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MECHANISMS OF PEROXIDIC OXYGEN TRANSFER TO ORGANIC SUBSTRATES

OXIDATION OF ORGANIC SULPHIDES BY CHROMIUM(VI)OXIDE DIPEROXIDE

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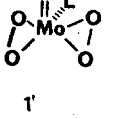
Abstract—The oxidation of organic sulphides (n-Bu_2S, $PhSCH_3$, Tolyl-SCH_3, p-$Cl\cdot C_6H_4SCH_3$, and Ph_2S) by $(HMPT)CrO(O_2)_2$ **1″** in $CHCl_3$ has been studied. The reaction produces the corresponding sulphoxides in nearly quantitative yields according to a 2:1 stoichiometry of sulphide to metaldiperoxide. A second-order-overall (order one in each of the reagents) kinetic law is obeyed. In parallel, the oxidation of organic sulphides by $(HMPT)MoO(O_2)_2$ **1′** has been studied. Kinetic data, the observed rate laws, and the effect of inhibitors (HMPT, DABCO) have pointed out that-although **1′** is significantly more reactive than **1″**—considerable similarity exists between the two metaldiperoxides, in that both appear to act as electrophilic oxidizers. Also, through ^1H, ^{31}P and ^{13}C NMR investigations have permitted to assess the relevance of equilibria $(HMPT)MO(O_2)_2 \rightleftharpoons MO(O_2)_2 + HMPT$ [with M = Mo(VI) or Cr(VI)] in solution, whereas no NMR evidence could be found for significant substrate coordination under the given conditions.

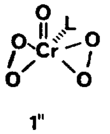
The crucial role played by transition metals in both industrial and biochemical processes involving molecular oxygen and/or hydrogen peroxide makes studies on the reactivity of metal–dioxygen complexes particularly relevant.[1] Several authors have claimed that η^2-dioxygen transition metal complexes ("side-on" metal peroxides) of Mo(VI), V(V), W(VI) and Ti(IV) are generated *in situ* during epoxidation of olefins using hydrogen peroxide and catalytic quantities of salts (or complexes) of these metals;[1-3] This implies that such peroxometal species may act as key intermediates in a whole family of catalitic oxidations.[1,4]

Mimoun *et al.* reported on the significant finding that molybdenum(VI)oxide diperoxide complexes such as **1′** can stoicheiometrically epoxidize olefins under anhydrous conditions in poorly coordinating organic solvents.[5] Since then kinetic studies on the oxidation of olefins, as well as of other organic substrates, by molybdenum(VI)oxide diperoxide species have proliferated[6-8]

Using ^{18}O-labeling techniques, Sharpless *et al.* demonstrated that the peroxo-oxygen of **1′** is exclusively transferred to olefins, the oxo-oxygen never being involved in the oxidation.[9] Apart from this feature, there has been considerable debate as to whether the reaction mechanism involves a direct attack of the organic substrate (an olefin, in the case at hand) at the peroxo-metal O–O bond or, rather, a sequence is followed which features the preliminary, rate-determining, coordination of the substrate to the metal.[1-3] In the latter case, the reaction would proceed through a nucleophilic attack by the coordinated oxygen to the substrate, thus forming a peroxometallacycle (five-membered, in the case of olefins); this, in turn, would then decompose by 1,3-di-polar cycloreversion, yielding the metal oxide and the oxidized substrate.[2]



1′



1″

With this in mind, we decided to explore the reactivity of chromium(VI)oxide diperoxide complexes **1″**. It is well established that aquochromium(VI)oxide diperoxide is readily formed when hydrogen peroxide is added to acidified solutions of dichromate or CrO_3; the significant equilibrium is:[10,11]

$$HCrO_4^- + 2H_2O_2 + H^+ \rightleftarrows H_2O\cdot CrO_5 + 2H_2O. \quad (1)$$

The equation above has a high equilibrium constant (K_f is of the order of $10^7\,M^{-3}$ at 25°), and the rate constant for the formation of $CrO_5(aq)$ is of the order of $10^3\,M^{-1}\,s^{-1}$ near pH 3.[10]

In aqueous solution, the blue peroxometal compound decomposes readily, and in a complex manner, to aquo chromium(III) species; however, it may be stabilized by extraction in complexing organic solvents (e.g. Et_2O) or by conversion to unstable solid complexes of nitrogen bases, like pyridine ($Py\cdot CrO_5$), 1,10-phenanthroline ($phen\cdot CrO_5$), or 2,2′-bipyridyl.[12,13] The X-ray analysis of these complexes has shown the close structural similarity of $L\cdot CrO(O_2)_2$ **1″** with analogous $L\cdot MoO(O_2)_2$ complexes.[2,14] For both peroxometal complexes a second coordination bond is considered weak and not essential, in that it is brought about with bidentate ligands only.

Although a number of chromium(VI) compounds find application in organic synthesis, just a few studies have appeared on the reactivity of $CrO(O_2)_2$ toward organic compounds. It was shown that alcohols can be oxidized to the corresponding carbonyl compounds, in high yield, by $Py\cdot CrO(O_2)_2$ in CH_2Cl_2.[15] Also, the possible involvement of singlet oxygen was hinted at in the reaction of $Et_2O\cdot CrO(O_2)_2$ with tetracyclone.[16]

Taking the view that organic sulphides are useful

Table 1. Comparison of spectroscopic data for hexamethylphosphorictriamide as a free species and as a ligand in chromium(VI)- and molybdenum(VI)-oxo diperoxo complexes in $CHCl_3$ (or $CDCl_3$)

Compound	temp. C	^1H NMR,[a] $\delta(C\underline{H}_3)$ (ppm)[b]	^{31}P NMR,[c] δ(ppm)[d]	^{13}C NMR $\delta(\underline{C}H_3)$,ppm	IR,[e] $\tilde{\nu}(cm^{-1})$
$[(CH_3)_2N]_3P{=}O \equiv$ HMPT	20°	2.64	28.2		1170(P=O)
	"				[1210(P=O)]
	-10°	2.65	26.8		
	-20°			36.86[f]	
$HMPT{\cdot}CrO(O_2)_2$	20°	2.82	35.30		1100(P=O)
	"				949.910(O-O)[g]
	-20°			37.12[f]	
$HMPT{\cdot}MoO(O_2)_2$	20°	2.79	34.12		[1190(P=O)]
	"				[875.865(O-O)]
	-10°	2.77	34.15		

[a] Me_4Si internal standard. [b] Doublet (1:1), with $J_{HCN^{31}P}$=9.4-9.7 hz. [c] 85% H_3PO_4 external standard. [d] Singlet, with ^1H noise decoupling. [e] Data in square brackets refer to spectra taken in nujol (see also ref. 14). [f] $J_{^{13}CP}$=3.9-3.8 Hz. [g] Cfr. also ref. 19 for IR spectral characteristics of $Py{\cdot}CrO(O_2)_2$ and $Bipy{\cdot}CrO(O_2)_2$.

model substrates to investigate the general features of nucleophilic attack at the O–O bond,[17] including "metal-ion-activated" peroxide bonds,[18] we undertook the present study on the reactivity of chromium(VI)oxide peroxide in organic solvents. We decided to begin by obtaining $HMPT{\cdot}CrO(O_2)_2$ (in 1″, L = HMPT) in order to be able to investigate, in parallel, the reactivity of the Mimoun's metal-peroxide 1′ toward the same substrates.

RESULTS AND DISCUSSIONS

Hexamethylphosphoramido molybdenum(VI) oxide diperoxide $(HMPT)MoO(O_2)_2$ 1′ is readily obtained by dehydration of $(HMPT)(H_2O)MoO(O_2)_2$; its synthesis, isolation and characterization has been reported by Mimoun *et al.*[14]

We performed the synthesis of $(HMPT)CrO(O_2)_2$ by reacting, at 2–8°, CrO_3 with H_2O_2 in a biphasic system of acidic (H_2SO_4, pH 2) water and chloroform containing hexamethylphosphorictriamide HMPT (in slight excess over the stoicheiometric). The reaction stoicheiometry is essentially that expressed by eqn (1); however, the blue aquochromium(VI)oxide diperoxide species, which formation is fast, is transferred into the organic phase by HMPT, while decomposition to aquochromium(III) species is negligibly small. By separating and drying P_2O_5 the organic phase, one affords deep blue solutions of $(HMPT)CrO(O_2)_2$, λ_{max} 580 ($\epsilon \sim 480$) and ~ 708 nm. Since attempts to isolate this metaldiperoxide species from $CHCl_3$ or CH_2Cl_2 solutions failed, due to the rapid decomposition of the peroxide, the $(HMPT)CrO(O_2)_2$ complex was characterized in solution by IR and NMR spectroscopy.

In Table 1 salient spectroscopic data of $(HMPT)CrO(O_2)_2$ and $(HMPT)MoO(O_2)_2$ are compared. It is not surprising that coordination of HMPT to Cr(VI) causes downfield shifts of ^1H- and ^{31}P-NMR resonances of the ligand (as well as displacement of IR P=O stretching to lower frequencies) which are significantly larger than for coördination to Mo(VI).[19]

Both $(HMPT)MoO(O_2)_2$ and $(HMPT)CrO(O_2)_2$ were found to oxidize sulphides to sulphoxide according to the stoicheiometry in eqn (2) [with M=Mo(VI) or Cr(VI)]

$$2R_2S + (HMPT)MO(O_2)_2 \rightarrow 2R_2S{=}O + MO_3 + HMPT \qquad (2)$$

The 2:1 stoicheiometry was shown by the nearly quantitative ($\geq 96\%$) yields of $n\text{-}Bu_2S{=}O$ or $p\text{-}CH_3C_6H_4\text{-}SO\text{-}CH_3$ (glc) in $CHCl_3$ or CH_2Cl_2 at 0–15°, with only trace amounts—if any—of sulphone being formed. In oxidations by $(HMPT)CrO(O_2)_2$ the UV maximum at 580 nm disappears, while maxima at 445 ($\epsilon \sim 300$) and 350 nm ($\epsilon \sim 1200$) arise which can be attributed to chromium trioxide $(HMPT)CrO_3$. Thus, just peroxide oxygen is being transferred to the sulphide, while chromium remains largely in the formal Cr(VI) state during the oxidations.

Table 2. Rate constants for the oxidation of representative organic sulphides by hexamethylphosphortriamido·chromium(VI)oxide peroxide in chloroform at 25.00 ± 0.05° [a]

Substrate	$10^4 \cdot [HMPT \cdot CrO_5]_o$, M	10^3[Sulphide], M	$10^3[HMPT]_o$,[b] M	$10^3[DABCO]_o$,[b] M	$10^3 k_1$,[c] s^{-1}	$10^2 k_2$,[d] $M^{-1}s^{-1}$
None	0.85	-	-	-	0.04	
	1.48	-	-	-	0.08	
	1.55	-	-	-	0.06	
	1.55	-	10.8	-	<0.01	
	1.60	-	-	-	0.07	
	1.60	-	-	-	0.08[e]	
	3.48	-	-	-	0.05	
$n\text{-}Bu_2S$	1.48	6.0	-	-	2.9	48.3
	1.48	12.0	-	-	5.8	48.3
	1.48	12.0	-	-	5.9	49.2
	1.48	22.0	-	-	10.4	47.3
	1.48	24.0	-	-	12.2	50.1
	1.48	48.0	-	-	25.1	52.3
	1.60	18.4	-	-	9.4	51.1
	1.60	18.4	-	-	9.8[e]	53.3[e]
	1.60	18.4	-	-	9.5[e]	51.6[e]
	3.48	48.0	-	-	24.9	51.9
	3.48	48.0	-	-	23.9	49.8
	9.52	48.0	-	-	22.6	47.1
						50.0±0.6[f]
	1.60	20.0	-	-	9.95	49.8
	1.60	20.0	-	0.34	10.2	51.0
	1.60	20.0	-	0.68	11.5	57.5
	1.55	-	-	7.4	8.0	-
	1.55	18.6	-	7.4	12.5[g]	67.2
	1.55	-	-	19.8	19.0	-
	1.55	18.6	-	19.8	15.2[h]	81.7
	1.67	47.5	-	-	24.0	50.5
	1.55	51.5	25.	-	1.15	2.23
	1.46	51.5	25.	-	1.14	2.21
	1.55	51.5	52.	-	0.703	1.365
	1.55	51.5	99.	-	0.42	0.815
	1.55	51.5	172.	-	0.32	0.621
$p\text{-}CH_3 \cdot C_6H_4 \cdot SCH_3$	1.67	20.3	-	-	0.20	0.96±0.025
	1.51	20.3	-	-	0.19	
	1.67	20.3	36.		0.049	0.23±0.01
	1.51	20.3	36.		0.044	
$C_6H_5 \cdot S \cdot CH_3$	1.67	19.4	-	-	0.14	0.745±0.025
	1.51	19.4	-	-	0.15	
	1.67	19.4	36.	-	0.030	0.152±0.003
	1.51	19.4	36.	-	0.029	
$p\text{-}Cl \cdot C_6H_4 \cdot SCH_3$	1.51	20.6	-	-	0.08	0.375±0.01
	1.68	19.4	-	-	0.07	
	1.51	20.6	36.	-	0.012	0 0606±0.00245
	1.51	20.6	36.	-	0.013	
$C_6H_5 \cdot S \cdot C_6H_5$	1.65	71.0	-	-	0.042	0.0592±0.0002
	1.75	96.0	-	-	0.057	

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[a] As determined by a spectrometric technique following the disappearance of the metal peroxide at 550 nm
[b] Initial concentration of added free ligand. [c] Obtained as $k_1 = k_1(obs) - k_1(dec)$; with $k_1(obs)$ and $k_1(dec)$ estimated from pseudo-first-order and first-order (respectively) integrated plots; [d] Individual k_2 values estimated as $k_1/[Sulphide]_o$; [e] Run carried out under inert gas (Ar) atmosphere; [f] Mean square error; [g] From $10^2 k_1(obs) = 20.5$ and $10^2 k_1(dec) = 8.0$ sec^{-1}; [h] From $10^2 k_1(obs) = 34.2$ and $k_1(dec) = 19.0$ sec^{-1} (see also note c.).

Kinetics

Reaction rates of blue chromium(VI)oxide diperoxide were determined in $CHCl_3$ at 25.0° by following the disappearance of the peroxometal at 580 nm. Using an excess of sulphide, excellent $-\ln(A_0 - A_\infty)$ vs time plots were observed, which were linear up to and beyond 80% completion; from these, pseudo-first-order rate constant (k_1) values were obtained (Table 2).

At constant initial concentration of sulphide (i.e. $[n\text{-}Bu_2S]_0 = 0.048$ M), close values of k_1 were obtained upon varying the initial concentration of the peroxometal from 1.48×10^{-4}, to 3.48×10^{-4}, to 9.52×10^{-4} M; this, coupled with the observation of linear $-\ln(A_0 - A_\infty)$ vs time plots ensures the order in chromium diperoxide in one. Inspection of data in Table 2 reveals that, for the oxidation of n-Bu_2S at constant peroxide initial concentration, k_1 values depend upon the excess initial concentration of substrate; indeed, a plot of log k_1 vs log $[n\text{-}Bu_2S]_0$ is linear with slope close to unity. Therefore, the rate law appears to be $R = k_2$[metalperoxide] [sulphide], with $k_2 \simeq k_1/[\text{sulphide}]_0$.

First-order kinetics were also observed for the decomposition of $CrO(O_2)_2$, which allowed us to estimate k_1(dec) values for each batch preparation of the peroxometal in $CHCl_3$. For oxidation of n-Bu_2S under pseudo-first-order conditions, k_1(dec) values were much smaller than the observed k_1 values (Table 2).

Carrying out reactions with exclusion of atmospheric oxygen i.e. under inert gas (Ar) atmosphere, has practically no effect on rates. This, coupled with the uncomplicated rate-law observed renders radical mechanisms unlikely.

Rate constant values k_2 listed in Table 2 show that

Table 3. Rate constants and/or initial rates for the oxidation of representative organic sulphides by hexamethylphosphorictriamido·molybdenum(VI)oxide peroxide in chloroform [a]

Substrate	temp., °C	$10^3[HMPT \cdot MoO_5]_0$, M	$10^3[\text{Sulphide}]_0$, M	$10^3[HMPT]_0$,[b] M	$10^2 \cdot k_1$,[c] sec^{-1}	$10^5 R_0$,[c] $M\ sec^{-1}$	$10^2 k_2$,[d] $M^{-1} sec^{-1}$
None	10°	5.05	-	-	<0.05	-	-
	0°	4.80	-	-	<0.02	-	-
n-Bu_2S	25°	-	-	-	-	-	(1150.±100.)[f]
	0°	5.09	13.6	-	-	25.	
	"	5.09	6.80	-	-	17.	350.
	"	4.90	4.10	-	-	9.0	312.
	"	5.09	3.40	-	-	7.3	317.
	"	4.90	2.60	-	-	4.6	-
	"	4.90	1.60	-	-	3.5	-
	"	8.34	3.30	-	-	12.4	-
	"	4.17	3.30	-	-	7.35	-
	"	3.30	3.30	-	-	5.00	350.
	"	2.05	3.30	-	-	2.60	333.
	"	4.53	7.35	-	-	-	316.
							330.±7.[g]
	"	4.53	7.35	35.0	-	-	190.
	"	4.40	7.60	36.3	-	-	188.
	"	4.53	7.35	109.	-	-	82.
	"	4.40	7.60	110.	-	-	79.
	"	4.40	7.60	204.	-	-	50.
	"	4.53	7.35	206.	-	-	49.
	10°	4.32	3.88	-	-	-	580.
	"	4.32	3.92	-	-	-	540.
							560±20.
	- 5°	-	-	-	-	-	(250±6.)[f]
p-$CH_3 \cdot C_6H_4 \cdot SCH_3$	- 5°	6.2	155.	-	3.48	-	23.5±1.5[h]
	- 5°	4.9	138.	-	3.47	-	

[a] As determined by a titrimetric technique (iodometry), following the disappearance of the metal peroxide.
[b] Initial concentration of the added free ligand; [c] Evaluated from pseudo-first-order kinetics plots.
[d] Unless otherwise noted k_2 values were evaluated from second-order kinetics plots, i.e. log[(a-x)/(b-x)] or 1/(a-x) vs. time. [e] Initial rates, estimated from peroxide concentration vs. time plots over the first 5-10% reaction. [f] Estimated from k_2 values at °0 and 10° by the Arrhenius equation (E_a=8.10±0.6 kcal mol^{-1}). [g] Mean square error. [h] Individual $k_2$values obtained as $k_1/[\text{Sulphide}]_0$.

substrate reactivity decrease in the order n-$Bu_2S > Ph{-}S{-}CH_3 > Ph_2S$; for substituted thioanisoles it is observed $p\text{-}CH_3{\cdot}C_6H_4{-}S{-}CH_3 > Ph{-}S{-}CH_3 > p\text{-}Cl{\cdot}C_6H_4{-}S{-}CH_3$, the k_2 values allowing one to roughly estimate a negative Hammett ρ value $\simeq -0.8$. This leaves no doubt that the sulphide substrate acts as a nucleophile while the chromium(VI)oxide diperoxide is the electrophilic partner.

Singlet oxygen quencher DABCO,[20,21] when added in three to sixfold excess over initial peroxide, does not depress the rates. Also, diphenyl sulphide (a substrate that is virtually inert toward $^1O_2{}^*$)[21,22] is oxidized by the chromium peroxide. This rules out the possibility of singlet oxygen being generated in the reaction.[16]

Ligand HMPT added in excess has a marked inhibitory effect on both chromium peroxide decomposition and rates of oxidation of sulphides (Table 2). For n-Bu_2S oxidation, a plot of k_2 vs 1/[HMPT] is linear over the range of concentration explored, yielding intercept $\simeq 0.4 \times 10^{-2}\,M^{-1}\,s^{-1}$ and slope $\simeq 0.45 \times 10^{-3}\,s^{-1}$.

The rates of the reaction between molybdenum(VI)oxide diperoxide and the model organic sulphides in $CHCl_3$ is much faster than oxidation by the analogous Cr(VI)diperoxide; they were determined following the loss of peroxidic titre with time at 0° in most of the cases.

Kinetic data are collected in Table 3. Initial rates R_0, calculated over the first 5–10% reaction, allow one to estimate reaction orders. At constant initial concentration of sulphide, i.e. 3.3×10^{-3} M n-Bu_2S, the dependence of R_0 upon varying initial concentration of the metalperoxide indicates the order in $MoO(O_2)_2$ is close to unity; in fact, a plot of log R_0 vs log $[MoO(O_2)_2]_0$ is linear with slope $\simeq 1.1$. Furthermore, keeping $[MoO(O_2)_2]_0$ nearly constant, but varying $[n\text{-}Bu_2S]_0$, R_0 values change as to indicate that the order in sulphide is also close to one. Therefore, the following second-order rate-law is likely to apply: $R = k_2[MoO(O_2)_2][\text{sulphide}]$.

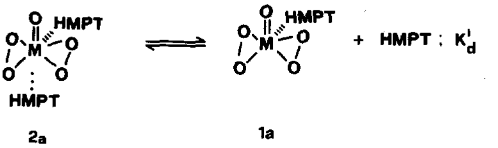
Integrated second-order-rate log [(a − x)(b − x)] vs time plots were linear up to 30–40% reaction; from these, rate constant values k_2 could be evaluated (Table 3). For the oxidation of n-Bu_2S, k_2 values at +25.0° and −5° could be estimated from rate data obtained at 0° and +10°. At −5°, n-Bu_2S is *ca* 11 times more reactive than $p{\cdot}CH_3{-}C_6H_4{-}S{-}CH_3$, which suggests that the molybdenum peroxide behaves as an electrophile.

Inspection of data in Table 3 reveals that, again, added ligand HMPT inhibits the rate; furthermore, added HMPT has the effect of yielding better integrated second-order kinetic plots, linear up to over 50% reaction. For the oxidation of n-Bu_2S at 0°, a plot of k_2 vs $1/[HMPT]_0$ has $\sim 0.22\,M^{-1}\,s^{-1}$ intercept and $\sim 0.060\,s^{-1}$ slope.

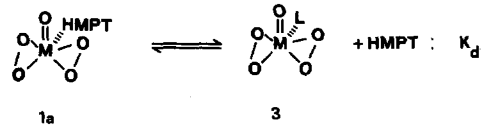
NMR experiments

Aiming to shed light into the number of the metal peroxide complexes and the equilibria involved in the systems at hand, several FT-NMR spectra of $(HMPT)MoO(O_2)_2$ and of $(HMPT)CrO(O_2)_2$, in $CDCl_3$ solutions were run by varying concentrations, both in the absence and in the presence of excess ligand HMPT.

Provided the structures of the metalperoxide complexes above in solution bear resemblance to the solid state,[12,14] the main equilibrium processes envisaged are represented by eqns (3) and (4).



(3)



(4)

In 3, L might be taken to represent a weakly coordinated solvent molecule or, practically, no ligand is present.

The ^{31}P-NMR spectrum (^{1}H noise decoupled) of 0.9×10^{-3} M $(HMPT)MoO(O_2)_2$ in $CDCl_3$ (at 20°) shows no resonance corresponding to the unbound HMPT ligand (cf Table 1). Addition of 0.9×10^{-3} M HMPT merely results in the appearance of a signal at δ28.2 ppm corresponding to free HMPT, *which integrates* 1:1 *with the complexed phosphorus ligand.* Addition of further HMPT (up to 10:1 excess over the peroxometal complex) has just the effect of enhancing the resonance intensity of unbound HMPT, with practically no change in chemical shifts. Lowering the temperature to −10° does not result in broadening of resonance signals or in significant changes in chemical shifts.

From this we conclude that, for chloroform solutions of $(HMPT)MoO(O_2)_2$, only equilibrium in eqn (4) applies. Indeed, lowering the $(HMPT)MoO(O_2)_2$ concentration to 0.8×10^{-4} M in $CDCl_3$ (at 20°), a peak corresponding to free HMPT appears, which integrates *ca* 3:10 with coordinated HMPT. From this, a dissociation constant of $K_d \simeq 0.5 \times 10^{-5}$ M can be roughly estimated for $(HMPT)MoO(O_2)_2$ in chloroform at +20°.

The ^{31}P–NMR spectra of solutions of $(HMPT)CrO(O_2)_2$ in $CDCl_3$ were run at −10° in order to minimize the decomposition to $(HMPT)CrO_3$, which might occur also during FT acquisition time. In separate experiments, we found that the latter chromium trioxide species in $CDCl_3$ solution gives rise to coordinated and unbound HMPT ^{31}P–NMR signals at δ 36.9 and 26.8 ppm, respectively; integration allowed to estimate a K_d'' value of *ca* 0.05 M for the equilibrium $(HMPT)CrO_3 \rightleftharpoons CrO_3 + HMPT$ at −10°.

The ^{31}P–NMR spectrum of 0.7×10^{-3} M $(HMPT)CrO(O_2)_2$, shows a signal at 35.2 ppm; a small downfield signal at 36.8 ppm is due to $\simeq 0.07 \times 10^{-3}$ $(HMPT)CrO_3$ formed during synthesis (at +10°) and decomposition of the chromium diperoxide species. Noteworthy, in this case a peak corresponding to unbound HMPT is also evident in the spectrum, which integrates *ca* 5.5:11 with the signal corresponding to HMPT bound to chromium(VI)oxide diperoxide. These data allow one to estimate $K_d \simeq 0.11 \times 10^{-3}$ M for equilibrium in eqn (4), relative to $(HMPT)CrO(O_2)_2$ in $CDCl_3$ at −10°.

Addition of HMPT results largely in increments of the ratios of unbound to complexed HMPT, which magnitude is consistent with the estimated value of K_d. No other peaks appear in the spectrum, nor significant broadening of the major peaks occurs. This, once again, points out just equilibrium in eqn (4) needs to be taken into account for the metal peroxide species under the reaction conditions.

The reaction of phenyl methylsulphide with $(HMPT)CrO(O_2)_2$ at −20° in chloroform is slow enough to permit monitoring by NMR. The ^{13}C NMR spectra in Fig. 1 show that, shortly after mixing, no change occurs in $PhS\text{–}\underline{C}H_3$ chemical shift when equimolar amounts of the sulphide and the chromium peroxide are reacted. The ^{13}C NMR chemical shifts of the free and complexed HMPT also remain unchanged. The scenario does not change when $(HMPT)CrO(O_2)_2$ is reacted with an over 15-fold excess for $PhSCH_3$. As the reaction is let to proceed the $\underline{C}H_3$ signal of the sulphide is slowly replaced by the sulphoxide $SO\text{–}\underline{C}H_3$ singlet resonance (at δ44.0 ppm), with no other significant variation in the spectrum.

Therefore, ^{13}C–NMR spectroscopy fails to reveal (under the given conditions) appreciable coordination of either the sulphide substrate or the sulphoxide product to the chromium peroxide.

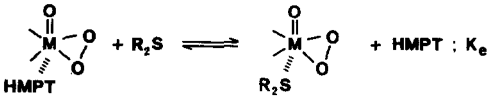
Reaction mechanism

The reaction stoicheiometry in eqn (2) suggests that the reduction of the side-bonded metal-diperoxide occurs in two sequential steps:

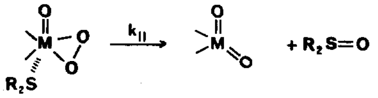
$$(HMPT)MO(O_2)_2 + R_2S \rightarrow (HMPT)MO_2(O_2) + R_2S{=}O \quad (5)$$

$$(HMPT)MO_2(O_2) + R_2S \rightarrow (HMPT)MO_3 + R_2S{=}O \quad (6)$$

Assuming, as the kinetics suggest, there is no significant difference in the rate of processes in eqns (5) and (6),[1,2,5,6] the kinetic data can be discussed adopting a simplified scheme involving the half-reaction shown in eqns (7) an (8).



1a **1b** (7)



1b (8)

This scheme, involving coordination of the substrate to the metal centre *prior* to peroxidic oxygen transfer, is practically identical to that advanced for the epoxidation of olefins by $(HMPT)MO(O_2)_2$ in aprotic solvents.[1–9]

Based on a Michaelis–Menten type treatment for the active intermediate **1b**, the following rate-law should hold:[23]

$$R = -\frac{d[\text{peroxide}]}{dt} = \frac{(k_{II}/2)[R_2S][\text{peroxide}]}{(1/K_p) + (1/K_dK_p)[HMPT]_0 + [R_2S]} \quad (9)$$

Here, K_d is the dissociation constant of the complex metalperoxide·HMPT [*cf* eqn (4)], and K_p is the formation constant of the kinetically active complex **1b**, as in: $R_2S + MO(O_2)_2 \rightleftharpoons [R_2S\cdot MO(O_2)_2]$; hence, $(1/K_p)$ would have the same meaning of the Michaelis constant K_m. Then, k_{II} is the limiting specific rate, which would be observed at very high ratios of sulphide to metalperoxide (where the order in substrate should approach zero).

At $[HMPT]_0 \simeq 0$, the rate law reduces to:

$$R \simeq \frac{(k_{II}/2)[R_2S][\text{peroxide}]}{(1/K_p) + [R_2S]} \quad (10)$$

Hence, it is seen one should not expect to observe first order in sulphide unless $(1/K_p) \gg [R_2S]$; in our case this means that, in order to accomodate the obser-

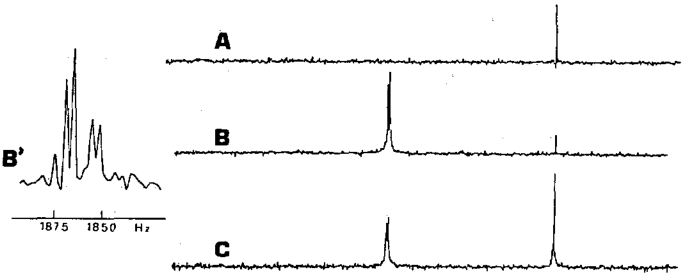
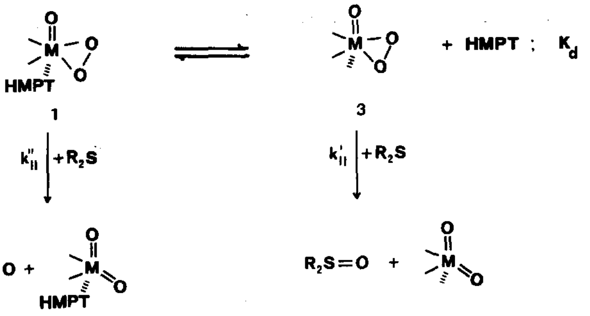


Fig. 1. A FT ^{31}C NMR spectrum (^{1}H noise decoupled) of $\simeq 0.4 \times 10^{-3}$ M $PhSCH_3$ in $CDCl_3$ (Me_4Si internal standard) at −20° (the sweep range chosen shows just the $S\text{–}\underline{C}H_3$ resonance at δ 15.6 ppm); **B**: same as A, but with $\simeq 0.4 \times 10^{-3}$ M $(HMPT)CrO(O_2)_2$ added [the **B**′ insert shows, from upfield to downfield the appearance of the unbound HMPT doublet, and of the partially overlapping $(HMPT)CrO(O_2)_2$ and $(HMPT)CrO_3$ doublets due to $OP(N(\underline{C}H_3)_2)_3$, with $J_{^{13}C^{31}P} \simeq 3.9$ Hz]; **C**: same as above, with $\simeq 5 \times 10^{-3}$ M $PhSCH_3$ and $\simeq 0.4 \times 10^{-3}$ M $(HMPT)CrO(O_2)_2$, at −20°, *ca.* 5 min. after mixing.



vation of order one in sulphide, it must be $K_p \ll 0.1\ M^{-1}$.

Comparing eqn (9) with the experimental rate-law, i.e. $R = k_2[R_2S][\text{Peroxide}]$, one obtains:

$$k_2 = \frac{(k_{II}/2)}{(1/K_p) + (1/K_dK_p)[\text{HMPT}]_0 + [R_2S]} \qquad (11)$$

Then, provided $([\text{HMPT}]_0/K_dK_p) \gg (1/K_p) + [R_2S]$, one can rationalize the observation of linear k_2 vs $1/[\text{HMPT}]_0$ plots (having slope = K_dK_p); these, however, should yield zero intercept, whereas it was pointed out above the plots experimentally observed present non-zero intercept values.

Therefore, an alternative mechanism can be considered which accomodates the data collected; this is shown below. The scheme implies a two-term rate-law of the type:

$$v = d[SO]/dt = (k'_{II}[3] + k''_{II}[1])[R_2S] \qquad (12)$$

Since it is $[\text{Peroxide}] = [MO(O_2)_2] + [(\text{HMPT})MO(O_2)_2]$, and $-(1/2)\,(d[\text{Peroxide}]/dt) = (d[SO]/dt)$, one is able to derive:

$$R = -\frac{d[\text{Peroxide}]}{dt} = \frac{1}{2}\cdot\left(\frac{k_{II}K_d + k_{II}[\text{HMPT}]_0}{K_d + [\text{HMPT}]_0}\right)[\text{Peroxide}][R_2S] \qquad (13)$$

This treatment of kinetic data is similar, in its essence, to that adopted by Bortolini *et al.* for the epoxidation of olefins by molybdenum(VI)peroxo-complexes in the presence of HMPT.[3,8]

We have seen that NMR data point out to a quite low dissociation for $(\text{HMPT})CrO(O_2)_2$ and for $(\text{HMPT})MoO(O_2)_2$ in chloroform, i.e. $K_d \simeq 10^{-3}$ and $\simeq 10^{-5}$ M, respectively. With $K_d \ll [\text{HMPT}]_0$, then, one obtains from eqn (13) the following expression for the observed second-order rate constant:

$$k_2 \simeq (k'_{II}K_d/2)(1/[\text{HMPT}]_0) + (1/2)k''_{II}. \qquad (14)$$

Now, eqn (14) predicts a non-zero intercept for k_2 vs $1/[\text{HMPT}]_0$ plots, as observed. From intercepts of such plots (see above), one estimates $k''_{II} \simeq 0.4$ and $0.008\ M^{-1}\,s^{-1}$ for the oxidation of n-Bu_2S by $(\text{HMPT})MoO(O_2)_2$ and $(\text{HMPT})CrO(O_2)_2$, respectively.

For sulphide oxidation by chromium diperoxide the slope of the k_2 vs $1/[\text{HMPT}]_0$ plot is $(k_I'K_d/2) \simeq 0.45 \times 10^{-3}\,s^{-1}$ (from eqn 14); assuming that, at $[\text{HMPT}]_0 \simeq 0$, the observed k_2 is $\simeq (k'_{II}/2)$ (from eqn 13), a $(k'_{II}/2)$ value of $\simeq 0.5\ M^{-1}\,s^{-1}$ (see Table 2), allows one to estimate $K_d \simeq 0.9 \times 10^{-3}$ M in $CHCl_3$ at 25°. Direct NMR measurements of the dissociation equilibrium $(\text{HMPT})CrO(O_2)_2 \rightleftharpoons CrO(O_2)_2 + \text{HMPT}$ gave a K_d value of $\simeq 0.11 \times 10^{-3}$ M in $CDCl_3$ at $-10°$ (see previous paragraph).

It was mentioned the k_2 vs $1/[\text{HMPT}]_0$ plot for sulphide oxidations by molybdenumdiperoxide at 0° has slope $\simeq 0.06\,s^{-1}$. For this metaldiperoxide both the fast kinetics and equilibrium constant measurements are affected by larger uncertainties. However, by following the same lines as above, on the grounds of K_d value of the order of 10^{-5} M, one might estimate that the rate constant k'_{II} for sulphide oxidation by $MoO(O_2)_2$ in $CHCl_3$ at 0° should be in excess of $10^3\ M^{-1}\,s^{-1}$.

It is apparent, therefore, that the kinetic data can be better accommodated by adopting Mechanism II instead that Mechanism I. In particular, Mechanism II bears the advantage that one does not need to invoke coordination of the sulphide to the metal-diperoxide, a process for which no NMR spectroscopic evidence has been found.

It should also be pointed out the evidence collected does not justify, for the system at hand, the hypothesis of more elaborate reaction mechanisms, such as e.g. the formation of a binary complex involving coordination of both HMPT and the sulphide at the metal center.[3,8] For one, the NMR experiments outlined in the previous paragraph yield no indication that such binary complexes are formed to any significant extent. Then, in principle, simple rate-laws presenting order one in substrate over a wide range of initial concentrations would not be expected.

The fact that preliminary coordination of the substrate does not play a major role is also suggested by the observation that, in the oxidation of phenyl methylsulphides by chromium(VI)oxide diperoxide, the p-CH_3 and p-Cl substitution have almost the same effect on rates both in the absence and in presence of added ligand HMPT, i.e. Hammett's $\rho \simeq -0.8$ and $\simeq -1$, respectively (see data in Table 2).[3,24]

CONCLUSION

Reaction stoicheiometries and kinetic rate-laws have indicated that considerable similarity exists in the reactivity toward organic sulphides of the so-far little studied chromium(VI)oxide diperoxide and the more throughly investigated molybdenum(VI)oxide diperoxide.[1-9]

In Table 4 rate constant values are summarized which allow one to compare the reactivity of the two

Table 4. Rates of oxidation of di-n-butyl sulphide by peroxide species in $CHCl_3$

Peroxide	temp.	$k_2, M^{-1} s^{-1}$
$MoO(O_2)_2$	+ 25°	11.5^{a}
	+ 10°	5.6
	0°	3.3
	− 5°	2.5^{a}
$CrO(O_2)_2$	+ 25°	0.5
t-BuOOH	+ 25°	$1.3 \times 10^{-4\ b}$
$\underline{m}$-Cl·C_6H_4·CO_3H	− 5°	$> 50.^{b,c}$

[a] See footnote *f* in Table 3. [b] R. Curci and L. Troisi, unpublished results.
[c] Value roughly estimated by initial rate measurements.

metal diperoxide species. The data point out that, at 25°, the molybdenum diperoxide is over 20 times more reactive than the analogous chromium compound. In line with this, one finds that the ratios (k_2Bu_2S/k_2PhSCH_3) are $\simeq 10$ (at −5°) and $\simeq 65$ (at 25°) (Tables 3 and 2) for diperoxomolybdenum and diperoxochromium, respectively, showing a lower selectivity for the more reactive peroxide.

As both metaldiperoxides appear to behave as electrophiles, the oxidation is likely to occur via nucleophilic attack by the substrate at the O–O bond of the "side-on" metaldiperoxide **1**.[1,3,9] Kinetics and NMR data have pointed out that oxidation via preliminary coordination of the substrate to the metal-peroxide[2,5,9] needs not to be envisaged here.

Data in Table 4 indicate that both metal diperoxide are vastly more reactive than t-butyl hydroperoxide (TBH), a reference standard peroxide that has been extensively employed in the oxidation of sulphides.[17,18] It is relevant, however, that the chromium(VI)—and the molybdenum(VI)—diperoxide appear to be less effective than m-chloroperoxobenzoic acid (MCPBA); in fact, in $CHCl_3$ at −5°, one can roughly estimate that MCBPA is more reactive than molybdenum(VI)diperoxide by a factor of over 40 (after a statistical factor of two is taken into account in comparing rates).

It is hard to rationalize this finding solely on the basis of different leaving group abilities (i.e. m-Cl·C_6H_4·CO_2H vs MoO_3 or CrO_3), akin to the model of nucleophilic attack at the O–O bond.[17]

It is likely, therefore, that a number of factors contribute to determine the trend observed. For one, we have shown that both $(HMPT)CrO(O_2)_2$ and $(HMPT)MoO(O_2)_2$ in solution are involved in equilibria that, by loss of the ligand HMPT, generate the "free" species $CrO(O_2)_2$ and $MoO(O_2)_2$. Rate data suggest that such metalperoxide species are remarkably more effective in electrophilic substrate oxidation than their precursors, which carry the electron-rich ligand HMPT.[3]

Clearly, in evaluating the reactivity of metal-diperoxide complexes of the kind examined here, one must be aware of the fact that more than a single peroxide species might be present in solution.[3,8,24] The various metal-peroxide species, then, might differ considerably in reactivity, not only depending on the nature of the metal centre, but also on the type and number of ligands.

It is hoped that further studies, now in progress, will be useful in shedding more light on the various aspects of oxidation mechanism by metal peroxides, including the possible occurrence of one-electron electron-transfer oxidation processes.

EXPERIMENTAL

Boiling and melting points are not corrected. The NMR spectra were obtained by using a Varian XL-200 instrument. IR spectra were run on a Perkin–Elmer 681 and UV-Vis spectra on a Varian-Cary 219 instrument. GLC analyses were performed employing a capillary column (0.25 μM SE-30, 30 M × 0.25 mM i.d., temp program) DANI 3800, equipped with a C-R1A Shimadzu integrator.

Materials. Commercial (Aldrich) di-n-butyl sulphide (b.p. 73–4°/14 mm) and diphenyl sulphide (b.p. 176–7°/10 mm) were purified by distillation. Phenyl methylsulphide (b.p. 78–9°/15 mm), p-tolyl methylsulphide (b.p. 97°/17 mm), and p-chlorophenyl methylsulphide (b.p. 135–6°/5 mm) were obtained by reported methods.[25] Di-n-butylsulphoxide [b.p. 140–2°/20 mm,[18] IR (CCl_4) 1038 cm^{-1} (S=O)] was obtained by oxidation of n-Bu_2S following a reported method;[26] the synthesis of Ph_2SO, p-CH_3·C_6H_4–SO–CH_3, p-Cl·C_6H_4–SO–CH_3, and Ph–SO–CH_3 has also been described.[26] Hexamethylphosphorictriamide (HMPT), chloroform, and other commercial reagents and solvents were purified by following standard procedures.

(Hexamethylphosphoramido)molybdenum(VI)oxide diperoxide $(HMPT)MoO(O_2)_2$ **1′**[14] By removal *in vacuo* of water (over P_2O_5), from $(HMPT)(H_2O)MoO(O_2)_2$.[6] The latter complex was obtained according to the procedure described by Mimoun.[14] IR and NMR data are reported in Table 1.

(Hexamethylphosphoramido)chromium(VI)oxide diperoxide $(HMPT)CrO(O_2)_2$ **1″** Analar grade chromic anhydride CrO_3(0.5 g, 5 mmol) was dissolved in acidic (pH 2, H_2SO_4) bidistilled water (100 ml). Freshly distilled chloroform (50 ml), containing purified HMPT (0.9 g, 5 mmol), was added; to the biphasic mixture, kept cold (2–4°) and well stirred, Analar grade 34% H_2O_2 (1 g) was added dropwise. The pH of the mixture was monitored and kept at pH 2 during the addition. After completing the addition, the organic phase (now deep blue) was quickly separated and dried (at 0°) over granular P_2O_5 (Granusic, Baker). Removal of water was checked by IR. Attempts to isolate

the complex (HMPT)$CrO(O_2)_2$ by *careful* removal of the solvent *in vacuo* (at 0°) yielded an instable deep blue peroxidic residue which decomposed on standing (CAUTION).[15,27] The chromium diperoxide complexes, therefore, have been characterized in solution: IR ($CHCl_3$): 2940(CH), 2860, 2810 (N-C), 1605, 1485, 1460, 1300, 1100 (P=O), 980 (P-N), 949, 910 (O-O), 750, 720; NMR: see Table 1; Vis ($CHCl_3$): max 580 nm ($\epsilon \simeq 480$) and $\simeq 720$ nm (shoulder), $\epsilon \simeq 350$).

Stoicheiometry. The oxidation of sulphide with (HMPT)$CrO(O_2)_2$ **1″** was shown to have a stoicheiometry of 2 mol sulphide to 1 mol **1″** by the nearly quantitative formation of the product sulphoxide. The following procedure is representative: to 0.046 g (0.315 mmol) of n-Bu_2S and 0.128 mmol of n-pentadecane (as GLC standard) in $CHCl_3$ (5 ml) at 0°, 5 ml of a 0.034 M solution (0.17 mmol, iodometric titre[17,24]) of the chromium diperoxide complex were added. The reaction was monitored by following the disappearance of the sulphide and the appearance of di-n-butyl sulphoxide by capillary column GLC (see above). After 3 h, the loss of peroxide was practically complete (iodometric titre), and the ratio of peak areas A(sulphoxide)/A(standard) showed (on a previously determined calibration curve) that 0.300 mmol (yield $\geq 95\%$) of sulphoxide had been produced.

Kinetics. Kinetic data involving (HMPT)$CrO(O_2)_2$ were obtained by standard spectrophotometric techniques: the change of absorbance with time at 580 nm (where reaction products are essentially transparent) was monitored by using a Zeiss DMR-21 recording spectrophotometer equipped with a thermostatic ($\pm 0.1°$) cell holder. Rate constants were obtained from first-order (or pseudo-first-order) integrated plots on the basis of the equation: $-\ln(A_t - A_\infty) = k_1 t - \ln(A_0 - A_\infty)$. To reproduce kinetic data, it is relevant to use recently distilled and dried $CHCl_3$ and freshly prepared (HMPT)$Cr(O_2)_2$ solutions. The decomposition of the chromium diperoxide complex obeys a first-order rate law.[10,11] We found, however, that—in our conditions—it is difficult to reproduce rate constants to better than $\pm 30\%$, when using different batches of (HMPT)$CrO(O_2)_2$ solution. For each batch preparation of (HMPT)$CrO(O_2)_2$ in $CHCl_3$, therefore, the decomposition of the peroxide was monitored in parallel with the substrate oxidation (under pseudo-first-order conditions); the k_1 values appearing in Table 2 were then obtained as $k_1(obs) - k_1(dec)$. Sulphide oxidations by (HMPT)$MoO(O_2)_2$ at constant temperature ($\pm 0.05°$) were monitored by following the disappearance of the peroxide (iodometric titre) according to techniques already reported.[8,17,18,24] In the absence of substrate, the peroxide decomposition is negligeably small in the given conditions. It is estimated that, owing to the relatively fast kinetics and the technique adopted, the k_2 value thus obtained are affected by a relatively large ($\pm 20\%$) systematic error.

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