min	14 (2)	19 (3)	23 (4)	62 (9)	0	0	58 (9)	80 (12)
	24 h	18 (3)	88 (13)	25 (4)	63 (10)	35 (5)	0	73 (11)	100 (15)
1b	30 min	4 (1)	31 (5)	26 (4)	73 (12)	33 (6)	0	44 (8)	31 (5)
	24 h	4 (1)	100 (17)	29 (5)	63 (10)	37 (6)	0	63 (11)	55 (9)
1c	30 min	23 (4)	47 (8)	19 (3)	100 (17)	11 (2)	0	45 (8)	76 (13)
	24 h	25 (4)	38 (7)	19 (3)	100 (17)	38 (7)	0	78 (13)	76 (13)
1d	30 min	8 (2)	36 (7)	17 (3)	52 (10)	26 (5)	0	50 (10)	43 (8)
	24 h	10 (2)	69 (13)	33 (6)	67 (13)	37 (7)	0	77 (15)	56 (11)
1e	30 min	3 (1)	62 (11)	15 (3)	69 (12)	34 (6)	0	88 (15)	46 (8)
	24 h	14 (2)	72 (12)	11 (2)	72 (12)	45 (8)	0	100 (17)	100 (17)
None	30 min	0	0	0	0	0	0	0	7
	24 h	0	0	0	0	14	0	0	16

^a Turnovers are shown in parentheses.

tive order, in terms of performance, of the catalysts appear to depend on which co-oxidant is used. Catalyst **1a** works best with NMO and Bu₄NIO₄, **1b** works best with NaOCl, NMO and Bu₄NIO₄, **1c** with NMO, PhIO and Bu₄NIO₄, **1d** with NMO and Bu₄NIO₄, and **1e** with NMO and Bu₄NIO₄. Clearly, NMO and Bu₄NIO₄ are the best overall general co-oxidants, whilst NaOCl and PhIO also perform well. Whereas Bu₄NIO₄ was noted to be very active as a stoichiometric oxidant for the primary alcohol, the reaction rates with the catalysts are significantly higher and the reactions go to completion, thus strongly suggesting that Bu₄NIO₄ functions mainly as a co-oxidant in the reactions involving compounds **1a–1e**. In most cases the catalytic reactions with the primary alcohol were faster than those with the secondary alcohol, with the exception of **1e** with PhIO and **1c** with NMO, the latter appearing to be a particularly effective combination.

Experiments were carried out to determine the maximum turnover limits of some of these catalysts. Thus, the quantity of catalyst used was halved to 10 mg and the quantity of alcohol and co-oxidant was doubled. Compounds **1b**, **1c** and **1e** were

examined with 1-hexanol and NMO and Bu₄NIO₄ as co-oxidant (Table 4). In the oxidation of 1-hexanol, all three of the catalysts showed an initial high rate of conversion with high turnovers when NMO was used as co-oxidant. The reaction rate levelled off rapidly after 3 h. Catalyst **1c** achieved a maximum of 52

Table 4
Summary of the catalytic reactions involving double quantities of 1-hexanol and half quantities of catalyst, showing percentage conversion/yield of hexanal

Complex	Reaction time	NMO ^a	Bu ₄ NIO ₄
1b	30 min	77 (52)	40 (28)
	3 h	85 (58)	93 (64)
	24 h	87 (59)	90 (61)
1c	30 min	65 (44)	50 (36)
	3 h	70 (48)	80 (56)
	24 h	78 (52)	100 (68)
1e	30 min	75 (51)	52 (36)
	3 h	82 (56)	88 (60)
	24 h	84 (56)	86 (59)

^a Turnovers are shown in parentheses.

Table 5
Summary of the catalytic reactions involving double quantities of 2-hexanol and half quantities of catalyst, showing percentage conversion (yield) of 2-hexanone

Complex	Reaction time	NMO ^a	Bu ₄ NIO ₄	NaOCl
1a	30 min	–	19 (11)	–
	3 h	–	38 (23)	–
	24 h	–	60 (36)	–
1b	30 min	–	–	14 (10)
	3 h	–	–	21 (14)
	24 h	–	–	25 (17)
1c	30 min	69 (47)	–	–
	3 h	100 (68)	–	–
	24 h	100 (68)	–	–
1e	30 min	–	30 (20)	–
	3 h	–	35 (24)	–
	24 h	–	54 (37)	–

^a Turnovers are shown in parentheses.

turnovers in 24 h, which equated to the number of turnovers achieved by the other two catalysts within 30 min. Compound **1b** now functioned as the best catalyst of those examined when NMO was used as co-oxidant, whilst it had appeared to be the poorest catalyst for this transformation under the conditions whose results are shown in Table 2. A possible reason for this behaviour is that although compound **1b** showed a slower rate of conversion of 1-hexanol to hexanal relative to the other catalysts, it has the ability to undergo more turnovers compared to the other compounds. This may be due to the structural stability of the fluorinated compound relative to the other compounds, which could increase the lifetime of the fluorinated compound under reaction conditions and consequently allow for easier re-oxidation of the reduced catalyst to its active form.

A different trend was observed for the oxidation reactions involving Bu₄NIO₄, with the initial reaction rate being slower than with NMO. Here the reaction involving **1b** was initially the slowest, but it had achieved the highest turnover of the three compounds studied after 3 h. Over time, compound **1c** was the most effective catalyst, however.

Similar experiments were carried out using the best catalyst/co-oxidant combinations for the oxidation of 2-hexanol to 2-hexanone from Table 3. These results are shown in Table 5. Clearly compound **1c** with NMO is the best combination of those examined under these conditions.

Although no specific trend in activity of the catalysts **1a–1e** could be determined from Tables 2 and 3, it could generally be concluded that compound **1c** functioned most effectively as a catalyst and that compound **1d** was the least effective. It was consequently decided to examine these two compounds as catalysts for the oxidation of a range of substrates using the co-oxidants NMO and Bu₄NIO₄, the latter being the most effective general co-oxidants from the range studied. The substrates were chosen to represent a wide spectrum of organic alcohols and further included an unsaturated chloride to determine if the oxidative system attacked halogens bonded to organic compounds. The range of substrates included the unsaturated aromatic primary alcohol (cinnamyl alcohol), its equivalent

unsaturated aromatic chloride (cinnamyl chloride), unsaturated primary alcohols (geraniol and crotyl alcohol), a saturated cyclic alcohol (cyclohexanol), a heteroatom containing aromatic alcohol (furfuryl alcohol) and finally a nitro-substituted alcohol (4-nitrobenzylalcohol) (Table 6). As previously, the co-oxidants themselves were also reacted with the substrates in the absence of catalyst to determine the degree of the direct reaction (Table 6).

Both **1c** and **1d** are efficient oxidants for the oxidation of cinnamyl alcohol, giving almost total conversion to cinnamyl aldehyde within 30 min of the start of the reaction. The double bond is not attacked and no other products are observed. Both co-oxidants on their own (especially NMO) give high conversions too, but at a slower rate and the reactions involving **1c** and **1d** are thus mostly catalytic.

The oxidation of cinnamyl chloride with **1c** and **1d** gave turnovers of one or less. These results are equal to or lower than when the co-oxidants are used alone. This suggests that the catalysts are inactive towards the oxidation of chloride in organic substrates. When NMO was used on its own, 30% of cinnamyl chloride was oxidised to cinnamyl aldehyde. This agrees with the literature which states that NMO reacts with activated halides [14,15]. The absence of a substantial yield of aldehyde in the reactions including the catalysts and NMO suggests that the catalysts inhibit the direct oxidation of organic halides by NMO.

Both **1c** and **1d** catalytically converted crotyl alcohol to croton aldehyde. The double bond was not attacked, nor was over-oxidation to the carboxylic acid observed. The co-oxidant Bu₄NIO₄ was best for this reaction and **1c** the better catalyst. The co-oxidants alone showed minimum reactivity.

Both **1c** and **1d**, combined with either NMO or Bu₄NIO₄, convert cyclohexanol to cyclohexanone rapidly and essentially quantitatively. No rupture of the cyclohexanol ring was observed. The co-oxidants alone showed low reactivity (<15% over 24 h).

Both **1c** and **1d** gave furfuraldehyde from furfuryl alcohol in 98% yield within 24 h with Bu₄NIO₄ as co-oxidant, although **1c** initially reacted more rapidly. In contrast **1d** was more effective than **1c** with NMO, although NMO is the poorer co-oxidant for this transformation. NMO is also fairly reactive on its own, unlike Bu₄NIO₄, giving the aldehyde in 21% yield after 30 min. No further products were observed for the above reactions, implying that the oxygen within the structure of the aromatic ring and the double bonds were not attacked. This suggests that the catalysts show specificity for the oxidation of the alcohol group.

Both catalysts were very effective in the oxidation of geraniol to citral with either co-oxidant, achieving, effectively, a quantitative conversion with no other oxidation or cleavage products observed. The co-oxidants on their own show conversions of 28% (NMO) and 10% (Bu₄NIO₄), respectively.

Finally, both catalysts with either co-oxidant convert 4-nitrobenzyl alcohol to 4-nitrobenzyl aldehyde in effectively 100% yield. For this alcohol, however, both co-oxidants (especially NMO) are rather active on their own. The nitro functional group is not attacked.

Table 6
Summary of the percentage conversions (yields) of substrates to their corresponding products with compounds **1c** and **1d** and the co-oxidants NMO and Bu₄NiO₄

Substrate	Product ^a	Reaction time	1c		1d		NMO ^b	Bu ₄ NiO ₄ ^b
			NMO ^c	Bu ₄ NiO ₄	NMO	Bu ₄ NiO ₄		
Cinnamyl alcohol	A	30 min	99 (17)	100 (17)	100 (19)	100 (19)	82	13
		3 h	100 (17)	100 (17)	100 (19)	100 (19)	77	25
Cinnamyl chloride	A	30 min	3 (<1)	5 (<1)	3 (<1)	3 (<1)	18	3
		3 h	2 (<1)	5 (<1)	1 (<1)	5 (1)	16	8
		24 h	2 (<1)	7 (1)	2 (<1)	9 (2)	30	30
Crotyl alcohol	A	30 min	51 (9)	53 (9)	45 (9)	20 (4)	0	6
		3 h	56 (10)	67 (11)	54 (10)	47 (9)	3	4
		24 h	57 (10)	100 (17)	57 (11)	74 (14)	3	3
Cyclohexanol	K	30 min	100 (17)	70 (11)	98 (19)	48 (9)	16	6
		3 h	100 (17)	100 (17)	100 (19)	98 (19)	15	13
Furfuryl alcohol	A	30 min	50 (9)	89 (15)	52 (10)	54 (10)	21	0
		3 h	55 (9)	93 (17)	64 (12)	77 (15)	23	5
		24 h	56 (10)	98 (17)	67 (13)	98 (19)	22	3
Geraniol	A	30 min	92 (16)	81 (14)	98 (19)	57 (11)	0	4
		3 h	97 (17)	100 (17)	100 (19)	100 (19)	2	5
4-Nitrobenzyl alcohol	A	30 min	99 (17)	96 (16)	95 (18)	99 (19)	70	25
		3 h	100 (17)	100 (17)	100 (19)	100 (19)	65	27

^a A: corresponding aldehyde product; K: corresponding ketone product.

^b In absence of catalyst.

^c Turnovers are shown in parentheses.

It can be concluded from the above study that **1c** and **1d** are efficient catalysts for a range of alcohol substrates. No sensitive linkages like double bonds, aromatic and saturated rings are cleaved, nor are heteroatoms or chlorides attacked. The inertness to double bonds was confirmed by the observation that these catalysts are inert to hexene. No significant difference in catalytic activity was noted between the fluorinated and protonated complexes **1c** and **1d**.

The yields referred to above are GC yields, isolated yields are a few percent lower due to product loss on work-up in our hands. The gravimetric determinations were done on scaled up reactions and the product was further identified by NMR spectroscopy (*versus* authentic samples).

Some preliminary studies were made to see if the catalysts could be supported on an insoluble support. Much effort has been expended over many years to combine the advantages of homogeneous and heterogeneous catalysts in this manner [16–20]. Compounds **1c** and **1d** were consequently supported on poly(4-vinylpyridine) (PVP) in the ratio of 1 mg catalyst to 10 mg PVP to give catalysts **2c** and **2d**. The IR data for the supported compounds shows a peak at 1105 cm⁻¹, assigned to the ν(C–O) stretch of the carboxylate group. A weak, though distinct, ν_{asym}(Ru=O) stretch is observed at approximately 878 cm⁻¹. Both these stretches are shifted to lower wavenumbers when compared to those of the unsupported compounds. Although the interaction between the supported Ru(VI) compounds and PVP was not studied, it is believed to involve an ionic interaction [21].

Reactions in two different solvents were examined, dichloromethane and toluene. Toluene was chosen because the compounds **1c** and **1d** do not dissolve in it and this should

reduce the possibility of leaching. Toluene is also known to cause swelling of the polymer beads, whilst CH₂Cl₂ does not [19,22].

The oxidation of cyclohexanol to cyclohexanone using the supported Ru(VI) catalysts **2c** and **2d** was investigated using NMO and Bu₄NiO₄ as co-oxidants. The same quantity of ruthenium was added as for the homogeneous reactions. Cyclohexanol was chosen because compounds **1c** and **1d** had previously shown 99–100% conversions with the same co-oxidants. The results are shown in Table 7. Mediocre conversions are observed in CH₂Cl₂, especially when compared to conversions obtained by the co-oxidants alone (Table 6). Both catalysts showed a slow rate of conversion of cyclohexanol to cyclohexanone in toluene at the beginning of the reaction, however, **2c** with NMO achieved a 40% yield of cyclohexanone after 24 h. Conversion with Bu₄NiO₄ was significantly lower as were the conversions achieved by **2d** with either co-oxidant. However, since almost no cyclohexanol is oxidised by the co-oxidants on

Table 7
Percentage conversion (yield) of cyclohexanol to cyclohexanone by the PVP-supported catalysts **2c** and **2d** in dichloromethane and toluene

Solvent	Reaction time	2c		2d	
		NMO ^a	Bu ₄ NiO ₄	NMO	Bu ₄ NiO ₄
Dichloromethane	30 min	14 (2)	29 (5)	22 (4)	15 (3)
	24 h	17 (3)	30 (3)	22 (4)	17 (3)
Toluene	30 min	4 (<1)	3 (<1)	4 (<1)	3 (<1)
	3 h	6 (1)	6 (1)	8 (1)	5 (1)
	24 h	40 (7)	13 (2)	20 (3)	21 (4)

^a Turnovers are shown in parentheses.

their own in toluene, both **2c** and **2d** appear to behave catalytically. The observed trend of a low rate of conversion at the beginning of the oxidations in toluene suggests that a solvent influence prevails. As the polymer swells active sites become more accessible and thus the rate of oxidation increases [19]. This trend was not observed for the reactions carried out in CH_2Cl_2 , adding support to this proposal. Since the mole quantity of supported material responsible for the above oxidations was not known, direct comparisons to catalysts **1c** and **1d** are difficult. The nature of the association between the catalyst and support was not investigated further, since this was just a preliminary study. It is conceivable that different co-oxidants or different supports, such as ion exchange resins, could be more effective.

4. Conclusion

In conclusion the fluoridated compounds can be obtained in significantly higher yield than their protonated equivalents and the former also appear to be the superior stoichiometric oxidants, in keeping with expectations from the IR data. All of these compounds are effective catalysts for the oxidation of 1- and 2-hexanol to hexanal and 2-hexanone, respectively, but no significant difference could be seen between the fluorinated and protonated compounds under catalytic conditions. Compounds **1c** and **1d** were also found to very effectively and selectively catalytically oxidise a range of alcohols without attacking other sensitive functional groups or heteroatoms, but again no significant difference is noted between the fluorinated and protonated compounds under catalytic conditions. It seems likely that the faster rate of oxidation by the fluorinated compounds is offset by a slower rate of re-oxidation.

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