Co^{II}-Induced Radical Oxidations by Peroxomolybdenum Complexes†

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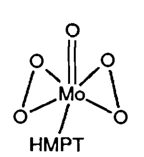
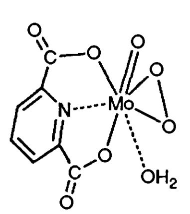
Peroxomolybdenum complexes, which are usually rather stable materials both in the solid state and in solution, may undergo a decomposition reaction yielding dioxygen when relatively small amounts of $Co(acac)_2$ are added to their solution in dichloroethane. Such a reaction is greatly dependent on the nature of the coordination sphere of the metal. In the series of neutral and anionic peroxomolybdenum species examined, the anionic complex MoO_5PICO (PICO = picolinate *N*-oxido anion) has been found to be more prone to decompose than the neutral ones. By contrast, electrochemical measurements indicate that the one-electron reduction of the neutral species occurs at less negative potentials than that of the anionic ones. Under the conditions which allow the decomposition of MoO_5PICO, the concomitant oxidation of organic substrates, *e.g.* alkanes and alkenes, takes place. The product analyses confirm that the peroxomolybdenum complex is acting as a radical oxidant. The role of Co^{II} not only in promoting the decomposition but also in taking part in a radical process is suggested by kinetic and electrochemical experiments.

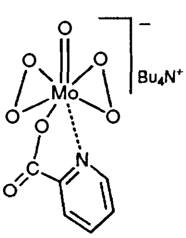
In the oxidation of organic substrates by peroxides, including transition metal peroxo complexes, two general mechanistic pathways can operate.[1] The distinction is based on the mode of cleavage of the oxygen–oxygen bond of the peroxide group which may occur either homolytically or heterolytically.[1–3] The latter reactivity for d^0 peroxo complexes, *i.e.* Ti^{IV}, V^V, Mo^{VI} and W^{VI} derivatives is very well documented.[1–6] By contrast, the information on homolytic processes involving d^0 peroxocomplexes is scarce.[7–10] It has been reported that some peroxovanadium complexes hydroxylate aromatic compounds to the corresponding monophenols[7,10,11] in a process which is clearly homolytic in nature. The promoting effect on such a reaction of one-electron donors such as Co^{II} derivatives has been demonstrated.[9] In this paper, we have explored the conditions which allow the occurrence of a radical reactivity in other d^0 peroxometal complexes.



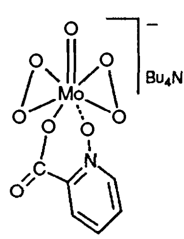
MoO_5HMPT



MoO_3DIPIC



MoO_5PIC



MoO_5PICO

Table 1 Decomposition of Mo^{VI} peroxo complexes (0.12 mmol) in DCE (10 cm^3) at 40 °C in the presence of $Co(acac)_2$

Complex	$Co(acac)_2$/mmol	*t*/h	O_{act} consumed[a] (%)
MoO_3DIPIC	0.0120	24	20
MoO_5HMPT	0.0120	24	80
MoO_5HMPT	0.0036	8	30
MoO_5PIC	0.0036	8	20
MoO_5PICO	0.0036	8	100

[a] O_{act} = 2[Complex].

In particular, we here report data on four peroxomolybdenum complexes, indicating that some of these species undergo a radical decomposition leading to dioxygen evolution. Such a decomposition requires either chemical or electrochemical promotion. When, in the decomposition reaction mixture, oxidizable substrates, *e.g.* alkanes or alkenes, are added, oxidized products are found whose nature supports the radical character of the process. On the basis of kinetic data and of electrochemical experiments, some mechanistic hypotheses can be discussed.

Results and Discussion

The results concerning the effect of the addition of $Co(acac)_2$ on the stability of peroxomolybdenum derivatives in dichloroethane (DCE) are reported in Table 1.

In the absence of Co^{II} all the molybdenum peroxocomplexes examined are remarkably stable in DCE; their concentration is almost unchanged after 24 h (0.12 mol dm^{-3} initial concentration of peroxo complex at 40 °C). When $Co(acac)_2$ is added, different behaviour is observed. Thus, the concentration of the complex MoO_3DIPIC (DIPIC = 2,6-dipicolinic acid dianion) does not change with the time, even in the presence of relatively large amounts of Co^{II}, as an indication that no reaction occurs between the two species. On the other hand, a decrease of the active oxygen content is observed for MoO_5HMPT (HMPT = hexamethylphosphoric triamide) and MoO_5PIC (PIC = picolinic acid anion). Such a decrease, however, stops after a *ca.*

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† Work taken in part from the Ph.D. Thesis of M. Bonchio, Padova University, 1992.

Table 2 Oxidation of alkanes and alkenes with the $MoO_5PICO/Co(acac)_2$[a] system in DCE (10 cm^3) at 40 °C

Substrate	Product	Yield (%)[b]
(*E*)-Stilbene	(*E*)-Stilbene oxide	25
	Benzaldehyde	trace
(*Z*)-Stilbene	(*Z*)-Stilbene oxide	1
	(*Z*)-Stilbene oxide	10
	Benzaldehyde	trace
Styrene	Styrene oxide	10
	Benzaldehyde	5
(*Z*)-Hex-3-ene	Hex-3-ene oxide	< 5[d]
Cyclooctene	Cyclooctene oxide	7
Cyclohexene	Cyclohexene oxide	7
	Cyclohex-2-enol	30
	Cyclohex-2-enone	76
Cyclohexene[c]	Cyclohexene oxide	4
	Cyclohex-2-enol	12
	Cyclohex-2-enone	32
Benzene	—	—
Diphenylmethane	—	—
Triphenylmethane	Triphenylmethanol	trace
Fluorene	Fluorenone	47

[a] MoO_5PICO 0.012 mmol; $Co(acac)_2$ 0.0036 mmol. [b] Yield calculated after complete disappearance of the oxidant and based on the O_{act} introduced, $O_{act} = 2[MoO_5PICO]$. [c] Reaction carried out under argon atmosphere. [d] (*Z*)-epoxide:(*E*)-epoxide = 1:3.

20–30% disappearance of the active oxygen when 0.036 mol dm^{-3} $Co(acac)_2$ is present. Note that the oxidant consumed largely exceeds the Co^{II} introduced. This finding suggests that the two peroxo molybdenum complexes oxidize Co^{II} to Co^{III} giving rise, also, to a short decomposition chain. In the presence of the same concentration of Co^{II}, a smooth decomposition of MoO_5PICO (PICO = picolinate *N*-oxido anion) takes place proceeding to completion and a quantitative evolution of dioxygen, based on the active oxygen of the peroxo complex initially added, is observed. In particular from a solution of 0.3 mmol of MoO_5PICO and 0.009 mmol of $Co(acac)_2$, in 25 cm^3 of DCE, 7.3 cm^3 of dioxygen, corresponding to 0.28 mmol, are produced at 40 °C. No information is, as yet, available on the nature of the species of molybdenum present at the end of the reaction. ^1H NMR analysis of the reaction mixture when the active oxygen is totally consumed suggests that paramagnetic species are absent; this follows from the observation that the peaks corresponding to the resonances of the protons of the ligand are sharp. Thus, it is likely that a Mo^{VI} complex, presumably a dimeric species as suggested later in this paper, is formed akin to other oxidation reactions involving peroxomolybdenum complexes.[1] The active oxygen decrease, as shown in Fig. 1, does not follow a simple kinetic pattern. In fact, after a first relatively fast disappearance of the oxidant, accounting for *ca.* 20% of the active oxygen initially added, the decomposition slows down.

Table 2 collects data referring to the oxidation of some representative alkanes and alkenes by the MoO_5PICO/Co^{II} system. Control experiments have demonstrated that both MoO_5PICO and $Co(acac)_2$, separately, do not react to any extent with the substrates examined.

The behaviour of the disappearance of the oxidant in the presence of all the substrates at all the concentrations used is almost identical to that observed in the decomposition experiments as an indication that the substrate is not involved in the rate law of the oxidation.

The data of Table 2 suggest that a novel oxidant is formed in solution capable of oxidizing both activated carbon–hydrogen bonds and variously substituted double bonds. The epoxidation of *Z*-olefins provides *E*-epoxides, at variance with the classical electrophilic epoxidations.[5] Moreover, in the oxidation of cyclohexene, together with the epoxide, which is the minor product, typical products of radical oxidation, *i.e.* cyclohex-2-enol and cyclohex-2-enone are obtained.[12] When cyclohexene is oxidized under air an overproduction of oxidized species is observed as a clear indication that autoxidative processes involving carbon centred radicals are taking place. The relative relevance of the two kinds of reactivity was examined by oxidizing 5*H*-dibenzo[*ad*]cycloheptene **1**. As shown in Scheme 1, the only product detected is the ketone **2** arising from the attack to the activated C–H bond in position 5 whereas the double bond remains untouched.

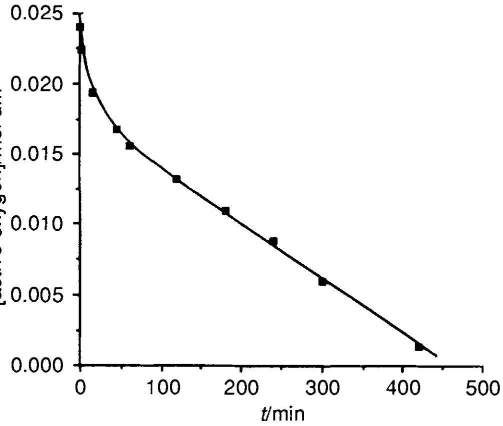
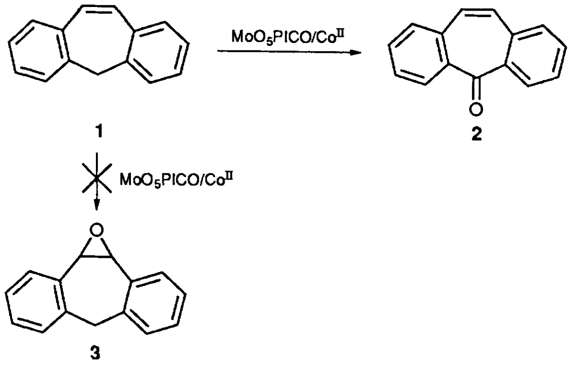


Fig. 1 Decrease of the active oxygen content as a function of time for the decomposition of MoO_5PICO (0.12 mol dm^{-3}) in DCE at 40 °C in the presence of $Co(acac)_2$ (0.036 mol dm^{-3})



Scheme 1

In the oxidation of **1**, as well as in that of fluorene, an intermediate alcohol is not detected. Whether this indicates that the oxidant has a peculiar oxidative behaviour or that simply the oxidation of the alcohol to ketone is faster than the hydroxylation of the parent hydrocarbon has not yet been ascertained.

The kinetics of the promoted decomposition of MoO_5PICO have been briefly examined. The initial rates of the two parts of the process, indicated as R_1 and R_2 respectively, at different MoO_5PICO and $Co(acac)_2$ initial concentrations have been measured. The results reported in Table 3 allow us to establish the corresponding rate laws.

It is observed that the rate law of the initiation is overall second-order, first-order in MoO_5PICO and first order in Co^{II} respectively, whereas the rate of the second part shows a linear dependence on Co^{II} concentration and a zero-order dependence on peroxo complex concentration thus suggesting a multistep mechanism.

The ability of peroxo complexes to act as one-electron acceptors has been estimated by measuring, by cyclic voltammetry, their reduction potentials $(E_p)_c$. The electrochemical process

Table 3 Initial rate values for the two parts of the MoO_5PICO decomposition reaction induced by $Co(acac)_2$ in DCE at 40 °C

	$MoO_5PICO/10^2$ mol dm^{-3}	$Co(acac)_2/10^2$ mol dm^{-3}	$R_1/10^6$ mol dm^{-3} s^{-1}	$R_2/10^6$ mol dm^{-3} s^{-1}
1	1.2	0	0	0
2	1.2	0.016	1.11	0.11
3	1.2	0.024	1.62	0.17
4	1.2	0.036	1.39	0.24
5	1.2	0.048	2.92	0.32
6	0.84	0.036	1.88	0.25
7	0.56	0.036	1.42	0.24

Table 4 Reduction peak potentials $(E_p)_c$, of a series of Mo^{VI} peroxo complexes, measured by cyclic voltammetry[a]

	Complex	$(E_p)_c$/V
1	MoO_3DIPIC	−1.40
2	MoO_5HMPT	−1.40
3	MoO_5PICO	−1.57
4	MoO_5PIC	−1.78

[a] Mo peroxo complex 0.001 mol dm^{-3} in DCE, supporting electrolyte TBAP 0.1 mol dm^{-3}, working electrode glassy carbon, ref. electrode SCE; scan rate 100 mV s^{-1}.

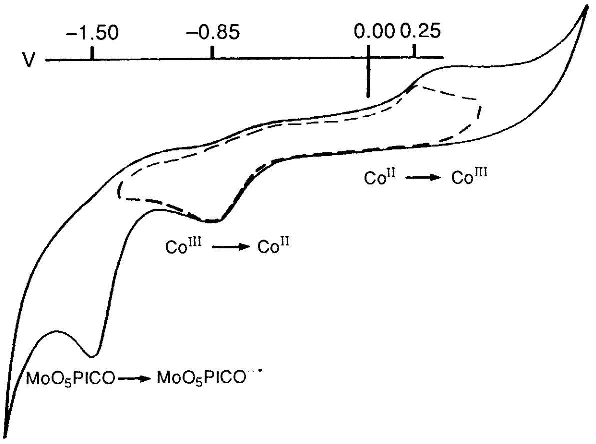


Fig. 2 Cyclic voltammetry of $MoO_5PICO/Co(acac)_2$ (1 × 10^{-3}/1 × 10^{-4} mol dm^{-3}) (——) and $Co(acac)_2$ (1 × 10^{-4} mol dm^{-3}) (– – –) in DCE; supporting electrolyte, TBAP (0.1 mol dm^{-3}); working electrode, glassy carbon; ref. electrode, SCE; scan rate 100 mV s^{-1}

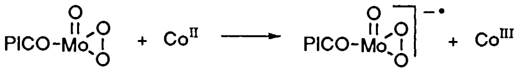
observed is an irreversible one, likely because of an immediate subsequent cleavage of the peroxide bond.[13] The $(E_p)_c$ values collected in Table 4 indicate that the complex whose decomposition in the presence of Co^{II} proceeds to completion, *i.e.* the anionic MoO_5PICO, is more difficult to reduce than neutral peroxo complexes.

Such electrochemical results simply indicate that the electron is more easily transferred to a neutral species than to an anionic one, very likely for electrostatic reasons. However in the context of the present study the behaviour observed suggests that in the decomposition of MoO_5PICO the role of Co^{II} cannot be merely in providing an electron to the peroxo complex.

This is further confirmed by the electrochemical experiment shown in Fig. 2, carried out on the system $MoO_5PICO/Co(acac)_3$, which is chemically inert. When in such a system Co^{II} is electrogenerated *in situ* by controlled potential electrolysis of the Co^{III} complex at −0.85 V, a decomposition reaction takes place whose behaviour is identical to that observed when the same amount of Co^{II}, as $Co(acac)_2$, is added in a separate experiment.

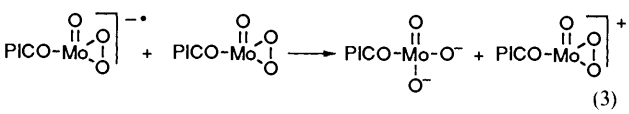
By contrast, if the electrochemical experiment is run in the absence of any cobalt derivative at the reduction potential of MoO_5PICO, *i.e.* −1.57 V, a much slower decomposition reaction is observed.

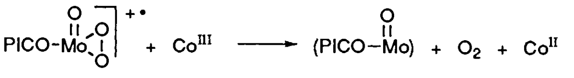
The complexity of the system and the limited number of compounds examined do not allow us to propose a mechanism explaining all the experimental findings. Nevertheless, some mechanistic considerations can be made. To this aim, a comparison with the well understood Fenton system,[14] in which, as in the present system, a peroxide, namely H_2O_2, reacts with a metal ion in low oxidation state, *i.e.* Fe^{II} is helpful. Therefore, the oxidation of Co^{II} to Co^{III} by the peroxo complex, indicated for the sake of simplicity, as $L_nMo(O_2)$, should proceed according to eqns. (1) and (2).


(1)


(2)

However, if these were the only steps occurring in the system, simply the stoichiometric consumption of the oxidant would be observed. On the contrary, with the possible exception of MoO_3DIPIC which is almost unreactive, the oxidant consumed is always more than the amount of Co^{II} added. Therefore, the following additional steps envisaging a chain decomposition leading to dioxygen should be considered [eqns. (3) and (4)].


(3)


(4)

Note that eqn. (4) takes into account the reduction of Co^{III} to Co^{II} as suggested by the kinetics. The fate of the coordinatively unsaturated species of Mo^{VI}, formed in eqn. (4), is not known. By analogy with similar systems,[7] their dimerisation may occur.

The electrochemical experiments suggest that the reaction of eqn. (1) should be faster for MoO_5HMPT than for MoO_5PICO. On the other hand, since in the case of MoO_5PICO, a species carrying two negative charges is formed upon reaction with Co^{II}, its oxidizing power toward Co^{II}, eqn. (2), should be much smaller than that of the species resulting from the monoreduction of a neutral peroxo complex. Since the chain length depends on both the rate of the initiation step, eqn. (1) and the termination step, eqn. (2), it may be argued that the chain length of the decomposition reaction is shorter for MoO_5HMPT than for MoO_5PICO mainly because the termination for the latter is a slow process. As far as MoO_3DIPIC and MoO_5PIC are concerned, it is likely that, together with a slow termination, also a slow initiation occurs. This could be due to the fact that the former is a coordinatively saturated species whereas the latter has the picolinato ligand which is more difficult to displace than the picolinate *N*-oxido one.[15] A corollary of this is that the reaction of eqn. (1) should be an associative process followed by the electron transfer.

The analogy between the Fenton reagent and the system studied here is, as anticipated, only a formal one. In fact, the important difference between the two systems is in the nature of the active species which in the former is HO•, whereas, in our case, it should be still a molybdenum derivative. Indeed, such a radical species, while exhibiting an oxidative behaviour similar to that of HO•, particularly in its ability to extract hydrogen atoms,[16] appears to be more selective than HO• as demonstrated by the data concerning the oxidation of the model substrates, particularly 5*H*-dibenzo[*ad*]cycloheptene **1**.

In conclusion, we obtained evidence that a homolytic reactivity can be promoted in anionic peroxomolybdenum complexes leading to the formation of radical species, whose nature is still unclear. Radical processes in anionic peroxomolybdenum complexes are not completely unprecedented.[9,17] As an example, evidence of homolytic reactions has been reported in diols' oxidation by MoO_5PICO.[17] Of course, several aspects of the system reported here need further clarification. Aside from a detailed mechanistic description, the role of the ligands coordinated to the metal and the synthetic applicability should be examined in detail.

Experimental

^1H NMR spectra were recorded at 250 MHz on a Bruker ACF instrument. Dioxygen evolution was measured by a thermostatted gas burette. Quantitative (internal standard) GLC analyses were carried out on 3% FFAP on Chromosorb WAW DMCS column, 2 m, for the oxidation of fluorene, diphenyl- and triphenyl-methane and stilbene; 15% Carbowax 20M on Chromosorb WAW DMCS column, 2 m, for styrene, cyclooctene, cyclohexene and (*Z*)-hex-3-ene; and an OV17 column, 2 m, for 5*H*-dibenzo[*ad*]cycloheptene. The active oxygen content in the decomposition reactions was determined by standard iodometry. All kinetic runs were carried out with temperature control better than ±0.05 °C.

All the peroxo complexes have been synthesized by literature methods.[4]

DCE was purified by standard procedures. All the substrates were commercially available materials purified by standard procedures. 5*H*-dibenzo[*ad*]cycloheptene was prepared following a literature procedure[18] by reduction of the commercially available dibenzo[*ad*]cyclohepten-5-one.

Cyclic voltammetry experiments were run with a EG&G-PAR 273 potentiostat/galvanostat with a EG&G-PAR universal programmer. A Hewlett Packard X-Y 7090 A plotter was used to record the current voltage output for 100 mV s^{-1} sweep rate. A conventional three-electrode system, consisting of a glassy carbon working electrode (Ø 3 mm), a platinum wire counter electrode and a saturated calomel electrode (SCE) as reference, was used. The solutions were usually 0.1 mol dm^{-3} TBAP and 1×10^{-3} mol dm^{-3} peroxo complex. All the solutions were deoxygenated by passing a nitrogen stream into the solution for at least 10 min prior to recording of the voltammetric data.

The controlled potential electrolysis experiments were run by using an AMEL Redel 552 potentiostat connected with an AMEL 731 digital current integrator. The working electrode was a glassy carbon plate (8 cm^2); a Ni coil, separated from the cell by a salt bridge, as counter electrode and a SCE as reference electrode were used.

Acknowledgements

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