

MECHANISM OF OXYGEN TRANSFER FROM PEROXO SPECIES

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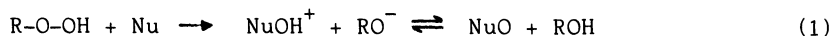
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Abstract - The mechanisms of the polar oxygen transfer from peroxo and metal peroxo species are critically reviewed. Evidence is given in favor of a multiplicity of reaction pathways depending on the experimental conditions and the nature of the reagents,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

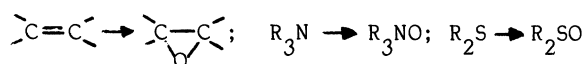
Within the domain of classical organic chemistry, two alternative mechanistic pathways for polar reactions, i.e. reactions which proceed by the heterolytic cleavage of the oxygen-oxygen bond, have been proposed:

Electrophilic oxygen transfer, which schematically may be written as:

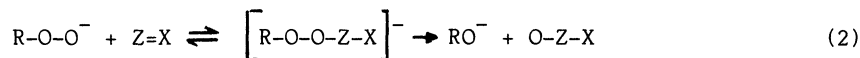


R = H, Alkyl, Acyl

Typical reactions are:

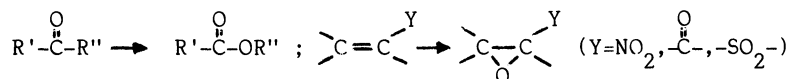


Nucleophilic oxygen transfer; a two-step process which involves the addition, often reversible, of the peroxo compound to the substrate and subsequent cleavage of the peroxide intermediate, as reported in Eq. 2:



R = H, Alkyl, Acyl

Typical reactions are:



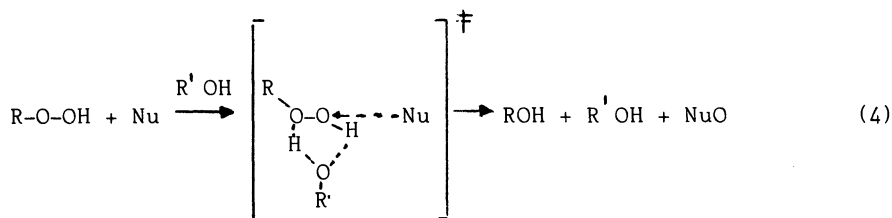
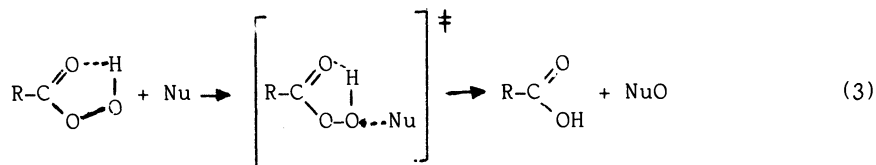
Several studies on such reactions have been carried out so that these mechanisms may be considered rather well established, even though a distinction between the two pathways may not be, in some cases, immediately evident. Beside that, proposals of a unified mechanism have been advanced (Ref. 5, 6). 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 transfer 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 peroxy acids and for H_2O_2 or RO_2H respectively:



R = H, Alkyl

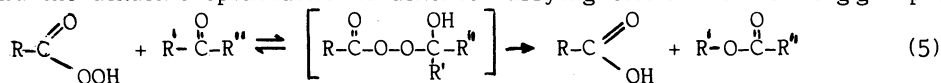
The electrophilic behavior of the peroxide oxygen and the removal of charge separation in the transition state by a hydrogen shift either internal (peroxocarboxylic acids) or external (H_2O_2 , RO_2H) is indicated, inter alia, by the Hammett rho values (sign and magnitude) determined by changing the 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 H_2O_2 and RO_2H , (by a factor of more than 10^5 , Ref. 7), the peculiar solvent effect observed and the experimental finding that the rates of oxidation by H_2O_2 or RO_2H are greatly enhanced by addition of acid whereas acid catalysis is rather inefficient in the oxidation by peroxocarboxylic acids (Ref. 8-10).

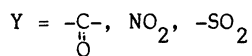
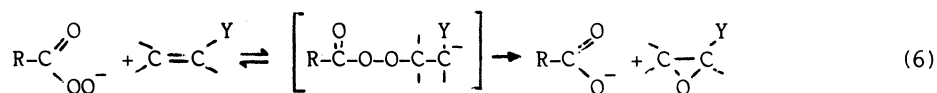
Some significant data are reported in Tables 1 and 2.

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 peroxyacids. In fact, peroxomonosulfuric H_2SO_5 and peroxomonophosphoric acid H_3PO_5 should 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 H_2SO_5 and similar reagents.

Well-known examples of nucleophilic oxygen transfer are the Baeyer-Villiger oxidation of ketones and the alkaline epoxidation of alkenes carrying electronwithdrawing groups.





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	$e(e^+)$	Ref.
$\text{X}-\text{C}_6\text{H}_4\text{CO}_3\text{H}$	$\begin{array}{c} \text{Ph} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array} \begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Ph} \end{array}$	+1.4	11
$\text{C}_6\text{H}_5\text{CO}_3\text{H}$	$\begin{array}{c} \text{X-Ar} \\ \diagdown \\ \text{C}=\text{C} \\ \diagup \\ \text{H} \end{array} \begin{array}{c} \text{H} \\ \diagup \\ \text{C} \\ \diagdown \\ \text{Ph} \end{array}$	-1.0	11
$\text{CH}_3\text{CO}_3\text{H}$	$\text{X}-\text{C}_6\text{H}_4-\text{NH}_2$	-1.9	12
$\text{C}_6\text{H}_5\text{CO}_3\text{H}$	$\text{X}-\text{C}_5\text{H}_3\text{N}$	-2.3	13
$\text{C}_6\text{H}_5\text{CO}_3\text{H}$	$(\text{X}-\text{C}_6\text{H}_4)_2-\text{S}$	-1.1	14
$\text{H}_2\text{O}_2/\text{H}^+$	$\text{X}-\text{C}_6\text{H}_4-\text{S}-\text{CH}_3$	-1.1	15

Typical electrophilic reaction

Br_2	$\text{X}-\text{C}_6\text{H}_4\text{CH}=\text{CH}_2$	-4.5	16
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TABLE 2. Rate data for some electrophilic oxidations

Oxidant	Substrate	Solvent	Relative Rate	Ref.
$C_6H_5CO_3H$	α -methylstyrene	C_6H_6	(1.00)	17
"	styrene	"	0.14	17
"	trans-stilbene	"	0.064	17
"	cyclohexene	"	4.3	17
"	1-methylcyclohexene	"	13.6	17
"	diphenylsulfide	"	2000.	14
"	diphenylsulfoxide	"	25.	14
CH_3CO_3H	>C=C<	CH_3CO_2H	(1.00)	18
"	$\text{>C=C(CH}_3\text{<}$	"	22.	18
"	$\text{>C=C(CH}_3\text{)}_2$	"	484.	18
CF_3CO_3H	trans-stilbene	$CHCl_3$	(1.00)	19
"	"	CCl_4	0.4	19
"	"	C_6H_6	0.525	19
"	"	$(CH_3)_3COH$	0.012	19

The data discussed so far might suggest that the nature of the substrate - more or less 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 $p\text{-X-C}_6\text{H}_4\text{-S(O)-C}_6\text{H}_5$ proceeds with the typical features of an electrophilic process (negative rho value) whereas, at higher pH, the nucleophilic pathway prevails (positive rho value). Moreover, the rate of oxidation has been shown to depend on the concentration of the peroxyanion, as illustrated, for $(p\text{-NO}_2\text{C}_6\text{H}_4)_2\text{SO}$, 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.

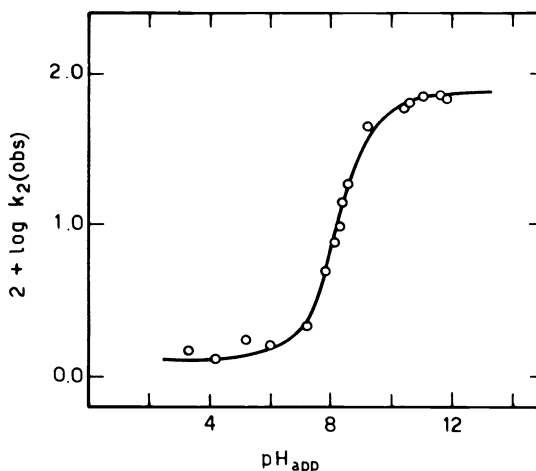
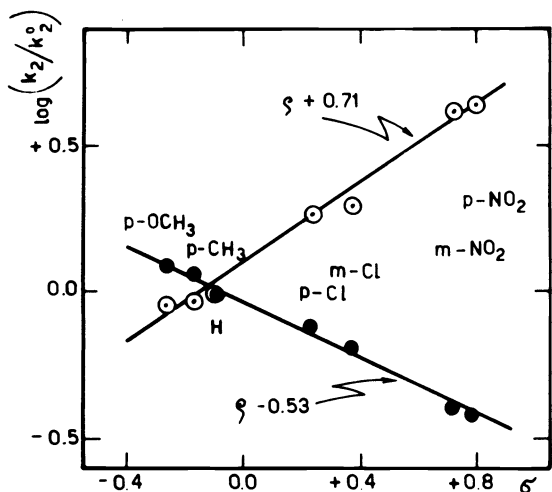
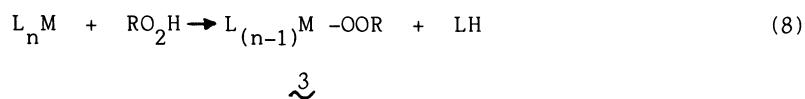
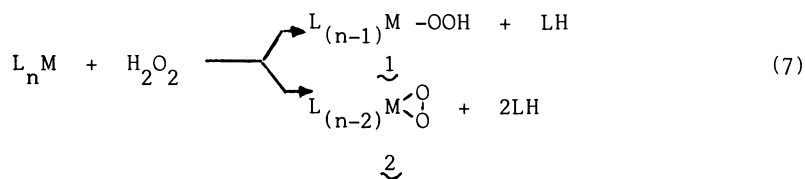


Fig. 1. Effect of the substituents on the rates of oxidation of $p\text{-X-C}_6\text{H}_4\text{-S(O)-C}_6\text{H}_5$ to the corresponding sulfone by $\text{C}_6\text{H}_5\text{CO}_3\text{H}$ in dioxane-water in acid (full circles) and alkaline (empty circles) media. Data from Ref. 23.

Fig.2. Rates of oxidation of $(p\text{-NO}_2\text{C}_6\text{H}_4)_2\text{SO}$ to the corresponding sulfone by $\text{C}_6\text{H}_5\text{CO}_3\text{H}$ in dioxane-water, as a function of the acidity of the medium. Data from Ref. 24.

Oxidation by metalperoxy compounds. Transition-metal peroxy species are the oxidizing agents in the transition-metal catalyzed oxidations with hydrogen peroxide and alkylhydroperoxides (Ref.25). These processes are particularly interesting, from an industrial standpoint (Ref.26), for the obvious reason that H_2O_2 and RO_2H are cheaper and safer reagents than peroxyacids. 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 peroxy 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 H_2O_2 or RO_2H 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 metalperoxy complexes are illustrated below:



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 H_2O_2 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 peroxy 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 $M-H_2O_2$ systems are attributable to the presence of an acid functionality, as in 1, (Ref.25) should be dismissed since structurally similar alkylperoxy 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 H_2O_2 to the metal ions mentioned above is remarkably large and, at any rate, much larger - by a factor of ca. 10^3 - than that of alkylhydroperoxides, in spite of the fact that H_2O_2 and RO_2H have similar nucleophilicity. In fact, these two peroxidic species add to carbonyl compounds and to a non-transition metal ion such as B^{3+} with a very similar, and rather small, association constant. These data are presented in Table 3. The interpretation is that H_2O_2

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

Substrate	$K_f(H_2O_2)/K_f(t-BuO_2H)$	Ref.
$CH_3-\overset{O}{\parallel}{C}-H$	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 peroxy compounds. Furthermore, the cyclic structure 2 is quite general, in the solid state, for peroxy complexes of several transition metals (Ref. 25).

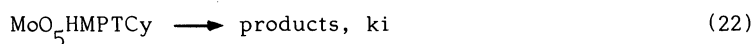
It may be interesting to discuss briefly the difference between transition metals and B^{3+} , which gives, with H_2O_2 , non cyclic adducts of the type 1. It should be noticed that the configuration at oxygens in cyclic peroxy compounds amounts to a cisoid structure which is largely disfavored in open 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,

TABLE 4. Oxidation of alkenes by metal peroxy species

Metal	Olefin	Relative Rate	Product	Ref.
V	1-octene	(1.00)	epoxide	41
"	trans-2-octene	6.6	"	41
Mo	1-octene	(1.00)	"	42
"	cis-trans-2-octene	4.3	"	42
Rh	1-hexene	(1.00)	ketone	38
"	2-hexene	0.07	"	38
Pd	1-hexene	(1.00)	"	39
"	2-hexene	no reaction	"	39

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



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

$$R = \frac{k_i K_{\text{Ass}} [\text{Cy}]_0 [\text{MoO}_5\text{HMPT}]_0}{1 + K_{\text{Ass}} [\text{Cy}]_0} \quad (23)$$

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 $\text{MoO}_5\text{HMPTCy}$ oxidize the substrate, the latter being less effective than the former. The derived rate-law in fact is:

$$R = \frac{k_2 [\text{Cy}]_0 [\text{MoO}_5\text{HMPT}]_0}{1 + K_{\text{Ass}} [\text{Cy}]_0} + \frac{k'_2 K_{\text{Ass}} [\text{Cy}]_0^2 [\text{MoO}_5\text{HMPT}]_0}{1 + K_{\text{Ass}} [\text{Cy}]_0} \quad (24)$$

where k_2 and k'_2 are the specific rate constants for the oxidation of cyclohexene with MoO_5HMPT and $\text{MoO}_5\text{HMPTCy}$. 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

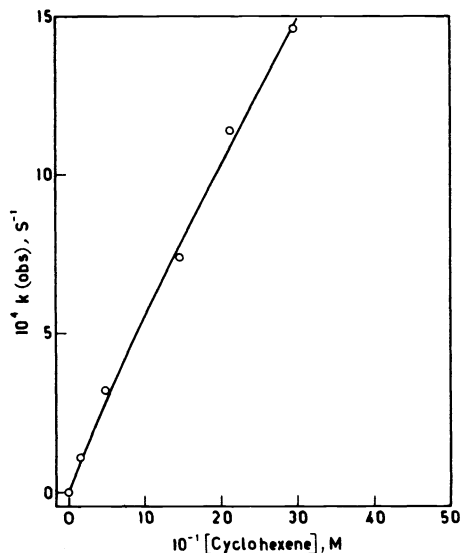


Fig. 3 Dependence of the rates of oxidation of cyclohexene by MoO_5HMPT , in DCE, at 25°C , on substrate initial concentration. The curve has been calculated from Eq. 24 by a computer program which sets the best k_2 , k'_2 and K_{Ass} values to fit the experimental points.

the peroxometal compound reduces its electrophilic ability, *i.e.* that $k'_2 < k_2$ appears reasonable. A 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,

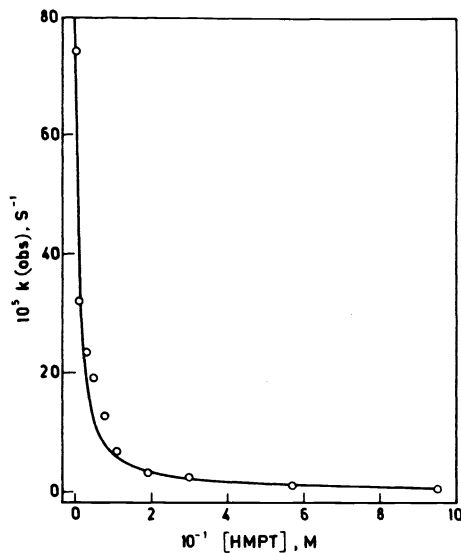


Fig. 4 Dependence of the rates of oxidation of cyclohexene by MoO_5HMPT in DCE, at 25°C , on the HMPT concentration. The curve has been calculated by a computer program from Eq. 25.

as well, is accounted for by the electrophilic scheme. In fact, upon addition of HMPT, $\text{MoO}_5(\text{HMPT})_2$ is formed which should be a very poor electrophilic oxidant; the rate-law⁵ in the presence of HMPT added, involves three terms as three oxidizing species, MoO_5HMPT , $\text{MoO}_5\text{HMPTCy}$ and $\text{MoO}_5(\text{HMPT})_2$ are present in solution and hence a three terms equation, Eq. 25, is derived:

$$R = \frac{k_2 [\text{Cy}]_0 [\text{MoO}_5\text{HMPT}]_0}{1 + K_{\text{Ass}} [\text{Cy}]_0 + K_{\text{Ass}} K_{\text{Ex}} [\text{HMPT}]_{\text{st}}} + \frac{k^1 K_{\text{Ass}} [\text{Cy}]_0^2 [\text{MoO}_5\text{HMPT}]_0}{1 + K_{\text{Ass}} [\text{Cy}]_0 + K_{\text{Ass}} K_{\text{Ex}} [\text{HMPT}]_{\text{st}}} + \frac{k^{11} K_{\text{Ass}} K_{\text{Ex}} [\text{Cy}]_0 [\text{MoO}_5\text{HMPT}]_0 [\text{HMPT}]_{\text{st}}}{1 + K_{\text{Ass}} [\text{Cy}]_0 + K_{\text{Ass}} K_{\text{Ex}} [\text{HMPT}]_{\text{st}}} \quad (25)$$

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 $\text{MoO}_5\text{CyHMPT}$. 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.

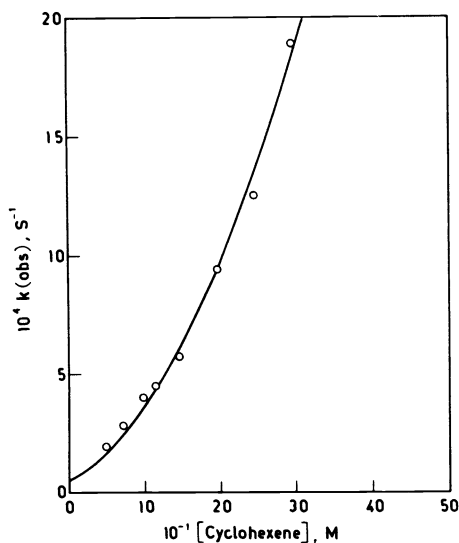


Fig. 5 Dependence of the rates of oxidation of cyclohexene by MoO_5HMPT in DCE, at 25°C, on substrate initial concentration, in the presence of HMPT 0.11 M. The curve has been calculated by a computer program from Eq. 25.

Let us discuss in more detail the structure of the molybdenum species. Diffractometric studies (Ref. 6) indicate that in MoO_5L_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 $\text{MoO}_5\text{HMPT}\cdot\text{H}_2\text{O}$, 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 peroxometallic cycle, 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 peroxy species does carry a strong ligand such as HMPT. In fact, monodentate ligands

related to HMPT may transfer MoO_5 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 MoO_5L ($\text{L}=(\text{CH}_3)_2\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\text{H}}{\text{C}}-\text{CH}_3$) 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, i.e. electrophilic transfer of a formal OH^+ 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				
49, 5 (1977)	671-673	In the "Recommended Reference Materials for the Realization of Physicochemical Properties - Section: Absorbance and Wavelength" infrared absorption bands were suggested as reference for wavenumber calibration. More recent revised data have been published by IUPAC in a book entitled <u>Tables of Wavenumbers for the Calibration of Infrared Spectrometers</u> 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.				
54, 1 (1982)	208, Abstract, line 2	<u>for</u> 'dexcy' <u>read</u> 'deoxy'				
	209, column 2, 3rd name	<u>for</u> 1,1,2,2-Tetrahydro <u>read</u> 1,1,2,2-Tetradehydro				
	210, column 1, 4th name	<u>for</u> 6,7,7,8-Tetrahydro <u>read</u> 6,7,7,8-Tetradehydro				
	214, column 2, structure for Cladinose	<table style="width: 100%; border: none;"> <tr> <td style="text-align: center; vertical-align: middle;"><u>for</u></td> <td style="text-align: center; vertical-align: middle;"> $\begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{OC}-\text{CH}_3 \\ \\ \text{HOCH} \\ \\ \text{CH}_3 \end{array}$ </td> <td style="text-align: center; vertical-align: middle;"><u>read</u></td> <td style="text-align: center; vertical-align: middle;"> $\begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{OC}-\text{CH}_3 \\ \\ \text{HOCH} \\ \\ \text{HOCH} \\ \\ \text{CH}_3 \end{array}$ </td> </tr> </table>	<u>for</u>	$ \begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{OC}-\text{CH}_3 \\ \\ \text{HOCH} \\ \\ \text{CH}_3 \end{array} $	<u>read</u>	$ \begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{OC}-\text{CH}_3 \\ \\ \text{HOCH} \\ \\ \text{HOCH} \\ \\ \text{CH}_3 \end{array} $
<u>for</u>	$ \begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{OC}-\text{CH}_3 \\ \\ \text{HOCH} \\ \\ \text{CH}_3 \end{array} $	<u>read</u>	$ \begin{array}{c} \text{CHO} \\ \\ \text{CH}_2 \\ \\ \text{CH}_3\text{OC}-\text{CH}_3 \\ \\ \text{HOCH} \\ \\ \text{HOCH} \\ \\ \text{CH}_3 \end{array} $			
54, 3 (1982)	681, Abstract, line 3	<u>for</u> TiO ₂ 1892±30 <u>read</u> TiO ₂ 1843±15 (in air) <u>for</u> ZnO ₂ 2710±25 <u>read</u> ZnO ₂ 2710±35				
54, 8 (1982)	1455, Table 1					
	(i) column -ΔH _h ^o for Hg ²⁺	<u>for</u> 1940 <u>read</u> 1845				
	(ii) footnote a to Table 1	<u>add</u> ΔH _h ^o of Hg ²⁺ has been misprinted in Ref. 19				
	1457, Table 2 column 1, last item	<u>for</u> BP ₄ ⁻ <u>read</u> BPh ₄ ⁻				
	1459, Table 3 column 1, 12th item	<u>for</u> Hg(l)/Hg ²⁺ <u>read</u> Hg(l)/Hg ₂ ²⁺				
54, 10 (1982)	1859, Eq.(14)	correct version is as follows:				

