Studies on Transition Metal Peroxo Complexes. Part 8.[1] The Nature of Peroxomolybdates and Peroxotungstates in Aqueous Solution†

Nicholas J. Campbell, Andrew C. Dengel, Catherine J. Edwards, and William P. Griffith *
Inorganic Chemistry Laboratories, Imperial College of Science and Technology, London SW7 2AY

The nature of the species formed in solutions of $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ (1—0.1 mol dm^{-3}) in the presence of H_2O_2 (5—0.5 mol dm^{-3}) from pH 12 to acid has been studied by Raman and i.r. spectroscopy and, for molybdenum-containing species, by ^{95}Mo n.m.r. spectroscopy. The polymerisation processes are far less complex in the presence of H_2O_2 than in its absence. The principal species are likely to be $[M(O_2)_4]^{2-}$, $[MO(O_2)_3]^{2-}$, $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$ and, at lower pH, complexes containing the $[MO(O_2)]^{2+}$ unit. Vibrational assignments are proposed for $K_2[M_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ (M = Mo or W) using ^{18}O and ^{2}H substitution. Parallel studies on the oxidation of alcohols and alkenes by $[MO_4]^{2-}$ in excess of H_2O_2 from pH 7 to 0.5 suggest that $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$ is the most effective oxidising species. Stoicheiometric oxidations of primary alcohols to aldehydes, of secondary alcohols to ketones, and of cyclohexene to its epoxide by $[PPh_4]_2[M_2O_3(O_2)_4]$ are briefly reported.

There has been much interest in the nature of the isopoly species formed by acidification of aqueous solutions of the molybdate ($[MoO_4]^{2-}$) and tungstate ($[WO_4]^{2-}$) ions, and a number of techniques have been applied to the problem.[2] However there are only scattered and often conflicting data on the nature of the species formed when $[MoO_4]^{2-}$ or $[WO_4]^{2-}$ is acidified in the presence of H_2O_2.[3] In this study we use Raman spectroscopy as a principal technique with supporting evidence from ^{95}Mo n.m.r. to study the nature of solute species in solutions of $[MO_4]^{2-}$ (M = Mo or W) in H_2O_2 at different pH and concentrations. These techniques have not been applied before to the study of polymerisation processes in peroxomolybdates and peroxotungstates, and indeed parallel Raman and n.m.r. studies have rarely been used together to probe solute structures, but both Raman[1,4,5] and n.m.r.[6] spectroscopy have been successfully separately applied to the problem of isopolymolybdates and isopolytungstates. We also use here the technique of comparing the Raman spectra of solid peroxo complexes which have known structures with the spectra of the solutions at different pH values, and have conducted a brief parallel survey on the oxidising ability of such solutions with respect to alcohols and alkenes.

Results and Discussion

(*a*) *Raman and* ^{95}Mo *N.M.R. Spectra of Species with Known Structures.*—In order to obtain information on the structures of the species in solution we need to obtain data on systems of known structure. A number of peroxo- and oxoperoxo-molybdates have been structurally characterised by *X*-ray methods but only two tungsten species. Those studied are $[Zn(NH_3)_4][Mo(O_2)_4]$,[7] $K_2[Mo_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$,[8] $[Hpy]_2[Mo_2O_3(O_2)_4(H_2O)_2]$ and $[Hpy]_2[Mo_2O_2(O_2H)_2(O_2)_4]$,[9] $K_2[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$;[10] there are also a number of 'isopolyperoxo' complexes, *viz.* $[NH_4]_4[Mo_3O_7(O_2)_4]\cdot 2H_2O$,[11] $K_4[Mo_4O_{12}(O_2)_2]$ and $K_6[Mo_7O_{22}(O_2)_2]\cdot 8H_2O$,[12] $K_6[Mo_5O_{10}(O_2)_8]\cdot 5H_2O$,[13] $K_5[Mo_7O_{21}(O_2)_2(OH)]\cdot 6H_2O$ and $[NH_4]_4[Mo_8O_{24}(O_2)_2(H_2O)_2]\cdot 4H_2O$,[11] $[NH_4]_8[Mo_{10}O_{22}(O_2)_{12}]\cdot 16H_2O$,[14] and $K_6[W_4O_8(O_2)_6(CO_3)]\cdot 6H_2O$.[15]

The data for $[M(O_2)_4]^{2-}$ and $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$ are listed in Table 1 and in SUP 56742. For the dimeric species $K_2[M_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ (M = Mo or W) we also have ^{18}O- and ^{2}H-substitution data to help in assignment of bands. It is generally agreed[1,16,17] that the stretching modes associated with the side-bonded peroxo ligand $\{\nu_{sym}(O\text{–}O)$, $\nu_{sym}[M(O_2)]$, and $\nu_{asym}[M(O_2)]\}$ are to be found near 880, 600, and 530 cm^{-1} respectively, the first two totally symmetric stretches being polarised in the Raman spectra of solutions of the complexes. Terminal M=O stretches are expected near 950 cm^{-1}, with the corresponding deformation near 300 cm^{-1}.[18] For binuclear species containing M_2O units, the symmetric and asymmetric M_2O stretches lie near 500 and 750 cm^{-1} respectively,[19,20] much dependent on the M–O–M angle.[21]

(*i*) $[M(O_2)_4]^{2-}$. These species are highly explosive, so it is very difficult to obtain their Raman spectra in particular. We and others have obtained Raman[16,22,23] and i.r.[22–26] data for $[M(O_2)_4]^{n-}$ species (M = Nb, Ta, Cr, Mo, or W); as a consequence of their dodecahedral (D_{2d}) symmetry[7] the spectra are relatively simple. In Table 1 we present data for salts of $[M(O_2)_4]^{2-}$ (M = Mo or W); Raman spectra of these explosive materials could not be obtained.

(*ii*) $K_2[M_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ (M = Mo *or* W). We have earlier reported the Raman spectra of both these salts in the solid state with partial assignment of bands as well as the i.r. spectra of the solids and solutions in $^{2}H_2O$ from 4 000 to 700 cm^{-1},[23] and there are further i.r. data for the salts.[25] We now report Raman and i.r. data for the normal, deuteriated, and ^{18}O-substituted complexes in the solid state and in aqueous solution (see Table 1 and SUP 56742).

It is apparent from these data that the bands near 960 cm^{-1} which are essentially unaffected by deuteriation but shift to lower wavenumber on ^{18}O substitution are likely to be due to ν(M=O) (calculated shifts on ^{18}O substitution are 47 cm^{-1}, close to the observed values). The three bands near 860 (Mo or W), 620 (W) and 580 (Mo), and 560 cm^{-1} (Mo or W), the first two of which are polarised for aqueous solutions, are essentially unaffected by deuteriation or ^{18}O substitution. Since the ^{18}O substitution was achieved by recrystallisation of $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$ from $H_2{}^{18}O$, which would not isotopically substitute the peroxo ligand, we may confidently assign these

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† *Supplementary data available* (No. SUP 56742, 11 pp.): Raman, i.r., and n.m.r. data; see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue, pp. xvii—xx.

Table 1. Vibrational spectral data (cm^{-1})[a] for $[M(O_2)_4]^{2-}$ and $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$ complexes

Species		$\nu(M{=}O)$	$\nu(O–O)$	ν_{asym}-(M_2O)	ν_{sym}-$[M(O_2)]$	ν_{asym}-$[M(O_2)]$	ν_{sym}-(M_2O)	$\nu[M(OH_2)]$	$\delta(M_2O)$
$Cs_2[W(O_2)_4]$	I.r.	825vs			560m	535m			
$[NH_4]_2[Mo(O_2)_4]$	I.r.	865vs			580m	525s			
$K_2[W_2O_3(O_2)_4(H_2O)_2]{\cdot}2H_2O$	I.r.	964vs	853s	765s	615m	560s		330m	
	Raman	955(10)	850(8)	762(2)	620(2)	557(5)	450(1)	317(2)	259(1)
	Raman[b]	960(10)p	854(7)p		622(3)p	559(2)dp		321(2)dp	
$K_2[W_2{}^{18}O_3(O_2)_4(H_2{}^{18}O)_2]{\cdot}2H_2{}^{18}O$	I.r.	905s	853s	715m	615m	560vs	405w		
	Raman	905(10)	853(7)	715w	620(2)	562(7)	405(1)	312(2)	
	Raman[c]	914(10)p	852(7)p		622(2)p	558(8)dp		311(3)dp	
$K_2[W_2O_3(O_2)_4({}^2H_2O)_2]{\cdot}2{}^2H_2O$	I.r.	966vs	852s	761s	615m	547s	447w	311m	
	Raman	956(10)	850(8)	761(3)	622(3)	565(7)	445(1)	310(2)	255(1)
$[PPh_4]_2[W_2O_3(O_2)_4]$	I.r.	962s	861m	722s	614m	576m	457w		
$K_2[Mo_2O_3(O_2)_4(H_2O)_2]{\cdot}2H_2O$	I.r.	961vs	855vs	715s	575s	531m	454w	335m	
	Raman	959(10) 950(9)	867(9)	723(2)	582(5)	533(4)	454(1)	344(4)	260(1)
	Raman[b]	967(10)p	871(8)p		573(3)p	540(10)p		317(3)	
$K_2[Mo_2{}^{18}O_3(O_2)_4(H_2{}^{18}O)_2]{\cdot}2H_2{}^{18}O$	I.r.	927vs	863s	675s	595s	530m		340m	
	Raman	926(8) 914(10)	867(7)		584(7)	535(8)	435(1)	341(4)	255(1)
	Raman[c]	921(8)p	872(9)p		574(4)p	539(10)dp		308(5)	
$K_2[Mo_2O_3(O_2)_4({}^2H_2O)_2]{\cdot}2{}^2H_2O$	I.r.	960vs	853vs	722s	578s	532m	450w	325w	
	Raman	958(10) 949(10)	866(9)	718(2)	588(5)	530(4)	448(1)	339(2)	256(1)
$[PPh_4]_2[Mo_2O_3(O_2)_4]$	I.r.	967s	873s 866 (sh)	722s	592m	533s	457w		
	Raman	960(10)	875(7)	726(2)	594(4)	559(5)			
	Raman[d]	965(10)	875(6)	725(1)	606(4)	560(5)			

[a] For solids. [b] Aqueous solution. [c] In $H_2{}^{18}O$ solution. [d] Acetonitrile solution.

bands to $\nu(O–O)$, $\nu_{sym}[M(O_2)]$, and $\nu_{asym}[M(O_2)]$ respectively. The only other bands shifting substantially on ^{18}O substitution are those at 762 and 450 cm^{-1} (W) and 715 and 454 cm^{-1} (Mo). These drop to 715 and 405 cm^{-1} (W) and to 675 and 435 cm^{-1} (Mo). We tentatively assign them to $\nu_{asym}(M_2O)$ and $\nu_{sym}(M_2O)$ respectively {for $[Cr_2O_7]^{2-}$ the $\nu_{asym}(Cr_2O)$ and $\nu_{sym}(Cr_2O)$ modes are at 730 and 572 cm^{-1} [19]}, and note that the shifts observed are larger for the tungsten complex. The calculated shifts {using the secular equations given by Wing and Callahan[21] and M–O–M angles of 136.1 and 139° respectively reported from *X*-ray data on $K_2[M_2O_3(O_2)_4(H_2O)_2]{\cdot}2H_2O$ (M = Mo[8] or W[10])} for the molybdenum complex are to 690 and 430 cm^{-1} for the $\nu_{asym}(M_2O)$ and $\nu_{sym}(M_2O)$ modes respectively; for the tungsten complex the shifts are to 732 and 426 cm^{-1}. The agreement between observed and calculated shifts is fair, especially in view of the approximations involved in the calculations;[21] the M–O–M angle in the solutions may well differ from those for the solids and thus affect the shifts.

The only bands to shift on deuteriation are those due to the metal–OH_2 stretch {$\nu[M(OH_2)]$}. For the tungsten dimer, this band is shifted from 330 to 311 cm^{-1} on deuteriation; for the molybdenum dimer the shift seen is from 335 to 325 cm^{-1} (calculated shifts 10 cm^{-1} in both cases).

(*b*) *Peroxotungstates in Aqueous Solution*.—We consider these first since, on account of the greater stability of the solutions, we were able to obtain many Raman spectra, though unfortunately very little ^{183}W n.m.r. data could be obtained because of the low receptivity of the ^{183}W nucleus. We used HCl to adjust the pH, but the use of $HClO_4$ or H_2SO_4 gave closely similar spectra. The H_2O_2:W ratios used were 5:1, 2:1, and 1:1; no complexes with a peroxide:metal ratio greater than 4:1 are known.[3] Detailed results are given in SUP 56742.

(*i*) pH 9—7. Above pH 9 we are unable to obtain solutions of sufficient stability to record good Raman spectra. Solutions containing H_2O_2:W ratios of 5:1 show (in addition to the O–O stretch of H_2O_2 at 876 cm^{-1}) polarised bands at 858 and 574 cm^{-1} which we assign to $\nu(O–O)$ and $\nu_{sym}[W(O_2)]$ of $[W(O_2)_4]^{2-}$; a weak depolarised band at 596 cm^{-1} probably arises from $\nu_{asym}[W(O_2)]$. These values are fairly close to those observed for solids containing $[W(O_2)_4]^{2-}$ (Table 1) and we thus conclude that $[W(O_2)_4]^{2-}$ is the principal species in such solutions, in agreement with other authors.[27,28] For solutions with H_2O_2:W ratios of 2:1 and 1:1 at pH 9—7 we observe additional Raman bands at 960 and 560 cm^{-1} which are likely to arise from $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ (see Table 1).

(*ii*) pH 7.0—1.3. For solutions containing 5:1 H_2O_2:W ratios the bands assigned above to $[W(O_2)_4]^{2-}$ persist down to pH 5.0, with additional bands (960, 770, and 323 cm^{-1}) assigned to $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$. From pH 5.0 to 1.3 the bands due to $[W(O_2)_4]^{2-}$ disappear and the Raman spectrum in this region is very similar to that of $K_2[W_2O_3(O_2)_4(H_2O)_2]{\cdot}2H_2O$ in solution. It is therefore likely that $[W_2O_3(O_2)_4(H_2O)_2]^{2-}$ is the principal solute species in the pH range 7.0—1.3; we have shown in earlier cryoscopic work that the anion in $K_2[W_2O_3(O_2)_4(H_2O)_2]{\cdot}2H_2O$ retains its structure in aqueous solution.[22,23] Formation of the dimer at pH 5 has also been shown potentiometrically[28] and cryoscopically.[29] Although the existence of triperoxo species such as $[WO(O_2)_3]^{2-}$ has been suggested,[30] our Raman data give no evidence for their existence; nor is there evidence for the proposed[27] protonated species $[HW_2(O_2)_8]^{3-}$. We find that solutions of $[WO_4]^{2-}$ in excess of H_2O_2 at pH 3.9, 2.5, and 1.7 have one narrow ^{183}W n.m.r. resonance, at δ −699 p.p.m. (*vs.* $\delta = 0$ for $[WO_4]^{2-}$), in the same position as that exhibited by an aqueous solution of $Na_2[W_2O_3(O_2)_4(H_2O)_2]{\cdot}2H_2O$.

(*iii*) *Below* pH 1.3. In this region the solutions become unstable and lose oxygen. The polarised Raman band formerly at 960 cm^{-1} shifts to 970 cm^{-1} and a new band at 883 cm^{-1} appears, which we assign to $\nu(O–O)$ in place of the band at 854 cm^{-1}. These changes could arise from formation of a monoperoxo complex such as the '$Na_2[WO_5]{\cdot}H_2O$'[31]

{perhaps better formulated as $Na_2[WO_3(O_2)(H_2O)]$}; however, we observe no splitting of ν(W=O) as would be expected[32] for a species containing *cis*-WO_2 or WO_3 groups and suggest that, in acid at least, the known species $[WO(O_2)Cl_4]^{2-}$ is formed. The i.r. bands reported for solid $Cs_2[WO(O_2)Cl_4]$[26] are close to the Raman bands which we observe for $[WO_4]^{2-}$ in excess of H_2O_2 below pH 1.3.

(*c*) *Peroxomolybdates in Aqueous Solution*.—For these we have been able to supplement our Raman data with ^{95}Mo n.m.r. data in most cases. As with the tungstate system, our work was done using 5:1, 2:1, and 1:1 H_2O_2:Mo ratios, and pH was adjusted using HCl.

(*i*) pH 9—5. Above pH 9 the deep red solutions were too unstable for Raman or ^{95}Mo n.m.r. measurements. It has been implied that di- or tri-peroxo species exist in such solutions,[33] but we believe that these are mixtures or decomposition products of the very unstable red $[Mo(O_2)_4]^{2-}$ ion. We and others[22–26] have measured the i.r. spectra of salts of $[Mo(O_2)_4]^{2-}$ (Table 1). The ^{95}Mo n.m.r. spectra of solutions from pH 8.8 to 8.2 containing excess of H_2O_2 show a sharp band at δ −426.5 p.p.m. (*vs.* δ = 0 for $[MoO_4]^{2-}$) together with a broader resonance at −496.0 p.p.m.; the latter grows at the expense of the former with time and probably arises from a decomposition product. For solutions containing 2:1 H_2O_2:Mo the sharp resonance at −426.0 p.p.m. was not observed. It is likely that this resonance arises from $[Mo(O_2)_4]^{2-}$, its sharpness arising from the relatively high symmetry about the metal atom {shown to be D_{2d} in $[Zn(NH_3)_4][Mo(O_2)_4]$[7]}.

From pH 7.2 to 5.0, the ^{95}Mo n.m.r. spectrum shows two resonances, a relatively sharp one at −492.3 p.p.m. and a much broader one at −266 p.p.m. The latter persists down to pH 2.5 and is probably due to $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$ (see below). The peak at −492.3 p.p.m. could arise from a triperoxo species $[MoO(O_2)_3]^{2-}$ or $[MoO(O_2)_3(H_2O)]^{2-}$. It has been suggested that such species exist near pH 8 on the basis of pH and potentiometric data,[33] and the very unstable red '$Cs_2[MoO_7]\cdot nH_2O$' (n = 3 or 0) has been reported.[33,34] We have previously shown that the claimed triperoxo species $[Hpy]_2[MO_7]$ (M = Mo or W)[35] are in fact $[Hpy]_2[M_2O_3(O_2)_4(H_2O)_2]\cdot H_2O$,[23] so clearly triperoxo species must be regarded with suspicion. The species '$Cs_2[MoO_7]\cdot nH_2O$' reported by Arkhipov *et al.*[33,34] was found by us to show complex i.r. and Raman spectra with bands due to O–O and Mo=O stretches, suggesting that it is a mixture of $Cs_2[Mo_2O_3(O_2)_4(H_2O)_2]$ and more complicated peroxomolybdate species. The broad resonance centred on δ −246 p.p.m. seen in the ^{95}Mo n.m.r. spectrum of these species reinforces this view. One solution of $[MoO_4]^{2-}$ in excess of H_2O_2 at pH 8.4 did show polarised bands at 959, 872, and 539 cm^{-1} which could be due to ν(Mo=O), ν(O–O), and $\nu_{sym}[Mo(O_2)]$ of a species such as $[MoO(O_2)_3]^{2-}$.

(*ii*) pH 5—2.5. The Raman spectra of 5:1 and of 2:1 H_2O_2:Mo solutions are all very similar in this region, and also show bands close to those observed for $K_2[Mo_2O_3(O_2)_4(H_2O)_2]$ in water (Table 1). The ^{95}Mo n.m.r. spectra over this range show a broad resonance at δ −263 p.p.m. (with the additional and sharper 'triperoxo' resonance mentioned above disappearing below pH 5.1). Dissolution of $K_2[Mo_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ in water gives a broad n.m.r. signal at −268 p.p.m. (pH 3), and it seems likely that the species $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$ is the principal one in this pH range. Our earlier cryoscopic data suggested, albeit with very weak solutions, that the species retains its binuclear character in aqueous solution.[22,23] It has been suggested, from potentiometric data, that dimerisation of peroxomolybdates is slow in aqueous solution.[36]

(*iii*) *Below* pH 2.5. Between pH 2.5 and 1.6 the broad ^{95}Mo n.m.r. peak at δ −263 p.p.m. shifts slightly downfield to −251 p.p.m., suggesting a protonation process (^{51}V n.m.r. peaks due to peroxovanadates shift downfield on protonation[37]), accompanied by minor shifts in the Raman spectrum. Species such as $[MoO(OH)(O_2)_2]$ may be formed at these lower pH values; such a species has been proposed on the basis of kinetic and spectrophotometric data.[38] We have recently shown by an *X*-ray crystal-structure determination that there is protonation of the μ-oxo bridge in $[NH_4]_3[V_2O_2(O_2)_4(OH)]$,[39] and the Raman and i.r. spectra of the latter complex show features similar to those of the $[MoO_4]^{2-}$–H_2O_2 system at low pH.

At pH 2.0 a new, sharper ^{95}Mo resonance appears at δ −155 p.p.m. in 5:1 solutions of H_2O_2:$[MoO_4]^{2-}$ (the latter being 1, 0.5, and 0.1 mol dm^{-3}), alongside the peak at −257 p.p.m.; at pH 0.8 the latter peak disappears. In the Raman spectrum of 5:1 H_2O_2:$[MoO_4]^{2-}$ solutions the Raman band assigned to $\nu_{asym}(Mo_2O)$ shifts from 630 (pH 2.0) to 652 cm^{-1} (pH 0.6), and disappears in concentrated HCl solutions, while ν(Mo=O) shifts from 976 (pH 2.0) to 980 cm^{-1} (pH 0.6 and below). Similar shifts occur when the pH of a solution of $K_2[Mo_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ is lowered. Although it is possible that monomeric diperoxo species $[MoO_2(O_2)_2]^{2-}$ have been formed {*e.g.* '$Cs_2[MoO_6]\cdot nH_2O$',[34] presumably $Cs_2[MoO_2(O_2)_2(H_2O)]$}, we observe no splitting of the ν(Mo=O) modes in the Raman as would be expected[32] for such species. It seems more likely that, at very low pH at least, where oxygen is seen to be lost from the solutions, monoperoxo species are formed. A number of these species has been claimed, *e.g.* '$[MoO_5]^{2-}$' {presumably $[MoO_3(O_2)]^{2-}$} in solutions for pH 5 to 0.5.[31,40] However, under the conditions of our work, it is likely that the known $[MoO(O_2)Cl_4]^{2-}$ will be formed at low pH.[41] We have reported the Raman spectrum of $Cs_2[MoO(O_2)Cl_4]$[16] and its Raman bands are close to those found in solutions of $[MoO_4]^{2-}$ in excess of H_2O_2 and concentrated HCl.

We have also measured the Raman spectra of $[NH_4]_8[Mo_{10}O_{22}(O_2)_{12}]\cdot 16H_2O$,[14] $[NH_4]_4[Mo_3O_7(O_2)_4]\cdot 2H_2O$,[11] and $K_6[Mo_7O_{22}(O_2)_2]\cdot 8H_2O$[12] in the solid state and in aqueous solution (see Experimental section; these known oxoperoxomolybdates were prepared by the methods of Stomberg and co-workers). In each case, the profiles of the spectra are similar for the solid state and the aqueous solution, suggesting retention of these isopolyperoxo structures in solution {in addition the ^{95}Mo n.m.r. spectrum of $[NH_4]_8[Mo_{10}O_{22}(O_2)_{12}]\cdot 16H_2O$ is complex}. However, on addition of H_2O_2, the complex Raman spectra disappear and are replaced by the spectra expected at the corresponding pH for solutions containing excess of hydrogen peroxide.

It would seem that, although these isopolyperoxo species clearly exist, precise Mo:H_2O_2 stoicheiometries and pH control are required for their preparation; similarly, while their structures are retained to a great degree in aqueous solution, the presence of excess of H_2O_2 serves to break them down into the simpler monomeric and dimeric oxoperoxomolybdate species discussed above.

All our ^{95}Mo shifts lie upfield of that of $[MoO_4]^{2-}$. Most oxomolybdate(VI) species give downfield shifts,[6] but strong σ donors do produce upfield shifts,[42] and for a peroxo complex this was first demonstrated for $[MoO(O_2)(CN)_4]^{2-}$ (δ −610 p.p.m. relative to δ = 0 for $[MoO_4]^{2-}$).[43] We have also shown that the peroxo species $[MoO(O_2)_2L]^{2-}$ (L = carboxylate) have ^{95}Mo shifts in the −240 p.p.m. region.[1]

(*d*) *Organic Oxidations by Peroxomolybdate and Peroxotungstate Solutions*.—The epoxidation of unsaturated carboxylic acids by H_2O_2 is catalysed by $[WO_4]^{2-}$ in aqueous solution at 50—65 °C and pH 4—5.5.[44,45] Under phase-transfer conditions $[MoO_4]^{2-}$ and $[WO_4]^{2-}$ in aqueous solution at

Table 2. Stoicheiometric oxidation of alcohols with $[PPh_4]_2[M_2O_3(O_2)_4]$ (M = Mo or W)[a]

Alcohol	Product[b]	t/h	Yield of carbonyl compound/%
p-Anisyl	A	3	97
p-Anisyl †	A	3	96
Benzyl	A	3	85
Vanillyl	A	3	89
Piperonyl	A	3	92
α-Tetralol	K	15	60
Cyclo-octanol	K	24	20
Cinnamyl	A	15	45
Geraniol	A	15	54
Citronellol	A	15	32

[a] All oxidations carried out in dichloromethane, and at room temperature, with a 1:1 substrate:oxidant molar ratio using $[PPh_4]_2[Mo_2O_3(O_2)_4]$ or †$[PPh_4]_2[W_2O_3(O_2)_4]$. [b] A = Corresponding aldehyde, K = corresponding ketone.

75 °C will catalyse the oxidation by H_2O_2 of primary alcohols to aldehydes and secondary alcohols to ketones: for $[MoO_4]^{2-}$ the optimum pH is 3.0 and for $[WO_4]^{2-}$ it is 1.4.[46] Our spectroscopic data given above indicate that $[M_2O_3(O_2)_4(H_2O_2)]^{2-}$ species will predominate at these pH values. In order to confirm this we have carried out a brief study of oxidation of benzylic alcohols, tetralol (1,2,3,4-tetrahydronaphthalen-1-ol), and cyclohexene by H_2O_2 in two-phase systems in the presence of $[MO_4]^{2-}$ (M = Mo or W) over a pH range and have also shown that $[PPh_4]_2[M_2O_3(O_2)_4]$ will, in CH_2Cl_2 solution, oxidise alcohols and epoxidise cyclohexene.

We find that oxidation of benzyl alcohol to benzaldehyde is effected by aqueous solutions of $[MO_4]^{2-}$ (M = Mo or W) with excess of H_2O_2 in a two-phase system with 1,2-dichloroethane and Aliquat $[NMe(C_8H_{17})_3Cl]$ at 75 °C most effectively at pH 3.0, in agreement with the results of Bortolini *et al.*,[46] thus at pH 1, 3, 5, and 7.5 the oxidation efficiency is 27, 58, 42, and 19% respectively for $[MoO_4]^{2-}$, and for $[WO_4]^{2-}$ at pH 0.5, 1, 3, 5, and 7.5 the corresponding figures are 66, 75, 82, 70, and 27% respectively.

It thus seems clear that $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$ is responsible for effecting these oxidations. Furthermore we find that solutions of $K_2[MoO_4]$ in excess of H_2O_2 at pH 3.0 warmed to 75 °C deposit crystals of pure $K_2[Mo_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ on cooling, and that the Raman spectrum of a solution of $K_2[MoO_4]$ in excess of H_2O_2 measured at pH 3.0 and 75 °C shows the bands typical of $[Mo_2O_3(O_2)_4(H_2O)_2]^{2-}$.

Finally, we have prepared the new salts $[PPh_4]_2[M_2O_3(O_2)_4]$ (M = Mo or W) by reaction of $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$ with PPh_4Cl, and studied their reactivities toward alcohols. They stoicheiometrically oxidise primary alcohols to aldehydes and secondary alcohols to ketones at ambient temperatures (see Table 2); cyclohexene is also oxidised to its epoxide and we believe that the low yields for oxidations of geraniol, citronellol (3,7-dimethyloct-6-en-1-ol), and cinnamyl alcohol are due to competing epoxidations. For $[PPh_4]_2[Mo_2O_3(O_2)_4]$ the reaction with alcohols is catalytic in a biphasic system without a phase-transfer catalyst, 4-methoxybenzyl alcohol thus being converted into the aldehyde in 46% yield at room temperature.

Our analytical data suggest that, unlike $K_2[Mo_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$, these tetraphenylphosphonium salts contain no co-ordinated water, so that the anion may have a quasi-seven-co-ordinate structure, as observed by us in $[NH_4]_3[V_2O_2(O_2)_4(OH)]\cdot H_2O$[39] where a weak interaction between a metal atom and a neighbouring peroxo ligand constitutes the seventh co-ordination position of a pentagonal bipyramid. If this is the case then in non-aqueous solvents such as CH_2Cl_2 a co-ordination site is likely to be vacant for oxidation reactions; it has been shown[47] that this is necessary for such reactions to proceed in molybdenum peroxo complexes. These new salts would therefore seem to be similar to $[PPh_3(CH_2Ph)]_2[W_2O_3(O_2)_4]$ prepared by Mimoun and co-workers,[48] a catalyst for the biphasic epoxidation of alkenes by H_2O_2 at 50 °C.

Conclusions

It appears that $[WO_4]^{2-}$ and $[MoO_4]^{2-}$ take similar pathways in their reactions with H_2O_2 over a pH range: at high pH (> 7) $[M(O_2)_4]^{2-}$ predominates, at intermediate pH (5—2) the dimer $[M_2O_3(O_2)_4(H_2O)_2]^{2-}$ is the major species, and at low pH, in the presence of HCl, *cis*-$[MoO(O_2)Cl_4]^{2-}$ is formed. There is some evidence in the case of molybdenum for the existence of species such as $[MoO(O_2)_3]^{2-}$ and $[Mo_2O_2(O_2)_4(OH)(H_2O)_2]^-$. For neither molybdenum nor tungsten does it seem likely that 'isopolyperoxo' species have an important role. Under the conditions used in our oxidation experiments it seems that $[M_2O_3(O_2)_4]^{2-}$ (M = Mo or W) are the most effective organic oxidants.

Experimental

Sodium molybdate and sodium tungstate were of AnalaR quality.

Preparations.—$K_2[M_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ (M = Mo *or* W). The method is based on that of Stomberg.[8] A solution of potassium molybdate (5.0 g, 21.0 mmol) in water (100 cm^3) was placed in an ice–water bath. Treatment with 30% H_2O_2 (10 cm^3) gave a dark red solution, to which dilute hydrochloric acid was added dropwise until the colour just turned bright yellow, at pH 4—5. A yellow crystalline solid appeared after 24 h at 5 °C, and was filtered off, washed with ethanol, and air-dried (Found: H, 1.3; K, 14.9; O_2^{2-}, 24.4. $H_8K_2Mo_2O_{15}$ requires H, 1.6; K, 15.1; O_2^{2-}, 24.7%).

The tungsten analogue was similarly prepared. A solution of potassium tungstate (2.0 g, 6.1 mmol) in water (15 cm^3) was treated with 30% H_2O_2 (10 cm^3). The yellow solution formed was treated with dilute HCl until it just turned colourless (pH 2.5). White crystals appeared on standing at 5 °C for 24 h, and were filtered off, washed with ethanol, and air-dried (Found: H, 1.0; K, 11.0; O_2^{2-}, 18.6. $H_8K_2O_{15}W$ requires H, 1.2; K, 11.3; O_2^{2-}, 18.4%).

Oxygen-18 substitution and deuteriation were achieved by recrystallisation of the above salts from $H_2{}^{18}O$ and ^2H_2O respectively, and the procedures used for the molybdenum species were typical. The salt $K_2[Mo_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ (0.1 g) was dissolved in $H_2{}^{18}O$ (1 cm^3) and the solution allowed to stand at room temperature for 24 h. The solution was then slowly evaporated to dryness on a vacuum line to yield the yellow solid $K_2[Mo_2{}^{18}O_3(O_2)_4(H_2{}^{18}O)_2]\cdot 2H_2{}^{18}O$. Yellow crystals of $K_2[Mo_2O_3(O_2)_4(^2H_2O)_2]\cdot 2{}^2H_2O$ were obtained by dissolving $K_2[Mo_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ in a minimum volume of ^2H_2O, and standing at 5 °C for 24 h.

$[PPh_4]_2[W_2O_3(O_2)_4]$. The salt $K_2[W_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ (0.50 g, 0.72 mmol) was dissolved in water (20 cm^3). Addition of tetraphenylphosphonium chloride (0.54 g, 1.44 mmol) with stirring gave a clear solution (pH 6.3), from which an off-white solid precipitated after 30 min. The solid was filtered off, washed with water (3 × 10 cm^3), and dried in a vacuum desiccator over silica gel (Found: C, 47.0; H, 3.2; O_2^{2-}, 10.1; P, 4.9. $C_{48}H_{40}O_{11}P_2W_2$ requires C, 47.2; H, 3.3; O_2^{2-}, 10.5; P, 5.1%).

$[PPh_4]_2[Mo_2O_3(O_2)_4]$. The salt $K_2[Mo_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ (1.0 g, 1.93 mmol) was dissolved in water (50 cm^3).

Addition, with stirring, of tetraphenylphosphonium chloride (1.45 g, 3.86 mmol) gave a flocculent yellow-white precipitate immediately (pH 5.4). The solid was filtered off, washed with water (3 × 10 cm^3), and dried in a vacuum desiccator over silica gel (Found: C, 56.0; H, 3.8; O_2^{2-}, 12.5; P, 6.1. $C_{48}H_{40}Mo_2O_{11}P_2$ requires C, 55.1; H, 3.9; O_2^{2-}, 12.2; P, 5.9%).

$[NBu_4]_2[Mo_2O_3(O_2)_4]$. The salt $K_2[Mo_2O_3(O_2)_4(H_2O)_2]\cdot 2H_2O$ (1.0 g, 1.93 mmol) was dissolved in water (30 cm^3), and the solution treated with tetrabutylammonium hydrogensulphate (1.31 g, 3.86 mmol) with stirring. The flocculent yellow precipitate was filtered off, washed with water (3 × 15 cm^3), and dried in a vacuum desiccator over silica gel. Recrystallisation from dichloromethane afforded a crystalline sample of the complex (Found: C, 44.2; H, 7.2; N, 2.9; O_2^{2-}, 15.6. $C_{32}H_{72}Mo_2N_2O_{11}$ requires C, 45.1; H, 8.5; N, 3.3; O_2^{2-}, 15.0%). Infrared and Raman spectra, cm^{-1}: i.r. (Nujol mull) 960s, 946s, 865s, 720m, 593m, 534m, 454w, and 332w; Raman (solid, KBr disc) 963 (10), 880 (6), 715 (1), 586 (4), 556 (6), 448 (3), 330 (1); (acetonitrile solution) 960 (10), 878 (7), 710 (3), 593 (3), and 558 (6) (numbers in parentheses are relative Raman intensities). The complex can be similarly prepared from tetrabutylammonium chloride, but the analogous tungsten complex could not be isolated using either tetrabutylammonium reagent.

$[NH_4]_8[Mo_{10}O_{22}(O_2)_{12}]\cdot 16H_2O$. The preparation was based on the method of Stomberg and co-workers.[14] Ammonium heptamolybdate, $[NH_4]_6[Mo_7O_{24}]\cdot 4H_2O$ (3.72 g, 3.0 mmol), was dissolved in water (1.5 cm^3) and the solution treated with 30% H_2O_2 (2.8 cm^3). The pH of the solution was adjusted to 2.8—3.0 using nitric acid (8 mol dm^{-3}). The dark yellow solution yielded yellow crystals after ethanol addition and storage at 5 °C; these were filtered off, washed with ethanol, and air-dried (Found: H, 2.4; N, 5.3; O_2^{2-}, 17.6. $H_{64}Mo_{10}N_8O_{62}$ requires H, 3.0; N, 5.3; O_2^{2-}, 18.0%). Infrared and Raman spectra, cm^{-1}: i.r. (Nujol mull) 953vs, 947s, 927s, 891vs, 872s, 849s, 730br, 686m, 622s, 554m, 472w, and 335w; Raman (solid, KBr disc) 967 (10), 957 (sh), 923 (4), 900 (3), 873 (3), 853 (1), 690 (2), 630 (2), 590 (4), 555 (7), 516(4), 474 (2), 366 (1), 334 (1), and 309br; (aqueous solution) 970 (10), 943 (8), 916 (4), 898 (2), 872 (4), 850 (4), 660 (2)br, 565 (4), 469 (2), 345 (3), and 302 (2).

$[NH_4]_4[Mo_3O_7(O_2)_4]\cdot 2H_2O$. The method was based on that of Trysberg and Stomberg.[11] A solution of ammonium heptamolybdate (15.45 g, 12.5 mmol) in water (25 cm^3) was treated with 60% H_2O_2 (0.52 cm^3, 12.5 mmol). The bright yellow solution (pH 5.5) was adjusted to pH 8 using ammonia solution. The solution was placed in a refrigerator, whereupon yellow crystals formed overnight. The crystals were filtered off, washed with ethanol, and air-dried (Found: H, 2.6; N, 7.9; O_2^{2-}, 19.7. $H_{20}Mo_3N_4O_{17}$ requires H, 3.2; N, 8.8; O_2^{2-}, 20.1%). Infrared and Raman spectra, cm^{-1}: i.r. (Nujol mull) 953s, 918s, 885s, 841m, 820w, 796w, 670br, 616m, 585w, 559m, 470m, and 315w; Raman (solid, KBr disc) 958 (8), 936 (10), 900 (8), 884 (6), 864 (4), 619 (2), 587 (3), 566 (5), 556 (sh), 400 (2), 363 (4), 336 (4), 314 (4), 237 (sh), and 219 (7); (aqueous solution) 957 (7), 934 (10), 897 (9), 874 (sh), 850 (2), 580 (sh), 558 (4), 353 (1), 317 (3), 306 (4), and 210 (2).

$K_6[Mo_7O_{22}(O_2)_2]\cdot 8H_2O$. The method of Stomberg *et al.*[12] was modified as follows. Potassium molybdate (12.38 g, 52.0 mmol) was dissolved in water (40 cm^3), and the solution treated with 60% H_2O_2 (2 cm^3). The effervescent yellow solution was treated with concentrated HCl (*ca.* 3.7 cm^3) until the pH was 6.2. Addition of ethanol and storage at −5 °C gave a yellow solid, which was filtered off, washed with ethanol, and air-dried (Found: H, 0.9; K, 15.6; O_2^{2-}, 4.2. $H_{16}K_6Mo_7O_{34}$ requires H, 1.1; K, 16.0; O_2^{2-}, 4.4%). Infrared and Raman spectra, cm^{-1}: i.r. (Nujol mull) 935s, 900vbr, 840s, 825m, 650vbr, 580s, 470m, and 368w; Raman (solid, KBr disc) 930 (10), 921 (4), 910 (6), 898 (8), 892 (8), 872 (6), 844 (2), 830 (1), 632 (1), 588 (1), 537 (3), 467 (1), 451 (2), 410 (2), 366 (5), 336 (3), 312 (4), and 225 (8); (aqueous solution) 945 (10), 939 (sh), 926 (5), 908 (4), 897 (5), 870br, 600br, 569 (2), 372 (3), 353 (2), 306 (2), 238 (sh), and 212 (2).

Stoicheiometric Oxidation of Alcohols using $[PPh_4]_2[M_2O_3(O_2)_4]$ (M = Mo *or* W).—The oxidation procedure for *p*-anisyl alcohol using the molybdenum complex is typical.

p-Anisyl alcohol (24.7 mg, 0.17 mmol) and $[PPh_4]_2[Mo_2O_3(O_2)_4]$ (187 mg, 0.179 mmol) were dissolved in dichloromethane (50 cm^3) in a round-bottom flask. The solution was stirred for 3 h, after which t.l.c. [diethyl ether–light petroleum, b.p. 40—60 °C (50:50)] showed the reaction to be complete. The solution was evaporated to dryness, and the residue extracted with diethyl ether (2 × 25 cm^3). The combined ether extracts were evaporated to dryness, and the product dissolved in the minimum volume of ethanol. The solution was treated with an acidic, saturated solution (10 cm^3) of 2,4-dinitrophenylhydrazine in methanol to yield the hydrazone derivative. This was filtered off, washed with cold water, and dried to constant weight.

Investigation of Competing Epoxidation: Reaction of Cyclohexene with $[NBu_4]_2[Mo_2O_3(O_2)_4]$.—Cyclohexene (7.5 mg, 0.091 mmol) and $[NBu_4]_2[Mo_2O_3(O_2)_4]$ (77.6 mg, 0.091 mmol) were dissolved in CD_3CN (2 cm^3) and the mixture stirred under nitrogen for 24 h, after which time the solution had changed from dark yellow to light yellow. The proton n.m.r. spectrum was measured [δ 5.50, t, CH=CH; 3.00, t, $\overline{CH_2CH_2O}$; 1.78m and 1.30m, cyclohexyl CH_2; p.p.m. relative to $SiMe_4$]. The ratio of integrals of the triplet at δ 5.50 to the triplet at δ 3.00 was *ca.* 1:14.

General.—Raman spectra were measured for solids on a KBr matrix as spinning discs or in solutions in spinning cells using a Spex Ramalog 5 spectrometer and a Coherent Radiation Innova 90 krypton-ion laser, with excitation at 6 471 and 5 648 Å. Infrared spectra were measured on a Perkin-Elmer 683 instrument, for solids as liquid paraffin films between caesium iodide plates or as aqueous solutions between calcium fluoride plates. The ^{95}Mo and ^{183}W n.m.r. spectra were measured on a Bruker WM250 instrument at 16.43 and 10.42 MHz respectively in 10-mm tubes with a 5-mm insert containing ^2H_2O for locking purposes.

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References

1 Part 7, A. C. Dengel, W. P. Griffith, R. D. Powell, and A. C. Skapski, *J. Chem. Soc., Dalton Trans.*, 1987, 991.
2 K-H. Tytko and O. Glemser, *Adv. Inorg. Chem. Radiochem.*, 1976, **19**, 239.
3 J. A. Connor and E. A. V. Ebsworth, *Adv. Inorg. Chem. Radiochem.*, 1964, **6**, 279.
4 K. Y. S. Ng and E. Gulari, *Polyhedron*, 1984, **3**, 1001.
5 K-H. Tytko and K. Schönfeld, *Z. Naturforsch., Teil B*, 1975, **30**, 471.
6 M. Minelli, J. H. Enemark, R. T. C. Brownlee, M. J. O'Connor, and A. G. Wedd, *Coord. Chem. Rev.*, 1985, **68**, 169.
7 R. Stomberg, *Acta Chem. Scand.*, 1969, **23**, 2755.
8 R. Stomberg, *Acta Chem. Scand.*, 1968, **22**, 1076.
9 J. M. LeCarpentier, A. Mitschler, and R. Weiss, *Acta Crystallogr., Sect. B*, 1972, **28**, 1288; J. M. Le Carpentier and R. Weiss, *Chem. Commun.*, 1968, 1260.
10 F. W. B. Einstein and B. R. Penfold, *Acta Crystallogr.*, 1964, **17**, 1127.
11 L. Trysberg and R. Stomberg, *Acta Chem. Scand., Ser. A*, 1981, **35**, 823.

12 R. Stomberg, L. Trysberg, and I. Larking, *Acta Chem. Scand.*, 1970, **24**, 2678; I. Larking and R. Stomberg, *ibid.*, 1972, **26**, 3708.

13 I. Persdotter, L. Trysberg, and R. Stomberg, *Acta Chem. Scand., Ser. A*, 1986, **40**, 1.

14 I. Persdotter, L. Trysberg, and R. Stomberg, *Acta Chem. Scand., Ser. A*, 1986, **40**, 83.

15 R. Stomberg, *Acta Chem. Scand., Ser. A*, 1985, **39**, 507.

16 W. P. Griffith and T. D. Wickins, *J. Chem. Soc. A*, 1968, 397.

17 W. Massa and G. Pausewang, *Z. Anorg. Allg. Chem.*, 1979, **456**, 169.

18 D. M. Adams, 'Metal–Ligand Vibrations,' Arnold, London, 1967.

19 D. V. Luu and M. Abeaoza, *C.R. Acad. Sci., Ser. B*, 1969, **269**, 208.

20 D. J. Hewkin and W. P. Griffith, *J. Chem. Soc. A*, 1966, 472.

21 R. M. Wing and R. P. Callahan, *Inorg. Chem.*, 1969, **8**, 871.

22 W. P. Griffith, *J. Chem. Soc.*, 1964, 5248.

23 W. P. Griffith, *J. Chem. Soc.*, 1963, 5345.

24 G. A. Bogdanov, N. A. Korotchenko, and L. I. Kozlova, *Russ. J. Phys. Chem.*, 1977, **51**, 1108.

25 G. P. Aleeva, L. A. Kotorlenko, and V. A. Lunenok-Burmakina, *J. Struct. Chem. (USSR)*, 1972, **13**, 590.

26 A. J. Menéz, F. Pétillon, and J. E. Guerchais, *C.R. Acad. Sci., Ser. C*, 1969, **269**, 1104; J. E. Guerchais and M-T. Youinou, *ibid.*, 1967, **264**, 1389.

27 N. A. Korotchenko, L. I. Zakharkina, L. I. Kozlova, and G. A. Bogdanov, *Russ. J. Chem. Phys.*, 1975, **49**, 739.

28 N. A. Korotchenko, K. K. Fomicheva, F. A. Bogdanov, and N. K. Ivanova, *Russ. J. Phys. Chem.*, 1976, **50**, 1551.

29 K. F. Jahr and M. Blanke, *Z. Anorg. Allg. Chem.*, 1953, **272**, 45.

30 R. I. Tereskhima and G. A. Bogdanov, *Izv. Ulyssch. Uchev. Khim., Tek.*, 1967, **10**, 843; *Chem. Abstr.*, 1968, **68**, 53786.

31 G. A. Bogdanov, T. M. Kurokhtina, N. A. Korotchenko, and G. P. Aleeva, *Russ. J. Phys. Chem.*, 1970, **44**, 673.

32 W. P. Griffith, *J. Chem. Soc. A*, 1969, 211.

33 A. V. Arkhipov, T. M. Kurokhtina, G. L. Petrova, and G. A. Bogdanov, *Russ. J. Inorg. Chem.*, 1979, **24**, 936.

34 A. V. Arkhipov, T. M. Kurokhtina, G. L. Petrova, G. A. Bogdanov, and M. O. Bronnikova, *Russ. J. Inorg. Chem.*, 1980, **25**, 1493.

35 R. G. Beiles, R. A. Safina, and E. M. Beiles, *Russ. J. Inorg. Chem.*, 1961, **6**, 825.

36 G. M. Vol'dman, V. A. Debina, A. N. Zelikman, and E. E. Kharlmova, *Russ. J. Inorg. Chem.*, 1979, **24**, 49.

37 A. T. Harrison and O. W. Howarth, *J. Chem. Soc., Dalton Trans.*, 1985, 1173.

38 A. F. Ghiron and R. C. Thompson, *Inorg. Chem.*, 1988, **27**, 4766.

39 N. J. Campbell, J. Flanagan, W. P. Griffith, and A. C. Skapski, *Transition Met. Chem. (Weinheim, Ger.)*, 1985, **10**, 353.

40 G. A. Bogdanov and M. V. Savina, *Russ. J. Phys. Chem.*, 1968, **42**, 1321.

41 E. Wendling, R. Rohmer, and R. Weiss, *Rev. Chim. Miner.*, 1964, **1**, 255.

42 B. Piggott, S. F. Wong, and D. J. Williams, *Inorg. Chim. Acta*, 1988, **141**, 275.

43 M. Postel, C. Brevard, H. Arzoumanian, and J. G. Riess, *J. Am. Chem. Soc.*, 1983, **105**, 4922.

44 G. B. Payne and P. H. Williams, *J. Org. Chem.*, 1959, **24**, 54.

45 K. S. Kirshenbaum and K. B. Sharpless, *J. Org. Chem.*, 1985, **50**, 1979.

46 O. Bortolini, V. Conte, V. di Furia, and G. Modena, *J. Org. Chem.*, 1986, **51**, 2661.

47 P. Chaumette, H. Mimoun, L. Saussine, J. Fischer, and A. Mitschler, *J. Organomet. Chem.*, 1983, **250**, 291.

48 J. Prandi, H. B. Kagan, and H. Mimoun, *Tetrahedron Lett.*, 1986, **27**, 2617.

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