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Mechanism of Alcohol Oxidations by Anionic Peroxomolybdenum Complexes

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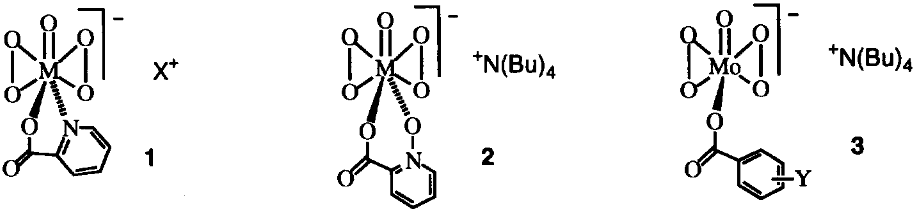
Abstract: The rates of oxidation of a series of primary and secondary alcohols to the corresponding carbonyl compounds by seven anionic peroxomolybdenum complexes, *i.e.* $[MoO(O_2)_2(C_5H_4NCOO)]^-$ $(Bu)_4N^+$ (**1a**), $[MoO(O_2)_2(C_5H_4NOCOO)]^-$ $(Bu)_4N^+$ (**2a**) and $[MoO(O_2)_2(X\text{-}C_6H_4COO)]^-$ $(Bu)_4N^+$ (X= H, p-NH_2, p-OMe, m-Cl, p-NO_2) (**3a-e**), have been measured under various experimental conditions. Different kinetic behaviors are exhibited by the various oxidants. In particular, different rate laws, activation parameters and kinetic isotope effects are found. Despite such differences a common general mechanistic scheme can be proposed, involving the association of the substrate to a free or releasable coordination site of the peroxocomplexes, leading to an intermediate present in a low, steady-state concentration. From such an alkoxo intermediate the carbonyl product is obtained through a series of steps whose nature is suggested only by indirect evidence. Two subsequent electron transfers to the oxidant from the coordinated alkoxo compound are considered the most likely mechanism.

INTRODUCTION

Previously we reported results demonstrating the synthetic significance of anionic peroxomolybdenum complexes as stoichiometric oxidants of the alcoholic function.[1,2] We showed that complex **2a**, which is one of the most active among those presented in Chart 1, is able to oxidize secondary alcohols to ketones and also primary ones to aldehydes without any overoxidation to carboxylic acids.[1]



1a: M=Mo, X^+=$N^+(Bu)_4$
1b: M=W, X^+=$N^+(Bu)_4$
1c: M=Mo, X^+=H^+
1d: M=W, X^+=H^+

2a: M=Mo
2b: M=W

3a: Y=H
3b: Y=p-NH_2
3c: Y=p-OMe
3d: Y=m-Cl
3e: Y=p-NO_2

Chart 1

Moreover, **2a** selectively oxidizes the alcoholic function of molecules in which other labile, *e.g.* oxirane ring, or oxidizable groups, *e.g.* double and triple bonds, are present.[2] As an additional advantage, **2a**, owing to its lipophilic character, is fairly soluble in non polar solvents, such as dichloroethane, DCE, where the oxidation reactions usually proceed at a convenient rate.[1]

We were also interested in the mechanism of the oxidative process which had received little attention. In fact, most of the mechanistic information was based on a kinetic study carried out by Mares *et al.* on the oxidation by hydrogen peroxide of secondary alcohols catalyzed by molybdenum **1c** and tungsten **1d** picolinate complexes, in methanol.[3] The excess of hydrogen peroxide over the catalyst was used to restore the peroxocomplexes. Such a study led to the mechanistic hypothesis according to which the association of the substrate to the metal occurs through the opening of the peroxo bridge followed by hydride abstraction from the alcohol.[3] A major point of concern about such a mechanism originated from our observation that the ligands coordinated to the metal play a crucial role in determining the reactivity of the peroxocomplexes.[4] As an example, we observed that under our experimental conditions **2a** was remarkably more reactive than **1a**.[4] Although some effect of the ligand on the opening of the peroxo bridge might be expected, we considered more likely the alternative that the large oxidation rate accelerations observed with **2a** compared with **1a** were due to the fact that the neutral tooth of **2a** is more easily removed by the substrate than that of **1a**.[5] In a recent paper we compared the oxidative behavior toward alcohols of a series of peroxomolybdenum complexes including neutral or anionic species either coordinatively saturated or unsaturated.[6] On the basis of such a comparison we concluded that the necessary requisites for alcohol oxidations by peroxomolybdenum derivatives are not only the occurrence of a free or releasable coordination site on the metal but also the anionic nature of the oxidant. The latter requisite was rationalized as arising from the nucleophilic catalysis operated by the anionic complex in the removal of the alcoholic hydrogen.[6] In this paper we extend our mechanistic investigation by presenting the results of kinetic studies on the oxidation of various alcohols by a series of anionic peroxomolybdenum and peroxotungsten complexes. In spite of an apparent large difference of oxidative behaviors, such results allow us to propose a common general mechanistic scheme. As far as the heart of the mechanism, *i.e.* the steps leading to the formation of the carbonyl compound is concerned, two possible alternatives, *i.e.* a polar reaction involving hydride abstraction from the substrate or a radical process in which a ketyl radical intermediate is formed have been considered.[7,8] Indirect but rather convincing evidence has been collected favoring the latter over the former process. Part of this work has been the subject of previous reports.[9,10]

RESULTS

The anionic peroxomolybdenum complexes employed in this investigation, together with some tungsten analogs examined for comparison purposes, are shown in Chart 1. The stoichiometry of the oxidation of cyclohexanol and 1-octanol by complexes **1a**, **2a** and **3a** had been studied previously.[6] Here, we have confirmed that, with the exception of complex **1b** which undergoes decomposition under the experimental conditions adopted, quantitative yields of the corresponding carbonyl compounds, cyclohexanone and octanal respectively, are obtained also with the other oxidants. The pertinent results are collected in Table 1. The rates of oxidation of the substrates were measured under pseudo-first-order conditions, by employing an excess of the alcohol over the peroxomolybdenum complexes. The course of the reactions was monitored by the increase of either cyclohexanone or octanal concentration with time by means of a gas chromatographic technique. Plots of $\ln[CO]_\infty/([CO]_\infty-[CO]_t)$ *vs* time were linear up to two half lives thus indicating a first order dependence of rates on the concentration of the oxidant. The pseudo first order rate constants $k_{obs.}$ listed in Table 1 are obtained as slopes of such plots. In some cases, particularly when 1-octanol is the substrate, a small but detectable positive intercept of the logarithmic plots was observed. The mechanistic significance of such a feature which could indicate the occurrence of an induction period will be discussed later on in this paper. The yields obtained indicate that both peroxo groups of the oxidant react with the substrate. Accordingly, the observed linearity of the logarithmic plots can be rationalized only by assuming an identical reactivity of the two groups or, alternatively and more likely, that a fast disproportionation of the monoperoxo complex resulting from the reaction of the first peroxo group to a diperoxo and an oxo molybdenum complex respectively occurs as suggested in similar systems.[11] From the data of Table 1 the following reactivity order for the various oxidants is obtained: **1b**<

1a<< **2b**< **2a** ≅ **3a**. Thus, at variance with previous results[3], though obtained under different conditions, in our system the molybdenum derivatives are better oxidants than the tungsten ones. Within the series of molybdenum peroxocomplexes the reactivity of **2** and **3** is similar, whereas **1** is definitely less reactive.

Table 1. Rate constants and yield values for the oxidation of 0.4 M Cyclohexanol and 0.4 M 1-octanol by various oxidants, 0.02 M in DCE, at 60 °C.

Oxidant	Substrate	$k_{obs.}x10^5$, sec^{-1}	Product, yield (%)
1a	cyclohexanol	2.4	cyclohexanone, 95
1b	cyclohexanol	1.4	cyclohexanone, 45
2a	cyclohexanol	460	cyclohexanone, 95
2b	cyclohexanol	160	cyclohexanone, 85
3a	cyclohexanol	524	cyclohexanone, 98
1a	1-octanol	3.6	octanal, 83
1b	1-octanol	1.4	octanal, 35
2a	1-octanol	108	octanal, 95
2b	1-octanol	52	octanal, 92

The kinetic order of the substrate has been determined for the oxidation of cyclohexanol by complexes **1a**, **2a** and **3a**. The dependence of $k_{obs.}$ values on substrate concentration is shown in Figure 1.

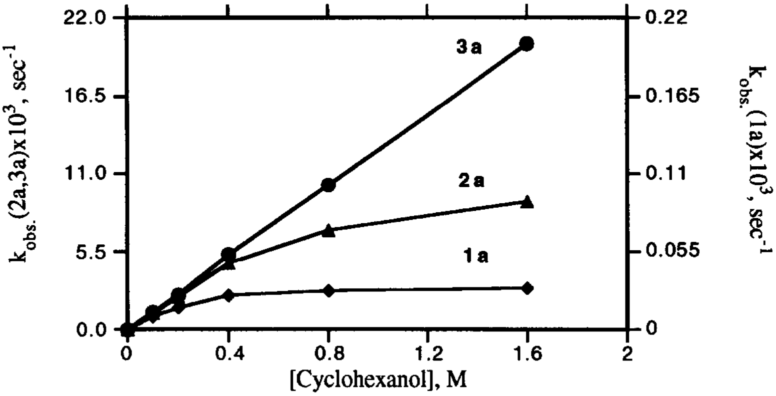


Figure 1: Plot of $k_{obs.}$ values versus alcohol concentration for the oxidation of cyclohexanol by complexes **1a**, **2a** and **3a**, 0.02 M in DCE, at 60 °C.

In the concentration interval explored a first order dependence of $k_{obs.}$ values on the substrate concentration is observed only for complex **3a**. The rates of oxidation by **1a** become very soon independent of substrate concentration and also for complex **2a** a tendency toward a less-than-one kinetic order of the substrate is observed. This finding might be indicative that a Michaelis-Menten type kinetic behavior is observed *i.e.* that an appreciable amount of a substrate-oxidant intermediate is formed leading eventually, at large substrate concentration, to the saturation of the oxidant.[12] However such a possibility is severely questioned by the fact that no deviation from the first order is observed for the coordinatively unsaturated complex **3a** in which saturation should be reached earlier than for complexes **1a** and **2a**. At any rate, the possibility of saturation for **2a** has been ruled out by direct experiments whose results are reported in Table 2.

Table 2. Competitive oxidation of 1-phenylethanol (Sub 1) and 2-butanol (Sub 2) by **2a**, 0.02 M in DCE, at 40 °C.

Sub 1 M	Sub 2 M	$(k_{obs.})_1 \times 10^4$ [a] sec^{-1}	$(k_{obs.})_2 \times 10^4$ [a] sec^{-1}	$(k_{obs.})_1/(k_{obs.})_2$	[Prod 1]∞/[Prod 2]∞
0.8	-	1.68	-	-	-
-	0.8	-	0.68	-	-
0.8	0.8	-	-	2.47	2.46

a: first order rate constants obtained from separate experiments.

Two different alcohols 1-phenylethanol and 2-butanol have been pitted against each other to compete for **2a**. If the two substrates were competing to form an appreciable concentration of an intermediate with the oxidant, the product distribution obtained should be different from that calculated from the rate constants measured in separate experiments.[13] In particular, the product ratio under saturation conditions would be that provided by Eq.1 if [Sub.1]=[Sub.2], in which K_1 and K_2 are the association constants of the two alcohols, whereas, if no saturation is taking place this ratio should simply be that of Eq.2.[13]

$$[\mathrm{Prod.1}]/[\mathrm{Prod.2}]=K_1k(_{obs.})_1/K_2k(_{obs.})_2 \quad (1)$$

$$[\mathrm{Prod.1}]/[\mathrm{Prod.2}]=k(_{obs.})_1/k(_{obs.})_2 \quad (2)$$

The data of Table 2 indicate that the product ratio obtained is, within the experimental error, identical to the ratio of the rate constants measured in separate experiments. This rules out that an intermediate is accumulating in solution unless the very unlikely possibility is considered that $K_1=K_2$. From the data of Table 2 it is observed that the difference of reactivity between the two alcohols employed, which are structurally rather different, is relatively small. This appears to be a general feature of these oxidations as demonstrated by the data reported in Table 3, collecting the rate constants for the oxidation of various alcohols by **2a**.

Table 3. Rate constants for the oxidation of various 0.4 M alcohols by **2a**, 0.02 M in DCE, at 60 °C.

Substrate	$k_{obs.} \times 10^3$, sec^{-1}
1-propanol	1.2
1-octanol	1.1
2-butanol	4.0
3,3-dimethyl-2-butanol	4.8
cyclopentanol	3.4
cyclohexanol	4.6

Even though the oxidation of secondary alcohols is faster than that of primary ones, the values of the rate constants reported in Table 3 span a rather small interval ranging from 1.1×10^{-3} sec^{-1} to 4.8×10^{-3} sec^{-1}. Steric effects play an unexpected role since it is observed that the more hindered substrate 3,3-dimethyl-2-butanol is oxidized faster than 2-butanol. This might result from a transition state effect due to the release of the strain in an intermediate formed previously along the reaction coordinate.

The effect of the substituents of the substrates and oxidants on the rates was deemed worthy of a more quantitative investigation. Thus the oxidation rates of a series of variously substituted benzylic alcohols with **2a** have been measured. As shown in Figure 2, these data may be correlated in a Hammett plot with the appropriate sigma values. The linear correlation is rather satisfactory (R=0.998) and a rho value of -0.27 is obtained. The rates of oxidation of cyclohexanol and 1-octanol with the series of peroxocomplexes **3a-e** have also measured.

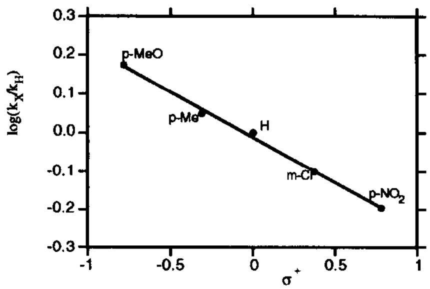


Figure 2: Hammett plot for the oxidation of variously substituted benzylic alcohols by complex **2a**, in DCE, at 50 °C.

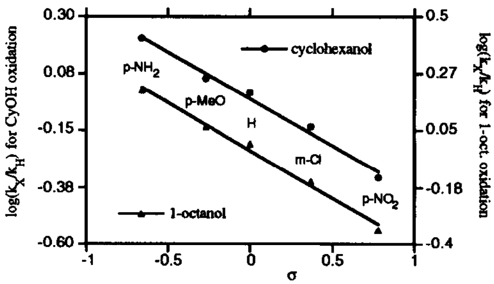


Figure 3: Hammett plots for the oxidation of cyclohexanol and 1-octanol by complexes **3a-e**, in DCE, at 60 °C.

The two straight lines (R=0.994 for cyclohexanol and R=0.993 for 1-octanol) of Figure 3 indicate that also in this case good Hammett plots are obtained from which the rho values of -0.37 (cyclohexanol) and -0.38 (1-octanol) are calculated. Interestingly, the sign of the rho values is the same as that obtained in the oxidation of substituted benzylic alcohols with **2a**. As an additional comment, it may be noted that all rho values are rather small.

Table 4 collects data which allow the determination of the kinetic isotope effect in the oxidation of cyclohexanol and 1-D-cyclohexanol by complexes **1a**, **2a** and **3a**.

Table 4. Rate constants and k_H/k_D values for the oxidation of 0.4 M cyclohexanol and 0.4 M 1-D-cyclohexanol by complexes **1a**, **2a** and **3a**, 0.02 M in DCE, at 60 °C.

Oxidant	Substrate	$k_{obs.}\times10^5$, sec^{-1}	k_H/k_D
1a	cyclohexanol	2.4	
1a	1-D-cyclohexanol	2.4	1.0
2a	cyclohexanol	464	
2a	1-D-cyclohexanol	232	2.0
3a	cyclohexanol	524	
3a	1-D-cyclohexanol	112	4.7

No KIE is observed for **1a** whereas k_H/k_D values of 2.0 and 4.7 for **2a** and **3a** respectively are measured. The activation parameters of the oxidation of 1-propanol, 2-butanol and cyclohexanol by complexes **1a**, **2a** and **3a** have also been obtained. They are listed in Table 5.

Table 5. Values of $k_{obs.}$, $\Delta H^{\neq}$ and $\Delta S^{\neq}$ for the oxidation of various 0.4 M alcohols by **1a**, **2a** and **3a**, 0.02 M in DCE.

Oxidant	Substrate	T, °C	$k_{obs.}x10^5$ sec^{-1}	$\Delta H^{\neq}$ $KJmole^{-1}$	$\Delta S^{\neq}$(25 °C) $JK^{-1}mole^{-1}$
2a	1-propanol	40	13.2		
2a	1-propanol	50	39.6	83	-20
2a	1-propanol	60	116		
2a	2-butanol	40	33.2		
2a	2-butanol	50	92	90	-16
2a	2-butanol	60	280		
2a	cyclohexanol	40	56		
2a	cyclohexanol	50	176	89	-15
2a	cyclohexanol	60	464		
3a	cyclohexanol	40	64		
3a	cyclohexanol	50	172	89	-15
3a	cyclohexanol	60	524		
1a	cyclohexanol	50	0.6		
1a	cyclohexanol	60	2.4	112	+6
1a	cyclohexanol	70	7.2		

Table 6. Rate constant values for the oxidation of 0.4 M 1-octanol by complexes **1a**, **2a** and **3a**, 0.02 M in DCE, in the presence of added ligand.

Oxidant	T, °C	Ligand	[Ligand], M	$k_{obs.}x10^5$, sec^{-1}
1a	60	-	0	3.6
1a	60	$(C_5H_4N)COOH$	5.1	3.5
1a	60	$(C_5H_4N)COO^-N^+(Bu)_4$	5.1	3.6
1a	60	$(C_5H_4N)COO^-N^+(Bu)_4$	11.1	3.5
2a	40	-	0	22.0
2a	40	$(C_5H_4NO)COOH$	5.0	4.2
2a	40	$(C_5H_4NO)COO^-N^+(Bu)_4$	5.0	29.2
2a	40	$(C_5H_4NO)COO^-N^+(Bu)_4$	11.6	32.0
3a	40	-	0	16.4
3a	40	$(C_6H_5)COO^-N^+(Bu)_4$	2.8	31.2
3a	40	$(C_6H_5)COO^-N^+(Bu)_4$	5.6	52.0
3a	40	$(C_6H_5)COO^-N^+(Bu)_4$	11.6	95.6

The $\Delta H^{\neq}$ and $\Delta S^{\neq}$ values are comparable for all the alcohols when **2a** and **3a** are the oxidants. In particular, rather small negative values of $\Delta S^{\neq}$ are obtained. When **1a** is the oxidant, a positive $\Delta S^{\neq}$ value is found.

The effect of added ligand on the reactivity of **1a**, **2a** and **3a** has been examined. Table 6 collects the results of such an investigation carried out on the oxidation of 1-octanol.

Added ligand, either in its acidic form or as tetrabutylammonium salt, has no effect on the oxidations by **1a**. In contrast, for **2a** added acid has a remarkable inhibitory effect whereas the salt causes a relatively small increase of the rates. Such an effect is more pronounced in the case of **3a** in which a 6-fold excess of the salt over the metal causes a *ca* 6-fold increase of the rates.

Finally, the effect of various additives and of the reaction conditions on the oxidation of various alcohols with **2a** and **3a** has been investigated. The results are collected in Table 7.

Table 7. Effect of various additives on rates and induction times for the oxidation of 1-propanol and 1-octanol 0.4 M by complex **2a** and **3a** 0.02 M, in DCE.

Substrate	Additive, M	Oxidant	T, °C	$k_{obs.}x10^5$, sec^{-1}	Induction Time min.
1-propanol	-	**2a**	40	13.2	5
1-propanol[a]	-	**2a**	40	12.8	5
1-propanol	-	**2a**	60	116	1
1-propanol	BHT, 0.02[b]	**2a**	60	116	1
1-propanol	AIBN, 0.02[c]	**2a**	60	108	1
1-propanol[d]	-	**2a**	60	152	1
1-octanol	-	**3a**	40	16.4	8
1-octanol	$Co(acac)_2$, 0.22	**3a**	40	17.2	6
1-octanol	$Co(acac)_2$, 0.45	**3a**	40	17.2	4
1-octanol	$Co(acac)_2$, 0.92	**3a**	40	17.6	1

a: reaction carried out under argon atmosphere. b: Butylated Hydroxy Toluene. c: α-Azoisobutyronitrile. d: nitrobenzene as solvent.

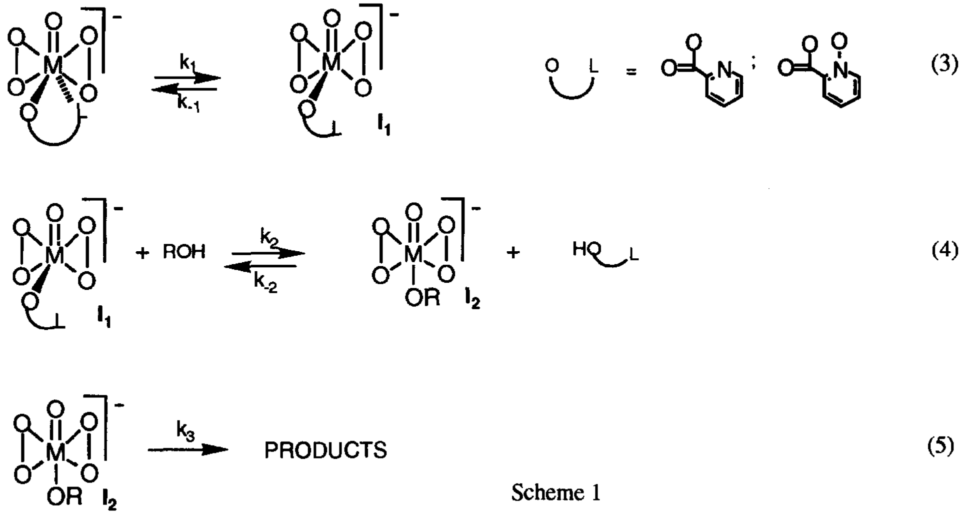
In particular, the modifications of reaction rates and induction times (see above) have been examined. Note that the species added and the parameters changed comform to the logic of checking the possibility of the occurrence of radical species. Along this line we also carried out the oxidation of cyclobutanol with **2a** under our standard conditions, obtaining quantitative yields of cyclobutanone. The cyclobutanol oxidation is a classical reactivity probe in this kind of chemistry.[7] In particular, if a free organic radical is involved, products deriving from the cleavage of the ring should be observed. Accordingly, cyclobutanone should be formed in minor amounts.[7] The fact that here we find only cyclobutanone as the product has mechanistic significance which will be discussed in the appropriate section.

DISCUSSION

The sensitivity of the oxidation reaction to the nature of the coordination sphere of the oxidant is good evidence of a mechanism involving the coordination of the substrate to the metal. For the two peroxocomplexes containing a bidentate ligand this is expected to occur through the opening of the neutral tooth of the ligand instead of the cleavage of the Mo-O peroxidic oxygen bond as previously suggested.[3] Accordingly, molybdenum and tungsten derivatives containing the picolinato ligand are less reactive than those containing the picolinate-N-oxido ligand or the monodentate carboxylato ligand, in agreement with the fact that the nitrogen of the picolinato anion is more tightly bound to the metal than the oxygen of the picolinate-N-oxido anion.[5] It is worthy of mention that in the oxidation of thioethers, which is a bimolecular reaction, the two peroxocomplexes **1a** and **2a** display an almost identical reactivity.[14] Furthermore, it has been shown that also glycols, which are firstly oxidized to ketoalcohols and then to α-diketones, enter the coordination sphere of **2a** by replacing the neutral tooth of the picolinate-N-oxido ligand.[15] Such a process takes place stepwise involving the first and then the second alcoholic group.[15] Finally, the activation parameters measured here and, in particular the small values of $\Delta S^{\neq}$ suggest that the reactants give rise in a fast process to an association complex before reaching the transition state of the product forming reaction.[16] On the other hand, such a complex does not accumulate in solution. Rather, its concentration ought to be always rather low since no real saturation of the oxidant by increasing the concentration of the substrate is observed. This is directly proved by the linearity of plots of $k_{obs.}$ versus cyclohexanol concentration shown in Figure 1 for complex **3a** and by the lack of competition between two different alcohols for the coordination to **2a** under the conditions which simulate the saturation of the complex. It should be noted that among the three complexes, **3a** is the most likely to reach saturation because of the presence of a free coordination site, whereas the other two oxidants are coordinatively saturated. Therefore, the tendency toward a less-than-one order in complexes **1a** and **2a** has to be accommodated within a mechanim different from that of the classical Michaelis-Menten kinetics. A very general scheme which rationalizes all the experimental findings is Scheme 1. Owing to the different kinetic behavior exhibited by the three peroxocomplexes, Scheme 1 must be adapted to the peculiarities of the three oxidants. In particular, in the case of complex **3a**, which bears a monodentate ligand, Eq.3 is clearly not operating. The inhibitory effect by the ligand added as acid in the oxidations by complexes **2a** and **3a**, confirms that the substrate enters the coordination sphere of the metal in a reversible process. Using steady-state approximation to the sequence of reactions 3-5, and in particular to the intermediates I_1 and I_2, the calculated rate law, where [L] is the concentration of free carboxylic acid, for the oxidations by **3a** is:

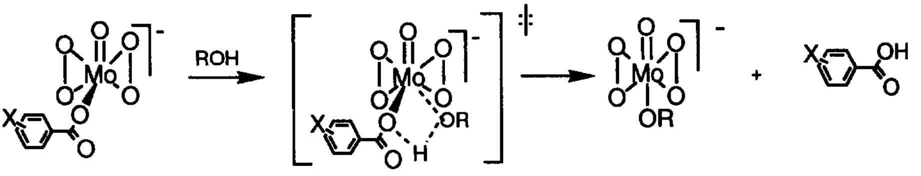
$$R(3a)=k_2k_3[Ox][ROH]/(k_3 + k_{-2}[L]) \qquad (6)$$

which agrees with the second order kinetic law observed. The occurrence of a KIE is expected under steady-state conditions owing to the presence of k_3 in the rate law. Also in agreement with Scheme 1 is the accelerating effect of the added salt on the oxidation rates since a nucleophilic catalysis in the removal of the alcoholic hydrogen is expected. The relatively small negative $\Delta S^{\neq}$ value is likely due to the contribution of the association equilibrium to the overall rate constant.



Scheme 1

The negative rho values obtained in the oxidation of cyclohexanol and 1-octanol by the series of complexes **3** is a rather unexpected observation which needs a comment. In fact, no matter which is the mechanism of oxidation, either a hydride abstraction from the carbon-hydrogen bond or an electron transfer from the substrate to the peroxometal complex followed by the loss of a proton, *i.e.* the two alternatives classically encountered in the oxidation of alcohols, the net result will be an increase of the electron density of the oxidant. On this basis one would expect a positive rho value. Since the opposite is observed, we suggest that a major role is played by the basicity of the carboxylate group of the ligand in the removal of the alcoholic hydrogen through a four centered transition state to form the alkoxo complex. Along this line, we may write Eq.4 at least for complexes **3** in a more detailed way than in Scheme 1:



(4)

Such a proposal is in agreement with the observation that the alcohol oxidation by peroxomolybdenum complexes is subject to nucleophylic catalysis.[6,8] In fact, it has already been found that alkoxo derivatives are more easily oxidized than the parent undissociated alcohols. This would also explain why anionic peroxomolybdenum complexes are better oxidants of the alcoholic function than the neutral derivatives.[6,8]As far as complex **1a** is concerned, all the evidence suggests that, even at relatively small excesses of the substrate over the oxidant, reactions 4-5 become faster than the unimolecular reaction 3 which involves the cleavage of the nitrogen-metal bond of the bidentate ligand. If this is the case, reaction 3 is the rate-limiting step and the corresponding rate law is:

$$R(1a)=k_1[Ox] \qquad (7)$$

Such a rate law accounts for the behavior shown in Figure 1 in which it is observed that the rates of oxidation by 1a become very early independent on substrate concentration. Indeed, such rates are even independent of the nature of the substrate, as shown by the data of Table 1. The rate law is also in agreement with the positive $\Delta S^{\neq}$ values obtained since they refer to a unimolecular process. Furthermore, no kinetic isotope effect should be observed and indeed this is experimentally found. Also the absence of any effect by added ligand is rationalized.The behavior of complex **2a** should be somehow in between those of complex **3a** and **1a**. Also for **2a** the association of the substrate to the metal, *i.e.* reaction 3, is operating. On the other hand, the opening of the vacant site is easier for **2a** than for **1a**. As a result, in the concentration interval explored, a rate limiting step does not exist. The rate law can be therefore calculated from Scheme 1 by applying the steady-state approximation to the intermediates $\mathbf{I_1}$ and $\mathbf{I_2}$. This leads to the expression:

$$R(\mathbf{2a})=k_1k_2k_3[Ox][ROH]/(k_{-1} + k_2[ROH])(k_3 + k_{-2}[L]) \qquad (8)$$

Eq.8 predicts that at relatively large substrate concentrations, which unfortunately are experimentally inecessible, the term k2[ROH] in the denominator should become larger than k_{-1}which then may be neglected. The resulting, simplified expression would be:

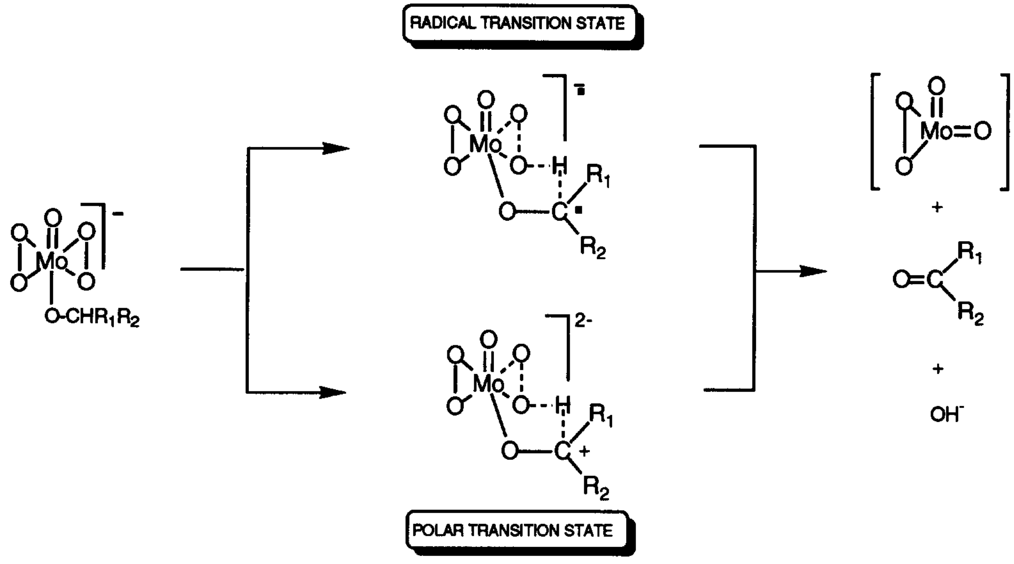
$$R(\mathbf{2a})=k_1k_3[Ox]/(k_3 + k_{-2}[L]) \qquad (9)$$

On the other hand, in a relatively large substrate concentration interval, the rate constants for the oxidation by **2a** shows a linear dependence on substrate concentration. This indicates that, in such an interval, the conditions holds that $k_{-1} >> k_2[ROH]$ so that the second term in the denominator of Eq.8 may be neglected and the rate law becomes:

$$R(\mathbf{2a}) = k_1k_2k_3[Ox][ROH]/(k_{-1}k_3 + k_{-1}k_{-2}[L]) \qquad (10)$$

Such a situation can hardly be obtained for complex **1a** since k_{-1} for the picolinate ligand is much larger than k_{-1} for the picolinate-N-oxido ligand whereas k_2 should be similar for the two complexes. For **2a** a KIE is again observed. Moreover, owing to the complexity of the observed rate constant which includes, together with k_3 also k_1, k_{-1}, k_2 and k_{-2} the value of the KIE is smaller for **2a** than for **3a**. Here, the rho value calculated by changing the substituents in the series of benzylic alcohols is -0.27. This confirms that the reaction is accelerated by electron donating substituents in line with the development of an electron deficiency of the substrate in the transition state.

The evidence on the nature of Eq.5, *i.e.* the process leading from the coordinated alkoxo derivative to the carbonyl compound is somehow conflicting. We have already mentioned that the most plausible alternatives are those shown in Scheme 2, *i.e.* either a polar or a radical reaction. For the sake of simplicity, in the scheme only the first electron transfer is indicated.



Scheme 2

On the basis of the data of Table 7 concerning the lack of effect of radical scavengers and of other results, namely the selective oxidation of cyclobutanol [7] the absence of any influence of dioxygen [15], the similarity of the rate constants measured in nitrobenzene, *i.e.* a classical radical trap, the presence of free carbon centered radicals in solution may be ruled out. On the other hand, the observation of a small but detectable induction period which is reduced or cancelled by the presence of a species capable of acting as one-electron donor toward the peroxocomplex, *i.e.* Co(II)[17,18] might be taken as evidence that an electron transfer is occurring within the coordination sphere of the peroxometal complex. In fact, since the reaction is promoted by one-electron donors, it may be envisaged that a radical chain process is operating. This is suggested basically by the occurrence of the induction period. On the other hand, the steady-state concentration of the chain carrier is reached very soon since the induction period is rather short.

Although we favor the occurrence of a coordinated ketyl radical, based also on previous investigations [15], it may be observed that a distinction between a polar and a radical reaction, the latter occurring within the coordination sphere of the oxidant and taking place through two subsequent and very close in time electron transfers, is not only difficult to make but it may be also of little significance.

CONCLUSION

The aim of this study was to establish the mechanism of the oxidation of alcohols by anionic peroxomolybdenum complexes. On the basis of the results obtained a mechanistic scheme is now available. It involves the association of the alcohol to the metal thus requiring the occurrence of a vacant site on the peroxocomplex. Such a site may be already available, as in the case of the peroxomolybdenum complex containing the carboxylate ligand, or it is formed via the removal of the neutral tooth of the bidentate ligand. The kinetic analysis strongly suggests that such a removal is an unimolecular reaction whose rate is a function of the strength of the bond between the neutral tooth and the metal. As a consequence, for complexes in which such a bond is rather strong, the liberation of the coordination site may be the rate limiting step of the oxidation reaction. The association of the alcohol requires its ionization operated by carboxylate group to form an alkoxo complex. From such a complex, the carbonyl compounds are formed through a pathway which, on the basis of indirect but convincing pieces of evidence, consists of two subsequent electron transfers to the oxidant taking place within the coordination sphere of the complex.

EXPERIMENTAL

Materials: Complexes **1**, **2** and **3** were obtained and purified ([Oact.]>95%, iodometric titre) according to published procedures.[1,6] Cyclohexanol and 1-octanol were high purity products (Aldrich), used as received. Benzylic (pMeO, p-Me, mCl and pNO_2) alcohols (Aldrich), were purified by cromatography (silica gel, dichlomethane). 1-D-cyclohexanol was prepared from cyclohexanone (2.0 gr, 20.4 mmol) by reduction with $NaBD_4$ (0.45 gr, 10.8 mmol) in ether. Chromatographic separation (silica gel, dichloromethane-ether 90:10) afforded 1.8 gr (90% yield) of 1-D-cyclohexanol. Picolinate, picolinate-*N*-oxido and benzoate tetrabutylammonium salts were prepared by mixing the appropriate carboxylic acid with a stoichiometric amount of tetrabutylammonium hydroxide (1.5 M solution in water). Water was then removed by distillation under vacuum. The remaining solid material was dissolved in dichlomethane and dried over $MgSO_4$. After removal of the solvent the organic salt was obtained.

Procedures: In a typical run, 6.0 mmol of substrate in 5 mL of DCE were added to a DCE solution (10 mL) containing the oxidant (0.3 mmol) and the internal GC standard (n-hexadecane for cyclohexanone and n-tetradecane for octanal respectively) in a glass reactor maintained at the desired temperature. Aliquots of the reaction mixture were withdrawn at various time intervals, quenched with $P(Ph)_3$ in excess, and the amount of the carbonyl product determined by GC analysis on a Carbowax 20 M 10 % (1.8 m column) on Chromosorb WAW-DMCS. Kinetic measurements were carried out under pseudo first order conditions by using an excess of the substrate over the oxidant, and monitoring the appearance of the product by GC. The pseudo-first order rate constants were obtained from plots of $\ln([\mathrm{Product}]_\infty-[\mathrm{Product}]_t)$ *vs* time, linear up to 80 % reaction. Duplicate runs agreed within ± 4% which can be considered the error of the rate constants reported.

REFERENCES

1. Bortolini, O.; Campestrini, S.; Di Furia, F.; Modena, G.; Valle, G.; *J. Org. Chem.*, **1987**, 52, 5467-5469.
2. Bortolini, O.; Campestrini, S.; Di Furia, F.; Modena, G.; *J. Org. Chem.*, **1990**, 55, 3658-3660.
3. Jacobson, S.E.; Muccigrosso, D.A.; Mares, F.; *J. Org. Chem.*, **1979**, 44, 921-924.
4. Bortolini, O.; Campestrini, S.; Di Furia, F.; Modena, G.; *The Role of Oxygen in Chemistry and Biochemistry*, Eds. Ando, W. and Moro-Oka, Y., *Studies in Organic Chemistry*, Elsevier Science Publishers B.V., Amsterdam, **1987**, 33, 237-242.
5. Campestrini, S.; Ph.D. Thesis, Padova University, **1988**.
6. Campestrini, S.; Di Furia, F.; Rossi, P.; Torboli, A.; Valle, G.; *J. Mol. Catal.*, **1993**, 83, 95-105.
7. Rocek, J.; Aylward, D.E.; *J. Am. Chem. Soc.*, **1975**, 97, 5452-5456.
8. Conte, V.; Di Furia, F.; Modena, G.; *J. Org. Chem.*, **1988**, 53, 1665-1669.
9. Campestrini, S.; Di Furia, F.; Modena, G.; Novello, F.; *Dioxygen Activation and Homogeneous Catalytic Oxidation*, Ed. Simandi, L.I.; Elsevier Science Publishers B.V., Amsterdam, **1991**, 375-384.
10. Campestrini, S.; Conte, V.; Di Furia, F.; Novello, F.; *Advances in Catalyst Design*, Eds. Graziani, M. and CNR Rao, World Scientific Publishing, Singapore, **1991**, 333-344.
11. Amato, G.; Arcoria, A.; Ballistreri, F.P.; Tomaselli, G.A.; Bortolini, O.; Conte, V.; Di Furia, F.; Modena, G.; Valle, G.; *J. Mol. Catal.*, **1986**, 37, 165-175.
12. Laidler , K.J.; *Chemical Kinetics*, Harper & Row Publishers, New York, third edition, **1987**, p.400.
13. Webb, J.L.; *Enzymes and Metabolic Inhibitors*, Academic Press, New York, **1963**, p.52-68.
14. Bortolini, O.; Campestrini, S.; Conte, V.; Di Furia, F.; Modena, G.; *J. Org. Chem.*, **1988**, 53, 5721-5724.
15. Campestrini, S.; Di Furia, F.; Novello, F.; *J. Mol. Catal.*, **1993**, 78, 159-168.
16. Bunnett, J.F.; *Investigation of Rates and Mechanism of Reactions*, Ed. Lewis, E.S.; Wiley, New York, N.Y., **1974**, Part I, p. 421.
17. Bonchio, M.; Conte, V.; Di Furia, F.; Modena, G.; *J. Org. Chem.*, **1989**, 54, 4368-4371.
18. Bonchio, M.; Conte, V.; Di Furia, F.; Carofiglio, T.; Magno, F.; Pastore, P.; *J. Chem. Soc. Perkin Trans. 2*, **1993**, 1923-1926.

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