

# One-Electron Oxidation of 2-Propanol by Vanadium and Molybdenum Peroxo Complexes

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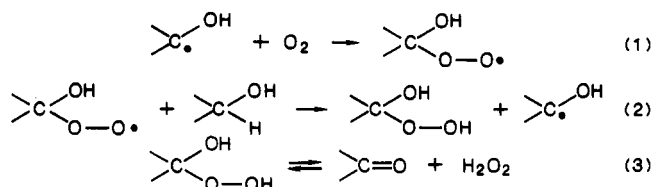
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Kinetic and <sup>18</sup>O-labeling evidence is presented of a radical pathway in the oxidation of 2-propanol to acetone by V(V)- and Mo(VI)-peroxo complexes. When the apparent pH of the reaction mixture is varied, thus affecting the relative amounts of neutral and anionic peroxo complexes, a different oxidative behavior of such species is observed. A mechanistic scheme is presented where the oxidation of the alcohol coordinated to the metal is proposed.

## Introduction

In a preliminary communication,<sup>2</sup> we reported experimental evidence of a radical pathway in the oxidation of alcohols, namely, ethanol and 2-propanol, by vanadium and molybdenum peroxo complexes.

In particular, we suggested the occurrence of a ketyl radical on the basis of the finding that, in the presence of dioxygen, hydrogen peroxide was formed,<sup>2</sup> as revealed by the stoichiometry as well as by <sup>18</sup>O-labeling experiments, likely via the autoxidative chain reaction:<sup>3</sup>



The unique role played by the peroxo complexes is demonstrated by the lack of any oxidative process when Mo(VI) or V(V) precursors, such as MoO<sub>2</sub>(acac)<sub>2</sub> or VO(OPr-*i*)<sub>3</sub>, are used under otherwise identical conditions but in the absence of hydrogen peroxide.<sup>2</sup> Moreover, when Mo(VI) or V(V) species are substituted with Fe(III), Co(II), and Cu(II) derivatives, a very different behavior is observed, resulting in a fast decomposition of hydrogen peroxide.<sup>2</sup> Therefore, the ability of vanadium and molybdenum peroxo species to act as mono-electron acceptors from alcohols has been revealed. This is indeed a novel feature which enlarges the scope of these reagents.<sup>4</sup>

We have now extended our investigation to the effect of the acidity of the alcoholic medium on the oxidation process. It is, in fact, well-known<sup>5,6</sup> that both peroxo-vanadium and peroxomolybdenum derivatives are acids. Therefore, depending on the experimental conditions, different concentrations of neutral and anionic peroxo species may occur, likely characterized by different oxi-

Table I. VO(OPr-*i*)<sub>3</sub>-Catalyzed Oxidation of 2-PrOH with H<sub>2</sub>O<sub>2</sub>.<sup>a</sup> Effect of Addition of 2-PrONa on the Reaction Rates

[2-PrONa] × 10 <sup>4</sup> M	R <sub>0</sub> ' <sup>b</sup> × 10 <sup>8</sup> M s <sup>-1</sup>
0.0	13.12
0.5	12.97
1.0	<0.11

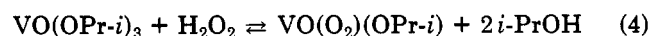
<sup>a</sup> [VO(OPr-*i*)<sub>3</sub>] = 1 × 10<sup>-4</sup> M, [H<sub>2</sub>O<sub>2</sub>] = 4.5 × 10<sup>-3</sup> M, [H<sub>2</sub>O] = 0.5 M. T = 25 °C. <sup>b</sup> R<sub>0</sub>' = d[C=O]/dt.

dative ability.<sup>7</sup> We report here the results of a kinetic study of the oxidation of 2-propanol at various acidities, together with potentiometric and <sup>18</sup>O-labeling experiments, which confirm the one-electron character of the process, underlining also the different behavior of V(V)- and Mo(VI)-peroxo species and of their anions.

## Results and Discussion

The oxidation of 2-propanol, which was also the solvent, with hydrogen peroxide in the presence of V(V) or Mo(VI) catalyst was followed by GC monitoring of the acetone formed and by iodometric titration of the hydrogen peroxide content. Details on the experimental conditions have been reported<sup>2</sup> previously and are summarized in the captions of the various figures. Although most of the work has been carried out for Mo(VI)-catalyzed oxidation, it may be appropriate to present here some data referring to VO(OPr-*i*)<sub>3</sub> catalyst. These are shown in Figures 1 and 2.

The involvement of dioxygen in the process is rather evident. In the reaction carried out under air, together with the formation of acetone, hydrogen peroxide is actually produced. When dioxygen is excluded, only the stoichiometric oxidation of 2-propanol is observed. Under these conditions, the linear dependence of both acetone formation and hydrogen peroxide disappearance as a function of time indicates pseudo-zero-order kinetics. This is due, as previously observed, to the large association constant of hydrogen peroxide to vanadium leading to the monoperoxometal species,<sup>8,9</sup> which is the actual oxidant in solution:



Owing to the kinetic complexity of the system where the

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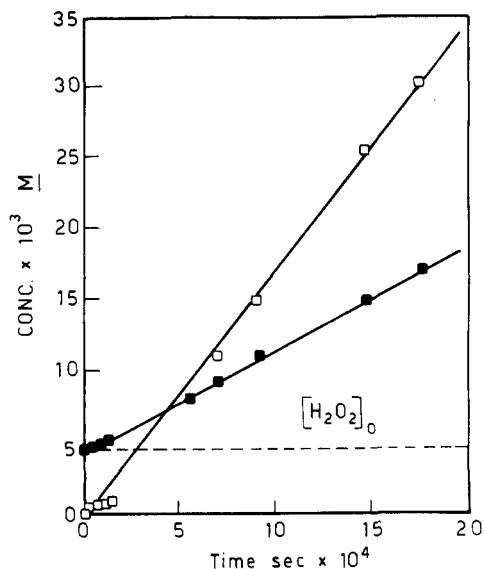
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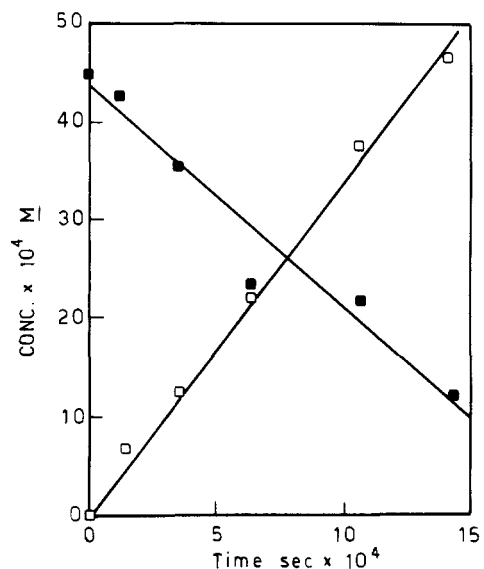
(b) Bortolini, O.; Di Furia, F.; Modena, G.; Seraglia, R. *J. Org. Chem.* 1985, 50, 2688-2690. (c) Bortolini, O.; Conte, V.; Di Furia, F.; Modena, G. *J. Org. Chem.* 1986, 51, 2661-2663.

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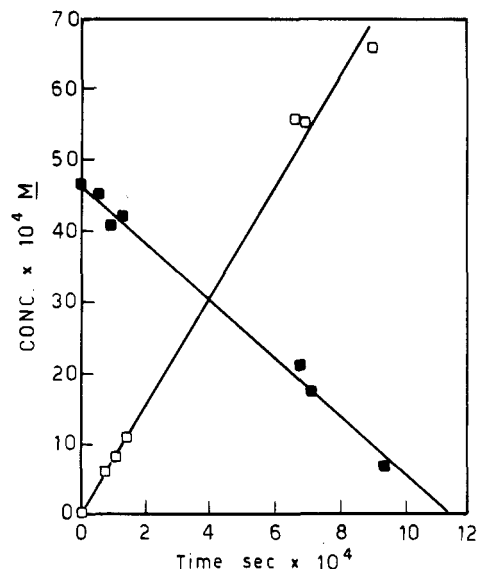
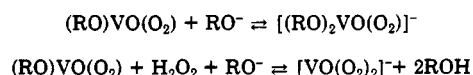
**Figure 1.** Rate of appearance of  $\text{H}_2\text{O}_2$  (■) and of acetone (□) in the oxidation of 2-PrOH with  $\text{H}_2\text{O}_2$  ( $4.5 \times 10^{-3}$  M) catalyzed by  $\text{VO}(\text{OPr-}i)_3$  ( $1 \times 10^{-4}$  M) in the presence of  $\text{H}_2\text{O}$  (0.5 M) and 2-PrOH as solvent at  $T = 25^\circ\text{C}$ , under air.



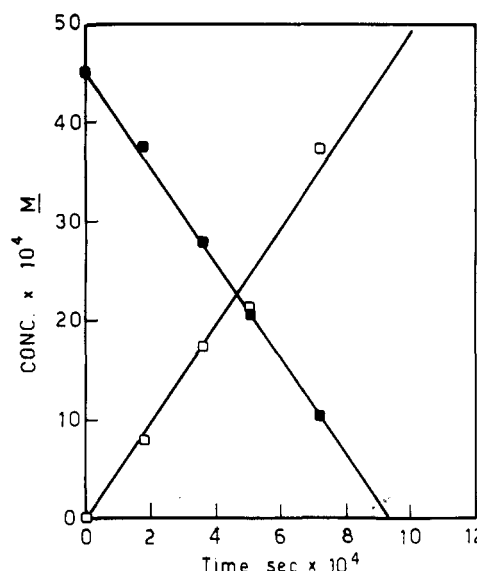
**Figure 2.** Rate of disappearance of  $\text{H}_2\text{O}_2$  (■) and appearance of acetone (□) in the oxidation of 2-PrOH with  $\text{H}_2\text{O}_2$  ( $4.5 \times 10^{-3}$  M) catalyzed by  $\text{VO}(\text{OPr-}i)_3$  ( $1 \times 10^{-4}$  M) in the presence of  $\text{H}_2\text{O}$  (0.5 M) and 2-PrOH as solvent at  $25^\circ\text{C}$ . The reaction was carried out in sealed vials after several vacuum-argon cycles.

content of hydrogen peroxide increases with time, we limited ourselves to examine the effect of added base (2-PrONa) on the rate of acetone formation under air. As shown in Table I, addition of 1 equiv of base almost suppresses the oxidation reaction. The effect of added base does not follow a simple behavior since it is observed that 0.5 equiv of 2-PrO<sup>-</sup> causes only a small decrease of the rate. This is largely due to the complex acid-base equilibria involved, which affect the nature of the peroxy species.<sup>9,10</sup> This system has been no further investigated. At any rate, the most relevant experimental result is that when 1 equiv of base is added, no acetone is formed and only a small loss

(10) As an example, the following equilibria may be envisaged:



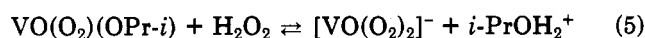
**Figure 3.** Rate of disappearance of  $\text{H}_2\text{O}_2$  (■) and appearance of acetone (□) in the oxidation of 2-PrOH with  $\text{H}_2\text{O}_2$  ( $4.5 \times 10^{-3}$  M) catalyzed by  $\text{MoO}_2(\text{acac})_2$  ( $1 \times 10^{-4}$  M) in the presence of  $\text{H}_2\text{O}$  (0.5 M) and 2-PrOH as solvent at  $T = 40^\circ\text{C}$ , under air.



**Figure 4.** Rate of disappearance of  $\text{H}_2\text{O}_2$  (■) and appearance of acetone (□) in the oxidation of 2-PrOH with  $\text{H}_2\text{O}_2$  ( $4.5 \times 10^{-3}$  M) catalyzed by  $\text{MoO}_2(\text{acac})_2$  ( $1 \times 10^{-4}$  M) in the presence of  $\text{H}_2\text{O}$  (0.5 M) and 2-PrOH as solvent at  $T = 40^\circ\text{C}$ . The reaction was carried out in sealed vials after several vacuum-argon cycles.

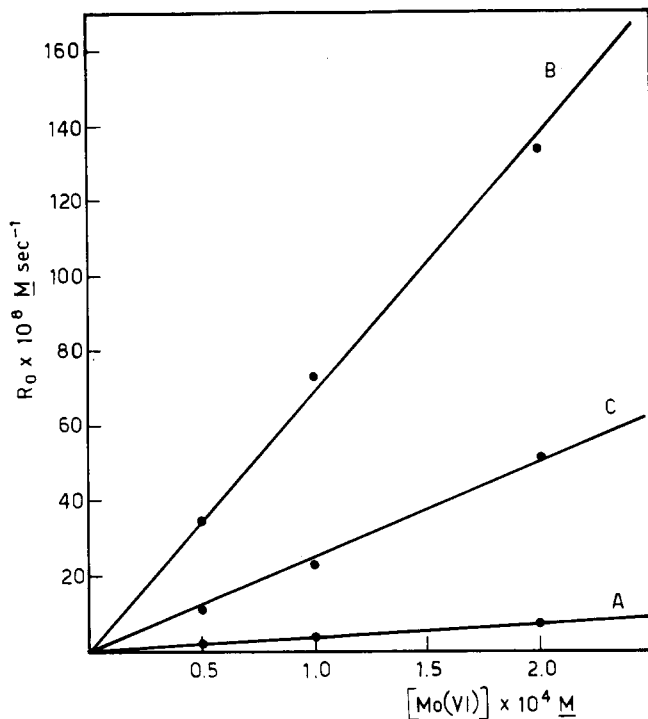
of hydrogen peroxide is observed (less than 10% in 30 h).

In order to explain this observation, it may be useful to recall that, under our experimental conditions, the excess of hydrogen peroxide over vanadium causes inter alia the formation, via an acid-dependent equilibrium, shifted to the right in basic solution, of an anionic diperoxovanadium species which should have no alkoxy groups bound to the metal.<sup>9</sup>



Independent evidence on the removal of alkoxy groups from the diperoxovanadium derivative has been obtained previously by means of a circular dichroism investigation.<sup>11</sup> Therefore, a rationale is that, in order to be oxidized, the

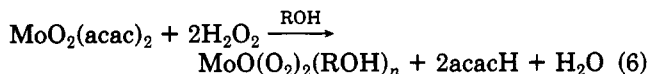
(11) Bortolini, O.; Di Furia, R.; Modena, G.; Scattolin, M. *Nouv. J. Chim.* 1982, 5, 537-540.



**Figure 5.** Mo(VI) kinetic order in the oxidation of 2-PrOH with  $\text{H}_2\text{O}_2$  ( $4.5 \times 10^{-3}$  M); 2-PrOH as solvent at  $T = 40^\circ\text{C}$ , under air. Plot A,  $[\text{2-PrONa}] = 0$ ; plot B,  $[\text{2-PrONa}] = [\text{Mo(VI)}]$ ; plot C,  $[\text{2-PrONa}] = 2[\text{Mo(VI)}]$ .

substrate must be bound, as an alkoxy group, to the metal. This has some relevance in the discussion that follows.

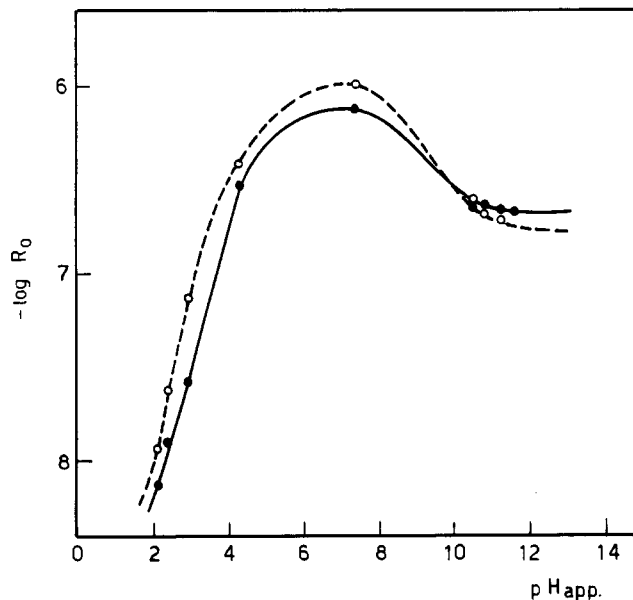
Turning now to the Mo(VI)-catalyzed oxidation, typical examples are shown in Figures 3 and 4 referring to the reaction under air and under argon respectively. In these experiments,  $\text{MoO}_2(\text{acac})_2$  has been used as precursor. Previous kinetic<sup>12</sup> and spectroscopic<sup>13</sup> studies have shown that, under our conditions, the ligand acetylacetonate is completely displaced from the metal, thus allowing the formation of an oxo-diperoxomolybdenum complex:



Other experiments have shown that different precursors, such as  $\text{MoO}_5\text{HMPT}$ , gave  $\text{MoO}(\text{O}_2)_2(\text{ROH})_n$ , and therefore an almost identical behavior is observed.

In the reaction under argon, in sealed vials and after several vacuum-argon cycles, 1 mol of acetone/mol of  $\text{H}_2\text{O}_2$  is formed. This is also an indication that little or no self-decomposition of hydrogen peroxide, catalyzed by Mo(VI) derivatives, occurs. On the other hand, the remarkable stability of  $\text{H}_2\text{O}_2$  in the presence of V(V) and Mo(VI) but in the absence of an oxidizable substrate has been previously reported.<sup>9</sup> As an example, in *t*-BuOH, under conditions identical with those adopted in this investigation, no self-decomposition of  $\text{H}_2\text{O}_2$  to  $\text{O}_2$  and  $\text{H}_2\text{O}$  is observed even for long reaction times (48 h or more).

When the same reaction is carried out in the presence of air, in an open vessel, the acetone produced exceeds, by a sizable amount, the hydrogen peroxide consumed. Noteworthy is the fact that the more-than-stoichiometric formation of acetone appears to become independent of the concentration of dioxygen.<sup>14</sup> In fact, the rates of

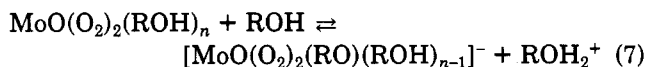


**Figure 6.** Trend of the  $-\log R_0$  vs  $\text{pH}_{\text{app}}$  of the reaction solution in the oxidation of 2-PrOH with  $\text{H}_2\text{O}_2$  ( $4.5 \times 10^{-3}$  M) catalyzed by  $\text{MoO}_2(\text{acac})_2$  ( $1 \times 10^{-4}$  M) in the presence of  $\text{H}_2\text{O}$  (0.5 M); 2-PrOH as solvent at  $T = 40^\circ\text{C}$ , under air. (●)  $R_0 = -d[\text{H}_2\text{O}_2]/dt$ ; (○)  $R_0 = d[\text{C}=\text{O}]/dt$ . The increase of the  $\text{pH}_{\text{app}}$  was obtained by adding to the reaction solutions increasing amounts of a ca. 0.1 M solution of 2-PrONa in 2-PrOH.

hydrogen peroxide consumption and acetone formation are the same on passing from air to dioxygen atmosphere. Moreover, the reactions under air are remarkably reproducible. It may be noticed that the plots of Figures 3 and 4 are linear, indicating also in this case, as previously observed for V(V), pseudo-zero-order kinetics due to the large association constant of metal-hydrogen peroxide.<sup>7a,8</sup>

Figure 5 (plot A) shows the results of experiments aimed at establishing the kinetic order in the catalyst. The linearity of the plot of Figure 5 indicates a first-order dependence on  $\text{MoO}_2(\text{acac})_2$  concentration.

The results presented so far refer to acidic,  $\text{pH}_{\text{app}}$  3 (as measured by a glass electrode<sup>15</sup>), conditions due to the Lewis acid character of diperoxo-molybdenum complex:<sup>16</sup>



When increasing amounts of 2-PrONa are added, thus moving toward alkaline solution, a remarkable effect on the oxidation rates as measured by disappearance of hydrogen peroxide is observed. These data are shown in the logarithmic plot of Figure 6.

The pseudo-zero-order rate constants increase by a factor of ca. 20 up to  $\text{pH}_{\text{app}}$  8 (corresponding to ca. 1 equiv of base) and then decrease, reaching a plateau at  $\text{pH}_{\text{app}} > 10$ .

It is noteworthy that in alkaline medium the more-than-stoichiometric production of acetone is suppressed. In fact, in the  $\text{pH}_{\text{app}}$  interval 8–13, the amount of acetone

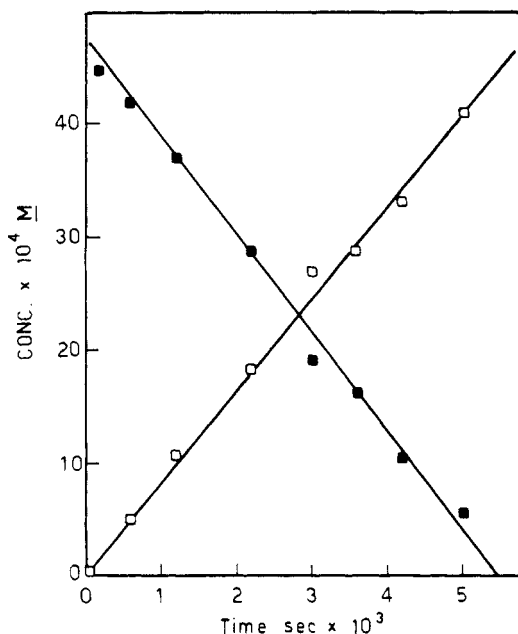
(14) In fact, even though the reaction between the ketyl radical and dioxygen, eq 1, ought to be almost diffusion controlled, an effect on the rate on varying the dioxygen concentration from 20% to pure dioxygen should be observed.

(15) Throughout the paper, the acidity of the medium is measured by the apparent pH of the solution according to a practice commonly used when working in nonaqueous media, even though no thermodynamic significance may be attached to the values reported. On the other hand, the alternative use of such small values of base concentration leads to large errors in determining the points of Figure 6.

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(13) Bortolini, O.; Bragante, L.; Di Furia, F.; Modena, G. *Can. J. Chem.* 1986, 64, 1189–1195.



**Figure 7.** Rate of disappearance of  $\text{H}_2\text{O}_2$  (■) and appearance of acetone (□) in the oxidation of 2-PrOH with  $\text{H}_2\text{O}_2$  ( $4.5 \times 10^{-3}$  M) catalyzed by  $\text{MoO}_2(\text{acac})_2$  ( $1 \times 10^{-4}$  M) in the presence of  $\text{H}_2\text{O}$  (0.5 M),  $\text{pH}_{\text{app}}$  9.5. 2-PrOH as solvent at  $T = 40^\circ\text{C}$ , under air.

formed corresponds, as shown in Figures 6 and 7, to the amount of hydrogen peroxide consumed. On the other hand, the linearity of plots of  $\text{H}_2\text{O}_2$  vs time is still observed and the kinetic order of the catalyst remains 1; see Figure 5 (plots B and C).

According to the equilibrium of eq 7,<sup>16</sup> the only effect expected for added base is an increase of the concentration of anionic peroxomolybdenum species until complete neutralization of the acid is reached, and consequently, an increase in the reaction rate might be expected. However, the behavior of the plot of log rate constants vs  $\text{pH}_{\text{app}}$  at relatively high  $\text{pH}_{\text{app}}$  values, i.e., the decrease of the rates after the maximum at  $\text{pH}_{\text{app}} > 8$  (see Figure 6), is not easily rationalized. In fact, the potentiometric titration of  $\text{MoO}(\text{O}_2)_2$  in 2-propanol, reported in a previous paper,<sup>13</sup> shows only one equivalent point, thus confirming that also in this solvent we are dealing with a monobasic acid complex. On the other hand, the evidence obtained here suggests that the anionic peroxomolybdenum formed upon neutralization of the acid undergoes a subsequent transformation leading to a species of lower oxidizing ability. This species should not be a simple dianion (vide infra). The occurrence of a dimeric or polymeric complex should be taken into account even though the order 1 in the catalyst is in better agreement with the absence of aggregation equilibria of the metal species. Formation of ion pairs between anionic peroxo complexes and alkaline cation favored by the low polarity of 2-propanol might also play a role, as discussed below.<sup>17</sup>

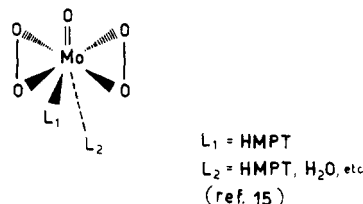
Moreover, the data referring to alkaline media appear to rule out any involvement of dioxygen leading to the formation of hydrogen peroxide. As a further evidence, we have confirmed, by using  $^{18}\text{O}$ -labeled hydrogen peroxide,<sup>2</sup> that no dilution of the label caused by formation of  $\text{H}_2\text{O}_2$  from reduction of dioxygen is observed, contrary to the results obtained in acidic medium.<sup>2</sup> The pertinent data are reported in Table II.

(17) It was found that in the  $\text{pH}_{\text{app}}$  region 8–13, conductometric titration of  $\text{Mo}(\text{VI})$ -peroxo complexes in the presence of excess  $\text{H}_2\text{O}_2$  shows a decrease of conductivity despite the increase of the ion concentration in solution. Conte, V. Ph.D. Thesis, University of Padova, 1987.

**Table II.**  $\text{MoO}_2(\text{acac})_2$ -Catalyzed Oxidation of 2-PrOH Carried Out with  $^{18}\text{O}$ -Labeled  $\text{H}_2\text{O}_2$ <sup>a</sup>

atmosphere	$\text{pH}_{\text{app}}$	time, h	% loss of $^{18}\text{O}$ label in residual $\text{H}_2\text{O}_2$ <sup>b</sup>
argon	2.9	20	0
air	2.9	20	26
air	10.5	8	0

<sup>a</sup>  $[\text{MoO}_2(\text{acac})_2] = 1 \times 10^{-4}$  M,  $[\text{H}_2\text{O}_2] = 4.5 \times 10^{-3}$  M,  $[\text{H}_2\text{O}] = 0.5$  M.  $T = 40^\circ\text{C}$ . <sup>b</sup> The preparation of  $^{18}\text{O}$ -labeled  $\text{H}_2\text{O}_2$  (~20% enrichment) and the determination of the label content by MS have been reported elsewhere.<sup>2</sup>



**Figure 8.**

Although we cannot provide, at the moment, a comprehensive rationale for the general behavior shown in Figure 6 and, in particular, for the decrease of oxidation rates after the maximum, we may offer a tentative mechanistic interpretation.

The experimental evidence suggests that the neutral oxo-diperoxomolybdenum complex, having at least one molecule of alcohol in the coordination sphere, may act as a one-electron oxidant. The fact that alcohol molecules are bound to the metal is indicated by several pieces of evidence: (i) All the structures of oxo-diperoxomolybdenum complexes determined by X-ray analysis<sup>18</sup> display a distorted pentagonal bipyramid arrangement where the four peroxo oxygens and a ligand lie in the equatorial plane, the oxo group occupies one of the two apical positions, and an extra ligand, e.g.,  $\text{H}_2\text{O}$ , is in the second one. In the absence of other ligands such as HMPT, DMF, etc., it is likely that both  $L_1$  and  $L_2$  are alcohol molecules (Figure 8). (ii) Since peroxomolybdenum complexes behave in alcoholic solutions as monobasic acids,<sup>13,16</sup> the presence of an acidic proton in the complex or, less likely but formally equivalent, the coordination of an alkoxy group is required. (iii) Peroxomolybdenum species, in the presence of a chiral alcohol, such as (-)-DET, behave as enantioselective oxidants toward prochiral sulfides<sup>19</sup> and olefins,<sup>20</sup> thus suggesting that indeed the alcohol is coordinated to the metal.

The very weak coordination of the second alcohol molecule ( $L_2$ ) in the apical position<sup>21</sup> could suggest that it does not play any role. It is, however, conceivable that, in fairly basic media, a second alkoxy group may substitute the neutral alcohol molecule forming a dianion, strongly ion paired<sup>17</sup> with  $\text{Na}^+$ . This might not show up in the potentiometric titration, exhibiting a reduced efficiency as oxidant compared to the monoanionic species.

The observed enhancement of oxidation rates with increasing basicity up to the addition of 1 equiv of base, corresponding to the complete formation of the monoanion, should indicate an easier removal of the electron from the alkoxy group than from the coordinated alcohol in spite

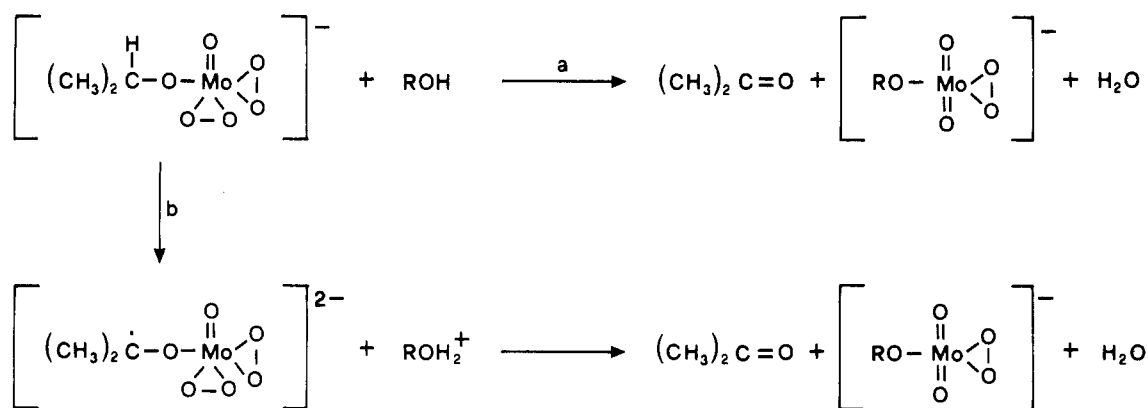
(18) Mimoun, H. *The Chemistry of Functional Groups: Peroxides*; Patai, S., Ed.; Wiley: New York, 1982; Chapter, 15, pp 463–482.

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(21) Le Carpentier, J. M.; Mitschler, A.; Weiss, R. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* 1972, B28, 1278–1288.

Chart I



of the fact that the electron acceptor is the negatively charged and hence less electrophilic peroxy anion.

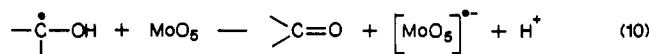
It must also be taken into account that, when only the peroxy anion is present, the reaction involving dioxygen is not observed anymore, thus suggesting that free-radical species do not occur. This feature may have at least two explanations: (a) the two subsequent one-electron steps are substituted by a two-electron process, i.e., a hydride transfer;<sup>7c,22,23</sup> (b) the removal of the second electron to form the carbonyl compound is faster than the reaction of the ketyl radical anion with dioxygen. The two alternatives may be schematically depicted as in Chart I.

Under the hypothesis that the oxidation, also in basic media, involves two subsequent one-electron steps, an appealing rationale of the difference between the oxidation of neutral alcohol and that of the alkoxy ion might be found in the different rates of ligand exchange if the detachment of the ketyl radical from the metal is so much faster than that of the ketyl radical anion, thus to make the second electron transfer faster than ligand exchange. Also, this implies that dioxygen should not react with the coordinated ketyl radical.

As to the fate of the species resulting from one-electron transfer to the peroxomolybdenum complex, the kinetics require its rapid disappearance. This could occur via disproportionation followed by regeneration of the peroxy species from the excess of H<sub>2</sub>O<sub>2</sub>:



It is also worth noticing that the autoxidative chain leading to the formation of hydrogen peroxide in the range of pH<sub>app</sub> up to ca. 8 is rather short. This is not surprising since the ketyl radical is not likely to survive many cycles in the presence of such a good oxidant as MoO<sub>5</sub>:



It should be noticed that, if the hypothesis of one-electron oxidation is accepted, the process of eq 10 ought to be the product-forming step in the reaction under argon where no interception of the ketyl radical by dioxygen is possible.

As anticipated above, the data reported here confirm the versatility of peroxometal complexes as oxidizing agents. In particular, the same species, i.e., MoO(O<sub>2</sub>)<sub>2</sub>(ROH)<sub>n</sub>, has been demonstrated to act as an electrophilic oxidant toward substrates such as alkenes<sup>24</sup> and thioethers<sup>25</sup> and as a one-electron acceptor in the reactions with alcohols.<sup>2</sup> Further studies on other peroxy complexes as well as on other one-electron-donor substrates are warranted.

### Experimental Section

**General Procedure.** The general procedure adopted for oxidation experiments has been previously reported.<sup>2</sup> In Figures 1-4, each point is the average of three independent experiments, which agreed within 5-7%.

Acetone was quantitatively determined by GLC (2-m column, packed with Carbowax 20 M, 15%, on Chromosorb W AW-DMCS, *n*-undecane internal standard).

Potentiometric titrations were carried out by stepwise addition of a freshly prepared solution of 2-PrONa, standardized with 0.01 M HCl, to a stirred solution (under argon) of the peroxy complex in 2-PrOH. The equilibrium potentials at the electrode were measured 30 s after the addition of the base.

**Materials and Instrumentation.** High-purity 2-propanol and acetone were obtained by standard procedures starting from commercial samples.

VO(OPr-*i*)<sub>3</sub> was prepared by a reported method<sup>26</sup> and purified by distillation (95 °C (10 mmHg)). MoO<sub>2</sub>(acac)<sub>2</sub>, a commercial product, was purified by recrystallization from acetone/acetylacetone, 1:4. Commercial H<sub>2</sub>O<sub>2</sub> (36% w/v; Carlo Erba) was used as received. The <sup>18</sup>O-enriched hydrogen peroxide was prepared by direct conversion of H<sub>2</sub>O vapor (~20% enrichment) in an electric discharge apparatus.<sup>27</sup>

Gas chromatographic analyses were performed on a Varian 3700 instrument equipped with a Vista CDS 401 or a Perkin-Elmer Sigma 10 integrator. Mass spectra were obtained by using a VG 16 M mass spectrometer. The determinations of the apparent pH values of the reaction mixtures as well as the potentiometric titrations were carried out by using a Metrohm 605 potentiometer equipped with a standard glass electrode.

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**Registry No.** MoO<sub>2</sub>(acac)<sub>2</sub>, 17524-05-9; VO(OPr-*i*)<sub>3</sub>, 5588-84-1; H<sub>2</sub>O<sub>2</sub>, 7722-84-1; 2-propanol, 67-63-0.

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