

Homogeneous-phase catalytic H₂O₂ oxidation of isobutyraldehyde using Keggin, Dawson and transition metal-substituted lacunary heteropolyanions

Ji Hu, Robert C. Burns*

School of Biological and Chemical Sciences, University of Newcastle, Callaghan, NSW 2308, Australia

Received 15 August 2001; accepted 15 January 2002

Abstract

The relative effectiveness of a range of heteropolyoxometalate catalysts with Keggin, Dawson and transition metal-substituted lacunary structures has been compared using the homogeneous-phase oxidation of isobutyraldehyde to isobutyric acid with H₂O₂ in acetonitrile at 50 °C. For the Keggin ([XM₁₂O₄₀]^{m-}, X = P(V), Co(III), Fe(III), Co(II), Zn(II), M = W(VI); X = P(V), M = Mo(VI) and Dawson ([X₂Mo₁₈O₆₂]^{m-}, X = P(V), S(VI)) structures, catalytic activity increased with decreasing anionic charge. In the case of the prototypical [PW₁₂O₄₀]³⁻ ion, kinetic studies indicated that there was association of the isobutyraldehyde and phosphopolyoxotungstate prior to oxidation of the former by H₂O₂. No fragmentation of the tungsten-containing species, such as [PW₁₂O₄₀]³⁻ and [CoW₁₂O₄₀]⁶⁻, occurred under the reaction conditions, as shown by ³¹P NMR and UV–VIS spectroscopy, respectively while both [PMo₁₂O₄₀]³⁻ and [P₂Mo₁₈O₆₂]⁶⁻ generated small amounts of peroxy-species based on ³¹P NMR studies. The transition metal-substituted lacunary polyoxomolybdate systems of the type [PZ(II)(Br)Mo₁₁O₃₉]⁶⁻, where Z = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II), are likely degraded to (PO₄[MoO(O₂)₂]₄)³⁻ and/or related species by H₂O₂, based on UV–VIS spectroscopic studies and on ³¹P NMR studies of diamagnetic [PZn(Br)Mo₁₁O₃₉]⁶⁻. The resulting products are only slightly more active catalysts than the Keggin anions (a maximum increase in activity by a factor of ~7). The initial rates of reaction followed the sequence Co(II) > Ni(II) > Zn(II) > Mn(III) > Cu(II), with Mn(II) undergoing oxidation by H₂O₂ under the reaction conditions. The order likely corresponds to a combination of the catalytic abilities of the transition metal-substituted lacunary anions in conjunction with their rates of decomposition by H₂O₂, and/or the catalytic abilities of the freed transition metals and peroxy-products themselves. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Homogeneous catalysis; Heteropolyoxometalate; Hydrogen peroxide; Oxidation

1. Introduction

Liquid-phase oxidations of organic substrates that are catalyzed by heteropolyoxometalates in either homogeneous or biphasic systems have been

studied using a wide range of oxidants including molecular oxygen, hydrogen peroxide, alkyl peroxides, iodosylarenes, etc. [1–6]. In such reactions, the multi-component heteropolyoxometalate redox catalysts are considered to be robust oxidation-resistant inorganic metalloporphyrin analogues. Of the above oxidants, the most environmentally benign are molecular oxygen and hydrogen peroxide [1,2]. While dioxygen contains 100% active oxygen and generates

* Corresponding author. Tel.: +61-2-49215479;

fax: +61-2-49215472.

E-mail address: csrcb@paracelsus.newcastle.edu.au (R.C. Burns).

no by-products, H_2O_2 has 47% active oxygen and the only by-product is water. The latter, therefore, represents an attractive oxidant for organic oxidations, and it is well known that molybdenum and tungsten compounds, such as their oxides, are active catalysts for oxidations using this species. In oxidation reactions the heteropolyoxometalates of molybdenum and tungsten catalyze the epoxidation of alkenes, and the oxidation of alcohols, diols, glycols, etc. under both homogeneous and biphasic conditions [1,2,7–11]. Moreover, peroxy derivatives of the polyoxometalates have been found to be active intermediates in these types of reactions [7,9].

Perhaps the best studied of the catalyst systems using H_2O_2 are those of Ishii and co-workers [12,13], and Venturello and co-workers [9,14,15]. These systems are, in the main, closely related to polyoxometalate systems in that the active catalyst appears to be $(\text{PO}_4[\text{WO}(\text{O}_2)_2]_4)^{3-}$ (or $[\text{PW}_4\text{O}_{24}]^{3-}$) which is analogous to the equivalent $(\text{PO}_4[\text{MoO}(\text{O}_2)_2]_4)^{3-}$ species originally reported by Beiles et al. [16]. The structure of the tungsten peroxy-species has been elucidated as the $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ salt [9]. Even when the source of the molybdenum and tungsten is the Keggin ion $[\text{PM}_{12}\text{O}_{40}]^{3-}$ (where $\text{M} = \text{Mo}, \text{W}$) it appears that the catalyst species is still $(\text{PO}_4[\text{MO}(\text{O}_2)_2]_4)^{3-}$ (where $\text{M} = \text{Mo}, \text{W}$), especially in biphasic systems, as these are generated by the breakdown of the corresponding heteropolyoxometalate anions. Indeed, there appears to be a large number of monomeric and polymeric peroxy-species related by a series of fast equilibria [17,18].

While the above studies indicate breakdown of the polyoxometalate framework of the Keggin structure of both $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and $[\text{PW}_{12}\text{O}_{40}]^{3-}$, there are examples of oxidations using H_2O_2 in which the framework remains intact. Thus, it has been shown that lacunary and transition metal-substituted 11-tungstates are better catalysts than $[\text{PW}_{12}\text{O}_{40}]^{3-}$ for the oxidation of cyclohexene in biphasic (1,2-dichloroethane/water) systems at 67°C [10]. Similarly, the heteropolyoxotungstate species $[\text{Fe}_4(\text{PW}_9\text{O}_{34})_2]^{10-}$ is stable towards H_2O_2 , and catalyzes the selective epoxidation of alkenes in aqueous acetonitrile at 20°C [19]. Moreover, species of the type $[\text{WM}_3(\text{H}_2\text{O})_2(\text{XW}_9\text{O}_{34})_2]^{12-}$, where $\text{X} = \text{M} = \text{Co}^{2+}$ and Zn^{2+} , appear resistant to hydrolysis and also to degradation by H_2O_2 , and are active in the

epoxidation of alkenes and the oxidation of alcohols [20].

Few of the above studies have addressed the differences between various types of heteropolyoxometalates or the mechanisms of the reactions through a kinetic study. The aim of the present work was to select an easily oxidizable model organic substrate and investigate its oxidation under *homogeneous* conditions by H_2O_2 , using a range of heteropolyoxometalates with different compositions, structures and charges. Some limited kinetic studies were also undertaken in order to shed light on the mechanism(s) by which oxidation is accomplished in the case of non-lacunary heteropolyoxometalates. The model substrate chosen was isobutyraldehyde, which is a by-product from the oxo synthesis of propene to give *n*-butyraldehyde, a raw material for plasticisers. It can, however, serve as a feedstock material for the synthesis of valuable methacrylic acid following conversion to methacrolein or isobutyric acid, while methacrylic acid yields methyl methacrylate following neutralization with methanol, and finally poly(methyl methacrylate) upon polymerization. The most comprehensive study of the oxidation of isobutyraldehyde to isobutyric acid is that reported by Emig et al. [21], who described the overall kinetics of the oxidation in aqueous solution using several catalysts, including an undefined cobalt heteropoly catalyst. That study employed oxygen gas as the oxidant, but no studies have reported the use of H_2O_2 as an oxidant for isobutyraldehyde.

2. Experimental

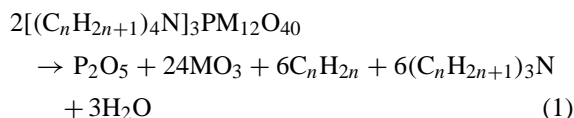
2.1. Syntheses of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{PMo}_{12}\text{O}_{40}$, $[\text{R}_4\text{N}]_3\text{PW}_{12}\text{O}_{40}$, [where $\text{R} = n\text{-C}_4\text{H}_9$ (^nBu), $n\text{-C}_6\text{H}_{13}$ (^nHx), $n\text{-C}_8\text{H}_{17}$ (^nOc)], $\text{H}[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{FeW}_{12}\text{O}_{40}$, $\text{H}_2[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{ZnW}_{12}\text{O}_{40}$, $\text{K}[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{Co(III)W}_{12}\text{O}_{40}$ and $\text{K}_2[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{Co(II)W}_{12}\text{O}_{40}$

All materials used were of analytical reagent grade and were obtained from Ajax (Univar), BDH or Aldrich. The compounds $[(n\text{-C}_4\text{H}_9)_4\text{N}]_3\text{PM}_{12}\text{O}_{40}$ (where $\text{M} = \text{Mo}, \text{W}$) $[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{FeW}_{12}\text{O}_{40}$ were prepared using the method of Rocchiccioli-Deltcheff et al. [22], while $\text{H}[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{FeW}_{12}\text{O}_{40}$ and $\text{H}_2[(n\text{-C}_4\text{H}_9)_4\text{N}]_4\text{ZnW}_{12}\text{O}_{40}$ were obtained using those of

Nomiya et al. [23], and Nomiya and Miwa [24], respectively. The potassium salts of $[\text{Co(II)W}_{12}\text{O}_{40}]^{6-}$ and $[\text{Co(III)W}_{12}\text{O}_{40}]^{5-}$ were obtained by the methods of Simmons [25] and Walmsley [26], respectively and were converted to $\text{K}_2(^n\text{Bu}_4\text{N})_4\text{Co(II)W}_{12}\text{O}_{40}$ and $\text{K}(^n\text{Bu}_4\text{N})_4\text{Co(III)W}_{12}\text{O}_{40}$ using a procedure similar to that described by Nomiya et al. [27] involving addition of a stoichiometric amount of $^n\text{Bu}_4\text{NBr}$ in aqueous solution, followed by filtration, washing with water and drying at 100°C . The compounds $(^n\text{Hx}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$ and $(^n\text{Oc}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$ were obtained by addition of a slight excess (5%) of $^n\text{Hx}_4\text{NBr}$ and $^n\text{Oc}_4\text{NBr}$ in aqueous solution (with added CH_3CN in the latter case), to concentrated aqueous solutions of $\text{H}_3\text{PW}_{12}\text{O}_{40}$ (the final solution for the $^n\text{Oc}_4\text{N}^+$ salt was 90:10 (v/v) $\text{H}_2\text{O}:\text{CH}_3\text{CN}$). The solids precipitated quite slowly and were stirred for 24 h to ensure complete precipitation. These were then filtered, washed with water and dried at 130°C . Analytical data for the compounds are given in Table 1 and are satisfactory.

The ^{31}P NMR of $(^n\text{Bu}_4\text{N})_3\text{PMo}_{12}\text{O}_{40}$ and $(^n\text{Bu}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$ in DMSO exhibited singlets at -2.73 and -14.20 ppm (from external 85% H_3PO_4), in agreement with reported data [28], indicating that only a single phosphorus-containing species was present in each case. The $(^n\text{Hx}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$ and $(^n\text{Oc}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$ compounds gave ^{31}P singlets at -14.39 and -14.35 ppm in DMSO, and are consistent with that of $(^n\text{Bu}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$, again indicating the presence of single phosphorus-containing com-

pounds. All three compounds exhibited IR spectra that showed the presence of the Keggin unit and agreed with reported data [22]. Thermogravimetric analysis (TGA) results on the phosphorus-containing species indicated that the compounds decomposed according to the equation:



where $\text{M} = \text{Mo}$ or W , and $n = 4$ (i.e. ^nBu), $n = 6$ (^nHx) and $n = 8$ (^nOc). The percentage mass losses (observed, calculated) up to 750°C (650°C for Mo-containing salts) were: $(^n\text{Bu}_4\text{N})_3\text{PMo}_{12}\text{O}_{40}$ (28.9, 29.5%), $(^n\text{Bu}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$ (20.7, 20.8%), $(^n\text{Hx}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$ (28.1, 27.6%) and $(^n\text{Oc}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$ (30.4, 31.8%). For the transition metal-centered species analogous equations can be written, but result in the involatile transition metal oxide products Fe_2O_3 , Co_2O_3 and ZnO , in addition to WO_3 . The percentage mass losses (observed, calculated) up to 750°C were: $\text{H}(^n\text{Bu}_4\text{N})_4\text{FeW}_{12}\text{O}_{40}$ (25.7, 26.1%), $\text{H}_2(^n\text{Bu}_4\text{N})_4\text{ZnW}_{12}\text{O}_{40}$ (25.5, 26.3%), $\text{K}(^n\text{Bu}_4\text{N})_4\text{Co(III)W}_{12}\text{O}_{40}$ (27.2, 25.6%) and $\text{K}_2(^n\text{Bu}_4\text{N})_4\text{Co(II)W}_{12}\text{O}_{40}$ (26.8, 25.1%). The latter two samples showed percentage mass losses slightly greater than expected. These slightly greater TGA mass losses, together with the slightly high C, H and N % for both compounds, suggest that they contained

Table 1
Analytical results (calculated values in parenthesis)^a

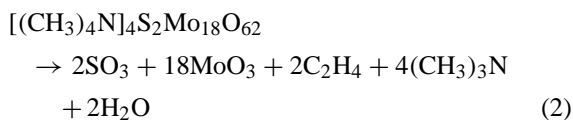
Compound	C (%)	H (%)	N (%)	X (%)	Z (%)	Mo or W (%)
$[(\text{C}_4\text{H}_9)_4\text{N}]_3[\text{PMo}_{12}\text{O}_{40}]$	22.3 (22.6)	4.2 (4.3)	1.6 (1.7)	–	–	45.0 (45.2)
$[(\text{C}_4\text{H}_9)_4\text{N}]_3[\text{PW}_{12}\text{O}_{40}]$	15.8 (16.0)	2.9 (3.0)	1.2 (1.2)	–	–	–
$[(\text{C}_6\text{H}_{13})_4\text{N}]_3[\text{PW}_{12}\text{O}_{40}]$	22.4 (22.0)	4.1 (4.0)	1.2 (1.1)	–	–	–
$[(\text{C}_8\text{H}_{17})_4\text{N}]_3[\text{PW}_{12}\text{O}_{40}]$	27.7 (27.0)	5.0 (4.8)	1.2 (1.0)	–	–	–
$\text{H}[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{FeW}_{12}\text{O}_{40}]$	19.7 (19.9)	3.7 (3.8)	1.5 (1.5)	1.5 (1.4)	–	–
$\text{K}[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{Co(III)W}_{12}\text{O}_{40}]$	21.9 (19.6)	4.1 (3.7)	1.5 (1.4)	1.5 (1.5)	–	–
$\text{H}_2[(\text{C}_4\text{H}_9)_4\text{N}]_3[\text{ZnW}_{12}\text{O}_{40}]$	18.5 (19.8)	3.4 (3.8)	1.5 (1.4)	1.7 (1.7)	–	–
$\text{K}_2[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{Co(II)W}_{12}\text{O}_{40}]$	20.6 (19.5)	3.9 (3.7)	1.5 (1.4)	1.4 (1.5)	–	–
$[(\text{CH}_3)_4\text{N}]_4[\text{S}_2\text{Mo}_{18}\text{O}_{62}]$	6.2 (6.4)	1.6 (1.6)	2.0 (1.8)	–	–	56.1 (56.1)
$\text{Na}_2[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{PMn(Br)Mo}_{11}\text{O}_{39}]$	27.4 (26.9)	5.5 (5.1)	2.0 (2.0)	–	1.7 (1.9)	36.2 (36.9)
$\text{Na}_2[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{PCo(Br)Mo}_{11}\text{O}_{39}]$	27.4 (26.8)	5.0 (5.1)	2.0 (2.0)	–	1.9 (2.1)	37.5 (36.8)
$\text{Na}_2[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{PNi(Br)Mo}_{11}\text{O}_{39}]$	27.2 (26.8)	5.2 (5.1)	1.9 (2.0)	–	1.9 (2.1)	36.7 (36.8)
$\text{Na}_2[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{PCu(Br)Mo}_{11}\text{O}_{39}]$	27.7 (26.8)	5.2 (5.1)	2.0 (2.0)	–	2.4 (2.2)	38.4 (36.8)
$\text{Na}_2[(\text{C}_4\text{H}_9)_4\text{N}]_4[\text{PZn(Br)Mo}_{11}\text{O}_{39}]$	27.2 (26.8)	5.3 (5.1)	1.9 (2.0)	–	2.3 (2.3)	37.0 (36.8)

^a X and Z refer to the central heteroatom and substituted addendum atom of the Keggin structure (i.e. $[\text{XM}_{12}\text{O}_{40}]^{m-}$) and transition metal-substituted lacunary Keggin structure (i.e. $[\text{XZ(Br)M}_{11}\text{O}_{39}]^{m-}$).

a little more than the expected four ${}^n\text{Bu}_4\text{N}^+$ cations (and, hence, less K^+) per anion, and thus, both formulae should be regarded as nominal. The compounds are, thus, primarily $\text{K}({}^n\text{Bu}_4\text{N})_4\text{Co(III)W}_{12}\text{O}_{40}$ with a little $({}^n\text{Bu}_4\text{N})_5\text{Co(III)W}_{12}\text{O}_{40}$ present ($\sim 5\text{--}7\%$) and primarily $\text{K}_2({}^n\text{Bu}_4\text{N})_4\text{Co(II)W}_{12}\text{O}_{40}$ with a little $\text{K}({}^n\text{Bu}_4\text{N})_5\text{Co(II)W}_{12}\text{O}_{40}$ present ($\sim 6\text{--}9\%$). The extra ${}^n\text{Bu}_4\text{N}^+$ cation in each case is likely attributable to the ratio of ${}^n\text{Bu}_4\text{NBr}$ to $[\text{Co(III)W}_{12}\text{O}_{40}]^{6-}$ and $[\text{Co(II)W}_{12}\text{O}_{40}]^{5-}$ used in the respective syntheses of the two compounds.

2.2. Syntheses of $[(\text{CH}_3)_4\text{N}]_6\text{P}_2\text{Mo}_{18}\text{O}_{62}$ and $[(\text{CH}_3)_4\text{N}]_4\text{S}_2\text{Mo}_{18}\text{O}_{62}$

The preparation and characterization of $[(\text{CH}_3)_4\text{N}]_6\text{P}_2\text{Mo}_{18}\text{O}_{62}\cdot 3\text{H}_2\text{O}$ [$(\text{CH}_3)_4\text{N}^+ = \text{Me}_4\text{N}^+$] has been described previously [29], while $(\text{Me}_4\text{N})_4\text{S}_2\text{Mo}_{18}\text{O}_{62}$ was synthesized using the methods of Hori and Himeno [30], and Cartie [31]. Analytical data are again given in Table 1. The latter compound had an IR spectrum that was identical with the reported data, while a TGA study up to 650°C indicated a mass loss of 16.3% compared to a calculated loss of 15.9% based on the equation:



2.3. Syntheses of $\text{Na}_5[\text{PZ}(\text{H}_2\text{O})\text{Mo}_{11}\text{O}_{39}]\cdot 5\text{H}_2\text{O}$ and $\text{Na}_2[{}^n\text{Bu}_4\text{N}]_4[\text{PZ}(\text{Br})\text{Mo}_{11}\text{O}_{39}]$ ($\text{Z} = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+})

The syntheses of the $\text{Na}_5[\text{PZ}(\text{H}_2\text{O})\text{Mo}_{11}\text{O}_{39}]\cdot 5\text{H}_2\text{O}$ (where $\text{Z} = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) salts were similar to those described by Qin et al. [32]. Solid samples of $\text{H}_3\text{PMo}_{12}\text{O}_{40}\cdot 23\text{H}_2\text{O}$ (11.3 g, 0.0050 mol) (water content determined by TGA) were dissolved in 20 ml aliquots of water. An equimolar amount of $\text{ZSO}_4\cdot n\text{H}_2\text{O}$ in 20 ml of water was added to each of the above solutions, respectively. The resulting solutions were heated to 50°C with stirring and the pH of each adjusted to about 4 using saturated NaHCO_3 solution. The solutions were heated subsequently for 30 min, yielding brown solutions for the Mn(II) and Co(II) preparations, yellow–green solutions for the Ni(II) and Cu(II) preparations and a light-green solution for the

Zn(II) preparation. They were evaporated at 50°C to give viscous solutions and put aside overnight. Colorless needle-shaped crystals of $\text{Na}_2\text{SO}_4\cdot 10\text{H}_2\text{O}$ appeared in each case. The solutions were filtered, and the filtrates placed in a desiccator for 1 or 2 days over silica gel, which resulted in the formation of block-shaped crystals in each case. Recrystallization from water (pH ~ 5) produced brown, block-shaped crystals corresponding to the Mn(II) and Co(II) salts, yellow–green crystals for the Ni(II) and Cu(II) salts and light-green crystals for the Zn(II) salt. The yields of the $\text{Na}_5[\text{PZ}(\text{H}_2\text{O})\text{Mo}_{11}\text{O}_{39}]\cdot 5\text{H}_2\text{O}$ salts (where $\text{Z} = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) were 4.4, 3.8, 5.8, 4.9 and 7.2 g, respectively. All compounds had IR spectra that agreed with the reported data [32].

Organic-soluble salts were obtained from the above sodium salts using the method of Qin et al. [33] and Lyon et al. [34]. Samples of the aqueous-soluble $\text{Na}_5[\text{PZ}(\text{H}_2\text{O})\text{Mo}_{11}\text{O}_{39}]\cdot 5\text{H}_2\text{O}$ compounds (1 g, ~ 0.0005 mol in each case) were dissolved in 5 ml aliquots of H_2O , respectively. In each case 5 ml of a solution of ${}^n\text{Bu}_4\text{NBr}$ was added to give a 6:1 ${}^n\text{Bu}_4\text{N}^+$:anion mole ratio and the crude product precipitated. The solids were isolated and the organic solvent soluble products were obtained by extraction with CH_2Cl_2 , followed by evacuation of the solvent and drying (yields 0.8–0.9 g).

From TGA studies the observed percentage mass losses up to 650°C were in the range 38–40%, suggesting that the compounds had less than the expected 6:1 ${}^n\text{Bu}_4\text{N}^+$:anion ratio (also assuming that the transition metals give MnO_2 , Co_2O_3 , NiO , CuO and ZnO and that the Br^- remains involatile as a transition metal bromide). Chemical analyzes, also given in Table 1, confirmed this result, and indicated that the formulae of all compounds were close to $\text{Na}_2({}^n\text{Bu}_4\text{N})_4[\text{PZ}(\text{Br})\text{Mo}_{11}\text{O}_{39}]$. The IR spectra showed that the anion vibrations were almost identical with those of their water soluble sodium salts, indicating that the anion had remained intact in each case. It would appear that even though a 6:1 ${}^n\text{Bu}_4\text{N}^+$:anion ratio was used in order to obtain the $({}^n\text{Bu}_4\text{N})_6[\text{PZ}(\text{Br})\text{Mo}_{11}\text{O}_{39}]$ salts, the most insoluble salts were those with less than six ${}^n\text{Bu}_4\text{N}^+$ ions, as found above for both $\text{K}_2({}^n\text{Bu}_4\text{N})_4\text{Co(II)W}_{12}\text{O}_{40}$ and $\text{K}({}^n\text{Bu}_4\text{N})_4\text{Co(III)W}_{12}\text{O}_{40}$. This may be related to the ratio of ${}^n\text{Bu}_4\text{NBr}$ to anion used in the syntheses, as suggested above, but could also be related to the

packing of the cations around the anions and limitations on the number of tetraalkylammonium cations that can be accommodated in a stable solid. Although the $\text{Na}_2(^n\text{Bu}_4\text{N})_4[\text{PZ}(\text{Br})\text{Mo}_{11}\text{O}_{39}]$ salts did not have the full complement of six $^n\text{Bu}_4\text{N}^+$ ions per anion, they were quite soluble in acetonitrile, the solvent used for the present oxidation studies.

2.4. Catalysis and analysis of products

All studies were performed in a 100 ml three-necked round bottom flask equipped with a Teflon-coated magnetic stirrer bar for mixing, and fitted with an inlet and outlet gas flow system, reflux condenser and rubber septum for sample withdrawal by syringe. A flow of nitrogen (BOC, ultra high purity) of 10 ml min^{-1} was continuously passed over the solution at all times. This was to remove any oxygen that formed from thermal decomposition of the hydrogen peroxide oxidant, as oxygen is capable of both catalytically and non-catalytically oxidizing isobutyraldehyde to isobutyric acid at the temperature employed in the present studies [21]. For each kinetic run, the flask was routinely charged with the catalyst (0.078 mmol), isobutyraldehyde (0.9 ml, 10 mmol) and acetonitrile as solvent (47.6 ml). The flask and contents were then immersed in an oil bath preheated to $\sim 50^\circ\text{C}$, and allowed to equilibrate at this temperature. The temperature of the solution inside the flask was $50(\pm 1)^\circ\text{C}$ and was monitored throughout each reaction. Each run was initiated by addition of a 1.5 times excess (over the isobutyraldehyde) of H_2O_2 (29–32% (v/v), 1.5 ml, 15 mmol), using a 1 ml precision gas-tight syringe (SGE), with vigorous stirring to avoid any build-up of a local concentration of the oxidant. The total volume of solution was 50 ml. Some studies were performed with varying amounts of H_2O_2 , but in these cases the volume of CH_3CN was adjusted so that the total volume of the solution remained at 50 ml.

The major reaction product was identified as isobutyric acid (generally greater than 90%), together with a minor amount of CO_2 , the latter being detected by infrared spectroscopy in the gas flow above the solution. No other conversion products could be detected. All reactions were monitored by determination of the isobutyraldehyde remaining in solution using gas chromatography (Pye Unicam Series 204, with a 1.5 m packed column of 3% FFAP plus 7% OV-17 on

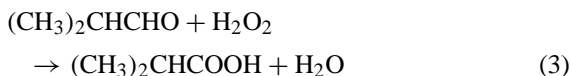
acid washed chromosorb W). The injector was set to a temperature of 170°C , the detector 175°C and the column 70°C . Isobutyric acid could be detected by raising the column temperature to 150°C . It should be noted that if there were any impurities that had similar retention times to acetonitrile (such as acetone [21]), they could not be observed. As the amount of CO_2 could not be easily quantified using the experimental design and the extent of conversion of isobutyraldehyde was generally low (see the following sections), all studies were followed using the extent of conversion of the isobutyraldehyde substrate. Samples of the actual solution (0.5 or 1 ml) were removed from the reaction vessel after appropriate time intervals (0–4 h following initiation of the reaction) using a 1 ml precision gas-tight syringe (SGE). These were diluted to 5 ml using CH_3CN and 1-butanol ($50 \mu\text{l}$) was added as an internal standard, followed by direct injection into the gas chromatograph.

Thermogravimetric analyzes were performed on a Stanton Redcroft TG-750 instrument coupled to a Eurotherm Model 94 temperature controller. Sample masses of 10–20 mg were used with a heating rate of $10^\circ\text{C min}^{-1}$ in an air atmosphere. Infrared spectra were recorded on a Bio-Rad FTS-7 Fourier transform spectrophotometer, with solid samples mounted as KBr discs. Solution ^{31}P NMR spectra were obtained with a Bruker AVANCE DPX-300 spectrometer operating at 121.49 MHz, with an external 85% H_3PO_4 reference. UV–VIS spectra were recorded on a Hitachi U-2000 spectrophotometer. Chemical analyzes were performed by the Australian National University Microanalysis Unit.

3. Results and discussion

A series of compounds containing Keggin, Dawson and transition metal-substituted lacunary species (the latter based on the Keggin structure) were synthesized in order to investigate the differences in homogeneous catalytic activity of various types of heteropolyoxometalate species with different compositions, structures and anionic charges in oxygen transfer reactions. For this purpose, the simple oxidation (actually the oxygenation) of the model substrate isobutyraldehyde to give isobutyric acid (Eq. (3)) in acetonitrile was selected as the probe reaction in the

present studies.



This oxidation was studied in a single-phase organic system, i.e. CH_3CN , so as to militate against possible breakdown of the heteropolyoxometalate systems under study.

In order to achieve the appropriate solubilities of the catalyst species, the compounds were synthesized as tetraalkylammonium salts, primarily as the ${}^n\text{Bu}_4\text{N}^+$ salts and, in some cases, with Me_4N^+ as the counter-cation. This was, in general, accomplished by simple metathetical exchange in aqueous solution with the appropriate tetraalkylammonium salt. This approach works well for both Keggin and Dawson anions, except that for the more highly charged Keggin anions it was found that not all of the original counter-cations could be replaced with tetraalkylammonium cations. Thus, for example, for anions of the type $[\text{XW}_{12}\text{O}_{40}]^{n-}$ (where $n = 5$ and 6), the counter-cations were a mixture of ${}^n\text{Bu}_4\text{N}^+$ and either H^+ or K^+ ions. Similar results were obtained for the transition metal-substituted lacunary species based on the Keggin structure, and generated species of the type $\text{Na}_2({}^n\text{Bu}_4\text{N})_4[\text{PZ}(\text{Br})\text{Mo}_{11}\text{O}_{39}]$ (where $Z = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}). While these latter species are soluble in organic solvents, it is likely that the Br^- would be essentially dissociated from the (formal) Z^{2+} addendum ion and replaced with a solvent molecule in CH_3CN solution. The extent of this dissociation has not been established in the present examples, but the loss of Br^- from the related transition metal-substituted lacunary Dawson species $\alpha_2\text{-}[\text{P}_2\text{Mn}(\text{III})(\text{Br})\text{W}_{17}\text{O}_{61}]^{7-}$ has been investigated in CH_2Cl_2 solution [34]. This yielded an association constant, K_{assoc} , of $48 \pm 9 \text{ M}^{-1}$ (at a concentration of $2 \times 10^{-3} \text{ M}$), with only 3% of the Br^- bound to the Mn(III) in the polyoxotungstate framework. Thus, the Br^- was extensively dissociated from the polyoxotungstate in CH_2Cl_2 . It is likely that the association constants for the transition metal-substituted lacunary species studied in the present work would be of the same order of magnitude. More importantly, it is highly unlikely that Br^- would be coordinated to the transition metal addendum ion in the considerably more polar CH_3CN [34], which is the

solvent employed in the present studies. Thus, the $[\text{PZ}(\text{Br})\text{Mo}_{11}\text{O}_{39}]^{6-}$ species should be regarded as pre-catalysts in these systems as they would generate $[\text{PZ}(\text{CH}_3\text{CN})\text{Mo}_{11}\text{O}_{39}]^{5-}$ ions, and that the site occupied by the solvent molecule (CH_3CN) may easily be replaced by other species, such as water. This, of course, assumes that they are not degraded by H_2O_2 under the reaction conditions, for which there is good evidence as discussed in the following sections.

The composition of the reaction mixtures used in the present studies was $[\text{isobutyraldehyde}] = 0.20 \text{ M}$, $[\text{H}_2\text{O}_2] = 0.29 \text{ M}$ and $[\text{catalyst}] = 1.56 \times 10^{-3} \text{ M}$. This gave an $\sim 50\%$ excess of H_2O_2 relative to isobutyraldehyde ($\text{H}_2\text{O}_2/\text{IBAL} = \sim 1.5$), as well as large excesses of both isobutyraldehyde to catalyst (isobutyraldehyde/catalyst = ~ 130) and H_2O_2 to catalyst ($\text{H}_2\text{O}_2/\text{catalyst} = \sim 185$). There was also an initial H_2O concentration of 1.28 M , which was introduced through the aqueous H_2O_2 , making the solvent effectively $\sim 98\%$ CH_3CN and $\sim 2\%$ H_2O . The aqueous H_2O_2 was slightly acidic ($\text{pH} \sim 3.5$), giving a nominal $[\text{H}^+]$ of $\sim 1 \times 10^{-5} \text{ M}$ in the solutions, which was considerably less than the actual heteropolyoxometalate concentration. Separate studies showed that at 50°C , less than 1.5% of the H_2O_2 was decomposed over the time the reactions were monitored (4 h). This was established by titration of aliquots of the reaction mixture with standardized KMnO_4 under acidic conditions. This increased to $\sim 27\%$ after 24 h. Thus, in the present study all reactions were followed for a maximum of 4 h although, as will be shown in the following sections, a concentration dependence term for H_2O_2 did not appear in the rate expression established by the limited kinetic studies for the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ ion. Some reactions were also performed with varying ratios of $\text{H}_2\text{O}_2/\text{isobutyraldehyde}$ and $\text{isobutyraldehyde}/\text{catalyst}$ to check on kinetic dependences, and these will be discussed in the following sections. In the studies of the transition metal-substituted lacunary species the (free) Br^- could have been oxidized to Br_2 , which might then have reacted with the substrate. While this reaction occurs readily in aqueous solution under acidic conditions, it is much slower in the absence of acid, conditions more appropriate to the present study. A separate UV–VIS spectroscopic study of the potential oxidation of ${}^n\text{Bu}_4\text{NBr}$ by H_2O_2 in CH_3CN at 50°C showed effectively no formation of Br_2 over the time-scale of the kinetic studies, suggesting that

this reaction is not important in the present context. Following the completion of this attempted reaction, addition of a few drops of concentrated H_2SO_4 to the solution at room temperature immediately generated a yellow–brown color, typical of the presence of Br_2 .

All rate constants were calculated from plots of the first-order expression $\ln(100/(100 - \% \text{ conversion}))$ versus time, and assume that the catalyst concentration was constant during the reactions. As the maximum conversion of isobutyraldehyde observed in the present studies was only 57% after 4 h, the ratio of isobutyraldehyde to catalyst was reduced only by a factor of ~ 0.5 , so that pseudo first-order conditions (with respect to the catalyst) were still fulfilled. However, it should be stressed that, with the exception of one system, not one of the reactions was followed for greater than one half-life, so that the assumption of first-order behavior may be incorrect, although unlikely. The above first-order expression generates a linear plot, the slope of which is the rate constant. Some plots, particularly for the transition metal-substituted lacunary species, were not linear, and the rate constants were obtained from the initial slopes of these plots. Kinetic dependence studies for $[\text{PW}_{12}\text{O}_{40}]^{3-}$ were also undertaken, as noted above, and this system was regarded as being representative of both the Keggin- and Dawson-type anions. A study of the effect of changing the counter-cation (${}^n\text{Bu}_4\text{N}^+$, ${}^n\text{Hx}_4\text{N}^+$ and ${}^n\text{Oc}_4\text{N}^+$) in the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ system was also investigated in order to examine the potential steric effects caused by ion-pairing (or even ion-triplet formation). No attempt was made in the present study to keep the ionic strength of the solutions constant, although contributions to this come only from the catalyst. However, with the charge on the anions varying from -3 to -6 (e.g. $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and $[\text{ZnW}_{12}\text{O}_{40}]^{6-}$) in an effectively non-aqueous solvent, even though it does have a relatively large dielectric constant (H_2O , 78.5; CH_3CN , 36.2 at 25°C), there were likely significant variations in ion-pairing between the heteropolyoxometalate anions and tetraalkylammonium cations for the different systems explored in the present study.

3.1. Catalysis studies of the Keggin and Dawson heteropolyoxometalate species

The catalytic activities of the Keggin- and Dawson-type anions, as measured by the % conversion

Table 2

Percentage conversion of isobutyraldehyde after 4 h and first-order rate constants for Keggin, Dawson and transition metal-substituted lacunary heteropolyoxometalate catalysts in the oxygenation of isobutyraldehyde in acetonitrile: [isobutyraldehyde] = 0.20 M, $[\text{H}_2\text{O}_2] = 0.29$ M, [catalyst] = 1.56×10^{-3} , $T = 50^\circ\text{C}$

Anion ^a	% Conversion (after 4 h)	First-order rate constant, k ($\times 10^6$; s^{-1})
Control (no anion)	<1.5	–
$[\text{S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$	31.3	26(2)
$[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{3-}$	5.3	3.8(5)
$[\text{PMo}_{12}\text{O}_{40}]^{3-}$	11.7	8.9(4)
$[\text{PW}_{12}\text{O}_{40}]^{3-}$	13.4	10.8(9)
$[\text{Co(III)W}_{12}\text{O}_{40}]^{5-}$	10.0	8.4(5)
$[\text{FeW}_{12}\text{O}_{40}]^{5-}$	5.9	4.2(2)
$[\text{Co(II)W}_{12}\text{O}_{40}]^{6-}$	8.5	6.5(7)
$[\text{ZnW}_{12}\text{O}_{40}]^{6-}$	7.0	5.2(4)
$[\text{PMn(Br)Mo}_{11}\text{O}_{39}]^{6- \text{ b}}$	29.0	31(2)
$[\text{PCo(Br)Mo}_{11}\text{O}_{39}]^{6- \text{ b}}$	57.1	67(3)
$[\text{PNi(Br)Mo}_{11}\text{O}_{39}]^{6- \text{ b}}$	51.3	56(3)
$[\text{PCu(Br)Mo}_{11}\text{O}_{39}]^{6- \text{ b}}$	10.5	13(1)
$[\text{PZn(Br)Mo}_{11}\text{O}_{39}]^{6- \text{ b}}$	45.7	51(3)

^a All $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ salts, except for $[\text{S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$ and $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ which were $(\text{CH}_3)_4\text{N}^+$ salts.

^b Anion is a pre-catalyst and degrades in the presence of H_2O_2 .

of isobutyraldehyde, are compared in Table 2 following 4 h of reaction, together with their first-order rate constants. Also included in this table are the results of a control study (i.e. no added catalyst). As examples of the % conversion and corresponding first-order linear $\ln(100/(100 - \% \text{ conversion}))$ versus time plots, the data for both $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and $[\text{PW}_{12}\text{O}_{40}]^{3-}$ are shown in Fig. 1. For the $\ln(100/(100 - \% \text{ conversion}))$ versus time plots the R^2 -values were ≥ 0.95 . The slight deviations from linearity are discussed in the following sections. All heteropolyoxometalate species exhibited some catalytic behavior, to a greater or lesser extent. The wide variation in the % conversion of isobutyraldehyde and the corresponding first-order rate constants over the range of catalysts employed suggests that a single peroxy-species, a possible result of fragmentation of the polyoxometalate, was not responsible for the catalytic activity. Thus, the observed results represent true differences in catalytic activity among the various catalysts. Examination of the data in Table 2 indicates a general trend, with a greater % conversion and higher first-order rate constant being observed with decreasing anionic charge. The dif-

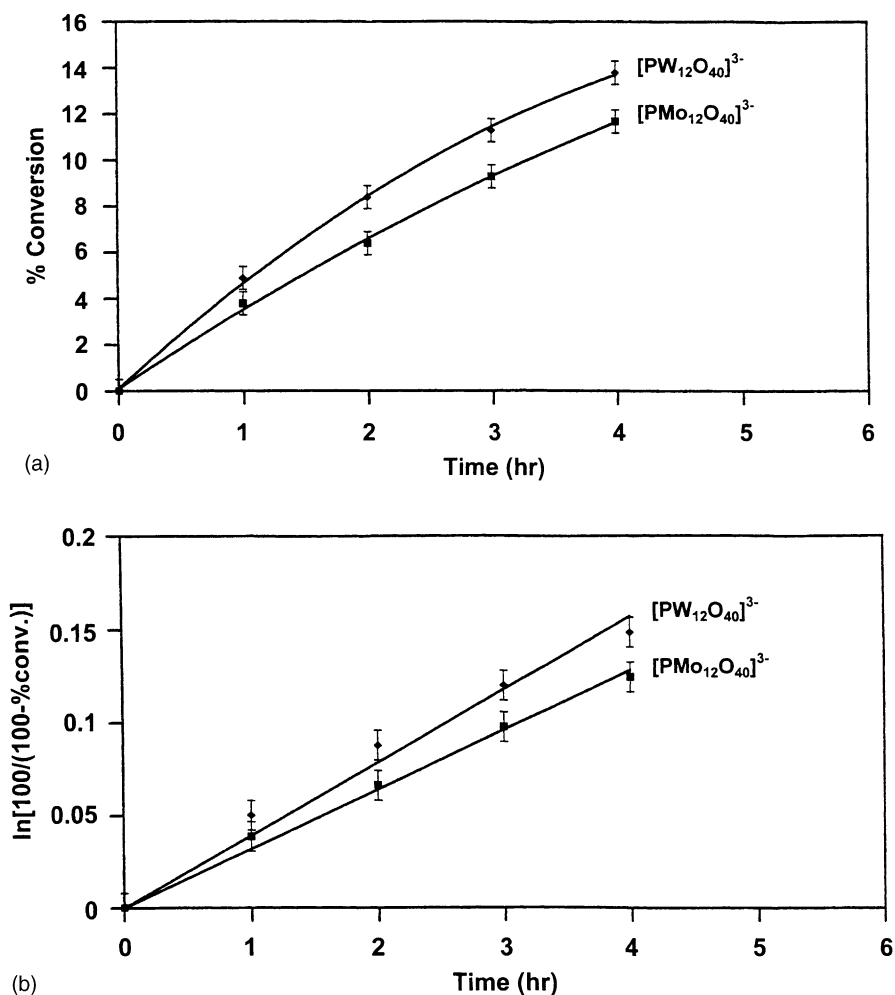


Fig. 1. (a) Percentage conversion vs. time and (b) corresponding first-order $\ln(100/(100 - \% \text{ conversion}))$ vs. time plots for the oxygenation of isobutyraldehyde by H₂O₂ in acetonitrile at 50 °C using the heteropolyoxometalate catalysts [PMo₁₂O₄₀]³⁻ and [PW₁₂O₄₀]³⁻.

ferent values observed for [Co(III)W₁₂O₄₀]⁵⁻ and [Co(II)W₁₂O₄₀]⁶⁻ reflect the different anion charges, as there was no evidence for the oxidation of Co(II) to Co(III) in [Co(II)W₁₂O₄₀]⁶⁻ under the reaction conditions (see the following sections), even though [Co(II)W₁₂O₄₀]⁶⁻ is fairly easily oxidized using a variety of oxidants [35]. The slightly low values for [Fe(III)W₁₂O₄₀]⁵⁻ in Table 2 may simply result from the different ionic makeup of the solutions containing the [XW₁₂O₄₀]ⁿ⁻ ($n = 5, 6$) ions as a result of variations among the counter-cations (i.e. ⁿBu₄N⁺ and either K⁺ or H⁺) or, alternatively, may represent

the limit of accuracy in these studies (i.e. control of temperature, concentrations, etc.) given the low % conversions of isobutyraldehyde found for this and related anions (<10% conversion after 4 h).

From the studies the following trends were observed (Eqs. (4)–(6)):

Dawson anions:



Keggin anions:

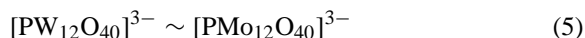
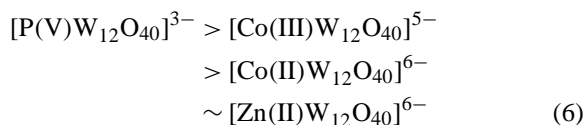


Table 3

Dependence of catalytic activity of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ on H_2O_2 and catalyst concentrations for the oxygenation of isobutyraldehyde in acetonitrile: [isobutyraldehyde] = 0.20 M, $T = 50^\circ\text{C}$

Catalyst	[Catalyst] (M) ^a	$[\text{H}_2\text{O}_2]$ (M)	First-order rate constant, k ($\times 10^6; \text{s}^{-1}$)
$[\text{PW}_{12}\text{O}_{40}]^{3-}$	1.56×10^{-3}	0.15	10.2(9)
	1.56×10^{-3}	0.29	10.8(9)
	1.56×10^{-3}	0.58	10.2(9)
	0.78×10^{-3}	0.29	5.7(5)

^a All $(n\text{-C}_4\text{H}_9)_4\text{N}^+$ salts.



In these ionic catalyst systems, the above relationships are plausibly related to greater electrostatic repulsion between the isobutyraldehyde and the polyoxometalate anion with increasing charge on the latter. Further discussion of these patterns is given in the following sections. For the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ ion the kinetic dependence of the first-order rate constant on both the H_2O_2 concentration and catalyst concentration were also investigated, and are presented in Table 3. This species is believed to be typical of the Keggin and Dawson groups as no evidence of major breakdown of these anions appears to occur, but the results of further studies are presented in the following sections. Interestingly, no dependence on H_2O_2 concentration was observed, while an effective first-order dependence on $[\text{PW}_{12}\text{O}_{40}]^{3-}$ was found, with a doubling of the first-order rate constant upon doubling of the catalyst concentration. The rate law, therefore, can be expressed as follows (Eq. (7)):

$$\begin{aligned}
 -\frac{d}{dt}[\text{isobutyraldehyde}] \\
 = [\text{isobutyraldehyde}][\text{PW}_{12}\text{O}_{40}]^{3-} \quad (7)
 \end{aligned}$$

The actual oxidation step must take place following the initial association of the isobutyraldehyde molecule with the heteropolyoxometalate anion, and must be kinetically faster than the association step. However, any non-catalytic oxidation of isobutyraldehyde must be even slower, as the control study indicated little conversion after 4 h. Attack on the isobutyraldehyde

substrate by H_2O_2 occurs following association, so that the present kinetic study cannot differentiate between a homolytic (i.e. radical) reaction, a heterolytic reaction involving nucleophilic attack, or even possibly peroxyacid formation. In view of the elevated temperature required to observe reaction, the former may be the most likely.

As the composition of the transition state in the rate-determining step does not involve H_2O_2 , the role of the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ ion appears to be that of a species that combines with the substrate prior to attack by the oxidant. This role presumably involves some alteration of the electron density distribution in the isobutyraldehyde, probably allowing facile attack by the oxidant on the latter, involving one of the above mechanisms. The rate of formation of the isobutyraldehyde–heteropolyoxometalate anion-pairing is slow, likely because of the anionic charge of the latter and the electron density on the carbonyl group, and the rate of formation is enhanced as the anionic charge decreases. The heteropolyoxometalate anion, thus, plays an indirect role in the catalysis, in that it does not appear to combine with H_2O_2 to give a peroxy-species (based on the Keggin structure) prior to reaction with the isobutyraldehyde.

While this is true for the heteropolyoxotungstates, some evidence for peroxy formation was obtained for the heteropolyoxomolybdates, and is discussed in the following sections. However, the possibility that reaction to give a peroxy-species occurs after the rate-determining step cannot be ruled out. The resulting peroxy-species would oxygenate the isobutyraldehyde to isobutyric acid and in turn regenerate the initial heteropolyoxometalate anion. It should also be noted that the slight deviations observed for the $\ln[100/(100 - \% \text{ conversion})]$ versus time plots ($R^2 \geq 0.95$) are likely attributable to competition between the substrate isobutyraldehyde and the product isobutyric acid for the catalyst. As the rates of association of both the substrate and product are likely to be similar in view of their related structures (perhaps a little less for isobutyric acid because of the extra oxygen atom with its accompanying lone pairs), any association of isobutyric acid with the heteropolyoxometalate will reduce the effective catalyst concentration in solution. This effect will increase as the isobutyraldehyde is progressively oxidized to

isobutyric acid and lead to deviations from first-order behavior.

In order to investigate possible fragmentation or potential peroxy formation of the $[\text{PM}_{12}\text{O}_{40}]^{3-}$ ($\text{M} = \text{Mo}, \text{W}$), $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ and $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ ions by H_2O_2 under the reaction conditions, ^{31}P NMR spectroscopic studies on $[\text{PW}_{12}\text{O}_{40}]^{3-}$, $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$, and UV–VIS studies of $[\text{CoW}_{12}\text{O}_{40}]^{6-}$, under the actual solution and temperature conditions, but in the absence of isobutyraldehyde, were undertaken. Under these conditions, no reaction of $[\text{PW}_{12}\text{O}_{40}]^{3-}$ with H_2O_2 was observed after 4 h. The chemical shift of the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ ion remained unchanged at -13.9 ppm, the same value found prior to addition of the H_2O_2 , and there was no evidence for the appearance of other ^{31}P signals, which would indicate fragmentation or formation of a peroxy-species. Previous studies under phase-transfer conditions from CDCl_3 to aqueous solution using $[(\text{C}_{18}\text{H}_{37} (75\%) + \text{C}_{16}\text{H}_{33} (25\%))_2\text{N}(\text{CH}_3)_2]^+$ have shown the formation of peroxy-species with chemical shifts values of -11.85 , -12.4 and -12.9 ppm after 45 min (the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ ion appeared at -14.9 ppm) at a $[\text{H}_2\text{O}_2]/[\text{W}] = \sim 1$, while with a large excess of H_2O_2 ($[\text{H}_2\text{O}_2]/[\text{W}] = 500$) the $(\text{PO}_4)[\text{WO}(\text{O}_2)_2]_4^{3-}$ ion ($\delta = \sim +3.6$ ppm) was observed, indicating complete breakdown of the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ ion [36]. Likewise, a solution of $[\text{Co}(\text{II})\text{W}_{12}\text{O}_{40}]^{6-}$ and H_2O_2 in acetonitrile at 50°C showed no change in the UV–VIS spectrum over a period of 4 h, or on standing at room temperature for over 1 week, indicating no evidence of fragmentation of the polyoxotungstate framework. However, both $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ (-2.39 ppm) and $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ (-1.92 ppm) solutions showed the formation of small, extra peaks at $+0.99$ and $+0.91$ ppm, respectively over a period of about 1 h. These peaks were less than 10% of the intensity of the peaks for the $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ ions and changed very little in intensity relative to the former signals following their initial appearance. The peaks are not attributable to $(\text{PO}_4)[\text{MoO}(\text{O}_2)_2]_4^{3-}$, as the chemical shift of this species occurs at $+7.8$ ppm (in CDCl_3) [36]. When water was used in place of H_2O_2 the peaks did not appear, indicating that they were indeed peroxy-species. These peroxy-species cannot be highly catalytically active in their own right, as no major deviations from first-order behavior were observed in the present studies. Based on the

above results, it is likely that the other tungstate-based $[\text{XW}_{12}\text{O}_{40}]^{n-}$ Keggin species (where $\text{X} = \text{Fe}^{3+}$, Co^{3+} and Zn^{2+}) investigated in the present work would have remained intact in acetonitrile solution under the conditions employed in this study, while the other Dawson structure, $[\text{S}_2\text{Mo}_{18}\text{O}_{62}]^{4-}$, would likely have shown some slight degradation as it is based on a polymerized molybdate framework.

The formation of an isobutyraldehyde–heteropolyoxometalate anion unit prior to oxygenation should be affected by any initial formation of an ion-pair (or even ion-triplet) between the counter-cation(s) and the anion in this predominantly organic medium, with a resulting steric hindrance acting against the formation of the substrate–anion unit. To investigate this possibility, the length of the alkyl chains on the tetraalkylammonium cations were varied in the series $(\text{R}_4\text{N})_3\text{PW}_{12}\text{O}_{40}$ (where $\text{R} = {}^n\text{Bu}_4\text{N}^+$, ${}^n\text{Hx}_4\text{N}^+$ and ${}^n\text{Oc}_4\text{N}^+$) to see whether or not a steric effect was observable, while keeping the anion constant. Ion-pair formation constants for the different tetraalkylammonium cations with $[\text{PW}_{12}\text{O}_{40}]^{3-}$ should not vary greatly, and thus, the results should reflect steric effects in the formation of the substrate–anion unit. The results of percentage conversion after 4 h for the three counter-cations examined were as follows: ${}^n\text{Bu}_4\text{N}^+$, 13.4%; ${}^n\text{Hx}_4\text{N}^+$, 12.8%; and ${}^n\text{Oc}_4\text{N}^+$, 11.5%. The variations suggest that increasing the size of the alkyl chain had a detrimental effect on the rate of reaction, although the effects are not large. This may be linked to increasing steric obstruction with alkyl chain length during formation of the substrate–anion unit.

As noted above, catalytic activity appears to correlate with the anion charge, with higher (negative) charge leading to lower activity. To investigate the effects of different anion charge on the activity of the various Dawson- and Keggin-type heteropolyoxometalate anions, the charge per oxygen atom may be compared as these atoms are located on the surface of the anion and, hence, form the environment experienced by an approaching substrate molecule. Some measure of this may be obtained by simply calculating the anion charge per oxygen atom. Thus, for example, comparing differences for the Dawson and Keggin species containing the same elements, i.e. $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ (anion charge/number of oxygen atoms = -0.097) and $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ (-0.075) indicates that the latter has a less negative charge,

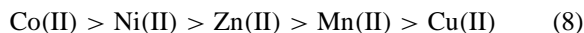
and hence, is a more active catalyst than the related Dawson species based on the correlation established earlier.

For species with the same anionic charge, such as $[\text{PW}_{12}\text{O}_{40}]^{3-}$ and $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, the greater activity of the former is likely related to the slight difference in net charges for the peripheral oxygen atoms, which would favor the former anion. However, sophisticated molecular orbital calculations, preferably in a solution environment, would be required to obtain these differences as the simple measure used earlier, i.e. anion charge/number of oxygen atoms, cannot differentiate between these anions. For the sequence of $[\text{XW}_{12}\text{O}_{40}]^{n-}$ ions (where $\text{X} = \text{P}^{5+}, \text{Co}^{3+}, \text{Co}^{2+}$ and Zn^{2+}), the anion charge/number of oxygen atoms becomes more negative from $[\text{PW}_{12}\text{O}_{40}]^{3-}$ to the other anions, which reflects the progressive decrease in catalytic activity on moving to higher net negative charges, and also highlights the similarities of the overall net charges of the transition metal-containing anions with anion charges of -5 (anion charge/number of oxygen atoms = -0.125) and -6 (anion charge/number of oxygen atoms = -0.15), and hence, with their similar catalytic activities.

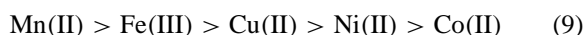
3.2. Catalysis studies of the transition metal-substituted lacunary Keggin-type phosphopolyoxomolybdate species

The first-order $\ln(100/(100 - \% \text{ conversion}))$ versus time plots for the transition metal-substituted lacunary phosphopolyoxomolybdates, $[\text{PZ}(\text{Br})\text{Mo}_{11}\text{O}_{39}]^{6-}$, where $\text{Z} = \text{Mn}^{2+}, \text{Co}^{2+}, \text{Ni}^{2+}, \text{Cu}^{2+}$ and Zn^{2+} , indicated considerably more deviation from linearity in each case than observed in the unsubstituted species, with regression analyzes for these studies giving R^2 -values of 0.89–0.94 for most compounds, and 0.83 for the Zn(II)-containing species. The large deviations from linearity observed in these systems suggested that the nature of the catalytic species was changing with time and that it was likely that considerable (or even total) degradation of the transition metal-substituted phosphopolyoxomolybdates over the timescale of the reactions had occurred. Evidence for degradation of these species by H_2O_2 is provided in the following sections. Thus, these species should be regarded as pre-catalysts in the present reactions.

All transition metal-substituted pre-catalysts were found to be more active than the unsubstituted $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ ion, with $[\text{PCu}(\text{Br})\text{Mo}_{11}\text{O}_{39}]^{6-}$ having about the same activity as $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ (based on the % conversion after 4 h). However, the increase in catalytic activity of these compounds was only a maximum of a factor of ~ 7 over that of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$, which indicates that the presence of the transition metal had very little effect. A trend in catalytic activity was observed that depended on the transition metal and followed the sequence:



This trend is very different to that observed for the oxidation of cyclohexene by molecular oxygen in 1,2-dichloroethane at 70°C using most of the same compounds as catalysts, which gave cyclohex-2-enol and cyclohex-2-enone as the major products, along with a little 1,2-epoxycyclohexane [33]. That study yielded the sequence:



Based on the distribution of reaction products in that study it was suggested that the oxidation reaction proceeded by a radical mechanism.

To explore the possible degradation of these species in the presence of H_2O_2 , ^{31}P NMR studies were undertaken on diamagnetic $[\text{PZn}(\text{Br})\text{Mo}_{11}\text{O}_{39}]^{6-}$. Even at room temperature, $[\text{PZn}(\text{Br})\text{Mo}_{11}\text{O}_{39}]^{6-}$ was found to react quickly with H_2O_2 , with the original signal at -1.36 ppm (assumed to arise from $[\text{PZn}(\text{CH}_3\text{CN})\text{Mo}_{11}\text{O}_{39}]^{5-}$, as noted earlier) disappearing and formation of a broad, asymmetric peak centered at about $+8.6$ ppm. This sharpened over several hours to a single peak at $+8.3$ ppm. The latter is consistent with the formation of $(\text{PO}_4[\text{MoO}(\text{O}_2)_2]_4)^{3-}$, which has been reported to exhibit a ^{31}P NMR signal at $+7.8$ ppm in CDCl_3 [35]. Presumably the broad peak that initially appeared was an intermediate in the formation of $(\text{PO}_4[\text{MoO}(\text{O}_2)_2]_4)^{3-}$, and may have been more catalytically active than the latter, thereby, accounting for the major deviation from linearity of the $\ln(100/(100 - \% \text{ conversion}))$ versus time plot for this anion.

The four remaining transition metal-substituted lacunary phosphopolyoxomolybdates all contain paramagnetic transition metal ions, so that ^{31}P NMR

Table 4

UV–VIS spectroscopic data and assignments for the $\text{Na}_2(\text{}^t\text{Bu}_4\text{N})_4[\text{PZ}(\text{Br})\text{Mo}_{11}\text{O}_{39}]$ salts ($\text{Z} = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) in acetonitrile before and after addition of H_2O_2

Anion ^a	λ (nm) (ϵ , $\text{M}^{-1} \text{cm}^{-1}$) and assignment ^{b,c}	After addition of H_2O_2 and heating to 50°C
$[\text{PMn}(\text{S})\text{Mo}_{11}\text{O}_{39}]^{5-}$	$<\sim 620$ br charge transfer transition from $\text{Mn}(\text{II}) \rightarrow$ polyoxometalate ^d ; $<\sim 470$ vs ^{e,f}	Oxidation \rightarrow $\text{Mn}(\text{III})$ 492 (230) and 645 br (38) split components of ${}^5\text{E}_g \rightarrow {}^5\text{T}_{2g}$; $<\sim 480$ vs ^f
$[\text{PCo}(\text{S})\text{Mo}_{11}\text{O}_{39}]^{5-}$	>1100 ^g ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{2g}(\text{P})$; 530 sh and 513 (186) ${}^4\text{T}_{1g}(\text{F}) \rightarrow {}^4\text{T}_{1g}(\text{F})$; $<\sim 470$ vs ^{e,f}	>1100 ; 530 sh and 512; $<\sim 480$ vs ^f
$[\text{PNi}(\text{S})\text{Mo}_{11}\text{O}_{39}]^{5-}$	>1100 ^g ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{2g}$; 785 (9) and 698 (13) spin-orbit split components of ${}^3\text{A}_{2g} \rightarrow {}^3\text{T}_{1g}(\text{F})$; $<\sim 470$ vs ^{e,f}	>1100 ; 710 and 623; $<\sim 500$ vs ^f
$[\text{PCu}(\text{S})\text{Mo}_{11}\text{O}_{39}]^{5-}$	832 br (43) ${}^2\text{E}_g \rightarrow {}^2\text{T}_{2g}$; $<\sim 470$ vs ^e	831 br; $<\sim 480$ vs
$[\text{PZn}(\text{S})\text{Mo}_{11}\text{O}_{39}]^{5-}$	$<\sim 460$ vs ^e	$<\sim 490$ vs

Concentrations: $\text{Na}_2(\text{}^t\text{Bu}_4\text{N})_4[\text{PZ}(\text{Br})\text{Mo}_{11}\text{O}_{39}] = 1.0 \times 10^{-2} \text{ M}$; H_2O_2 (when added) = $3.0 \times 10^{-2} \text{ M}$.

^a S = CH_3CN .

^b Notations—vs: very strong; br: broad; sh: shoulder.

^c Assignments are given on the basis of O_h symmetry, although the transition metal site has an in-built axial distortion and C_s symmetry.

^d Obscures the spin-forbidden d–d transitions of $\text{Mn}(\text{II})$.

^e Charge transfer transition, $\text{O} \rightarrow \text{Mo}(\text{VI})$.

^f Base of peak obscured by the lower wavelength bands in the spectrum.

^g Cannot be obtained as it is out of the range of the spectrophotometer.

studies were not feasible. Consequently, UV–VIS spectroscopic studies of the compounds before and after addition of H_2O_2 were recorded. The data are given in Table 4. The assignments for the spectra are taken from the extensive UV–VIS spectroscopic studies that have been reported on transition metal-substituted lacunary anions based on both the Keggin and Dawson structures, i.e. $[\text{XZ}(\text{H}_2\text{O})\text{M}_{11}\text{O}_{39}]^{n-}$ and $[\text{X}_2\text{Z}(\text{H}_2\text{O})\text{M}_{17}\text{O}_{61}]^{n-}$, where $\text{X} = \text{Zn}^{2+}$, B^{3+} , Si^{4+} , Ge^{4+} , P^{5+} or As^{5+} ; $\text{Z} = \text{Mn}^{2+}$, Co^{2+} , Ni^{2+} , Cu^{2+} , Zn^{2+} , Mn^{3+} or Co^{3+} , $\text{M} = \text{Mo}$ or W) [37–39].

The present study was complicated by the very strong $\text{O} \rightarrow \text{Mo}(\text{VI})$ charge transfer band in the formal phosphopolyoxomolybdate unit, $[\text{PMo}_{11}\text{O}_{39}]^{7-}$, which shows a strong absorbance below ~ 460 nm. This was evident in all of the spectra, and is typified by the UV–VIS spectrum of the $\text{Zn}(\text{II})$ -substituted phosphopolyoxometalate anion. Evidence for a shift (~ 30 nm) of the absorption edge to higher wavelengths was noted following addition of H_2O_2 in the case of $[\text{PZn}(\text{Br})\text{Mo}_{11}\text{O}_{39}]^{6-}$. This is consistent with the formation of $(\text{PO}_4[\text{MoO}(\text{O}_2)_2]_4)^{3-}$, as this anion is bright yellow in color [35]. However, this shift was more difficult to observe for the other anions, generally because of overlap with other transitions, although a shift could be detected for the $\text{Cu}(\text{II})$ system.

The only anion that showed oxidation of the transition metal-substituted addendum ion was the $\text{Mn}(\text{II})$ -containing anion. Oxidation of $\text{Mn}(\text{II})$ to $\text{Mn}(\text{III})$ by H_2O_2 took only a few minutes at room temperature. The $\text{Co}(\text{II})$ and $\text{Cu}(\text{II})$ spectra showed little difference in peak maxima following addition of H_2O_2 , while for the $\text{Ni}(\text{II})$ solution the peaks shifted to lower energies, which is consistent with replacement of O-donor atoms of the ligands by N-donor atoms of the CH_3CN solvent as a result of breakdown of the anion. Previous studies had shown that water alone had almost no effect on the positions and intensities of the peak maxima. It is, thus, likely that the $\text{Ni}(\text{II})$ -substituted lacunary phosphopolyoxomolybdate compound was decomposed by H_2O_2 , while no firm conclusions can be drawn regarding the $\text{Mn}(\text{III})$, $\text{Co}(\text{II})$ and $\text{Cu}(\text{II})$ systems, although the latter also appears to have been degraded. On standing overnight, however, white solids appeared in the case of the $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$ and $\text{Zn}(\text{II})$ systems, and yellow crystals (probably containing $(\text{PO}_4[\text{MoO}(\text{O}_2)_2]_4)^{3-}$) after several days. It is, thus, likely that the anions are degraded by H_2O_2 at somewhat different rates. In view of the ${}^{31}\text{P}$ and UV–VIS evidence detailed above, it is likely that all anions began to fragment under the conditions of the reactions (50°C) as soon as the H_2O_2 was added, and almost certainly decomposed

over the course of their reactions. Thus, the observed non-linear $\ln(100/(100 - \% \text{ conversion}))$ versus time plots likely represent a combination of several factors: (a) the actual catalytic abilities of the transition metal-substituted lacunary phosphopolyoxomolybdate compounds, being limited by the rate of their decomposition by H_2O_2 , and (b) the catalytic abilities of the product species, including $(\text{PO}_4[\text{MoO}(\text{O}_2)_2]_4)^{3-}$, and those of the freed transition metals that originally occupied the lacunary sites. In view of the complexity and changing nature of the reaction mixtures, no conclusions can be drawn as to the mechanism of reaction that occurs between the substrate isobutyraldehyde and the oxidant H_2O_2 in these reactions.

4. Conclusions

The homogeneous catalytic oxidation of isobutyraldehyde to isobutyric acid using H_2O_2 in acetonitrile solution at 50°C has been examined using a variety of heteropolyoxometalate catalysts with Keggin, Dawson and transition metal-substituted lacunary structures, the latter based on the Keggin structure. There was no evidence for fragmentation of any polyoxotungstate framework under the reaction conditions, while the polyoxomolybdate frameworks of $[\text{PMo}_{12}\text{O}_{40}]^{3-}$ and $[\text{P}_2\text{Mo}_{18}\text{O}_{62}]^{6-}$ exhibited some minor breakdown to yield peroxy-species. The polyoxomolybdate-based transition metal-substituted lacunary species, $[\text{PZ}(\text{II})(\text{Br})\text{Mo}_{11}\text{O}_{39}]^{6-}$, where $\text{Z} = \text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$, all likely underwent complete degradation to give peroxy-species based on ^{31}P NMR and UV–VIS evidence, likely yielding $(\text{PO}_4[\text{MoO}(\text{O}_2)_2]_4)^{3-}$ as one product. Thus, species of this type with a polyoxomolybdate framework would appear to be of little application in studies involving H_2O_2 oxidation, despite the use of solution conditions designed to maximize their stability.

Kinetic studies on $[\text{PW}_{12}\text{O}_{40}]^{3-}$ showed that the rate expression was first-order in catalyst and was zero-order in oxidant. Actual oxidation of the isobutyraldehyde, therefore, occurs following interaction with the anion, according to these studies. For the Keggin and Dawson species catalytic activity increased with decreasing anionic charge, which suggests that the catalytic activity depended on the extent of electrostatic repulsion between the isobutyraldehyde and

the anion, and hence, the rate of formation of an encounter complex. It is also likely that ion-pairing plays some role under these (effectively) non-aqueous solution conditions, as shown by a comparison of the rates of oxidation of the $^n\text{Bu}_4\text{N}^+$, $^n\text{Hx}_4\text{N}^+$ and $^n\text{Oc}_4\text{N}^+$ salts of the $[\text{PW}_{12}\text{O}_{40}]^{3-}$ ion.

Acknowledgements

Dr. J. Hu would like to acknowledge the University of Newcastle for the award of a UNRS and an OPRS.

References

- [1] C.L. Hill, C.M. Prosser-McCartha, *Coordination Chem. Rev.* 143 (1995) 407.
- [2] C.L. Hill, G.-S. Kim, C.M. Prosser-McCartha, D. Judd, in: M.T. Pope, A. Müller (Eds.), *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity*, Kluwer, Dordrecht, 1994, p. 359.
- [3] I.V. Kozhevnikov, *Chem. Rev.* 98 (1998) 171.
- [4] T. Okuhara, N. Mizuno, M. Misono, *Adv. Catal.* 41 (1996) 113.
- [5] D.K. Lyon, W.K. Miller, T. Novet, P.J. Domaille, E. Evitt, D.C. Johnson, R.G. Finke, *J. Am. Chem. Soc.* 113 (1991) 7209.
- [6] D. Mansuy, J.-F. Bartoli, P. Battioni, D.K. Lyon, R.G. Finke, *J. Am. Chem. Soc.* 113 (1991) 7222.
- [7] N. Mizuno, M. Misono, *J. Mol. Catal.* 64 (1990) 1.
- [8] N.I. Kuznetsova, L.G. Detusheva, L.I. Kuznetsova, M.A. Fetoto, V.A. Likholobov, *Kinet. Katal.* 33 (1992) 516.
- [9] C. Venturello, R. D'Aloisio, J.C. Bart, M. Ricci, *J. Mol. Catal.* 32 (1985) 107.
- [10] M. Schwegler, M. Floor, H. van Bekkum, *Tetrahedron Lett.* 29 (1988) 823.
- [11] H. Furukawa, T. Nakamura, H. Inagaki, E. Nishikawa, C. Imai, M. Misono, *Chem. Lett.* (1988) 877.
- [12] Y. Ishii, K. Yamawaki, T. Ura, H. Yamada, T. Yoshida, M. Ogawa, *J. Org. Chem.* 53 (1988) 3587.
- [13] S. Satoshi, S. Watase, Y. Katayama, Y. Sakata, Y. Nishiyama, Y. Ishii, *J. Org. Chem.* 59 (1994) 5681.
- [14] C. Venturello, R. D'Aloisio, *J. Org. Chem.* 53 (1988) 1553.
- [15] C. Venturello, M. Ricci, *J. Org. Chem.* 51 (1986) 1599.
- [16] R.G. Beiles, Z.E. Rozmanova, O.B. Andreeva, *Russ. J. Inorg. Chem.* 14 (1969) 1122.
- [17] L. Salles, C. Aubrey, R. Thouvenot, F. Robert, C. Doremieux-Morin, G. Chottard, H. Ledon, Y. Jeannin, J.M. Brégeault, *Inorg. Chem.* 33 (1994) 871.
- [18] L.J. Csanyi, K. Jaky, *J. Mol. Catal.* 61 (1990) 75.
- [19] A.M. Khenkin, C.L. Craig, *Mendeleev Commun.* (1993) 140.
- [20] R. Neumann, M. Gara, *J. Am. Chem. Soc.* 116 (1994) 5509.
- [21] G. Emig, T. Haeberle, W. Hoss, O. Watzenberger, *Chem. Eng. Technol.* 11 (1988) 120.

- [22] C. Rocchiccioli-Deltcheff, M. Fournier, R. Franck, R. Thouvenot, *Inorg. Chem.* 22 (1983) 207.
- [23] K. Nomiya, M. Miwa, R. Kobayashi, M. Asio, *Bull. Chem. Soc. Jpn.* 54 (1981) 2983.
- [24] K. Nomiya, M. Miwa, *Polyhedron* 2 (1983) 955.
- [25] V. Simmons, Ph.D. Thesis, Boston University, Boston, 1963.
- [26] F. Walmsley, *J. Chem. Educ.* 69 (1992) 936.
- [27] K. Nomiya, R. Kobayashi, M. Miwa, *Bull. Chem. Soc. Jpn.* 56 (1983) 2272.
- [28] R. Massart, R. Contant, J.M. Fruchart, J.P. Ciabrini, M. Fournier, *Inorg. Chem.* 16 (1977) 2916.
- [29] J. Hu, R.C. Burns, J.-P. Guerbois, *J. Mol. Catal. A: Chem.* 152 (2000) 141.
- [30] T. Hori, S. Himeno, *Chem. Lett.* (1987) 53.
- [31] B. Cartie, *J. Chem. Res.* (1988) 2282.
- [32] D. Qin, G. Wang, M. Li, Y. Wu, Wuji Huaque Quebao (Chin. *J. Inorg. Chem.*) 8 (1992) 124.
- [33] D. Qin, G. Wang, Y. Wu, in: V.C. Corberán, S.V. Bellón (Eds.), *New Developments in Selective Oxidation II*, Elsevier, Amsterdam, 1994, p. 603.
- [34] D.K. Lyon, W.K. Miller, T. Novet, P.J. Domaille, E. Evitt, D.C. Johnson, R.G. Finke, *J. Am. Chem. Soc.* 113 (1991) 7209.
- [35] A.L. Nolan, R.C. Burns, G.A. Lawrance, *J. Chem. Soc., Dalton Trans.* (1998) 3041.
- [36] C. Aubry, G. Chottard, N. Platzer, J.-M. Brégeault, R. Thouvenot, F. Chauveau, C. Huet, H. Ledon, *Inorg. Chem.* 30 (1991) 4409.
- [37] T.J.R. Weakley, S.A. Malik, *J. Inorg. Nucl. Chem.* 29 (1967) 2935.
- [38] S.A. Malik, T.J.R. Weakley, *J. Chem. Soc. A* (1968) 2647.
- [39] C.M. Tourné, G.F. Tourné, S.A. Malik, T.J.R. Weakley, *J. Inorg. Nucl. Chem.* 32 (1970) 3875.