MECHANISM OF OXYGEN TRANSFER FROM PEROXO SPECIES

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Abstract - The mechanisms of the polar oxygen transfer from peroxo and metal peroxo species are critically reviewed. Evidence is given in favor of a multiplicity of reaction pathways depending on the experimental conditions and the nature of the reagents, particularly in the case of metalperoxo species.

The process of oxygen transfer from peroxo compounds to organic substrates has several theoretical and practical implications (Ref. 1-4).

Within the domain of classical organic chemistry, two alternative mechanistic pathways for polar reactions, i.e. reactions which proceed by the heterolytic cleavage of the oxygen-oxygen bond, have been proposed:

Electrophilic oxygen transfer, which schematically may be written as:

$$R-O-OH + Nu \longrightarrow NuOH^{+} + RO^{-} \rightleftharpoons NuO + ROH$$
 (1)

R = H, Alkyl, Acyl

Typical reactions are:

$$C = C \rightarrow C \rightarrow R_3 N \rightarrow R_3 NO; R_2 S \rightarrow R_2 SO$$

Nucleophilic oxygen transfer; a two-step process which involves the addition, often reversible, of the peroxo compound to the substrate and subsequent cleavage of the perox ide intermediate, as reported in Eq. 2:

$$R-O-O^{-} + Z=X \rightleftharpoons \left[R-O-O-Z-X\right]^{-} \rightarrow RO^{-} + O-Z-X$$
 (2)

R = H,Alkyl,Acyl

Typical reactions are:

$$R'-\ddot{C}-R'' \longrightarrow R'-\ddot{C}-OR'' ; \subset C = C \xrightarrow{Y} C \xrightarrow{Q} (Y=NO_2, -\ddot{C}-, -SO_2-)$$

Several studies on such reactions have been carried out so that these mechanisms may be considered rather well established, even though a distinction between the two pathways may not be, in some cases, immediately evident. Beside that, proposals of an unified mechanism have been advanced (Ref.5,6). This aspect is becoming "hot" again in connection with the reactivity of metalperoxo compounds, since the presence of a metal

ion might introduce a further element of uncertainty.

Let us examine in some more detail the two mechanisms and the pertinent experimental data.

The most typical and best studied reactions proceeding by an electrophilic oxygen tran sfer are the oxidations of substrates such as alkenes, sulfides, tertiary amines by peroxocarboxylic acids and by hydrogen peroxide or alkylhydroperoxides.

The last two oxidants usually require acids catalysis. Several pieces of evidence suggest the following mechanisms for peroxo acids and for H_2O_2 or RO_2H rescreetively:

$$R-O-OH + Nu \xrightarrow{R'OH} \begin{bmatrix} R \\ O-O & - & - & - & Nu \\ H \\ O' & R' \end{bmatrix} \xrightarrow{\dagger} ROH + R'OH + NuO$$
 (4)

R = H, Alkyl

The electrophilic behavior of the peroxide oxygen and the removal of charge separation in the transition state by a hydrogen shift either internal (peroxocarboxylic acids) or external (H₂O₂, RO₂H) is indicated, inter alia, by the Hammett rho values (sign and magnitude) determined by changing the substituents in both the oxidants and the substrates. Also consistent with the mechanism proposed are the higher reactivity of the more alkyl substituted, and hence more nucleophilic, double bonds, the much greater efficiency of peroxocarboxylic acids as compared with that of H₂O₂ and RO₂H, (by a factor of more than 10°, Ref. 7), the peculiar solvent effect observed and the experimental finding that the rates of oxidation by H₂O₂ or RO₂H are greatly enhanced by addition of acid whereas acid catalysis is rather inefficient in the oxidation by peroxocarboxylic acids (Ref. 8-10).

Some significant data are reported in Tables 1 and 2.

The behavior of peroxocarboxylic acids and, in particular, the fact that they are the most powerful oxidants in this class of peroxides, deserves a further comment. Indeed, their very large reactivity must be related in some way to the acidity of the corresponding carboxylic acid. Accordingly, trifluoroperacetic acid is a much better oxidant, by a factor of ca. 100, than peracetic acid (Ref. 4b).

It should be noticed, however, that this correlation does not extend to inorganic per-oxoacids. In fact, peroxomonosulfuric H₂SO₂ and peroxomonophosphoric acid H₃PO₅should be, both, much more effective than peroxocarboxylic acids, whereas they usually behave as modest electrophilic oxidants (Ref. 20,21). Therefore it is likely that a major role in determining the effectiveness of peroxocarboxylic acids is played by the easy removal of the peroxidic proton by hydrogen bonding to the carbonyl group, which avoids charge separation. Evidently this process is much less efficient in H₂SO₅ and similar reagents.

Well-known examples of <u>nucleophilic oxygen transfer</u> are the Baeyer-Villiger oxidation of ketones and the alkaline epoxidation of alkenes carrying electron with drawing groups.

$$R-C = \begin{pmatrix} O & O & O \\ OOH & R-C-R'' & \rightleftharpoons & \left[R-C-O-O-C-R'' \right] & \rightarrow & R-C & OH & R'-O-C-R'' \end{pmatrix}$$
(5)

$$Y = -C-, NO_2, -SO_2$$

The occurrence of an intermediate peroxide, which may be in some cases rather stable and the rate-determining character of the second step have been well documented (Ref. 4a,22).

TABLE 1. Electrophilic oxidations

Oxidant	Substrate	Q(€)	Ref.	
x-c ₆ ^H ₄ co ₃ ^H	$Ph \\ C = C \\ Ph$	+1.4	11	
с ₆ н ₅ со ₃ н	X-Ar $C = C$ Ph	-1.0	11	
сн ₃ со ₃ н	X-C ₆ H ₄ -NH ₂	-1.9	12	
с ₆ н ₅ со ₃ н	x-c ₅ H ₃ N	-2.3	13	
с ₆ н ₅ со ₃ н	(X-C ₆ H ₄) ₂ -S	-1.1	14	
н ₂ 0 ₂ /н ⁺	x-c ₆ H ₄ -s-cH ₃	-1.1	15	

Typical electrophilic reaction

 $^{3}r_{2}$ 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2 2

TABLE 2. Rate data for some electrophilic oxidations

Oxidant	Substrate	Solvent	Relative Rate	Ref.
с ₆ ^н 5 ^{со} 3 ^н	≪-methylstyrene	с ₆ н ₆	(1.00)	17
11	styrene	11	0.14	17
"	trans-stilbene	***	0.064	17
11	cyclohexene	**	4.3	17
11	1-methylcyclohexene		13.6	17
**	diphenylsulfide	11	2000.	14
11	diphenylsulfoxide	11	25.	14
сн ₃ со ₃ н)c = c(сн ₃ со ₂ н	(1.00)	18
	c = c	11	22.	18
n	$c = c < cH_3$ $c = c < cH_3$ cH_3	"	484.	18
CF ₃ CO ₃ H	trans-stilbene	CHC1 ₃	(1.00)	19
11	11	CC1 ₄	0.4	19
11	"	^C 6 ^H 6	0.525	19
**	11	(СН ₃) ₃ СОН	0.012	19

The data discussed so far might suggest that the nature of the substrate – more orless keen to nucleophilic attack – is more important than the nature of the peroxospecies in determining the mechanism of oxygen transfer. There is, however, at least one example which shows that the same substrate may undergo either electrophilic or nucleophilic oxidation. These are the organic sulfoxides, oxidized to the corresponding sulfones by peroxobenzoic acid (Ref. 23). As shown in Fig. 1, at low pH, where the peracid is not dissociated, the oxidation of p-X-CH₂ S(O)-CH₂ proceeds with the typical features of an electrophilic process (negative rho value) whereas, at higher pH, the nuclephilic pathway prevails (positive rho value). Moreover, the rate of oxidation has been shown to depend on the concentration of the peroxoanion, as illustrated, for (p-NO₂CH₂)SO, in Fig. 2 (Ref. 24).

This is a rather unique example, as it is generally found that a substrate is either oxidized under electrophilic or nucleophilic conditions.

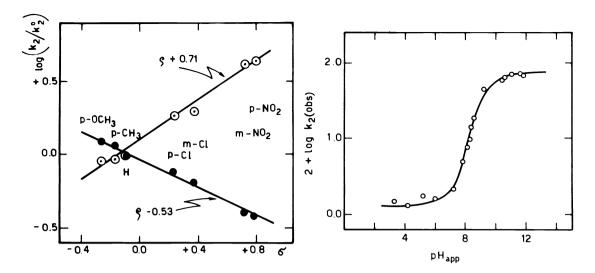


Fig. 1. Effect of the substituents on the rates of oxidation of p-X-C₆H₂-S(0)-C₆H₅ to the corresponding sulfone by C₆H₅CO₃H in dioxane-water in acid (full circles) and alkaline (empty circles) media. Data from Ref. 23.

Fig.2. Rates of oxidation of $(p-N0.C_0H_2)$ SO to the corresponding sulfone by ${}^{2}_{6}H_{5}^{+}CO_{3}H_{5}^{-}$ in dioxane-water, as a function of the $\frac{a}{c}$ cidity of the medium. Data from Ref. 24.

Oxidation by metalperoxo compounds. Transition-metal peroxo species are the oxidizing agents in the transition-metal catalyzed oxidations with hydrogen peroxide and alkylhy droperoxides (Ref.25). These processes are particularly interesting, from an industrial standpoint (Ref.26), for the obvious reason that H₂O₂ and RO₂H are cheaper and safer reagents than peroxoacids. Beside a more general interest related to the problem of molecular oxygen activation (Ref.25) and biological oxidations (Ref.25), an appealing potentiality of metal-catalyzed oxidation systems is that metal peroxo species have almost always other coordination sites which may be occupied by chiral ligands. This approach to enantioselective oxidation has already given positive results, from the initial experiments carried out with chiral alcohols as cosolvents (Ref.27) and the use of specially designed ligands (Ref.28) to the recent results of almost enantiospecific syntheses (e.e. > 95%), even though limited to the epoxidation of allylic alcohols (Ref.29). We shall examine below the features of peroxocompounds formed by interaction of H₂O₂or RO₂H with metal ions in their highest oxidation states. The chemistry of dioxygen complexes, formed by addition of molecular oxygen to the appropriate metal ion, will not be discussed here.

The processes leading to the formation of metalperoxo complexes are illustrated below:

$$L_{n}^{M} + H_{2}^{O_{2}} \xrightarrow{L_{(n-1)}^{M} -OOH} + LH$$

$$L_{(n-2)}^{M} \xrightarrow{O} + 2LH$$

$$2.$$
(7)

$$L_{n}M + RO_{2}H \longrightarrow L_{(n-1)}M - OOR + LH$$
(8)

where M is a transition metal ion and HL a monodentate ligand (Ref.25).

Species carrying two or more peroxide groups may also be formed (Ref.30). However, for the sake of simplicity, they are not considered in the following discussion. The adducts of H₂O₂ might have either the open, peracid-like, structure 1 or the cyclic, side-bonded, structure 2 (Ref.25). On the other hand only the structure 3 is conceivable for the adducts of alkylhydroperoxides. In general, the peroxo complexes of metal ions such as Ti(IV), V(V), Mo(VI), and W(VI), are all good oxidants towards alkenes, sulfides, tertiary amines, etc.(Ref.25). Therefore, the earlier suggestion that the oxidizing properties of M-H₂O₂ systems are attributable to the presence of an acid functionality, as in 1, (Ref.25) should be dismissed since structurally similar alkylperoxo compounds of the type 3 have similar characteristics.

Recent kinetic and thermodynamic studies (Ref.31) suggest that the preferred structure for the hydrogen peroxide adducts to transition metal ions is the cyclic one. In particular it has been observed that the binding constant of $\rm H_2O_2$ to the metal ions mentioned above is remarkably large and, at any rate, much larger – by a factor of <u>ca.</u> 10^3 – than that of alkylhydroperoxides, in spite of the fact that $\rm H_2O_2$ and $\rm RO_2H$ have similar nucleophilicity. In fact, these two peroxidic species add to carbonyl compounds and to a non-transition metal ion such as $\rm B^{3^+}$ with a very similar, and rather small, as sociation constant. These data are presented in Table 3. The interpretation is that $\rm H_2O_2$

TABLE 3. Association constants (Kf, M^{-1}) of X-OOH to various substrates (X=H, t-Bu)

Substrate	Kf (H ₂ O ₂)/Kf (t-BuO ₂ H)	Ref.	
о сн ₃ -с-н	2	32,33	
B(OH) 4	2	34,31e	
VO(OEt) ₃	> 1000	31e,35	

behaves as a bidentate ligand, as far as coordination to a transition metal ion is concerned, yielding cyclic peroxo compounds. Furthermore, the cyclic structure 2 is quite general, in the solid state, for peroxo complexes of several transition metals (Ref. 25). It may be interesting to discuss briefly the difference between transition metals and B³⁺, which gives, with H₂O₂, non cyclic adducts of the type 1. It should

It may be interesting to discuss briefly the difference between transition metals and B^{3+} , which gives, with H_2O_2 , non cyclic adducts of the type 1. It should be noticed that the configuration at oxygens in cyclic peroxo compounds amounts to a cisoid structure which is largely disfavored in open chain peroxides (Ref.4a). It seems, therefore, quite likely that the empty d-orbitals of the transition metal play a major role in stabilizing this structure, possibly by an interaction with the filled antibonding orbital on oxygens. Also, the possibility for metals such as Mo(VI) or V(V) of larger coordination numbers than B^{3+} could be a factor favoring the side-on coordination of H_2O_2 .

For a complete analysis of these oxidizing systems it is necessary to take into account the possibility that the cyclic species 2 is in equilibrium with the peracid-like species 1, as in Eq.9 and that 1, even present in very low concentration, is the real oxidizing agent. This circumstance cannot be ruled out but it appears rather unlikely. On the other hand the cyclic peroxospecies are expected to be remarkably efficient. Indeed,

$$M \stackrel{O}{\stackrel{}{\stackrel{}}{\stackrel{}}} + HX \rightleftharpoons M \stackrel{O-OH}{\stackrel{}{\stackrel{}}{\stackrel{}}}$$

$$(9)$$

X = OH, OOH etc.

we have already mentioned that monoperoxosulfuric acid, which may be considered a very good model for species like 1, is a rather poor electrophilic oxidant in spite of the fact that the leaving group, SO_4 , is particularly good. A peculiar feature of monoperoxosulfuric acid, which is worth mentioning also because it sheds light on the reactivity of cyclic peroxospecies, is that, in the presence of carbonyl compounds, HSO_5 becomes an effective oxidant of nucleophilic substrates such as olefins (Ref.36). This happens, as shown below, because of the formation of the highly reactive dioxirane intermediate (Ref.36b,c):

Mechanism of oxygen transfer from peroxometal complexes. Two alternative mechanistic pathways have been proposed, as shown here for olefin epoxidation (Ref.25).

SCHEME A.

$$M \downarrow O + C = C \longrightarrow M \downarrow O \qquad \qquad M=O + C - C \qquad (11)$$

$$M^{O} \cap R + C = C \longrightarrow \begin{bmatrix} C & C & T \\ M & O & T \\ O & C & T \end{bmatrix}$$

$$M \rightarrow M \rightarrow C + C \longrightarrow C \longrightarrow C$$

$$(12)$$

SCHEME B.

$$M^{O} \circ R + C = C \Leftrightarrow M^{O} \circ R \to M^{O} \circ$$

The processes depicted in Scheme A simply amount to an electrophilic oxygen transfer which, in the case of alkylperoxo complexes, is accompanied by a 1-2 shift of the metal (Ref.37). Taking into account the tendency of metalperoxo species to coordinate the nucleophilic substrate (Ref.6), Scheme A should be slightly modified. In particular the possibility must be considered that also the substrate-complexed peroxo species 5, formed according to Eq. 15, behaves as an oxidant

$$M \downarrow 0 + C = C \Rightarrow M \downarrow 0 + S
C = C \Rightarrow S$$
(15)

(where S is a solvent molecule or a neutral ligand). It is evident that Scheme A envisages a kind of reactivity of metalperoxo compounds very similar to that of peroxoacids and ${\rm H_2O_2}$ or ${\rm RO_2H}$ in the electrophilic oxidations. This, together with the fact that it accomodates for all the experimental observations, made in such systems, render very appealing the mechanistic hypothesis of Scheme A.

The oxidative pathway depicted in Scheme B is also reasonable. It implies that the substrate, by coordination to the metal, reverts its original character becoming electrophilic. Thus a nucleophilic attack by the peroxide oxygen may occur. Indeed, if structures such as 6 are considered, it becomes clear that Scheme B might be an example of nu

cleophilic intramolecular oxidation. The critical step should be the formation of the peroxometallocycle 4 (or the pseudo-peroxometallocycle 4) which collapses to products in a fast step. Therefore, the rate-limiting step could be either the insertion of the substrate into the metal-oxygen bond or the coordination of the nucleophile to the metal. As it will be discussed below, also this mechanism accounts for most of the experimental data available.

Let us analyze in detail the properties of the peroxometallocycle, which is the crucial intermediate. It has been invoked in the epoxidation of alkenes by Mo(VI) and V(V) peroxospecies (Ref.6) as well as in the oxidation of terminal olefins to methyl ketones, mainly by Rh and Pd peroxo species (Ref.6,38,39). The rationale was offered that depending on the nature of the metal, two alternative decomposition routes are possible (Ref.6,38,39)

M = V(V), Mo(VI)

(1-2 carbon-carbon hydride shift)

M = Rh(III)

The decomposition pathway leading to epoxide Eq. 17, finds its obvious parallel, even though an opposite flow of the electrons might be predicted, in the intermediate of the alkaline epoxidation of alkenes, \underline{cfr} Eq. 6, however no direct evidence of peroxometallocycles of V(V) or Mo(VI) has ever been obtained. Some evidence does exist for Rh and Pd peroxometallocycles (Ref.6,38,39) but the decomposition mechanism suggested, Eq. 18, has left some doubts since it has no precedents in the chemistry of peroxide compounds.

We tought that a likely alternative would have been a ß-elimination or a process similar to the decomposition of the peroxide intermediate in the Baeyer-Villiger oxidation of ketones (Ref.4a) and of cumyl hydroperoxide to give acetone and phenol (Ref.1):

The presence of the base B, which might be simply a solvent molecule, may not be necessary since a 1-2 carbon-oxygen shift of the hydrogen may occur. This hypothesis has been checked by using alkenes deuterated in the appropriate position or carrying out the reaction in deuterated ethanol.

We have found (Ref.40) that in the Rh catalyzed oxidation of terminal olefins to methyletones, the outcome of our experiments suggests that the hydrogen migration (Eq.18-20) is mediated by the solvent.

This may suggest that, whether metalperoxocycles are formed, they decompose to carbonyl compounds by a route which is rather common for peroxides (Ref.1-4) and, consequently, the mechanistic pathway leading to epoxides might be different from that involving a peroxometallocycle. This is confirmed by the different order of reactivity of the alkenes in the two processes.

In fact, Rh and Pd peroxo species react almost exclusively with terminal olefins to give methylketones, being almost unreactive toward alkyl substituted double bonds whereas V and Mo peroxo species, similarly to organic peroxoacids, react faster with the more alkyl substituted olefins.

Some pertinent data are collected in Table 4.

These results suggest that in the reaction leading to methylketones steric factors play a major role, whereas in that leading to epoxides, electronic effects dominate. This, in turn, may indicate that the role of substrate coordination in the two processes is different.

Despite the considerations discussed above, most of the experimental results may be,more or less easily, accommodated in either one of the two mechanistic hypotheses. Therefore, we looked for obtaining less equivocal and more differentiating evidence from a detailed kinetic study.

We have approached the problem by evaluating the kinetic consequences of the two alternative mechanisms in order to establish which one fits better the experimental data. The model reaction choosen was the epoxidation of cyclohexene with MoO₅ HMPT in dichloroethane, which was originally investigated by Mimoun et al. (Ref.42). They found and we have confirmed, (Ref.40), that the kinetic behavior is somewhat complex, being the order in the substrate smaller than one. This might result from a preequilibrium process

TABLE	4.	Oxidation	of	alkenes	by	metal	peroxo	species
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Metal	Olefin	Relative Rate	Product	Ref.	
V	1-octene	(1.00)	epoxide	41	
	trans-2-octene	6.6	"	41	
Мо	1-octene	(1.00)	11	42	
11	cis-trans-2-octene	4.3	11	42	
Rh	1-hexene	(1.00)	ketone	38	
11	2-hexene	0.07	"	38	
Pd	1-hexene	(1.00)	11	39	
11	2-hexene	no reaction	11	39	

preceding the oxygen transfer as it is suggested in Scheme B reported previously, giving schematically:

$$Cy + MoO_5HMPT \implies MoO_5 HMPTCy, K_{Ass}$$
 (21)

$$MoO_SHMPTCy \longrightarrow products, ki$$
 (22)

that leads to the following rate law, Eq. 23:

$$R = \frac{kiK_{Ass} \left[Cy \right]_{\circ} \left[MoO_{5} HMPT \right]_{\circ}}{1 + K_{Ass} \left[Cy \right]_{\circ}}$$
(23)

which is consistent with the experimental data. However, it may be easily shown that also the electrophilic mechanism explains this behavior under the assumption that both MoO_5HMPT and $MoO_5HMPTCy$ oxidize the substrate, the latter being less effective than the former. The derived rate-law in fact is:

$$R = \frac{k_2 \left[Cy \right]_{\circ} \left[MoO_5 HMPT \right]_{\circ}}{1 + K_{Ass} \left[Cy \right]_{\circ}} + \frac{k_2' K_{Ass} \left[Cy \right]_{\circ}^2 \left[MoO_5 HMPT \right]_{\circ}}{1 + K_{Ass} \left[Cy \right]_{\circ}}$$
(24)

where k_2 and k_1 are the specific rate constants for the oxidation of cyclohexene with MoO_HMPT and MoO_HMPTCy.It is noteworthy that Eq. 24 fits very well the experimental data, as shown in Figure 3. Thus, the assumption that coordination of the olefin to

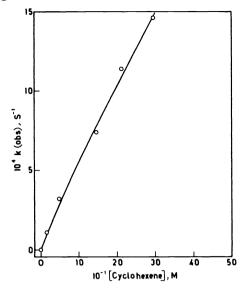


Fig. 3 Dependence of the rates of oxidation of cyclohexene by MoO_5HMPT , in DCE, at 25°C, on substrate initial concentration. The curve has been calculated from Eq. 24 by a computer program which sets the best k_2 , k_2' and k_1' and k_2' values to fit the experimental points.

the peroxometal compound reduces its electrophilic ability, i.e. that $k_2 < k_2$ appears reasonable. An useful tool in such systems is to add a strong, non oxidizable ligand, typically HMPT itself, and to study its effect on oxidation rates (Ref.44). On the basis of the mechanism which involves intramolecular oxidation of the coordinated substrate one may immediately predict that increasing amounts of added HMPT will continuously inhibit the reaction because of the displacement by HMPT of the coordinated olefin to give $\text{MoO}_5(\text{HMPT})_2$. Indeed, this is the behavior observed. However this feature,

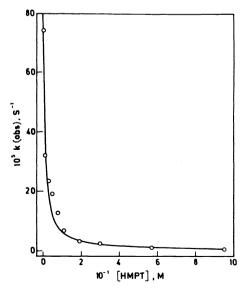


Fig. 4 Dependence of the rates of oxidation of cyclohexene by MoO_1HMPT in DCE, at 25°C, on the HMPT concentration. The curve has been calculated by a computer program from Eq. 25.

as well, is accounted for by the electrophilic scheme. In fact, upon addition of HMPT, MoO_(HMPT) is formed which should be a very poor electrophilic oxidant; the rate-law in the presence of HMPT added, involves three terms as three oxidizing species, MoO_HMPT, MoO_HMPTCy and MoO_(HMPT) are present in solution and hence a three terms equation, Eq. 25, is derived:

$$R = \frac{k_{2} \left[\text{Cy} \right]_{0} \left[\text{MoO}_{5} \text{HMPT} \right]_{0}}{1 + K_{Ass} \left[\text{Cy} \right]_{0} + K_{Ass} \left[\text{Ex} \right]_{0} + \frac{k_{2}^{\dagger} K_{Ass} \left[\text{Cy} \right]_{0}^{2} \left[\text{MoO}_{5} \text{HMPT} \right]_{0}}{1 + K_{Ass} \left[\text{Cy} \right]_{0} + K_{Ass} \left[\text{Ex} \right]_{0} + \frac{k_{2}^{\dagger} K_{Ass} \left[\text{Cy} \right]_{0} + K_{Ass} \left[\text{Cy} \right]_{0}$$

In Figure 4 it is shown how such an expression agrees with the experimental results, in particular with the effect of addition of HMPT on oxidation rates. There is however a particular behavior which cannot be rationalized within the intramolecular mechanism. This is the apparent order in cyclohexene, larger than one, which is observed in the presence of an excess of HMPT, (Figure 5). There is no possibility for an intramolecular oxidative process to account for such experimental finding whereas the electrophilic mechanism does involve a quadratic term, i.e. the oxidation carried out by MoO₅CyHMPT. As shown in Figure 5, a good coincidence of the experimental points with the curve calculated according to this hypothesis is again observed. As a conclusion, the kinetic analysis confirm the mechanistic ambiguity discussed before providing only an indirect evidence, which should be carefully tested in other systems, favoring the electrophilic mechanism.

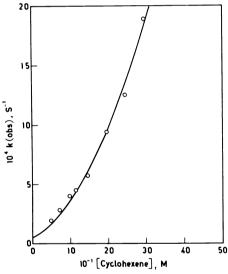


Fig. 5 Dependence of the rates of oxidation of cyclohexene by MoO₅HMPT in DCE, at 25°C, on substrate initial concentration, in the presence of HMPT 0.11 \underline{M} . The curve has been calculated by a computer program from Eq. 25.

Let us discuss in more detail the structure of the molybdenum species. Difrattometric studies (Ref. 6) indicate that in $MoQ_L^1L_2$ the two coordination sites are not equivalent. One ligand is strongly bound, whereas the other is only weakly bound. As a matter of fact, in $MoQ_bHMPTH_bQ_b$, the water may be removed under vacuum. These structural features may suggest that the coordination of the olefin, which is a prerequisite for the formation of the peroxometallocycle, occurs by removal or shift of HMPT to the weakly bonding site. The rate laws derived under this hypothesis are not significantly different from those previously discussed (Ref. 42) and therefore the conclusions reached above are not infirmed. However, there is independent evidence that the active peroxo species does carry a strong ligand such as HMPT. In fact, monodentate ligands

related to HMPT may transfer MoO₅ from aqueous to organic phase and still maintain the oxidizing power of the peroxocomplex (Ref. 43). Furthermore, if they are chiral, they may perform an enantioselective oxidation (Ref. 40). This finds a correspondence with the asymmetric induction obtained with MoO₅L (L=(CH₃)₂N-C- $\frac{1}{0}$ HCH₃) under stoichiometric conditions (Ref. 28c).

The possibility that this species may act as a bidentate ligand and hence remain coordinated at one center, which should be the weak coordination site, does not seem consistent with the fairly large induction observed (e.e. > 30%).

Support for a nucleophilic character of the peroxide oxygen in peroxocarboxylic acids has been sought in the results of theoretical calculations (Ref. 45) which indicate that in peroxocarboxylic acids both peroxide oxygens carry a fractional negative charge, the positive charges being localized on the hydrogens and the carbonyl carbon. However, these results cannot be assumed as an evidence favoring nucleophilic oxidation mechanism such as the one proposed (Ref. 6). Certainly, the chlorine atom in the chlorine molecule is not positive, and any calculations will indicate so, but still it is a strong electrophile, in the presence of a nucleophilic substrate, as all the halogens are.

Under many points of view, hydrogen peroxide may be considered similar to chlorine, even though the former must be less electrophilic than the latter; still, a similar chemical behavior may be expected, <u>i.e.</u> electrophilic transfer of a formal OH^{\dagger} fragment. This reaction has to be acid catalyzed and indeed it is. On the other hand it is very hard to envisage an alternative pathway which implies that H_2O_2 acts as a nucleophile toward substrates such as sulfides and amines.

As it emerges from the above discussion, the claim for an unified mechanism does not seem enough substantiated. On the contrary, from this analysis, the need of a variety of intermediates, transition states and mechanisms for different reactions giving sometime different products, clearly arises.

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ERRATA

Volume, Issue and Year	Page no. and location	Correction				
<u>49</u> , 5 (1977)	671-673	In the "Recommended Reference Materials for the Realization of Physicochemical Properties - Section Absorbance and Wavelength" infrared absorption bankwere suggested as reference for wavenumber calibration a book entitled Tables of Wavenumbers for the Calibration of Infrared Spectrometers compiled by A.R.H. COLE (Pergamon Press, Oxford, 1977). Wavenumbers appearing in sections II/8, II/9, II/10 and II/11 of Recommendations on Reference Materials should be replaced by the values published by COLE				
<u>54</u> , 1 (1982)	208, Abstract, line 2	<u>for</u> 'dexcy' <u>read</u> 'deoxy'				
	209, column 2, 3rd name	for 1,1,2,2-Tetrahydro read 1,1,2,2-Tetradehydro				
	210, column 1, 4th name	for 6,7,7,8-Tetrahydro read 6,7,7,8-Tetradehydro				
	214, column 2, structure for Cladinose	CHO CH2 CH2 For CH ₃ OC-CH ₃ HOCH CH ₃ CH ₃ OC-CH ₃ HOCH HOCH CH ₃ CH ₃ CH ₃ OC-CH ₃ CH ₃ CH ₃ OC-CH ₃ HOCH CH ₃				
<u>54</u> , 3 (1982)	681, Abstract, line 3	for TiO ₂ 1892 [±] 30 <u>read</u> TiO ₂ 1843 [±] 15 (in air) for ZnO ₂ 2710 [±] 25 read ZnO ₂ 2710 [±] 35				
<u>54</u> , 8 (1982)	1455, Table 1 (i) column -ΔH ^O for Hg ²⁺ h (ii) footnote a	<u>for</u> 1940 <u>read</u> 1845				
	to Table 1 1457, Table 2 column 1, last item	add ΔH_h^0 of Hg^{2+} has been misprinted in Ref. 19 for BP_4^- read BPh_4^-				
	1459, Table 3 column 1, 12th item	<u>for</u> Hg(l)/Hg ²⁺ <u>read</u> Hg(l)/Hg ²⁺				
<u>54</u> , 10 (1982)	1859, Eq.(14)	correct version is as follows:				
	M ^O OR +	$C = C = M^{O} OR \rightarrow M^{O} O \rightarrow M - OR + C - C $ $C = C = C \qquad C \rightarrow C \qquad (14)$				
		4 '				