Oxidation of Tertiary Amines by Chromium(VI) Oxide Diperoxide

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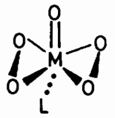
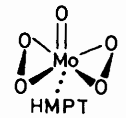
The oxidation of tertiary amines Et_3N and *p*-$MeOC_6H_4NMe_2$ (DMPA) by $(L)CrO(O_2)_2$ (**1″**) and by $(OPN_3Me_6)MoO(O_2)_2$ (**1′**) in $CHCl_3$ has been investigated. Although the amines are converted into the corresponding *N*-oxides in good (70–95%) yields in 2:1 stoicheiometry with respect to the peroxide, the oxidation of DMPA by (**1″**) also produces *p*-$MeOC_6H_4NHMe$. The rate law observed and the inhibitory effect of added OPN_3Me_6 (hexamethylphosphoric triamide) suggest a mechanism involving preliminary co-ordination of the amine to the metal; this is also supported by ^{31}P n.m.r. experiments. Comparison of the oxidation rates of the amines with those of organic sulphides, e.s.r. experiments, and the observed appreciable competitive dealkylation of DMPA, all point to a mechanism having some single-electron-transfer (SET) character.

In metal peroxide chemistry, few systems are as interesting and significant as those involving co-ordination of dioxygen to transition-metal ions.[1,2] Transition-metal peroxocomplexes of Groups IVb, Vb, and VIb are well known for their ability to afford selective oxidations of a variety of organic substrates.[1–3] Indeed, high-valent d^0 transition-metal peroxocomplexes (**1**) ('side-on') are believed to be involved as intermediates in many important processes of organic synthesis as well as in biological oxidations.[1–5] Although in recent years several careful investigations have tried to establish the oxidation mechanism by these species, some aspects of the peroxide oxygen-transfer step remain the object of debate.[1–3,6,7]


(**1**)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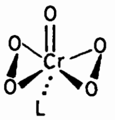
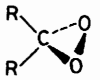
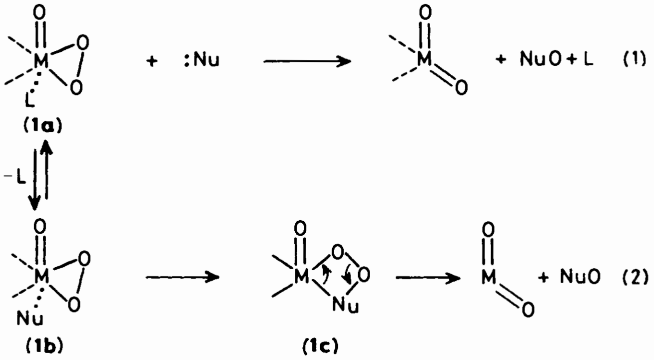

(**1″**)


(**2**)

(L = Me_6N_3PO, Ph_3PO)

In fact, akin to the mechanism well established for acyclic peroxides,[8] as well as for dioxiranes (**2**) (the three-membered ring carbon analogues of 'side-on' metal peroxides),[9] the most straightforward mechanism of oxidation by (**1**) would involve an S_N2-type displacement by the nucleophilic substrate at the peroxide O–O bond [Scheme 1, equation (1)].[1,2,7,8] Nucleophilic attack at the oxygen of the O–N bond has also been invoked for oxygen transfer to organic substrates from sulphonyloxaziridines.[10] As an alternative to this view, Mimoun was the first to propose a peroxymetallation mechanism that would involve first the co-ordination of substrate to the metal, then its insertion into the metal–oxygen bond to form a pseudocyclic intermediate (**1c**) [Scheme 1, equation (2)].[3]

In a previous paper, we reported on the oxidation of organic sulphides by the chromium(VI) and by molybdenum(VI) diperoxides (**1″**) and (**1′**), presenting stringent kinetic and spectroscopic evidence that militates against the Mimoun's mechanism.[1] On the road to explore the reactivity of chromium peroxides, we then turned our attention to the oxidation of tertiary amines by (**1″**), and, in comparison, by its molybdenum(VI) analogue (**1′**). The subject is of general interest since amine oxidation is a ubiquitous process which can be effected by a variety of chemical oxidants,[11,12] including peroxides,[13] as well as electrochemically,[14] photochemically,[15] and enzymatically.[16] To establish the mechanism of amine oxidation by metal peroxides was also challenging, since it represents one case where the Mimoun mechanism cannot hold. This, in fact, would involve formation of a pseudocycle (**1c**) encompassing a *pentacovalent* nitrogen (Nu = $R^1R^2R^3N$ in Scheme 1). We believe the kinetic, spectroscopic, and stoicheiometry data presented herein for the oxidation of tertiary amines are helpful in shedding further light into significant details of peroxidic oxygen transfer from metal peroxides to organic substrates.



Scheme 1.

Results and Discussion

Triethylamine and *N,N*-dimethyl-*p*-anisidine (DMPA) were chosen as model tertiary amine substrates to probe the reactivity of metal peroxocomplexes (**1′**) and (**1″**); the structure of these 'side-on' metal peroxides in solution has been the subject of several spectroscopic investigations,[1,3,17] including ^{17}O n.m.r. spectroscopy.[18]

Stoicheiometry experiments that were run in $CHCl_3$ or CH_2Cl_2 at 0–5 °C (to minimize peroxide decomposition)[1] demonstrated that (**1′**) and (**1″**) can convert the tertiary amines into the corresponding *N*-oxide in good (70–95%) yields according to the 1:2 stoicheiometry shown in equation (3).

Table 1. Representative rate constants for the oxidation of two tertiary amines by (HMPT)$CrO(O_2)_2$ in chloroform.

Substrate	T/°C	$[\text{peroxide}]_0$/ 10^{-3} mol dm^{-3}	$[\text{amine}]_0$/ 10^{-3} mol dm^{-3}	$[\text{HMPT}]_0{}^{a}$/ 10^{-3} mol dm^{-3}	$k_1{}^{b}/10^{-3}$ s^{-1}
None	+25	0.350			0.06[c]
Et_3N	+25	0.175	0.32		1.12[d,e]
	+25	0.175	0.48		1.60[d]
	+25	0.175	0.75		2.20[d]
	+25	0.175	2.20		4.30
	+25	(0.180)[f]	2.20		(5.20)[f]
	+25	0.175	11.0		8.30
	+25	0.175	11.0		(12.5)[g]
	+25	0.175	91.1		13.7
	+25	0.520	91.1		13.9
	+25	0.105	91.1		13.5[h]
	+25	0.175	4.4		5.40
	+25	0.175	4.4	42	5.00
	+25	0.175	4.4	50	4.75
	+25	0.175	4.4	65	4.50
	+25	0.175	4.4	116	4.20
	+25	0.175	4.4	223	3.35
	+25	0.175	4.4	468	1.98
DMPA	−5	1.90			1.42
	−5	1.90	27.5		1.95
	−5	3.80	80		2.05
	−5	1.90	80		2.10
	−5	1.90	100		2.15
	−5	1.80	150		1.80
	−5	1.80	48	50.5	0.60
	+10	1.60	48		3.92
	+10	1.60	19.5		4.10
	+10	1.60	27.0		5.00
	+10	1.60	88.0		5.10
			120		
	+25				(11.0 ± 0.6)[i]

[a] Initial concentration of added free ligand. [b] As estimated from pseudo-first order integrated plots, unless noted otherwise. [c] From first-order integrated plots.[1] [d] Estimated as $k_1 = (R_0/[\text{peroxide}]_0)$, with R_0 = initial rate as obtained from [peroxide]–time plots. [e] Assuming first order in the amine, this value allows one to estimate $k_2 = (k_1/[Et_3N]_0) \cong 3.5$ dm^3 mol^{-1} s^{-1}. [f] The peroxide complex $(Ph_3PO)CrO(O_2)_2$ was used as the oxidant instead than (HMPT)$CrO(O_2)_2$. [g] In the presence of 6×10^{-3} mol dm^{-3} DABCO (*cf.* ref. 1). [h] Run carried out under dry N_2. [i] Estimated from data at −5 and +10 °C of $k_{max.}$, yielding $E_a \cong 8.7$ kcal mol^{-1}.

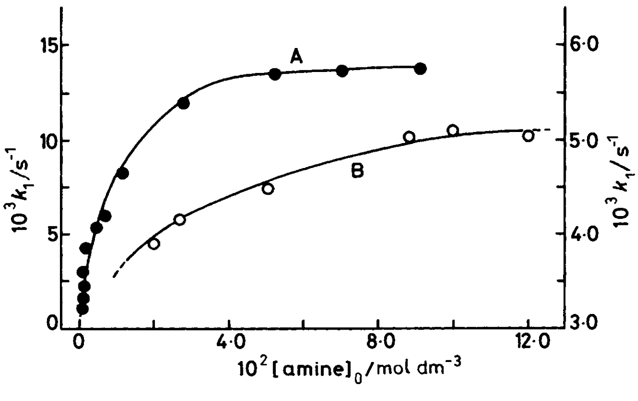


Figure 1. Variation of the pseudo-first-order rate constant of oxidation of Et_3N (curve A, left ordinate scale, T 25.0 °C) and of DMPA (curve B, right ordinate scale, T 10.0 °C) by (HMPT)-$CrO(O_2)_2$ in $CHCl_3$ with increasing initial substate concentration.

$$(L)MO(O_2)_2 + 2\,R^1R^2R^3N \longrightarrow MO_3 + 2\,R^1R^2R^3N^+\text{–}O^- + L \quad (3)$$

In the case of the chromium peroxocomplexes (**1**″), we find the reaction stoicheiometry (3) can be verified if the reaction is run with a six- to ten-fold excess of the amine over the peroxide and analysing the reaction mixtures at 65–80% conversion of peroxide. And this to avoid overlap with the incursion of side-reactions such as deoxygenation of the *N*-oxide at the expense of the metal.[19] Under these conditions, part of the *N*-oxide is formed as a $(R^1R^2R^3NO)MO_3$ complex, and the overall *N*-oxide produced is better determined by using h.p.l.c.

The yields in *N*-oxide were considerably higher (85–95%) for the conversion of Et_3N into $Et_3N^+\text{–}O^-$ than for the oxidation of DMPA; in the case of the aromatic amine, in fact, the *N*-oxide produced (yield 70–80%) was almost invariably accompanied by some *N*-methyl-*p*-anisidine by-product, in 18–5% yield. Thus, competitive with *N*-oxidation, oxidative dealkylation of the aromatic tertiary amine also takes place. No effort was made to optimize the yield of the dealkylation product.

Kinetics.—In the majority of cases reaction rates were determined under pseudo-first-order conditions, with the amine being in large excess over the metal peroxide. In the reaction of blue chromium(VI) oxide diperoxide (**1**″) with Et_3N, the disappearance of the peroxide was followed at 580 nm, according to a spectrophotometric technique already described.[1] In the reaction of (**1**″) with DMPA, formation of DMPA *N*-oxide (which is scarcely soluble in $CHCl_3$) prevented the spectrophotometric determination of the rate constants, so that the change of peroxide concentration with time was followed titrimetrically (iodometry).[1] Due to interference by the

Table 2. Representative rate constants for the oxidation of two tertiary amines by $(HMPT)MoO(O_2)_2$ in chloroform at 25.0 °C.

Substrate	$[\text{peroxide}]_0$/ 10^{-3} mol dm^{-3}	$[\text{amine}]_0$/ 10^{-3} mol dm^{-3}	$[\text{HMPT}]_0$[a]/ 10^{-3} mol dm^{-3}	k_1[b]/10^{-3} s^{-1}	k_2[c]/ 10^{-2} dm^3 mol^{-1} s^{-1}
None	1.50			<0.005	
Et_3N	1.10	15.0		1.38	9.2
	1.10	30.0		3.00	10
	1.10	114		9.10	(8.0)[d]
	1.10	210		10.8	(5.1)[d]
	3.50	210		10.6	(5.0)[d]
	1.10	76		6.40	(8.4)[d]
	1.10	76	180	3.05	
	1.10	76	365	1.95	
	1.10	76	545	1.40	
	1.10	76	725	1.02	
DMPA	3.05	53		0.51	
	4.05	53		0.53	
	4.05	210		3.00	
	4.05	300		3.20	

[a,b] See footnotes on Table 1. [c] Estimated as $k_1 = (k_2/[Et_3N]_0)$. [d] log k_1 *versus* log $[Et_3N]_0$ plots indicate a pronounced negative deviation from first order in the amine after $[Et_3N]_0 \cong 110 \times 10^{-3}$ mol dm^{-3}.

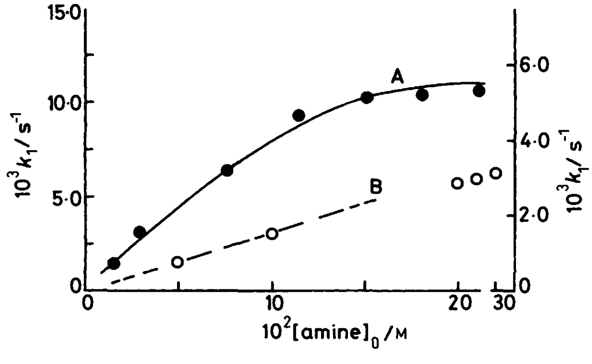


Figure 2. Variation of the pseudo-first-order rate of oxidation of Et_3N (curve **A**, left ordinate scale) and of DMPA (curve **B**, right ordinate scale) by $(HMPT)MoO(O_2)_2$ in $CHCl_3$ at 25 °C with increasing initial substrate concentration.

N-oxide produced, pseudo-first-order integrated plots were observed to be linear over the first 30–60% reaction only. Owing to the higher initial concentrations of reactants demanded by the titrimetric technique, DMPA oxidation by (**1″**) is a trifle too fast to be followed conveniently at 25 °C, so that kinetic runs were performed at −5 and +10 °C. The reaction of the molybdenum diperoxide (**1′**) with both amine substrates were also monitored titrimetrically.[1] Some rate data are collected in Tables 1 and 2, while a larger set of kinetic constants is reported in Figure 1 and 2; the Figures also serve to illustrate the particular trend of variation in rate constants with increasing initial concentration of the substrate.

Inspection of the rate data reveals that, in all of the cases examined, the order in peroxide is close to unity; the k_1 values in fact are practically independent of initial peroxide concentration. The kinetic order in amine, instead, appears to be less than unity, approaching zero at high substrate concentrations (Figures 1 and 2). For instance, in the case of oxidation of Et_3N by (**1″**), a plot of log k against log $[\text{amine}]_0$ gives an initial slope of *ca.* 0.8 that decreases steadily as the initial concentration of the substrate is increased, and becomes practically zero for Et_3N concentrations higher than *ca.* 5×10^{-2} mol dm^{-3}. The same trend is observed in the oxidation of Et_3N by the molybdenum peroxocomplex (**1′**), although in this case deviations from first order in the substrate become pronounced at higher amine concentrations, *i.e.* 0.2–0.4 mol dm^{-3}. The kinetic order in DMPA appears to be fractional and less than unity in the reaction with both metal peroxocomplexes (**1″**) and (**1′**) over the range of concentrations explored (Figure 1 and 2).

On the basis of a steady-state treatment of rates already discussed for the oxidation of sulphides by metal peroxides,[1] the kinetic behaviour observed in the present case (*i.e.*, kinetic order in the substrate changing from about one to zero, yielding a limiting $k_{\text{max.}}$ value at sufficiently high substrate concentrations), might be accommodated by a scheme involving co-ordination of the amine to the metal *prior* to peroxide oxygen transfer. Then, the rate law (4) should hold where HMPT is hexamethylphosphoric triamide.

$$R = -\frac{d[\text{peroxide}]_0}{dt} = \frac{(k_{\text{II}}/2)\,[\text{amine}]_0\,[\text{peroxide}]}{(1/K_e)\,[\text{HMPT}]_0 + [\text{amine}]_0} \qquad (4)$$

In equation (4), K_e relates to the equilibrium constant for ligand displacement by the amine and $(k_{\text{II}}/2)$ is the limiting rate attained at sufficiently high substrate concentration, so that $[\text{amine}]_0 \gg (1/K_e)[\text{HMPT}]_0$.

The rate law (4) predicts inhibition of rates by excess of HMPT, which was indeed observed (Tables 1 and 2). The observed pseudo-first-order rate constant values $k_1^{\text{obs.}}$ should be related to the concentration of excess of ligand HMPT as in equation (5).[1]

$$(1/k_1^{\text{obs.}}) = \{[\text{HMPT}]_0/(k_{\text{II}}/2)K_e[\text{amine}]_0\} + [1/(k_{\text{II}}/2)] \qquad (5)$$

For the oxidation of Et_3N by (**1″**) at 25 °C, at constant $[Et_3N]_0$ 4.4×10^{-3} mol dm^{-3}, but varying the excess of HMPT from 0.04 to 0.47 mol dm^{-3} (Table 1), a linear plot of $(1/k_1)$ *vs.* $[\text{HMPT}]_0$ could be obtained; this allows one to calculate, from the values of intercept and slope, $(k_{\text{II}}/2)$ $(6 \pm 2) \times 10^{-3}$ s^{-1} and K_e $(1.4 \pm 0.4) \times 10^{-3}$. For the oxidation of Et_3N by the molybdenum peroxocomplex (**1′**) at 25 °C, a similar treatment of the kinetic data collected at constant amine initial concentration with varying excess HMPT (Table 2) yields $(k_{\text{II}}/2) \cong (1.1 \pm 0.2) \times 10^{-2}$ s^{-1} and $K_e \cong 1.05 \pm 0.2$.

In order to compare the reactivity of the metal peroxides at hand with that of non-metal peroxides in the same solvent, we have also measured the oxidation rates of Et_3N by bis-

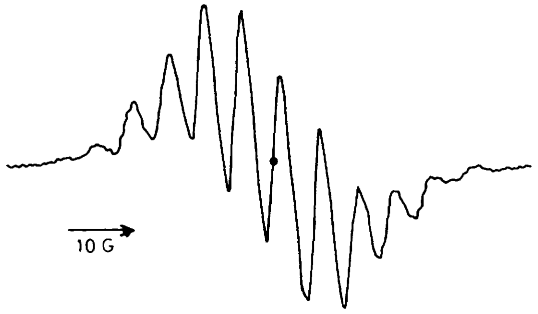


Figure 3. E.s.r. spectrum of the transient radical species arising in the reaction of *ca.* 0.1 mol dm^{-3} DMPA with *ca.* 0.035 mol dm^{-3} (HMPT)$CrO(O_2)_2$ in $CHCl_3$-MeCN, after mixing under vacuum at 263 K (microwave frequency 9.50 GHz); the dot marks the centre of the spectrum.

(trimethylsilyl)peroxide[20] and by *m*-chloroperbenzoic acid (MCPBA). These organic peroxides were chosen because they yield an uncomplicated rate law in $CHCl_3$,[8,20] an overall second-order (first-order each in the peroxide and Et_3N) rate law was found to hold, yielding k_2 7.3 × 10^{-4} dm^3 mol^{-1} s^{-1} for the reaction of Et_3N with $Me_3SiOOSiMe_3$ at 25 °C. The reaction of the amine with MCPBA was too fast to follow titrimetrically at 25 °C; thus, kinetic runs had to be performed at low temperatures by taking just a few points, which led to a rough estimate of rate constants as $k_2 \cong 2.4 \times 10^2$ dm^3 mol^{-1} s^{-1} at −23.5 °C and 3.2 × 10^2 dm^3 mol^{-1} s^{-1} at −10.1 °C. Based on these values, the rate constant for Et_3N oxidation by MCPBA in $CHCl_3$ at 25 °C should be roughly of the order of 6 × 10^2 dm^3 mol^{-1} s^{-1}.

Spectroscopy Experiments.—By using a combination of spectroscopic techniques, useful hints were obtained concerning reaction mechanisms. We have already reported that equilibria such as (HMPT)$CrO(O_2)_2 \rightleftharpoons CrO(O_2)_2$ + HMPT can be conveniently monitored by ^{31}P n.m.r. spectroscopy since distinct ^{31}P signals are found for both bound and free ligand HMPT, respectively, at δ 36.9 and 26.8 p.p.m.[1] At −13 °C, with *ca.* 0.6 × 10^{-3} mol dm^{-3} (HMPT)$CrO(O_2)_2$ initial concentration, these integrate roughly in the ratio 1.5:1; addition of 0.4 × 10^{-3} mol dm^{-3} Et_3N results in considerable enhancement of the signal for free HMPT, with an integration ratio close to *ca.* 0.3:1 after 60–90 s. This strongly suggests co-ordination of the amine to the metal by displacement of HMPT.[1] Attempts to run similar n.m.r. experiments by using DMPA instead of Et_3N gave poor results due to significant broadening of ^{31}P signals upon addition of the aromatic amine to solutions of (**1″**) in chloroform.

Electronic spectra also suggest preliminary co-ordination of the amine to the metal. As an example, the well defined maximum of (**1″**) (L = HMPT) at 580 nm (0.2 × 10^{-3} mol dm^{-3} in $CHCl_3$) can be observed to undergo a rapid blue-shift to *ca.* 568 nm upon addition of DMPA in moderate excess (1 × 10^{-3} mol dm^{-3}), and this before any significant amine oxidation occurs.

That organic radicals are generated in the reaction is supported by e.s.r. experiments. In fact, addition of DMPA to (**1″**), in degassed solvent at low temperatures, allows the spectrum in Figure 3 to be observed;* under the given conditions the e.s.r. signals (*a* 6.7 G) vanish 10–15 min after mixing.

Although the observed e.s.r. spectrum is poorly resolved, it bears much resemblance to that of *NNN′*-trimethyl-*N′*-(4-methoxyphenyl)-1,4-phenylendiamine radical cation arising from single-electron-transfer (SET) oxidation of DMPA with $Tl(OAc)_3$.[22] The radical species might be envisaged to result from nucleophilic attack on DMPA$^{+\bullet}$ by *p*-$MeOC_6H_4NHMe$ (the primary dealkylation product).[16,21,23]

Reaction Mechanisms.—Table 3 collects a summary of rate data to focus on the relevant features of a tertiary amine oxidation by metal peroxides by comparison with oxidation of sulphides.

In order to propose a reasonable mechanism, the following points need to be taken into account.

(*i*) In oxidations by $Me_3SiOOSiMe_3$ (an organic peroxide serving as a convenient reference)[20] the reactivity order observed is that expected on the basis of straightforward nucleophilic attack by the substrate at the peroxide O–O bond,[8] *i.e.* DMPA $\ll$ Et_3N < sulphide; this is in line with the higher reactivity of sulphur with respect to nitrogen nucleophiles. We have also estimated that the ratio $k_2(Bu^n{}_2S)/k_2(Et_3N)$ should be close to 2.5 for oxidation by MCPBA (a reactive, rather unselective, electrophilic oxidant).[8]

(*ii*) For molybdenum(VI) oxide diperoxide (**1′**), sulphide oxidation is considerably faster than amine oxidation, *e.g.* $k_2(Bu^n{}_2S)/k_2(Et_3N) \cong 10^{-2}$.

(*iii*) In the case of oxidations by the chromium diperoxide complex (**1″**), contrary to predictions based on substrate nucleophilicity, one finds $Et_3N > Bu^n{}_2S$.

(*iv*) Based on k_2 values listed in Table 3, oxidation of Et_3N by the chromium peroxide is more effective than by $MoO(O_2)_2$, which is the exact opposite to $Bu^n{}_2S$ oxidation.

(*v*) At variance with observations for the oxidation of organic sulphides by (**1″**) and (**1′**), in this case there is ample kinetic, as well as spectroscopic, evidence that tertiary amines yield rapid co-ordination at the metal centre of (**1″**) and of (**1′**) by displacement of HMPT ligand, although with different equilibrium constants (*i.e.*, $K_e \cong 10^3$ and $\cong 1$, respectively); the $k_{1\,\text{max.}}$ values should be related to the reactivity of the (amine)$MO(O_2)_2$ complexes which evolve into the observed oxidation products. Inspection of the data in Table 3 reveals that the limiting rate values for Et_3N and DMPA oxidation by the chromium peroxocomplex are quite close.

Our observations cannot be accommodated within a single reaction mechanism. It is obvious that more than one path should be available for metal peroxocomplexes and electron-donor substrates to evolve into the observed products. This is also suggested by the observation of oxidative dealkylation of DMPA in competition with *N*-oxidation in the reaction with (**1″**) (see above). In this case, radical species deriving from DMPA$^{+\bullet}$ could also be revealed by e.s.r. spectroscopy.

In recent years, a number of peroxide reactions once thought to occur *via* purely ionic paths have been shown to involve, at least in part, SET processes[13,24,25] and new, clear-cut cases are being continuously presented.[26] Factors governing SET *versus* polar pathways have been reviewed by Pross,[24] and, largely due to the investigations by Kochi and his co-workers,[2,26] the impact of SET mechanism in organometallic chemistry has been extensive. We have already pointed out that transition-metal peroxides are obvious candidates for SET processes with suitable electron-donor partners,[6] and systems envisaging such a mechanistic approach have been reported.[28]

A somewhat simplified outline of oxidative pathways available for the reaction of simple electron-donor substrates with 'side-on' transition-metal peroxocomplexes is presented in Scheme 2. Here, just one of the two peroxide moieties is drawn, for clarity; this, however, would involve the questionable assumption that, with effective electron-donors, there is no

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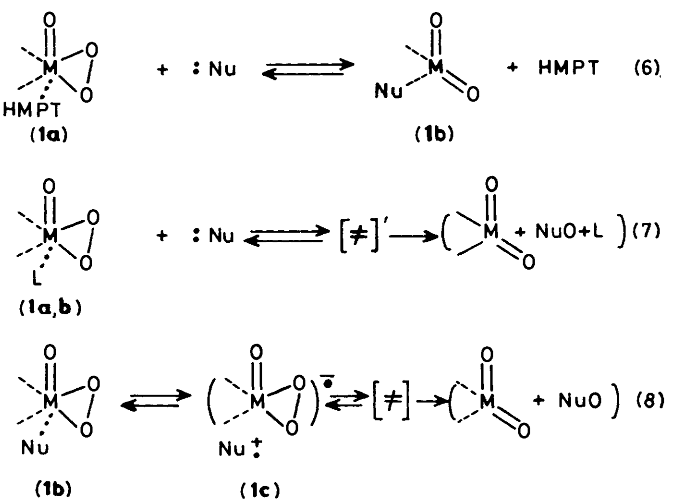
* In monitoring the reaction between DMPA and (HMPT)$CrO(O_2)_2$, in addition to the signal at $\langle g \rangle$ 2.0027 (Figure 3), another signal centred at $\langle g \rangle$ 1.972 (with splitting *a* 20.5 G) could also be detected; this can be tentatively attributed to Cr^V (*cf.*, *I* 3/2 for ^{53}Cr in 9.55% natural abundance).[21]

Table 3. Rates of oxidation of some nucleophilic organic substrates by chromium(VI) and molybdenum(VI) oxide diperoxide as compared to a reference organic peroxide in chloroform at 25.0 °.

		$(L)CrO(O_2)_2$[a]	$(L)MoO(O_2)_2$[a]	$Me_3SiOOSiMe_3$
DMPA	$k_{1\,max.}/10^{-3}$ s^{-1}	11	3.2	
	$k_2/10^{-2}$ dm^3 mol^{-1} s^{-1}	*b*	*b*	0.034×10^{-2}[c]
Et_3N	$k_{1\,max.}/10^{-2}$ s^{-1}	13.9	10.8	
	$k_2/10^{-2}$ dm^3 mol^{-1} s^{-1}	350	10	7.3×10^{-2}
$Bu^n{}_2S$	$k_2/10^{-2}$ dm^3 mol^{-1} s^{-1}	50[f]	1 150[f]	24.0×10^{-2}[c–e]

[a] In all cases, L = HMPT in the metal peroxide complexes which are precursors of the reactive species. [b] Second-order rate constants could not be estimated in this case owing to a kinetic order < 1 in the substrate (see text). [c] Data from ref. 20. [d] Rate constant value refers to substrate thioxane. [e] The oxidation rate of $Bu^n{}_2S$ by MCPBA in $CHCl_3$ at 25.0 °C was roughly estimated as $k_2 \cong 1\,500$ l mol^{-1} s^{-1}. [f] Data from ref. 1.



Scheme 2.

significant difference in reactivity of diperoxide species (**1**) with respect to that of their first-reduction product $MO_2(O)_2$.[1–3,6,7] Neglecting apical co-ordination or formation of (Nu)(HMPT)-$MO(O_2)_2$ complexes, in equation (6) amine co-ordination to the metal is envisaged to occur in the equatorial plane containing the O–O bond in order to meet the stereoelectronic requirements for subsequent O–O oxygen transfer.[29,30] The latter is schematized in equation (7) and amounts to nucleophilic attack at the O–O bond, as in the electrophilic oxidation of donor substrates by a variety of simple and complex peroxides;[1,2,7,8] reaction products are shown in parentheses since both the amine and the *N*-oxide formed might be involved in complexation equilibria with the reduced metal peroxide, *i.e.* MO_3. Competitive s.e.t. pathways can be summarized as in equation (8).

Here, a key feature is the formation of a distinct pair of oppositely charged radical ions (**1c**); in essence, the pattern is similar to a general one envisaging preliminary formation of an 'encounter complex' between an acceptor A and a given donor D, *i.e.* $D + A \rightleftharpoons D\cdots A \rightleftharpoons D^{+\bullet}\cdots{}^{-\bullet}A \rightleftharpoons$ products.[24,25] Based on gas-phase ionization potentials, the formation of a pair of radical ions should be more favoured for amines than for sulphides (*cf. I* 8.43, 7.50, and 7.12 eV for Et_2S, Et_2N, and $PhNMe_2$, respectively).[31] Then, in order to estimate the free-energy change associated with the net electron-transfer in the present case, one would need electron-affinities or solution-phase reduction potentials of the metal peroxide complexes; to our knowledge, these data are not available for (**1″**) and (**1′**). However, a value of $E_{\frac{1}{2}}$ −0.09 V. has been reported by Kadish *et al.* for the reversible first reduction potential of $(TmTP)Mo(O_2)_2$ in CH_2Cl_2.[32] By coupling this value with $E_{\frac{1}{2}}$ +0.42 V. for DMPA $\longrightarrow$ $DMPA^{+\bullet}$ (in MeOH–water),[15b] and arbitrarily neglecting solvent change and the Coulombic attraction term in the Weller equation,[33] one comes out with an estimate of ΔG° *ca.* 7.5 kcal mol^{-1} for the reversible SET $DMPA + MoO(O_2)_2 \rightleftharpoons DMPA^{+\bullet} + MoO(O_2)_2{}^{-\bullet}$. Thus, the process is only modestly endergonic; however, for both the molybdenum and the chromium peroxocomplex, the group transfer required to yield products from (**1c**) should make the process in equation (8) exergonic as a whole.[24,34]

One might even speculate that some major reorganization of the pair (**1c**) should occur during its evolution into products. One possibility involves the rupture of the metal–oxygen bond, as in Scheme 3.

It is interesting that with the aromatic amine DMPA, radical delocalization should provide extra stabilization and an increased lifetime of the radical-cation–radical-anion pair; then, some leakage from (**1c** or **d**) might be expected to occur, giving rise to radical pathways such as amine oxidative dealkylation.[13c] This was indeed observed in one case.

It was pointed out that the detection of e.s.r.-active intermediates and the observation of radical pathway products cannot be taken *per se* as proof of an SET mechanism;[13c] in fact, this may not reflect the transition state (t.s.) for the given reaction. On the other hand, the t.s. for direct nucleophilic attack at the O–O bond of the metal peroxide [$(\neq)'$, equation (7)] might itself assume significant SET character,[13c,26b] and the possibility of having a polar–SET mechanistic spectrum is recognized.[24] In oxidations by metal peroxides borderline cases are expected because, with easily reducible transition-metal complexes and with more electron-donating substrates, the mechanism could shift from S_N2-like [equation (7)] to marked S.E.T. character [equation (8)]. Since the dichotomy here advanced might have a number of significant implications in the rationalization of the reactivity of 'side-on' metal peroxocomplexes,* further work is warranted to test its general applicability.

Experimental

B.p.s and m.p.s are not corrected. The n.m.r. spectra were run

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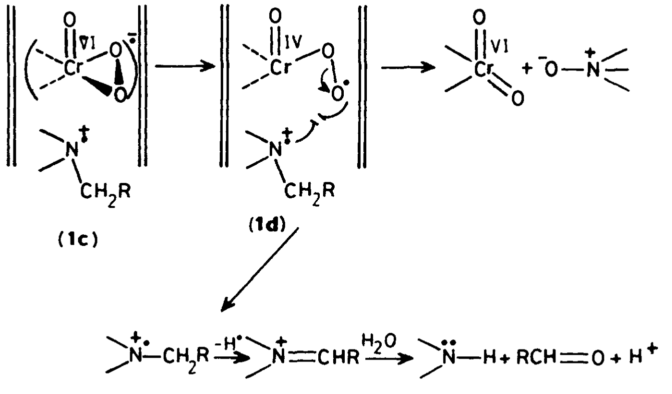
* We have remarked that Mimoun's peroxometallacycle mechanism[3] cannot apply to the oxidation of tertiary amines. In a possible generalization of the process outlined in Scheme 3, however, during oxidation of suitable alkenes or ketones with (**1**) the reorganized pair (**1c**) may also collapse to yield peroxometallacycles;[2,3] here, the case of formation of radical ions pairs should be a key factor (for the occurrence of SET processes in the reaction of alkenes with transition-metal oxides, see, *e.g.* ref. 35). The breaking of the peroxide  $\left(M\begin{smallmatrix}O\\ |\\ O\end{smallmatrix}\right)^{-\bullet} \rightleftharpoons \left(M\begin{smallmatrix}O^-\\ \\ O^\bullet\end{smallmatrix}\right)$ bond on the other hand, might open the path to the formation of insertion products.[2]



Scheme 3.

on a Varian XL-200 (^{1}H, 200 MHz; ^{31}P, 80.96 MHz) instrument; e.s.r. experiments were performed on a Varian E109 instrument. The u.v.-visible and i.r. spectra were taken on a Varian DMS (or Perkin-Elmer 555) spectrophotometer and on a Perkin-Elmer 681 instrument, respectively. The g.l.c. analyses were performed on a capillary-column Dani 3800 chromatograph; analytical h.p.l.c. was carried out by using a Perkin-Elmer 3B instrument, with LC-85B detector and autocontrol.

Materials.—The synthesis and characterization of (HMPT)-$CrO(O_2)_2$ (**1″**) and of (HMPT)$MoO(O_2)_2$ (**1′**) have been described:[1,18] (Ph_3PO)$CrO(O_2)_2$ was obtained as reported by Mimoun *et al.*[17] The syntheses of bis(trimethylsilyl)peroxide, *N*,*N*-dimethyl-*p*-anisidine (DMPA), and of dimethyl-(*p*-methoxyphenyl)amine oxide have been described.[20] Triethylamine oxide was obtained by following a literature procedure as a deliquescent, highly hygroscopic material:[36] $\nu_{max.}$(Nujol) 1 270 and 952 (N–O) cm^{-1};[37] it was characterized by its picrate adduct, m.p. 164 °C (lit.,[38] 165 °C). Bis(triethylamine oxido)-chromium trioxide was prepared by reaction of CrO_3 (5 mmol) with excess of Et_3NO (25 mmol) in dry chloroform at 0–5 °C, with stirring (30 min); removal of the solvent *in vacuo* and washing of the brown-red residue with dry Et_2O afforded a microcrystalline solid, m.p. 101–103 °C; $\nu_{max.}$(Nujol) 1 200 and 945 cm^{-1} (N–O $\cdots$ Cr); δ($CDCl_3$, Me_4Si) 3.30 (2 H, br q, *J* 7 Hz) and 1.40 (3 H, br t, *J* 7 Hz). Commercial (Aldrich) *N*-methyl-*p*-anisidine, *m*-chloroperbenzoic acid, and other materials and solvents were purified by following standard procedures.[1]

Stoicheiometry.—The stoicheiometry in equation (3) was determined by reacting (**1″**) or (**1′**) (0.2–0.4 mmol; iodometric titre) with excess (2.4–8.0 mmol) Et_3N or DMPA in $CHCl_3$ or CH_2Cl_2 (15–30 cm^3) at 0–5 °C. After 60–90% reaction (iodometric titre), the residual amine was determined by g.l.c. (0.25 μm SE-30, 30 m × 0.25 mm i.d. capillary column) by the internal standard method; the amount of *N*-oxide produced was estimated by using reverse-phase h.p.lc. (10 μm C-18, 25 cm × 4.6 mm i.d. analytical column, MeCN–water 3:2 mobile phase). The yields of triethylamine *N*-oxide were obtained from the concentrations of free Et_3NO and bonded $(Et_3NO)_2CrO_3$. In the case of DMPA oxidations, the amount of *N*-methyl-*p*-anisidine by-product was determined by g.l.c.

Kinetics.—The spectrophotometric and titrimetric techniques adopted, as well as details concerning kinetic runs using metal peroxocomplexes (**1′**) and (**1″**), have been described previously.[1] Due to the general difficulties met with amine oxidation, the rate constants appearing in Tables 1 and 2 might be affected, in some instance, by an error as large as ±30%. The rate constants for amine oxidation by MCPBA should be taken as very rough estimates since the titrimetric technique adopted is not best suited to follow these fast reactions.

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References

1 R. Curci, S. Giannattasio, O. Sciacovelli, and L. Troisi, *Tetrahedron*, 1984, **40**, 2763 and references therein.
2 R. A. Sheldon and J. K. Kochi, 'Metal Catalyzed Oxidations of Organic Compounds,' Academic Press, New York, 1981 and references therein.
3 (*a*) H. Mimoun, in 'The Chemistry of Peroxides,' ed. S. Patai, Wiley-Interscience, New York, 1983, ch. 15, pp. 463–482; (*b*) *Angew. Chem., Int. Ed. Engl.*, 1982, **21**, 734.
4 J. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 280.
5 (*a*) R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, 1979, **79**, 139; (*b*) T. Matsuura, *Tetrahedron*, 1977, **33**, 2869.
6 R. Curci, G. Fusco, O. Sciavovelli, and L. Troisi, presented at the International Symposium on Activation of Dioxygen and Homogeneous Catalytic Oxidations, Galzignano, 1984; Abstracts L9, 33; SET oxidations involving metal peroxocomplexes were reported there for the first time.
7 F. Di Furia and G. Modena, *Pure Appl. Chem.*, 1982, **54**, 1853.
8 R. Curci and J. O. Edwards, in 'Organic Peroxides,' ed. D. Swern, Wiley-Interscience, New York, 1970, vol. 1, pp. 199–264.
9 L. Cassidei, M. Fiorentino, R. Mello, O. Sciacovelli, and R. Curci, *J. Org. Chem.*, 1987, **52**, 699; see also references to previous articles.
10 F. A. Davies, M. E. Harakal, and S. B. Awad, *J. Am. Chem. Soc.*, 1983, **105**, 3123.
11 (*a*) A. J. Sisti and S. R. Milstein, *J. Org. Chem.*, 1974, **39**, 3932; (*b*) E. F. Pratt and T. P. McGovern, *ibid.*, 1964, **29**, 1540; (*c*) J. R. Lindsay Smith and L. A. V. Mead, *J. Chem. Soc., Perkin Trans. 2*, 1973, 206.
12 Y. L. Chow, W. C. Danen, S. F. Nelsen, and D. H. Rosenblatt, *Chem. Rev.*, 1978, **78**, 243.
13 (*a*) D. G. Pobedimskii, *Russ. Chem. Rev.*, 1971, **40**, 142; (*b*) R. W. R. Humphrey, *J. Org. Chem.*, 1983, **48**, 1483; (*c*) W. A. Pryor and W. H. Hendrickson, *J. Am. Chem. Soc.*, 1983, **105**, 7114; (*d*) R. W. Hoffmann and R. Cadena, *ibid.*, 1977, **99**, 8226; (*e*) Y. Ogata, K. Tomizawa, and T. Morikawa, *J. Org. Chem.*, 1979, **44**, 352.
14 (*a*) J. R. Lindsay Smith and D. Masheder, *J. Chem. Soc., Perkin Trans. 2*, 1976, 47; (*b*) P. J. Smith and C. L. Mann, *J. Org. Chem.*, 1969, **34**, 1821.
15 (*a*) F. D. Lewis, T.-I. Ho, and J. T. Simpson, *J. Org. Chem.*, 1981, **46**, 1077; (*b*) I. Saito, T. Matsuura, and K. Inoue, *J. Am. Chem. Soc.*, 1983, **105**, 3200.
16 B. Kalyanaraman and K. Sivarajah, in 'Free Radicals in Biology,' ed. W. A. Pryor, Academic Press, New York, 1984, vol. 6, pp. 149–198.
17 E. Daire, H. Mimoun, and L. Saussine, *Nouv. J. Chim.*, 1984, **8**, 271.
18 R. Curci, G. Fusco, O. Sciavovelli, and L. Troisi, *J. Mol. Catal.*, 1985, **32**, 251.
19 See *e.g.* (*a*) L. T. Burka, F. P. Guengerich, R. J. Willard, and T. L. McDonald, *J. Am. Chem. Soc.*, 1985, **107**, 2549; (*b*) P. Shannon and T. C. Bruice, *ibid.*, 1981, **103**, 4580; (*c*) W.-H. Wong, D. Ostovic, and T. C. Bruice, *ibid.*, 1987, **109**, 3428; see also references to previous articles.
20 R. Curci, R. Mello, and L. Troisi, *Tetrahedron*, 1986, **42**, 877.
21 F. Ciminale, R. Curci, and L. Troisi, unpublished results.
22 F. Ciminale, R. Curci, M. Portacci, and L. Troisi, *Tetrahedron Lett.*, 1988, **29**, 2463.
23 R. N. Adams, *Acc. Chem. Res.*, 1969, **2**, 175.
24 A. Pross, *Acc. Chem. Res.*, 1985, **18**, 212.

25 (*a*) C. Walling, *J. Am. Chem. Soc.*, 1980, **102**, 6855; G. B. Schuster; (*b*) *ibid.*, 1979, **101**, 5851; (*c*) *Acc. Chem. Res.*, 1979, **12**, 366.

26 See, *e.g.* (*a*) R. E. Ball, A. Chako, J. O. Edwards, and G. Levy, *Inorg. Chim. Acta*, 1985, **99**, 49; (*b*) A. E. Miller, J. J. Bischoff, C. Bizub, P. Luminoso, and S. Smiley, *J. Am. Chem. Soc.*, 1986, **108**, 7773; (*c*) S. Oae, Y. Watanabe, and K. Fujimori, *Tetrahedron Lett.*, 1982, **23**, 1189; (*d*) K. G. Taylor and S. Nuggehalli, presented at the 194th ACS National Meeting, New Orleans, 1987, Abstracts, ORGN 14.

27 (*a*) K. Srinivasan, P. Michaud, and J. K. Kochi, *J. Am. Chem. Soc.*, 1986, **108**, 2303; (*b*) E. G. Samsel, K. Srinivasan, and J. K. Kochi, *ibid.*, 1985, **107**, 7606; see also references to previous papers.

28 O. Bortolini, V. Conte, F. Di Furia, and G. Modena, *Nouv. J. Chim.*, 1985, **9**, 147.

29 R. D. Bach, G. J. Wolber, and B. A. Coddens, *J. Am. Chem. Soc.*, 1984, **106**, 6098.

30 K. J. Jørgensen and R. Hoffmann, *Acta Chem. Scand., Ser. B.*, 1986, **40**, 411.

31 R. G. Pearson, *J. Am. Chem. Soc.*, 1986, **108**, 6109.

32 K. M. Kadish, D. Chang, T. Malinski, and H. Ledon, *Inorg. Chem.*, 1983, **22**, 3492.

33 D. Rehm and A. Weller, *Isr. J. Chem.*, 1970, **8**, 259.

34 D. P. Riley and P. E. Correa, *J. Org. Chem.*, 1985, **50**, 1563.

35 T. G. Traylor and A. R. Miksztal, *J. Am. Chem. Soc.*, 1987, **109**, 2770.

36 V. N. Below and K. K. Savich, *Zh. Obshch. Khim.*, 1947, **17**, 257.

37 S. H. Hunter, V. M. Langford, G. A. Rodley, and C. T. Wilkins, *J. Chem. Soc., A*, 1968, 305.

38 W. Strecker and M. Baltes, *Chem. Ber.*, 1921, **54**, 2693.

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