Reactions of Heteropolyanions in Non-polar Solvents. Part 3.[1] Activation of Dioxygen by Manganese(II) Centres in Polytungstates. Oxidation of Hindered Phenols†

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The heteropolyanions $[XW_{11}O_{39}\{Mn^{II}(OH_2)\}]^{n-}$ [X = P(**1**), Si (**2**), Ge (**3**), or B (**4**)] and α_2-$[P_2W_{17}O_{61}\{Mn^{II}(OH_2)\}]^{8-}$ (**5**) have been transferred into non-polar solvents (benzene, toluene) with the aid of tetraheptylammonium bromide or other phase-transfer agents. Following dehydration of their non-polar solutions, anions (**2**) and (**3**) show reactivity towards dioxygen. At temperatures below −35 [(**2**)] and *ca.* 22 °C [(**3**)] oxygenation produces a reversible colour change ($\lambda_{max.}$ 475, 585 nm); above these temperatures oxygenation results in irreversible oxidation to the manganese(III) heteropolyanions ($\lambda_{max.}$ 520 nm). The coloured oxygenated product is e.s.r.-inactive and is not formed in polar solvents nor in the presence of other polar solutes such as alcohols, pyridine, *etc.* Traces of water are, however, necessary for the formation of the colour, which intensifies as the temperature is lowered, and it is proposed that a weak dioxygen adduct is stabilised by a hydrogen-bonded water molecule. The rapid oxidation of anhydrous (**2**) by dioxygen was carried out in the presence of the spin trap 5,5-dimethyl-1-pyrroline *N*-oxide (dmpo). E.s.r. spectra indicate the transient formation of a polyanion–O_2–dmpo complex that decomposes to oxidised polyanion and dmpo–$O_2H^{\bullet}$. Solutions of anions (**2**), (**3**), and (**5**) catalyse the oxidation of 2,6- and 2,4,6-substituted phenols to benzoquinones or polyphenyl ethers, and e.s.r. evidence of polyanion–O_2–phenoxy radical complex formation is adduced. Comparisons are drawn with the chemistry of dioxygen complexes of cobalt(II). Anion (**1**) is neither oxygenated nor oxidised by O_2, and (**4**) is rapidly oxidised at −70 °C. Both behaviours are understandable in terms of the manganese(III)–manganese(II) redox potentials.

In recent years considerable attention has been directed towards the chemistry and potential applications of heteropolyanions,[2] especially with respect to catalysis.‡ Previous work from our laboratory has shown that it is possible to transfer highly charged polyanions into non-polar solvents and that such solutions exhibit new kinds of reactivity for these compounds.[1,4] One particularly exciting development concerns the use of polyanions of the type $[XM_{11}O_{39}\{M(OH_2)\}]^{n-}$ in which a 'surface' M atom can be dehydrated and become co-ordinatively unsaturated. The resulting anion, $[XM_{11}O_{39}M]^{n-}$, can then be considered as an inorganic metalloporphyrin analogue, as others have also since noted.[3g] In this connection we communicated[4a] some preliminary results concerning the reactivity of certain heteropolytungstates towards dioxygen. The present paper provides more details and demonstrates the activation of dioxygen by these heteropolyanions.

Results and Discussion

Of the heteropolyanions studied, $[PW_{11}O_{39}\{Mn(OH_2)\}]^{5-}$ (**1**), $[SiW_{11}O_{39}\{Mn(OH_2)\}]^{6-}$ (**2**), $[GeW_{11}O_{39}\{Mn(OH_2)\}]^{6-}$ (**3**), and $[BW_{11}O_{39}\{Mn(OH_2)\}]^{7-}$ (**4**) have structures in which an $Mn^{II}OH_2$ group has replaced $W^{VI}O$ in the well known Keggin structure[2] observed for dodecatungstates like $[PW_{12}O_{40}]^{3-}$, and α_2-$[P_2W_{17}O_{61}\{Mn(OH_2)\}]^{8-}$ (**5**) is similarly related to the structure of $[P_2W_{18}O_{62}]^{6-}$, the α_2 prefix signifying substitution at one of the apical tungsten sites of the Dawson structure.[2] The water ligand in (**1**)—(**5**) therefore occupies a position on the surface of the heteropolyanion. In their original studies of these complexes, Weakley, Tourné, and co-workers[5a,b] showed that oxidation to manganese(III) analogues was possible and reported the following manganese(III)–manganese(II) potentials: (**1**), +0.88; (**2**), +0.65; (**3**), +0.81; (**4**), +0.43; (**5**), +0.69 V *vs.* normal hydrogen electrode (n.h.e.). Oxidation of (**4**) could be achieved by bubbling air through an aqueous solution, but the other anions required more vigorous oxidation with disulphate.

When they have been transferred into a non-polar solvent like benzene or toluene with the aid of tetraheptylammonium bromide (Experimental section), anions (**2**)—(**5**) are oxidised to the manganese(III) state by passage of a stream of O_2. The rate of oxidation increases in the order (**4**) ('instantaneously' at −70 °C) > (**2**) > (**3**) ≫ (**5**) (incomplete after 12 h at ambient temperature).§ Anions (**2**) and (**3**) were selected for further investigation.

Oxygenation and Oxidation Experiments.—Electronic spectroscopy. The colour of a solution of anion (**3**) in toluene–$N(C_7H_{15})_4Br$ changes from yellow to orange (Figure 1) when the solution is 'dried' as described in the Experimental section. Addition of a drop of water to the dried solution restores the original colour and spectrum. We attribute the colour change to

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† *Non-S.I. units employed:* atm = 101 325 Pa, Torr ≈ 133 Pa, G = 10^{-4} T.

‡ Research activity is high in this area and has not been comprehensively reviewed recently. Recent papers from some different research groups (alphabetically by first author) that are currently active and provide an *entree* to the literature are listed in ref. 3 of the present paper.

§ The position of anion (**3**) in this series is not consistent with that inferred from its aqueous redox potential. There is no compelling reason why there should be a direct relationship between kinetic activity and *E*, although it is puzzling that the potentials of (**2**) and (**3**) should differ so much.

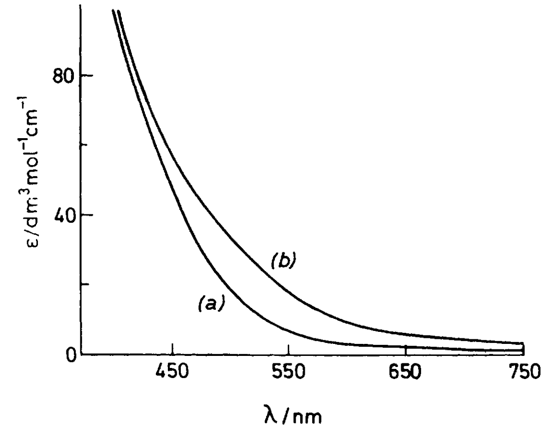

Figure 1. Electronic spectrum of $[GeW_{11}O_{39}\{Mn(OH_2)\}]^{6-}$ in toluene–$N(C_7H_{15})_4Br$ before (*a*) and after (*b*) dehydration as described in the Experimental section. Addition of a drop of water to the dehydrated solution restores the spectrum (*a*)

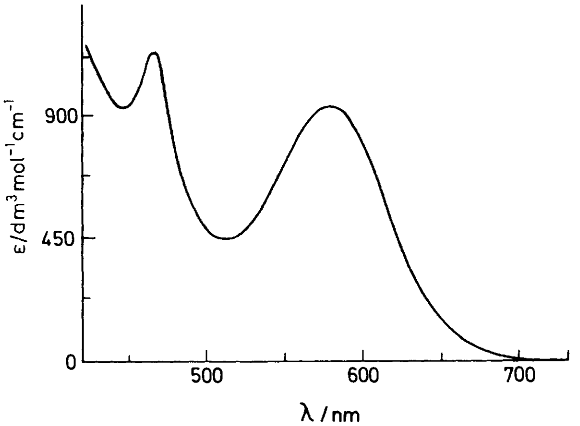

Figure 2. Electronic spectrum of 0.50 mmol dm^{-3} $[GeW_{11}O_{39}Mn]^{6-}$ in toluene–$N(C_7H_{15})_4Br$ glass at 77 K after oxygenation at −15 °C. Path length 0.1 mm

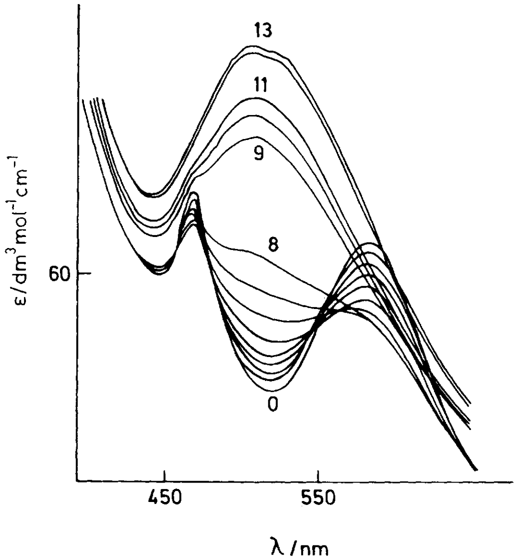

Figure 3. Spectral changes for an oxygenated toluene solution of 10.0 mmol dm^{-3} $[GeW_{11}O_{39}Mn]^{6-}$ stored at room temperature. Curves are labelled serially and correspond to a total elapsed time of 50 h

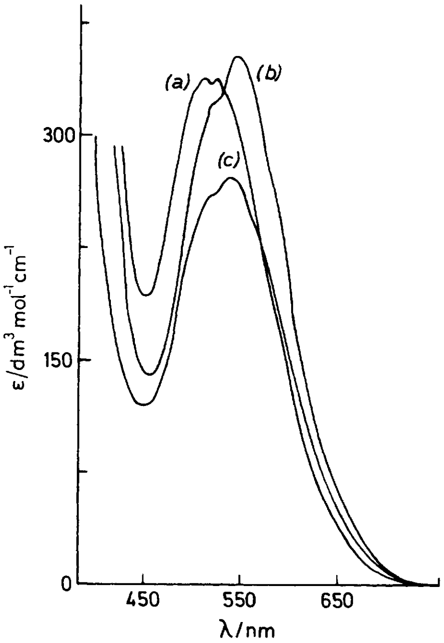

Figure 4. Electronic spectra recorded in toluene–$N(C_7H_{15})_4Br$: (*a*) freshly extracted $[GeW_{11}O_{39}\{Mn^{III}(OH_2)\}]^{5-}$; (*b*) the same solution after dehydration by nitrogen aspiration for 2 h; (*c*) a solution of $[GeW_{11}O_{39}Mn]^{6-}$ after oxygenation and ageing to complete oxidation

a partial dehydration (1). Such a dehydration following similar

$$[GeW_{11}O_{39}\{Mn(OH_2)\}]^{6-} \rightleftharpoons [GeW_{11}O_{39}Mn]^{6-} + H_2O \quad (1)$$

treatment was unambiguously demonstrated for the analogous cobalt(II)-substituted heteropolyanions since the ligand-field spectra of six- and five-co-ordinate Co^{II} are diagnostic.[4a] When molecular oxygen is bubbled through the dried solution of (**3**) at room temperature there is a rapid (< 5 s) colour change to green. The spectrum of the green solution is similar to that shown in Figure 2, but with about 5% of its intensity. If the green solution is cooled or if oxygenation is carried out at lower temperatures, the spectrum intensifies (the solution appears purple) and approaches that shown in Figure 2. The temperature effect is completely reversible. When argon or dinitrogen is bubbled through the oxygenated solution the original orange colour is restored, within 5 s at 20 °C but requiring up to 90 s at lower temperatures. The oxygenation–deoxygenation cycle is quantitatively reversible based on spectral intensities and is repeatable several times over a period of 5 h. After prolonged (overnight) exposure to dioxygen at room temperature there is evidence of irreversible oxidation to the manganese(III) heteropolyanion ($\lambda_{max.}$ 520 nm). Spectral changes, recorded over *ca.* 50 h, are shown in Figure 3. The tungstosilicate analogue (**2**) undergoes this behaviour much more rapidly (see below). The spectrum of a 'dried' solution of the authentic manganese(III) polyanion, $[GeW_{11}O_{39}\{Mn^{III}(OH_2)\}]^{5-}$, in toluene–$N(C_7H_{15})_4Br$ is shown in Figure 4, together with that of an O_2-oxidised solution of the manganese(II) complex. Both solutions have very weak manganese(II) e.s.r. spectra (see below) indicating incomplete oxidation (or partial reduction in the organic solvent). In aqueous solution the manganese(III) heteropolyanion is e.s.r.-silent, as expected. Even allowing for different chromophore concentrations in the two spectra of Figure 4, it is evident that there are slight differences. These differences *might* be attributable to the presence of different

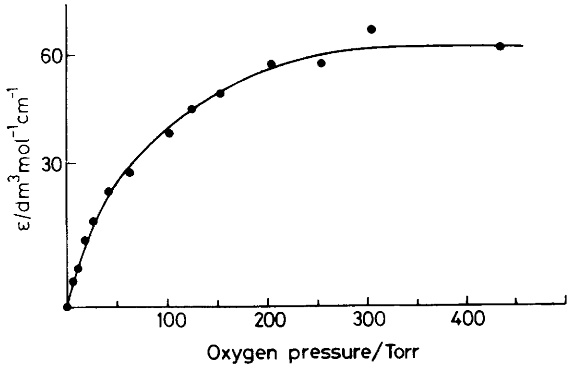

Figure 5. Effect of oxygen partial pressure on the 585-nm absorbance of a solution of $[GeW_{11}O_{39}Mn]^{6-}$ in toluene–$N(C_7H_{15})_4Br$ at 0 °C

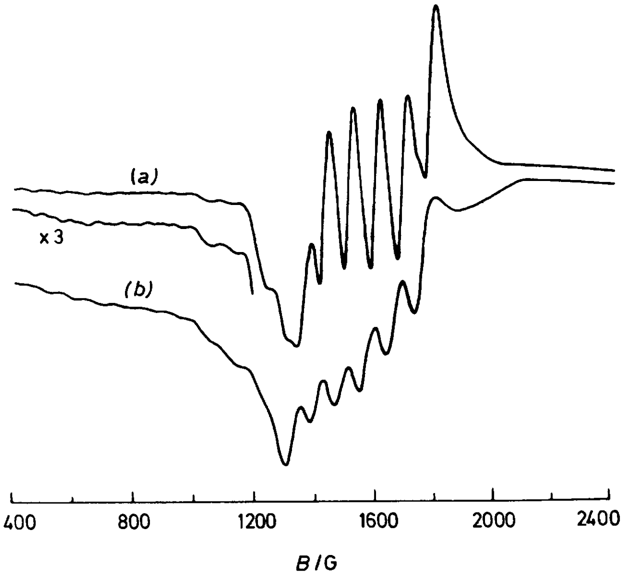

Figure 6. *X*-Band e.s.r. spectra in toluene–$N(C_7H_{15})_4Br$ at 77 K: (*a*) 'dried' $[GeW_{11}O_{39}\{Mn(OH_2)\}]^{6-}$ and (*b*) the product after oxygenation for 1 min at −14 °C, recorded at a gain of six times that of spectrum (*a*)

terminal ligands in the two cases, *e.g.* water *vs.* hydroxide or hydroperoxide for the O_2-oxidised solution (see discussion of the spin-trapping experiments below).*

Addition of polar substances such as water, pyridine, methanol, acetone, acetonitrile, and phenol rapidly bleaches the green or purple oxygenated solutions and restores the yellow colour of the original heteropolyanion. The presence of these molecules in the original solution is sufficient to prevent colour changes on oxygenation. Furthermore, if the heteropolyanion is phase-transferred in the presence of chloride ion (*e.g.* with Aliquat 336® or tetraheptylammonium chloride) the resulting solutions are unaffected by oxygenation. These results show that one condition for the colour change is direct inner-sphere contact of O_2 with Mn. Other observations indicate that *some* water is also required. Karl Fischer coulometric titration of solutions dried by aspiration of dry Ar, followed by Dean-Stark distillation as described in the Experimental section, revealed *ca.* 60 μg water per cm³ or about 0.5 mol water per mol heteropolyanion. If the solutions are more rigorously dried by treatment with acetone dimethyl acetal, followed by solvent-stripping and redissolution in fresh dry toluene, no colour change is observed upon oxygenation. The amount of residual water noted above suggests the possibility that the active complex might be a water-bridged dimer. Molecular weight measurements are impractical for polyelectrolyte solutes such as these, but the strong six-line e.s.r. spectrum of the dehydrated solution and the spin-only magnetic moment determined by the Evans method [5c] lead us to favour a monomer.

The behaviour of solutions of the Si-centred anion, (**2**), towards oxygen is similar to that described for (**3**) except that the former anion is much more reactive. The colour change upon oxygenation is fully reversible between −35 and −75 °C but at higher temperatures the irreversible oxidation also occurs and above *ca.* 0 °C oxidation is the only detectable behaviour. At room temperature the oxidation is virtually instantaneous when the solution has been dried, but even a freshly phase-transferred (hydrated) solution is oxidised after about 15 min of oxygen treatment. If pyridine is added to the dried toluene solution, oxidation is slowed still further and some 3 h of oxygenation is necessary to achieve a colour change. In contrast, *aqueous* solutions of (**2**) are unaffected by prolonged passage of oxygen.[5a,b]

Stoicheiometry of oxygenation. Attempts were made to measure the stoicheiometry of the oxygenation of the Ge-centred anion, (**3**), in toluene–$N(C_7H_{15})_4Br$ at 0 °C by direct gas uptake or by means of an oxygen electrode as described in the Experimental section. Both methods gave variable results† within the range of 0.06—0.15 mol O_2 per mol of heteropolyanion when 1—10 mmol dm⁻³ solutions were equilibrated against 1 atm of O_2 at 0 °C. The effect of oxygen partial pressure upon the solution absorbance at 585 nm (corresponding to the maximum in Figure 1) is shown in Figure 5. Apparent saturation occurs at an oxygen pressure of 400 Torr for a 10 mmol dm⁻³ solution at 3 °C. If the oxygen-saturated solution is cooled to 77 K the absorbance increases about ten-fold (*cf.* Figure 2).

Other measurements. It is tempting to consider that the species responsible for the electronic spectrum of Figure 2 is some form of oxygen adduct, for which other precedents exist with manganese complexes,[6] indeed the spectra of the oxygenated solutions are remarkably similar to those reported by McAuliffe and co-workers[6h–j] for $[MnX_2(PR_3)_2]$–O_2 adducts, which however are thought to be pseudo-tetrahedral species. In the present case little can be done to characterise the adduct more fully. The apparent degree of conversion (*ca.* 10%) indicated by the oxygen-uptake experiments is supported by magnetic susceptibility measurements. Upon oxygenation at −15 °C the magnetic moment diminishes by 12%, and is restored to its original value when the solution is deoxygenated by passage of N_2. We have examined oxygenated solutions at −20 to 0 °C by resonance Raman spectroscopy but cannot detect any absorptions not obscured by solvent peaks that can be attributed to superoxo or peroxo species. There is no detectable change of the e.s.r. spectrum, measured at 77 K (see Figure 6) of dried solutions of anion (**2**) or (**3**) immediately following oxygenation (in this respect the complexes differ from those reported by McAuliffe) although such solutions have the electronic spectrum shown in Figure 2. The e.s.r. (but not the electronic) spectrum is affected when oxygenation is carried out at −10 to −15 °C for a minute or so, or at room temperature for 15—30 min. As shown in Figure 6(*b*), the e.s.r. spectrum of such solutions is much weaker and is characterised by a different

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* There is no good precedent for this statement however. In aqueous solution the spectra of $[Mn(H_2O)_6]^{3+}$ and $[Mn(H_2O)_5(OH)]^{2+}$ differ only in intensity (C. F. Wells and G. Davies, *J. Chem. Soc. A*, 1967, 1858), presumably as a result of loss of symmetry.

† The variability can probably be traced to the relatively large blank values. The solubility of dioxygen in toluene–$N(C_7H_{15})_4Br$ is comparable to the concentration of the heteropolyanion.

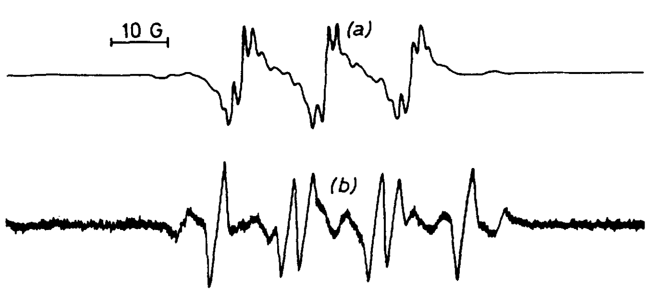


Figure 7. Room-temperature *X*-band e.s.r. spectra of 0.1 mol dm^{-3} dmpo and KO_2–18-crown-6. Solvent: (*a*) toluene, (*b*) 0.1 mol dm^{-3} $N(C_7H_{15})_4Br$ in toluene

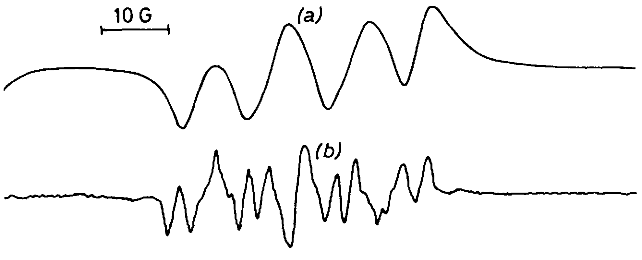


Figure 8. *X*-Band e.s.r. spectra of 10 mmol dm^{-3} $[SiW_{11}O_{39}Mn]^{6-}$ in toluene–$N(C_7H_{15})_4Br$–0.1 mol dm^{-3} dmpo after oxygenation for 1 min: (*a*) immediately after oxygenation, (*b*) after 15 min

hyperfine splitting (88.5 *vs.* 86.3 G for the original spectrum). The spectrum shown in Figure 6(*a*) is completely restored after passage of N_2, and we tentatively attribute the spectral change to the effects of saturation of the solution by oxygen. Interaction of O_2 with the manganese centre must be very weak since the colour change is observed only in the absence of any polar species that can compete for co-ordination to manganese. Since the presence of some water is necessary for the development of the colour, the strong temperature dependence of the absorbance leads us to speculate that a ternary six-co-ordinate complex involving Mn^{II}, co-ordinated O_2, and a hydrogen-bonded water molecule might be responsible for the colour. We have observed that hydration of, *e.g.*, green $[SiW_{11}O_{39}Co]^{6-}$ to red $[SiW_{11}O_{39}\{Co(OH_2)\}]^{6-}$ in toluene is strongly enhanced at lower temperatures. Hydrogen-bonding interactions involving metal-bound dioxygen are well established.[7]

Oxygen Activation.—Spin trapping. They very rapid oxidation of the Si-centred anion, (**2**), by dioxygen suggests the possibility of superoxide ion formation. Experiments were carried out with the spin trap 5,5-dimethyl-1-pyrroline *N*-oxide (dmpo). In Figure 7 are shown the e.s.r. spectra of KO_2–18-crown-6 (1,4,7,10,13,16-hexaoxacyclo-octadecane) in toluene and toluene–$N(C_7H_{15})_4Br$, in the presence of 0.1 mol dm^{-3} dmpo. The spectrum in toluene [$A(N)$ 13, $A(H_\beta)$ 5.5, and $A(H_\gamma)$ 1.25 G] is in good agreement with that reported for the superoxide adduct of dmpo in benzene [$A(N)$ 12.9 and $A(H_\beta)$ 6.9 G].[8] The spectrum in toluene–$N(C_7H_{15})_4Br$ is shown in Figure 7(*b*) [$A(N)$ 13.2 and $A(H_\beta)$ 11 G] and is stable for at least 24 h, in contrast to the spectrum in toluene alone which decays after about 3 min. The stable spectrum has parameters close to that reported for dmpo–$O_2^{\bullet}$ in water [$A(N)$ 14.3, $A(H_\beta)$ 11.7, and $A(H_\gamma)$ 1.25 G][9] and may well identify the adduct of dmpo with $HO^{\bullet}$, formed by decompositon of dmpo–$O_2H^{\bullet}$.

Addition of dmpo (*ca.* 0.1 mol dm^{-3}) to a dried 10 mmol dm^{-3} solution of (**2**) in toluene–$N(C_7H_{15})_4Br$ yielded a solution with no observable e.s.r. spectrum in the $g = 2$ region. After oxygenation for 1 min (instantaneous colour change) the upper e.s.r. spectrum shown in Figure 8 was produced. This spectrum began to be transformed after about 3 min and ultimately resulted in the lower spectrum shown in Figure 8. The final spectrum may be resolved into a mixture of the lower spectrum of Figure 7 and a three-line spectrum attributed to the oxidation product of the spin trap, 5,5-dimethyl-2-pyrrolidone-1-oxyl (dmpox) [$A(N) = 13$ G[10]]. When the experiment was repeated with a longer period of oxygenation (5—10 min) no transient spectra were observed on completion, and the spectrum of dmpox only was produced.

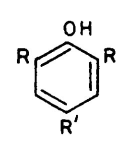
The transient broad spectrum shown in Figure 8 was simulated with $A(N) = 12.5$ and $A(H_\beta) = 7.75$ G and is plausibly attributed to the adduct of dmpo with $[SiW_{11}O_{39}Mn^{III}O_2^{\bullet}]^{6-}$ or a hydrated/protonated form of this, as suggested for an analogous adduct of a Co^{III}–O_2 complex.[10] The line broadening in the present case results from enhanced relaxation by nearby paramagnetic Mn^{III} and/or from slow tumbling caused by the attached large heteropolyanion. A similar adduct, with phenoxy radicals, has been implicated in the oxidations of phenols with cobalt dioxygen complexes.[11] Decomposition of the manganese(III) superoxo adduct to give $[SiW_{11}O_{39}\{Mn^{III}(OH)\}]^{6-}$ and dmpo–$O_2H^{\bullet}$ ($\longrightarrow$ dmpo–$OH^{\bullet}$?) could account for the subsequent spectral changes.

Phenol oxidations. Addition of phenols to dried (orange) solutions of anions (**2**) and (**3**) in toluene–$N(C_7H_{15})_4Br$ restored the yellow colour of the hydrated anions as was noted above with the addition of other polar substances. The e.s.r. spectra of the polyanion–phenol mixtures, measured at 77 K, showed two overlapping sets of six hyperfine lines at $g = ca.$ 4.3, one corresponding to the original polyanion [*cf.* Figure 6(*a*)] and the second attributed to a phenol–polyanion complex. The relative intensities of the two sets of lines varied with the phenol/polyanion ratio, but complete saturation was not achieved with up to a 200-fold excess of phenol. Comparison of the reaction of (**2**) with 2,6-dimethylphenol and 2,6-di-t-butylphenol indicated that the latter, as expected in view of its bulky substituents, was less effective at modifying the colour and e.s.r. spectrum of the polyanion solution.

In addition to phenol itself, five methyl- and t-butyl-substituted phenols were studied. When polyanion–phenol solutions in toluene–$N(C_7H_{15})_4Br$ were oxygenated, a colour change (to brown-green) occurred within *ca.* 5 to 600 s if the phenol was substituted in the 2 and 6 positions. The colour change was most rapid with the t-butyl-substituted phenols. With 3,5-dimethylphenol and unsubstituted phenol the colour change was much slower and less extensive, *e.g.* no change was observed with (**3**) and 3,5-dimethylphenol after oxygenation for 30 min at 0 °C, but a slight colour appeared when the solution was allowed to stand overnight. Examination of the coloured solutions by thin-layer chromatography, ^1H and ^{13}C n.m.r. spectroscopy revealed various phenol oxidation products. The cleanest reaction occurred with 2,6-dimethylphenol (**B**) which yielded only the polyether [^1H 2.05 (6 H) and 6.69 (2 H); ^{13}C 17.50, 115.67, 133.86, 146.80, and 156.20 p.p.m.; ν(C–O) 1 190 cm^{-1}], and which was easily separated from starting material by elution with benzene on a silica gel column. The major products from the other active phenols were the corresponding benzoquinones. The results of a series of comparative experiments are summarised in the Table.

Oxidation of phenols by molecular oxygen catalysed by metal complexes that are known to bind dioxygen reversibly [*e.g.* cobalt(II) Schiff-base complexes, manganese porphyrins] has been intensively studied in recent years.[11,12] The products listed in the Table are among those observed in the earlier studies and strongly suggest that similar mechanisms (see below) pertain in the tungstomanganate-catalysed oxidations. The initial step in any mechanism is of course the generation of the phenoxy radical, and in the cases of phenols (**D**)—(**F**), characteristic e.s.r.

Table. Phenol oxidations[a] catalysed by $[SiW_{11}O_{39}Mn]^{6-}$

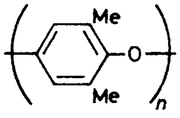


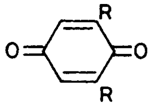
(A) R = R′ = H
(B) R = Me, R′ = H
(C) R = R′ = Me
(D) R = Bu^t, R′ = H
(E) R = Bu^t, R′ = Me
(F) R = R′ = Bu^t

Phenol	Conversion (%)	Product[b] (proportion)
(A)	0	
(B)	*ca.* 0	Traces of (i)
(B)	31[c]	(i) (100)
(C)	0	
(D)	100	(ii) (83), (iii) (17)
(E)	87	(ii) (75), (iv) (9), (v) (7)[d]
(F)	96	(vi) (4)[e]

[a] Reactions carried out in toluene–$N(C_7H_{15})_4Br$ as described in the text: ambient temperature; oxygen partial pressure, 1 atm; 2 h, unless stated otherwise.

[b]


(i)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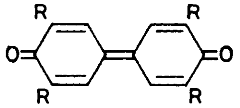
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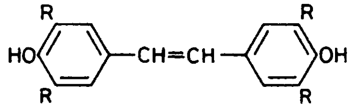
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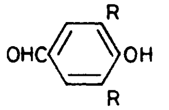
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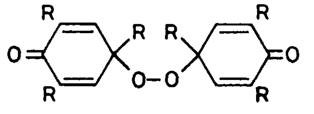
(vi)

[c] Above solution after 24 h. [d] Unidentified products, 9%. [e] Two unidentified products, 89 and 7%.

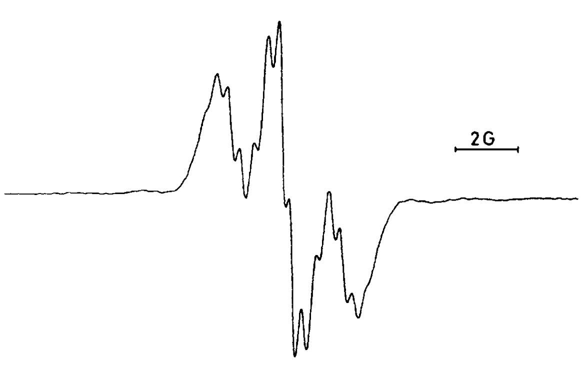

Figure 9. *X*-Band e.s.r. spectrum of the 2,4,6-tris(t-butyl)phenoxy radical produced by oxygenation of a toluene solution of the corresponding phenol (F) in the presence of $[SiW_{11}O_{39}Mn]^{6-}$

spectra[13] of the corresponding radicals were observed after a few seconds of oxygenation. Lifetimes for the radicals under these conditions ranged from >24 h (F) to *ca.* 1 min (D).

Control experiments in which the heteropolyanion was omitted, or was replaced by $[SiW_{12}O_{40}]^{4-}$ or by $[SiW_{11}O_{39}\{Mn^{III}(OH_2)\}]^{5-}$ yielded no colour changes, radicals, or phenol oxidation products. In another control a solution of anion (2) in toluene–$N(C_7H_{15})_4Br$ was oxygenated for 3 h to yield the manganese(III) polyanion, (B) was added, and oxygenation was continued for a further 2.5 h. Although the red-purple colour of Mn^{III} changed to brown-green after a few minutes, no trace of phenol oxidation product was detected. This experiment demonstrates that (*a*) $[SiW_{11}O_{39}\{Mn^{III}(OH_2)\}]^{5-}$ that has been prepared in aqueous solution and phase-transferred into toluene is not identical to the manganese(III) heteropolyanion that has been produced by O_2 oxidation of $[SiW_{11}O_{39}Mn]^{6-}$ *in situ*, and which perhaps is $[SiW_{11}O_{39}\{Mn^{III}(OH)\}]^{6-}$, (*b*) the brown-green colour is formed only in the presence of the O_2-oxidised manganese(III) polyanion and phenol, and (*c*) neither manganese(III) species alone is able to generate the phenoxy radical required to initiate autoxidation.

A few experiments were carried out with anions (1) and (5) with phenol (F). In the case of the 1:11 heteropolyanion, (1), oxygenation produced no colour change or radical formation, and the e.s.r. spectrum at 77 K showed no extra lines that might indicate complex formation with the phenol. With the 2:17 anion, (5), oxygenation for 1 min at room temperature led to the formation of a broad (6 G) featureless e.s.r. signal at $g = 2$. A similar broad signal was observed in the early stages of oxygenation of mixtures of $[SiW_{11}O_{39}Mn]^{6-}$ and (F); after 5—10 min the spectrum narrowed into the fully hyperfine-resolved spectrum of the radical of (F) (Figure 9). In both cases, the initial broad signals were attributed to radical-polyanion complexes analogous to that observed for the spin trap (Figure 8).

Conclusions

It seems clear that the activity of the heteropolyanions in toluene is determined by the facility with which the terminal water ligand on manganese(II) is lost, and by the manganese(II)–manganese(III) redox potential. Although we cannot directly detect the loss of the terminal water ligand, activity towards oxygenation and oxidation is not observed in aqueous solutions, nor when the phase-transferred solutions contain a significant amount of water. Furthermore such activity is repressed when other potential ligands (alcohols, pyridine, *etc.*) are present. The yield of the coloured product of oxygenation of the Si- and Ge-centred anions is not increased above about 10% by increase of the oxygen partial pressure, but is increased by lowering the temperature of the oxygen-saturated solution. Since no colour is produced when water is rigorously removed, and since we have observed with analogous heteropolytungstates of Co^{II} and Cu^{II} in toluene solutions that a water ligand becomes more tightly associated with M^{II} as the temperature is lowered, we speculate that the coloured species is a dioxygen adduct of the polyanion, stabilised by a hydrogen-bonded water molecule. An analogous situation has been proposed for the [methylbis(3-salicylideneaminopropyl)amine]-cobalt(II)–O_2 complex stabilised with trifluoroethanol.[10] The spin-trapping experiments demonstrate that O_2 becomes activated towards superoxide when associated with the heteropolyanion. Since the final product is undoubtedly Mn^{III}, it seems plausible to assume that an inner-sphere electron-transfer process has taken place. The same process can be considered for the phenol oxidations, in which an '$Mn^{III}O_2$' moiety abstracts a hydrogen atom from the phenol, thereby, initiating the radical autoxidation in a manner suggested for other systems.[11,12,14] The relatively large yield of benzoquinone from phenols (D) and (E) suggests that the polyanion–O_2 species attacks the *para* position of the phenols in a fashion analogous to that proposed for cobalt(II)–dioxygen complexes.[11,12]

Experimental

Materials.—The potassium salts of $[XW_{11}O_{39}\{Mn^{II}(OH_2)\}]^{n-}$ (X = P, Si, Ge, or B), α_2-$[P_2W_{17}O_{61}\{Mn^{II}(OH_2)\}]^{8-}$, and the guanidinium salts of $[XW_{11}O_{39}\{Mn^{III}(OH_2)\}]^{(n-1)-}$ were prepared according to literature procedures.[4] The phase-transfer agents, tetraheptylammonium bromide and chloride, were obtained from Eastman and Aldrich respectively; methyltrioctylammonium chloride (Aliquat 336®) was a gift from Sherex Chemical Co. Benzene, toluene, and xylenes (spectragrade) were generally used without further purification, unless 'extra dry' conditions were required. In this case the solvents were distilled over sodium–benzophenone and passed through a column of alumina (Woelm N-Super I) under N_2, and stored over sodium on a vacuum line. Extra dry N_2 (99.997%, < 1 p.p.m. water) and extra dry O_2 (99.8%) were used for the dehydration and oxygenation experiments.

Phase Transfer.—The general procedure was as follows. An unbuffered 10 mmol dm^{-3} aqueous solution of the heteropolyanion was shaken briefly with an equal volume of 0.1 mol dm^{-3} $N(C_7H_{15})_4Br$ in benzene or toluene. Since all the heteropolyanions were coloured, it was easy to observe the complete transfer from the aqueous to the organic layer. After the two phases had been allowed to settle for 10 min they were separated. The organic layer at this stage was discovered, *via* Karl Fischer titration, to contain between 4 000 and 5 000 μg water per cm^3 or about 25 H_2O per heteropolyanion. A control experiment showed that the bulk of this water is transferred by the phase-transfer agent, and is presumed to be contained in reverse micelles. The water content was reduced to *ca.* 60 μg cm^{-3} (0.4 H_2O per heteropolyanion) by a 2-h aspiration of dry N_2 followed by a 1-h reflux under N_2 in a Dean-Stark apparatus. Alternatively, the water was removed (to about the same level) by repeated stripping of the solvent on a rotary evaporator and redissolution in fresh dry solvent. The heteropolyanions could be transferred back into water by shaking the toluene solutions with 0.1 mol dm^{-3} $NaClO_4$ or KI. Potassium hyperoxide (KO_2) solutions in benzene or toluene were prepared using 18-crown-6 or dicyclohexyl-18-crown-6 (eicosahydrodibenzo[*b,k*][1,4,7,10,13,16]hexaoxacyclo-octadecane). For example, for 28 mmol dm^{-3} KO_2 in toluene, the solid (9.7 mg) was added to 28 mmol dm^{-3} crown ether (5 cm^3) in toluene, and the mixture sonicated for 6 h.

Spectroscopy.—Electronic spectra were recorded on Cary 14 or Hewlett-Packard 8415A instruments. A jacketted 1.000-cm quartz cell through which was circulated an appropriate coolant (acetone–solid CO_2 or ethyl acetate–liquid nitrogen) was used for spectra at −80 to 20°C. Spectra at 77 K were measured in a VLT-2 unit (Research and Industrial Instruments Co.) using an FH-01 cell of 0.1 mm path length. Spectra under different partial pressures of oxygen were measured in the jacketted cell connected to a simple manifold through which N_2, O_2, or a vacuum could be connected to the cell. The total pressure above the cell was recorded with a mercury manometer. In a typical experiment the solution was introduced into the evacuated cell under an atmosphere of N_2 and allowed to reach thermal equilibrium (*ca.* 15 min). The N_2 was pumped off and the desired pressures of N_2 and O_2 were admitted through the manifold. The spectrum was recorded at intervals until three consecutive scans were identical. This usually required 45—60 min. The gases were then pumped out and a new set of pressures of O_2 and N_2 applied. Vibrational spectra were run on Perkin-Elmer 225 or 457 spectrometers using KBr discs or a 0.050-cm cell with AgCl windows. *X*-Band e.s.r. spectra were recorded on a Varian E-4 spectrometer equipped with a TM_{110} rectangular cavity and an E-4557-9 variable temperature accessory. An immersion Dewar was used for spectra at 77 K. Spectra were simulated using a program described by Perkins *et al.*[15] Proton and ^{13}C n.m.r. spectra were recorded on a Bruker AM-300WB spectrometer. Magnetic susceptibilities of polyanion solutions were estimated by the Evans method[5c] using a Bruker WH-90 spectrometer and coaxial cells WGS-BL and 507-PP (Wilmad).

Other Measurements.—The oxygen uptake of toluene–$N(C_7H_{15})_4Br$ solutions with or without heteropolyanion was measured by (*a*) a gas burette or (*b*) an oxygen electrode. The gas burette procedure employed a modification of the apparatus described by McAuliffe *et al.*[6i] In a typical experiment, a pre-evacuated flask (100 cm^3) was charged with solution (80 cm^3). After thermal equilibration [most measurements were made in an ice–water bath (0 °C)] the flask was opened to an oxygen-filled gas burette and reservoir (1 000 cm^3) that had also been thermally equilibrated. After 2—3 h oxygen absorption was complete and the burette level read with a cathetometer. In the oxygen electrode procedure, the oxygenated toluene solution (10 cm^3) was syringed into nitrogen-saturated 0.1 mol dm^{-3} $NaClO_4$ (280 cm^3) contained in a septum-closed bottle. After vigorous magnetic stirring for 1 min, the phases were allowed to separate for 5 min. A stopcock sealed into the side of the bottle was opened and allowed most of the lower (aqueous) layer to be transferred to another bottle containing a precalibrated oxygen electrode (Orion Research, model 97-08). The transfer procedure was necessary to avoid contact of the electrode's membrane with the organic solvent.

Water was determined by Karl Fischer titration using Hydranal® reagents (Crescent Chemical Co.) and by coulometry with a 658 KF processor (Sybron/Brinkmann Instruments). Chromatography was carried out with Baker-flex IB-F silica gel sheets, or for preparative t.l.c. on precoated silica gel 60 F_{254} plates, using benzene as the mobile phase. Liquid chromatograms were recorded on a Perkin-Elmer series 10 chromatograph connected to a Waters Associates model 440 absorbance detector.

Phenol Oxidations.—Comparative experiments were carried out under 1 atm O_2 at 25 °C. A stock solution of heteropolyanion was prepared in toluene (50 cm^3) by transferring $K_6[SiW_{11}O_{39}\{Mn(OH_2)\}]\cdot 21H_2O$ (1.6814 g, 0.50 mmol) dissolved in water (50 cm^3), with the aid of $N(C_7H_{15})_4Br$ (1.4728 g, 3.0 mmol) in toluene (50 cm^3). After removal of excess of water, 10-cm^3 aliquots were withdrawn, mixed with the appropriate phenol (0.5 mmol), and placed in a round-bottom flask (500 cm^3) that was attached to a shaker and a pressure manifold/manometer. The flask was evacuated and flushed three times with argon, a pressure of 1 atm oxygen was applied, and the flask shaken vigorously for 2 h. The resulting solution was analysed by high-performance liquid chromatography, using 10% dichloromethane in hexanes as the eluant.

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