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Catalytic oxidation of hydrocarbons by trinuclear μ-oxo-bridged ruthenium-acetate clusters: Radical *versus* non-radical mechanisms

Genebaldo S. Nunes [a,*], Anamaria D.P. Alexiou [b], Henrique E. Toma [b,*]

[a] *Universidade Estadual do Sudoeste da Bahia, Itapetinga, Bahia, CEP 45700-000, Brazil*
[b] *Instituto de Química, Universidade de São Paulo, C. Postal 26077 CEP 05513-970, São Paulo, SP, Brazil*

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ABSTRACT

The $[Ru_3O(H_3CCO_2)_6(py)_2(L)]PF_6$ clusters, where L = methanol or dimethyl sulfoxide, can be activated by peroxide or oxygen donor species, such as *tert*-butyl hydroperoxide (TBHP) or iodosylbenzene (PhIO), respectively, generating reactive intermediates of the type $[Ru_3^{IV,IV,III}=O]^+$. In this way, they catalyse the oxidation of cyclohexane or cyclohexene by TBHP and PhIO, *via* oxygen atom transfer, rather than by the alternative oxygen radical mechanism characteristic of this type of complexes. In addition to their ability to perform efficient olefin epoxydation catalysis, these clusters also promote the cleavage of the C–H bond in hydrocarbons, resembling the oxidation catalysis by metal porphyrins.

1. Introduction

Hydrocarbons and other organic compounds can undergo selective catalytic oxidation by transition metal complexes, resembling in many ways the enzymatic oxidations involving, for instance, cytochrome P-450 [1–9]. In this context, ruthenium(II or III) complexes containing a variety of ligands, including polypyridine and Schiff-bases, can be activated by several oxidants to yield ruthenium(IV, V, or VI)-oxo (Ru=O) species as active intermediates in hydride, hydrogen- or oxygen-transfer, C–H insertion or proton-coupled electron transfer reactions [2,4,5,7,9–12]. It should be noticed that in high oxidation states, e.g. $Ru^{IV}(d^4)$, $Ru^{V}(d^3)$, and $Ru^{VI}(d^2)$, the vacancies in the $d_\pi(Ru)$ levels can be stabilized by $2p_\pi(O) \rightarrow d_\pi$ electron donation, thus favoring the Ru=O bond formation [1,2,11,12].

Trinuclear oxo-bridged ruthenium carboxylate clusters (Fig. 1) of the type $[Ru_3O(RCO_2)_6L_3]^n$ (where $R = CH_3$, C_2H_5; $L = H_2O$, PPh_3, py, $n = 0, +1$) have been reported to be effective catalysts in the oxidation of alcohols, cyclohexene and cyclohexane, acting by an outer sphere mechanism involving the formation of radical species from the peroxide reagents [13–16].

Recently, we reported on the chemistry of a novel ruthenium-oxo species, e.g. $[Ru_3^{IV,IV,III}O(H_3CCO_2)_6(py)_2O]^+$ or $[Ru_3^{IV,IV,III}=O]^+$, resulting from proton-coupled redox processes associated with the $[Ru_3^{III,III,III}O(H_3CCO_2)_6(py)_2(H_2O)]^+$ cluster [17] (Figs. 1b and 1c). Such complex exhibited an enhanced electrocatalytic activity in the oxidation of benzyl alcohol, with the participation of $[Ru_3^{IV,IV,III}=O]^+$ species (Fig. 1c). However, their generation from $[Ru_3^{III,III,III}O(H_3CCO_2)_6(py)_2(L)]^+$ precursors in the presence of oxidizing agents in organic solvents, has not been successful up to the present time. As a matter of fact, a good leaving group L is required for the formation of $[Ru_3^{III,III,III}O(H_3CCO_2)_6(py)_2]^+$ species exhibiting an empty site for the transfer of oxygen from O-donor agents (e.g., peroxides and iodosylbenzene). In the lack of a suitable leaving group, the outer-sphere electron transfer mechanism should predominate, proceeding through free radical species, as previously reported in the literature [13–16]. According to our preliminary tests, most conventional ligands, including the coordinated water molecule in the $[Ru_3^{III,III,III}O(H_3CCO_2)_6(py)_2(H_2O)]^+$ complex, are not labile enough for this purpose. Therefore, a special strategy is required to generate a good leaving group from $[Ru_3^{III,III,III}O(H_3CCO_2)_6(py)_2(L)]^+$. Accordingly, we have selected the $[Ru_3O(H_3CCO_2)_6(py)_2L]^+$ clusters containing the ligands $L = CH_3OH$ and $(CH_3)_2SO$ as precursor complexes, and performed the oxidation of cyclohexene and cyclohexane, in the presence of iodosylbenzene or *tert*-butyl hydroperoxide. The CH_3OH and $(CH_3)_2SO$ ligands can be rapidly oxidized in the reaction media, yielding weakly coordinating acetaldehyde and $(CH_3)_2SO_2$ ligands. Therefore, they can provide effective leaving groups, allowing the direct activation of the $[Ru_3^{III,III,III}O(H_3CCO_2)_6(py)_2]^+$ species by the oxygen donor agents. To evaluate this hypothesis, we investigated their

* Corresponding author.
E-mail addresses: genebaldo@gmail.com (G.S. Nunes), henetoma@iq.usp.br (H.E. Toma).

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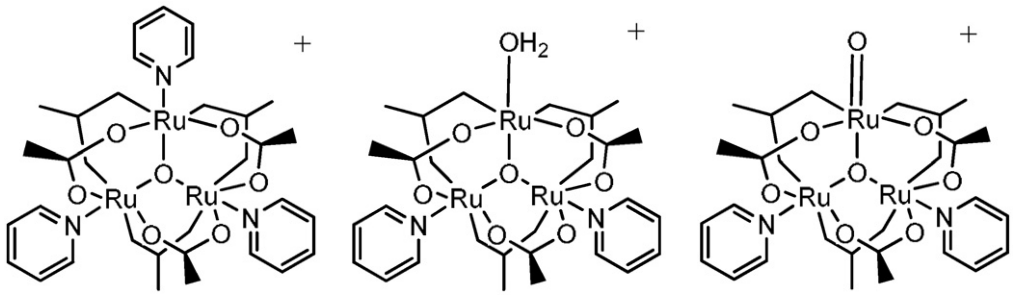


(a) (b) (c)

Fig. 1. Structural representation of the $[Ru_3O(H_3CCO_2)_6(py)_3]^+$ (a), $[Ru_3O(H_3CCO_2)_6(py)_2(H_2O)]^+$ (b) and $[Ru_3O(H_3CCO_2)_6(py)_2O]^+$ or $[Ru_3^{IV,IV,III}{=}O]^+$ (c) complexes.

inner-sphere catalytic performance in comparison with the outer sphere $[Ru_3^{III,III,III}O(H_3CCO_2)_6(py)_3]^+$ analogue.

2. Experimental

2.1. Materials and instrumentation

All reagents and solvents were of analytical grade and used as supplied. $[Ru_3O(H_3CCO_2)_6(py)_2L]PF_6$, L = CH_3OH, dmso, $(CH_3)_2SO$, py (pyridine) and $[Ru_3O(H_3CCO_2)_6(py)_2(H_2O)]Cl$ were prepared according to previously described procedures [13,17–19]. Iodosylbenzene was obtained by the hydrolysis of iodosyl benzene diacetate [20,21]. The purity of *tert*-butyl hydroperoxide solution and PhIO was determined by iodometric assays.

The oxidation reactions of cyclohexene and cyclohexane were carried out in 5 mL vials capped with a teflon-coated septum, at 25 °C, under a nitrogen atmosphere, with magnetic stirring. In a typical procedure, the catalyst, the substrate, *n*-octane (internal standard) and the oxygen donor (PhIO or TBHP) were added to 3 mL dichloromethane. After 2 or 3 h, respectively, the products were analyzed by gas chromatography using a Shimadzu model CG-17A equipment with flame ionization detector and OV-1701 0.50 μm capillary column (30 m × 0.25 mm), and *n*-octane as internal standard. The reaction yields were calculated in relation to the starting amount of oxygen donor.

The effect of oxygen donors on the electronic properties of the catalyst was studied by means of UV–vis spectroscopy, using a Hewlett–Packard model 8453-A diode array equipment, in the 190–1100 nm range. Typically, 3 mL solutions of the $[Ru_3O(H_3CCO_2)_6(py)_2(CH_3OH)]PF_6$ cluster (2.0×10^{-4} mol dm^{-3}) in CH_2Cl_2 were employed for monitoring the electronic spectra before and after the addition of TBHP (3×10^{-5} mol) or PhIO (1×10^{-5} mol).

3. Results and discussion

The $[Ru_3O(H_3CCO_2)_6(py)_2(CH_3OH)]PF_6$ cluster has a blue color, displaying characteristic bands at 600 and 690 nm (Fig. 2) ascribed to intra cluster (IC) metal–metal electronic transitions [13]. The dichloromethane solution of the complex containing TBHP or PhIO exhibits green color and its spectrum reveals two bands at 591 and 772 nm (Fig. 2) reflecting the formation of the $[Ru_3^{IV,IV,III}{=}O]^+$ oxidized clusters [17]. Such species have been previously detected in electrochemical studies involving proton-coupled redox processes in $[Ru_3^{III,III,III}O(H_3CCO_2)_6(py)_2(H_2O)]^+$.

3.1. Oxidation of cyclohexene

The results of the cyclohexene oxidation using $[Ru_3O(H_3CCO_2)_6(py)_2(CH_3OH)]PF_6$ (A) or $[Ru_3O(H_3CCO_2)_6(py)_3]PF_6$ (B) as catalysts, and iodosylbenzene as oxygen donor, can be seen in Table 1. The

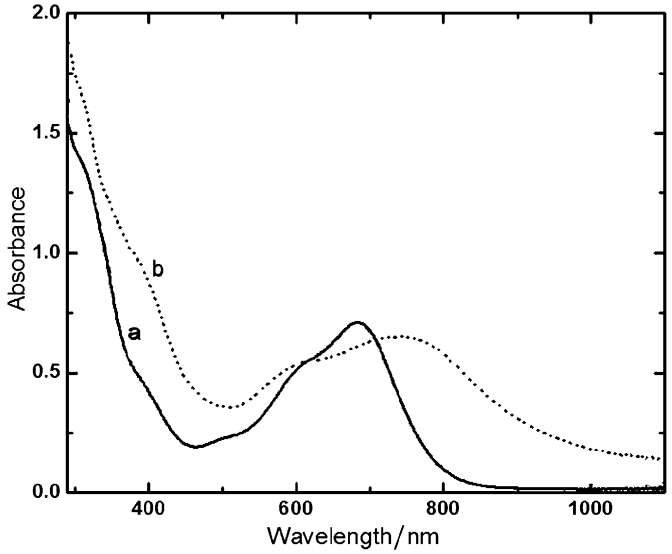


Fig. 2. UV–vis spectra of 2×10^{-4} mol dm^{-3} solutions of the $[Ru_3O(H_3CCO_2)_6(py)_2(CH_3OH)]PF_6$ cluster in CH_2Cl_2, before (a) and after (b) addition of TBHP (3×10^{-5} mol).

Table 1
Oxidation of cyclohexene with PhIO catalyzed by $Ru_3O(H_3CCO_2)_6(py)_2(CH_3OH)]PF_6$ (A) or $[Ru_3O(H_3CCO_2)_6(py)_3]PF_6$ (B).[a]

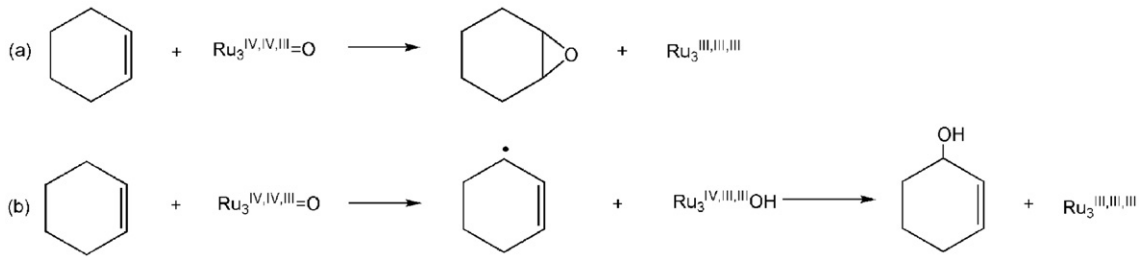
Catalyst	Yield (%)[b]		
	Epoxide	Alcohol	Ketone
A	48 (±2)	0.87 (±0.05)	16.3 (±0.8)
B	1.6 (±0.1)	–	–

[a] 2×10^{-6} mol of catalyst, 4.4×10^{-3} mol of cyclohexene, 9.6×10^{-5} mol of iodosylbenzene (99.3%) in 3 mL of dichloromethane, $T = 25$ °C, $t = 2$ h.

[b] Based on the starting amount of iodosylbenzene.

reaction catalyzed by the $[Ru_3O(H_3CCO_2)_6(py)_2(CH_3OH)]PF_6$ cluster yielded 1,2-epoxycyclohexane as epoxidation product, and 2-cyclohexen-1-ol and 2-cyclohexen-1-one as allylic oxidation products. In this catalytic system, the alcohol is easily oxidized to ketone. Under similar conditions, the $[Ru_3O(H_3CCO_2)_6(py)_3]PF_6$ cluster yielded no significant amount of products. In addition, when the catalysis by $[Ru_3O(H_3CCO_2)_6(py)_2(CH_3OH)]PF_6$ was carried out in a coordinating solvent such as acetonitrile, only trace amounts of products were obtained. These results indicate that the catalytic intermediate is only generated when the cluster has a substitutionally labile terminal ligand, in order to allow its activation by the O-transfer agent.

By transferring an oxygen atom to the labile position of the cluster, iodosylbenzene can give rise to the catalytic intermediate $[Ru_3^{IV,IV,III}{=}O]^+$ which preferentially attacks the C=C bond producing the epoxide product (Scheme 1a). The $[Ru_3^{IV,IV,III}{=}O]^+$ species



Scheme 1. Cyclohexene oxidation catalyzed by $[Ru_3^{IV,IV,III}{=}O]^+$ species, or $[Ru_3O(H_3CCO_2)(py)_2O]^+$.

Table 2
Oxidation of cyclohexane catalyzed by the clusters $[Ru_3O(H_3CCO_2)_6(py)_2L]^{n+}$ in the presence of *tert*-butyl hydroperoxide (TBPH).[a]

Ligand (L)	μmol		TON		Ratio ol:one
	ol	one	ol	one	
CH_3OH	8.7 (±0.4)	4.4 (±0.2)	13.7 (±0.6)	7.0 (±0.3)	2.0 (±0.1)
H_2O	1.9 (±0.1)	1.0 (±0.1)	2.9 (±0.1)	2.0 (±0.1)	1.6 (±0.1)
dmso	6.4 (±0.3)	3.2 (±0.1)	10.1 (±0.5)	5.0 (±0.3)	2.0 (±0.1)

[a] 6.3×10^{-7} mol of catalyst, 2×10^{-3} mol of cyclohexane, 2.2×10^{-4} mol of ROOH (80%) in 3 mL of dichloromethane, $T = 25\,^{\circ}C$. TON = moles of products per mol of catalyst ($t = 3$ h).

can also abstract a hydrogen atom from the C–H bond forming the 2-cyclohexen-1-yl radical, in an intermediary step, which is then rebounded, generating the corresponding alcohol (Scheme 1b). The formation of the 2-cyclohexen-1-one in significant amounts can be explained by a ruthenium-catalyzed oxidative dehydrogenation pathway from the allylic alcohol [22,23], in parallel with the reaction of the 2-cyclohexen-1-yl radical with the PhIO.

Okumura et al. [6] have discussed the role of the coordination structures of ruthenium complexes and their catalytic activity toward oxygen-transfer reactions, with special emphasis on the axial ligand. They observed from ESI-MS measurements that weakly coordinated ligands (L) such as dmso and 4-cyanopyridine are easily converted into Ru^{VI}=O species in the presence of PhIO. However, strongly coordinated dmapy (4-*N*,*N*-dimethylaminopyridine) prevents such ligand-exchange reaction. Stultz et al. have reported that the Ru^{IV}=O species attacks preferentially the C–H bond rather than olefin double bond, yielding alcohol, and that the low-valent metal-oxo species has radical character [24]. On the other hand, epoxidation seems to predominate at the higher oxidation state of ruthenium-oxo species, such as Ru^{V}=O or Ru^{VI}=O [10,25–28]. In our case, the predominant epoxidation activity of $[Ru_3^{IV,IV,III}{=}O]$ resembles that of the high-valent Ru^{V}=O or Ru^{IV}–O· species, indicating an unusual synergistic effect in the electronically deficient cluster moiety.

3.2. Oxidation of cyclohexane

The oxidation of cyclohexane with *tert*-butyl hydroperoxide in dichloromethane, catalyzed by the $[Ru_3O(H_3CCO_2)_6(py)_2(L)]PF_6$ clusters (L = CH_3OH or dmso), leads to the formation of cyclohexanol and cyclohexanone (Table 2) in different yields.

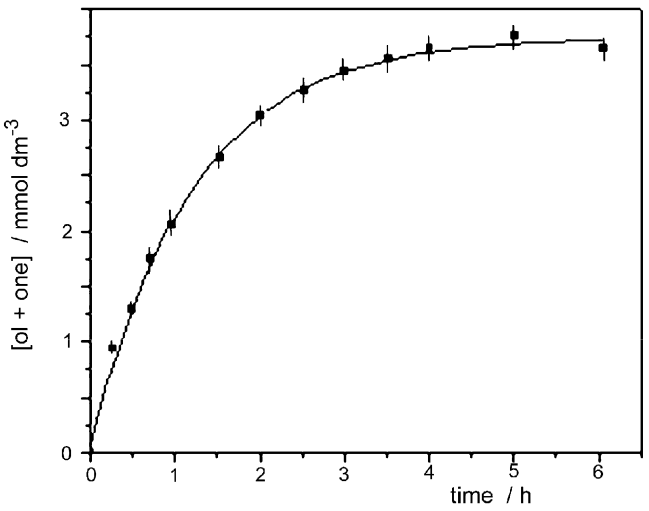


Fig. 3. Variation of the products concentration as a function of the time in the oxidation of cyclohexane by *tert*-butyl hydroperoxide using $[Ru_3O(H_3CCO_2)_6(py)_2(CH_3OH)]PF_6$ as catalyst. Conditions: 6.7×10^{-7} mol of cluster, 2.4×10^{-4} mol of TBHP, 2.0×10^{-3} mol of cyclohexane in 3 mL of dichloromethane, at 25 °C.

In the case of L = H_2O, the observed yields are at least three times smaller than for the methanol and dmso complexes. Tembe and Ganeshpure [16] have reported a similar catalytic activity for the $[Ru_3O(H_3CCO_2)_6(py)_3]PF_6$ cluster in the oxidation of cyclohexane by *tert*-butyl hydroperoxide, and proposed a mechanism involving the formation of radicals from the homolytic cleavage of peroxide. This type of mechanism is inhibited by CCl_4, which is a well known radical scavenger

As shown in Table 2, the behavior of the dimethyl sulfoxide complex is comparable to that of the CH_3OH analogue. In this complex, the dmso ligand is coordinated by means of the O atom [13]. In contrast to the H_2O and py species, both ligands are relatively labile and can also undergo further oxidation to acetaldehyde or dimethylsulfone, which would be even better leaving groups. Focusing on the CH_3OH case, one can see in Table 3, that the addition the CCl_4 does not inhibit the catalysis, reinforcing the involvement of a non radical mechanism involving the catalytic intermediate $[Ru_3^{IV,IV,III}{=}O]^+$. It is interesting to note that this oxo-catalytic species reacts with cyclohexane, cleaving the C–H bond in

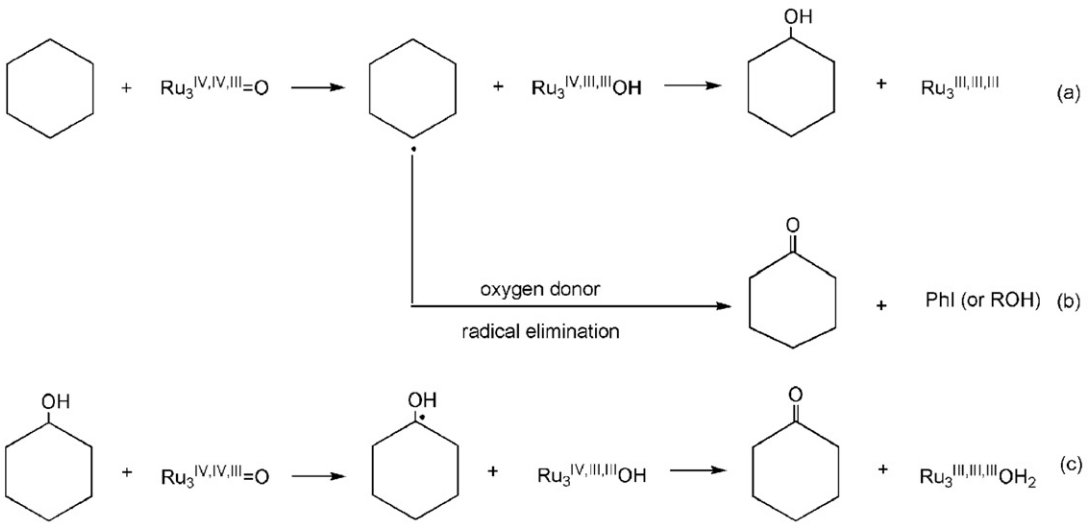
Table 3
Oxidation of cyclohexane catalyzed by $[Ru_3O(H_3CCO_2)_6(py)_2(CH_3OH)]PF_6$ in the presence of *tert*-butyl hydroperoxide (TBPH).[a]

Condition[b]	Cyclohexanol		Cyclohexanone		Chlorocyclohexane		Ratio ol:one
	(%)[b]	TON	(%)[c]	TON	(%)[c]	TON	
1	3.4 (±0.2)	2.7 (±0.1)	2.4 (±0.1)	1.9 (±0.1)	–	–	11.4 (±0.1)
2	3.2 (±0.2)	2.5 (±0.1)	1.9 (±0.1)	1.4 (±0.1)	0.8 (±0.1)	0.7 (±0.1)	1.8 (±0.1)

[a] 2.68×10^{-6} mol of catalyst, 2.0×10^{-3} mol of cyclohexane, 2.4×10^{-4} mol of TBPH in 3 mL of dichloromethane, $T = 25\,^{\circ}C$. TON = moles of products per mol of catalyst ($t = 2$ h). Catalyst: TBHP: cyclohexane (mol ratio) ~1:100:1000.

[b] Condition: 1—without CCl_4; 2—in the presence of CCl_4 (2 mL of CH_2Cl_2 and 1 mL of CCl_4).

[c] Yield based on starting TBHP amount. Relative error: ±2%.



Scheme 2. Cyclohexane oxidation catalyzed by the oxo species $[Ru_3O(H_3CCO_2)_6(py)_2O]^+$, or $[Ru_3^{IV,IV,III}{=}O]^+$.

Table 4
Effect of the oxygen donor agent in the oxidation of the cyclohexane catalyzed by $[Ru_3O(H_3CCO_2)_6(py)_2(CH_3OH)]PF_6$.[a]

Oxygen donor	Cyclohexanol		Cyclohexanone		Ratio ol:ona
	%[b]	TON	%	TON	
TBHP[c]	3.2 (±0.2)	2.7 (±0.1)	2.4 (±0.1)	1.9 (±0.1)	1.4 (±0.1)
PhIO[d]	7.7 (±0.4)	6.9 (±0.4)	16.7 (±0.8)	15.1 (0.7)	0.46 (0.03)

[a] 2.68×10^{-6} mol of cluster, $t = 2$ h.
[b] Based on the starting oxygen donor amount.
[c] Catalyst:oxygen donor:cyclohexane mol ratio = 1:83:746.
[d] Catalyst:oxygen donor:cyclohexane mol ratio = 1:74:746.

a similar way observed for porphyrins (Scheme 2) [25–33]. Formation of cyclohexanone can be explained by the oxidation of the cyclohexanol product or by the reaction of the cyclohexyl radical formed near the catalytic site, with the oxygen donor. In the presence of the radical scavenger CCl_4, cyclohexyl can also react to form chlorocyclohexane [34–36]. As a matter of fact, this pathway has been detected, as shown in Table 3.

The kinetics of the cluster catalyzed oxidation of cyclohexane by *tert*-butyl hydroperoxide have been investigated. A typical result, expressed by the plot of product concentration (ol + one) *versus* time, is illustrated in Fig. 3. From the linear plot of $\ln[P\infty - P]$ (where $P\infty$ is the final total concentration of products) *versus* time, a first order kinetic constant of $7.7 \pm 0.5 \times 10^{-6}$ s^{-1} ($R = 0.998$) has been obtained in this case.

In Table 4 one can compare the yields of cyclohexane oxidation for the two oxygen donors. The results show that iodosylbenzene is more efficient than *tert*-butyl hydroperoxide, being able to activate the catalyst in a higher number of cycles, but yielding predominantly cyclohexanone.

4. Conclusions

The $[Ru_3O(H_3CCO_2)_6(py)_2(L)]PF_6$ clusters where L = methanol, dimethyl sulfoxide, can be activated by peroxide or oxygen donor species, such as *tert*-butyl hydroperoxide or iodosylbenzene, respectively, generating reactive intermediates of the type $[Ru_3^{IV,IV,III}{=}O]^+$. This species preferentially reacts with the C=C bond in cyclohexene, producing the epoxide in high yields, and also is able to abstract a hydrogen atom from the C–H bond, forming the radical 2-cyclohexen-1-yl, in an intermediate step, before it is converted into the corresponding alcohol. The formation of the 2-cyclohexen-1-one in significant amount can be explained by a ruthenium-catalyzed oxidative dehydrogenation of the allylic alcohol, or by the reaction of the intermediate radical 2-cyclohexen-1-yl with the oxygen donor species.

The methanol and dmso complexes also catalyse the oxidation of cyclohexane by TBHP and PhIO by means of the cleavage of the C–H bond followed by oxygen atom transfer, rather than by the alternative oxygen radical mechanism characteristic of this type of complexes.

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