THE UNIVERSITY OF SHEFFIELD

Department of Chemistry

PALLADIUM AND HETEROPOLYACID CATALYSED OXIDATION OF BUTENE TO BUTANONE

Submitted for degree of Doctor of Philosophy

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To my husband, Graham.

"There is nothing love cannot face; there is no
limit to its faith, its hope and its endurance."

Corinthians Chapter 13, Verse 7.

Acknowledgements

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Palladium and Heteropolyacid Catalysed Oxidation of Butene to Butanone

Suzanne F.Davison

Summary

Mixed heteropolyacids of the $H_{3+n}PMo_{12-n}V_nO_{40}$ series have been prepared and their solution properties studied by n.m.r. and electronic spectroscopy. It was found that except for n=0 or 1 these compounds exist largely as mixtures of P-Mo-V heteropolyacids in aqueous media. No evidence was found for the existence of discrete compounds where $n>3$. Detailed ^{31}P, ^{51}V and ^{17}O n.m.r. spectroscopic studies of $H_4PMo_{11}VO_{40}$ and $H_5PMo_{10}V_2O_{40}$ have been carried out. It has been shown that $H_4PMo_{11}VO_{40}$ retains the Keggin structure and the existence of isomeric forms of $H_5PMo_{10}V_2O_{40}$ has been confirmed.

The usefulness of such mixed heteropolyacids as reoxidation catalysts in the $PdSO_4$ catalysed oxidation of but-1-ene to butan-2-one was studied. Their activity was limited by the rate of oxidation of the reduced forms by O_2 and this was found to increase with the vanadium content of the heteropolyacid. Systems containing only vanadium were found not to be reoxidised by O_2, but $H_3PMo_{12}O_{40}$ and suitable mixtures of MoO_4^{2-} and PO_4^{3-} were reasonably good co-catalysts under defined conditions of concentration and acidity, for example, turnover numbers of 36 based on palladium were achieved with $H_3PMo_{12}O_{40}$ (4.13×10^{-3}M), $PdSO_4$ (4.95×10^{-3}M) in 1MH_2SO_4.

The composition of solutions of $H_3PMo_{12}O_{40}$ (oxidised and reduced forms) has been investigated by n.m.r. and visible spectroscopy. In dilute acidic solution the main components were shown, by the use of lanthanide shift reagents, to be free phosphoric acid and an isomolybdate species. Evidence was also found for the existence of other minor, phosphorus containing species at higher temperatures. Interaction with aldehydes was found to inhibit reoxidation of the reduced species.

Some experiments have been performed on a continuous reactor with some success.

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CHAPTER 1

Introduction

1.1 Commercial processes for producing butan-2-one

The major commercial process for the manufacture of butan-2-one may be summarised as follows.(1)

(1) Hydrolysis of n-butenes via sulphonation to butan-2-ol.

$$\begin{tikzcd}
C_4H_8 + (\text{conc})H_2SO_4 \arrow[r, shift left] \arrow[d, "C_4H_8"] & C_4H_9OSO_3H \arrow[l, shift left] \arrow[d, "H_2O"] \\
C_4H_9OSO_2OC_4H_9 \arrow[r, "H_2O"] & C_4H_9OH + (\text{dil})H_2SO_4
\end{tikzcd}$$

(2) Dehydrogenation of butan-2-ol to butan-2-one.

$$C_4H_9OH \xrightarrow[ZnO]{400^{\circ}C} CH_3CH_2COCH_3$$

In most commercial plants dehydrogenation of butan-2-ol is carried out in a vapour phase reactor over a ZnO catalyst which has been specially treated to reduce dehydration reactions. The temperatures used are around 400°C and the pressure lies in the 15-45 p.s.i. range.

This process uses a lot of energy for the reconcentration of sulphuric acid and the high temperatures needed for dehydrogenation of butan-2-ol. Obviously a low temperature direct oxidation of n-butenes to butan-2-one, as is presently used for the manufacture of acetaldehyde from ethene, (the Wacker process[1]), would be very attractive. Many patents have appeared on this theme but as yet butan-2-one is not produced commercially by this type of method because of problems with chlorinated side products and slow reaction rates.

1.2 Palladium catalysed oxidation of olefins to aldehydes and ketones

1.2.1 Wacker reaction

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[1] Named after the firm (Wackerchemie GmbH) where it was first developed.

The stoichiometry of the Wacker reaction is as follows:

$$C_2H_4 + PdCl_2 + H_2O \longrightarrow CH_3CHO + Pd^o + 2HCl \tag{1}$$

$$Pd^o + 2CuCl_2 \longrightarrow PdCl_2 + Cu_2Cl_2 \tag{2}$$

$$\underline{Cu_2Cl_2 + 2HCl + \tfrac{1}{2}O_2 \longrightarrow 2CuCl_2 + H_2O} \tag{3}$$

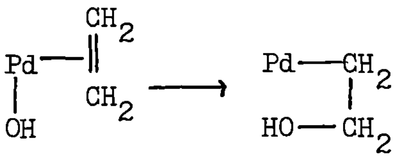
$$C_2H_4 + \tfrac{1}{2}O_2 \longrightarrow CH_3CHO$$

The reaction in equation (1) has been known since 1894(2) but it was not until 1959 that it was combined with reactions (2) and (3) by Smidt and co-workers(3)(4) to give the catalytic cycle indicated above. As a result of extensive studies the mechanism of reaction (1) is fairly well understood. A summary is shown in Figure 1a.

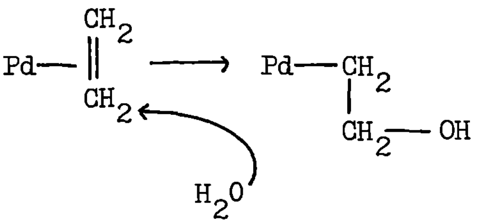
Steps 1 to 4 are generally agreed and are consistent with the accepted kinetics and the rate expression.(5)

$$\frac{-d\,[C_2H_4]}{dt} = \frac{k^{1}K_1\,[PdCl_4{}^{2-}]\,[C_2H_4]}{[H^+]\,[Cl^-]^2}$$

Formation of 5, the hydroxyethyl palladium intermediate, may occur by a cis-addition of OH^- from within the palladium co-ordination sphere, again in agreement with the kinetics.



However, studies of the stereochemistry(6)(7) using cis- and trans-CHD=CHD indicate that trans-addition by an external nucleophile is also possible.



More recent studies by Henry and Gragor(8) show that the conditions used

The Wacker Reaction

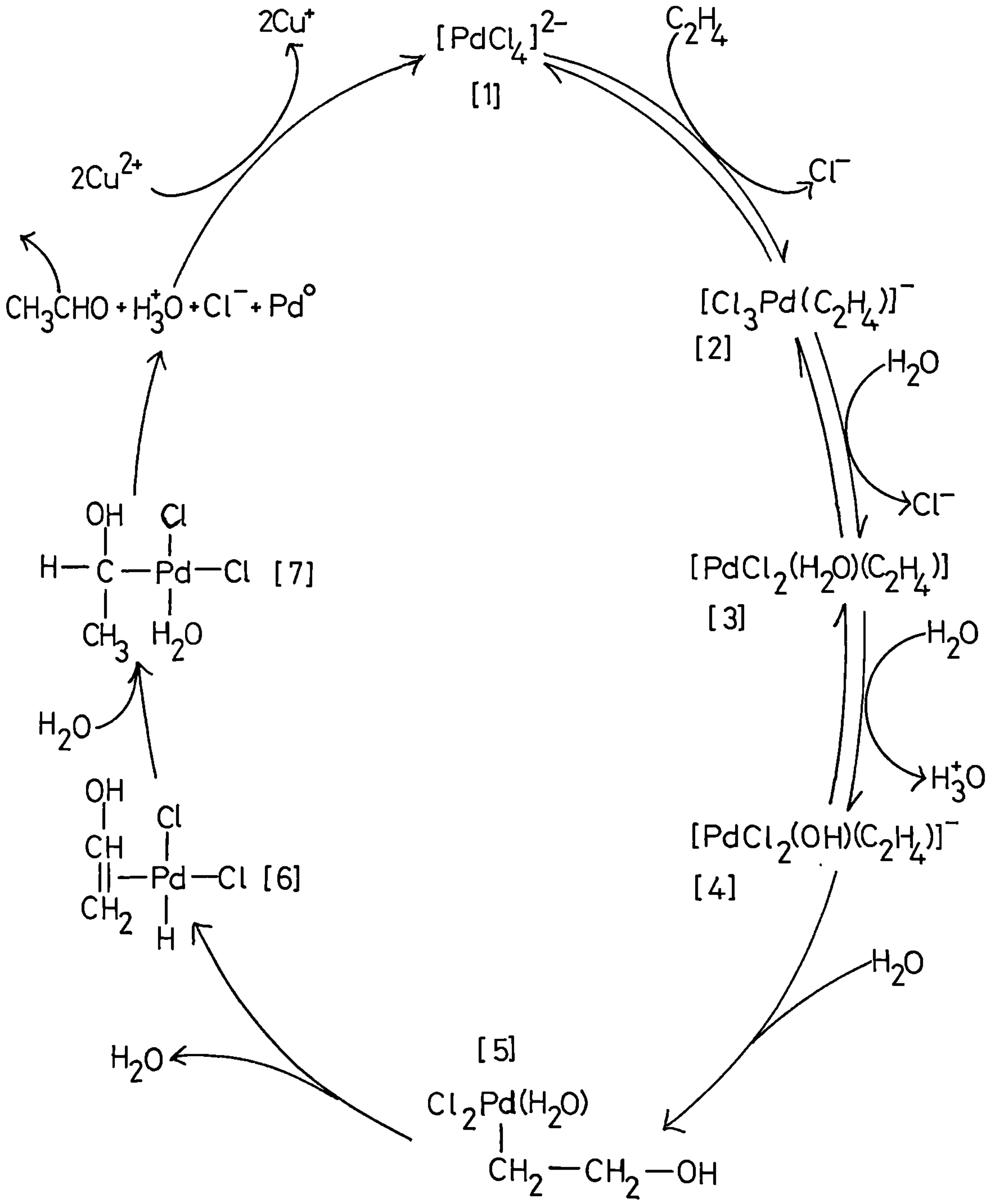
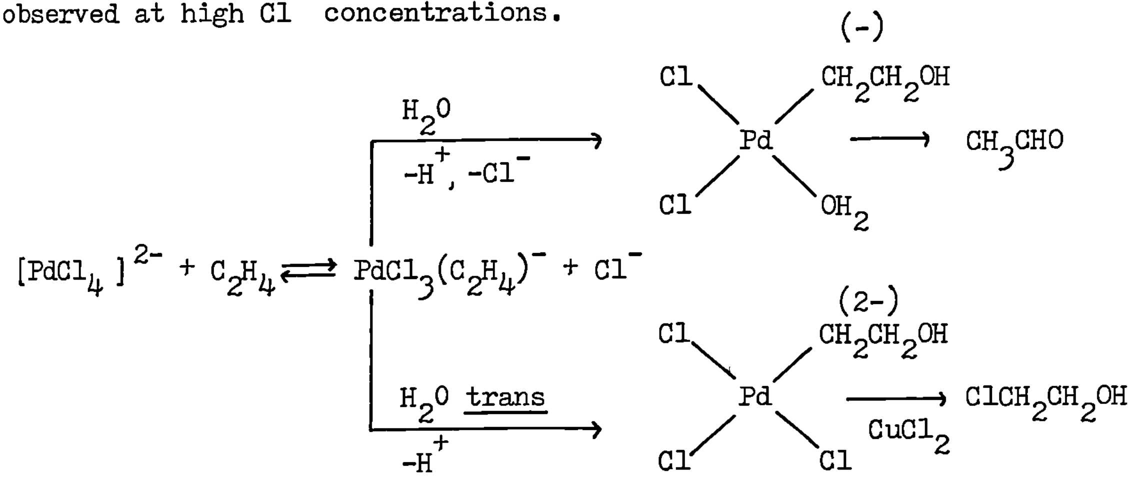


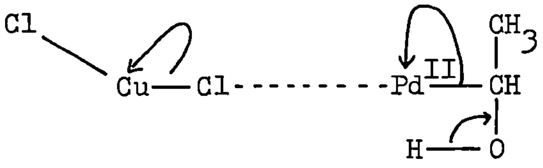
Figure 1a,

in these stereochemical studies, that is high chloride ion concentrations, may lead to an alternative reaction path. They suggest two paths, one of which leads to aldehyde, the other leading to chlorohydrins. This also gives some explanation for the chlorinated side products which are observed at high Cl^- concentrations.



Steps 5 to 7 agree with the observation that when the reaction is carried out in D_2O no deuterium appears in the product. This shows that all the hydrogen in the product must come from ethylene.

The interaction between palladium and the reoxidant, usually $CuCl_2$, is much less well understood. It is known that (9) the presence of chloride ions decreases the normal potential of the Pd^0/Pd^{2+} couple and simultaneously increases the potential of the Cu^+/Cu^{2+} couple by stabilising Pd^{2+} and Cu^+ by complexing. Hence Cu^{2+} in the absence of chloride is a bad reoxidant. A suggestion (10) that the reoxidation occurs via an interaction between the σ-bonded intermediate (7) and $CuCl_2$, in which $CuCl_2$ removes electrons from the Pd(II) as the Pd(II)-carbon bond is broken has been proposed.



1.2.2. Chloride Free Systems

The oxidation of ethene to acetaldehyde in aqueous media has also been studied in the absence of chloride ions(11,12). These studies have used p-benzoquinone to reoxidise the palladium. The mechanism of this reaction is not understood but the following scheme has been proposed by Matveev.

$$\begin{aligned} Pd^{II}aq + C_2H_4 + H_2O &\longrightarrow Pd^{o} + CH_3CHO + 2H^{+} \\ Pd^{o} + C_2H_4 &\rightleftharpoons Pd^{o}(C_2H_4) \\ Pd^{o}(C_2H_4) + C_2H_4 &\rightleftharpoons Pd^{o}(C_2H_4)_2 \end{aligned}$$

$$\begin{aligned} Pd^{o}(C_2H_4)_n + Q &\rightleftharpoons Pd^{o}(C_2H_4)_n\,Q \\ Pd^{o}(C_2H_4)_n\,Q + H^{+} &\rightleftharpoons Pd^{o}(C_2H_4)_n\,Q(H^{+}) \\ Pd^{o}(C_2H_4)_n Q(H^{+}) &\longrightarrow Pd^{2+}(C_2H_4)_n + HQ^{-} \end{aligned}$$

$n = 1,2$

Q = benzoquinone

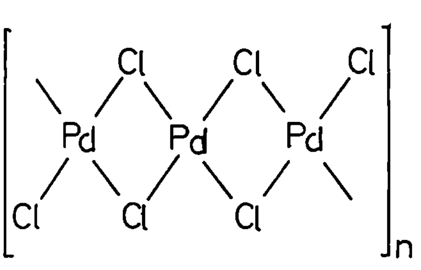
At low ethene concentrations a palladium(I) intermediate $Pd_2Q\,(H)_2^{2+}$ was also suggested to participate.

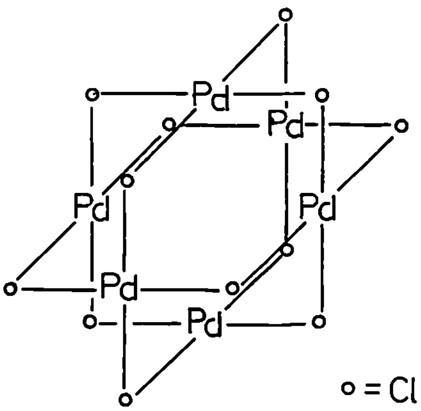
The rate determining step of the reaction in the absence of chloride was proposed to be the reoxidation of Pd (0) to Pd(II) (i.e. the reverse of that in the chloride systems). This would explain the enhancement of the rate at higher H^{+} concentration and the increase in rate on the addition of small amounts of chloride ion.

1.2.3. Butene Oxidation

Most of the patents dealing with direct oxidation of butene use palladium(II) salts and a reoxidation catalyst. The most used palladium(II) salts are $PdCl_2$, $Pd(OAc)_2$ and $PdSO_4$.

$PdCl_2$ is known in two forms(13,14), the α-form which is polymeric and the β-form which consists of discrete clusters of six palladium atoms.

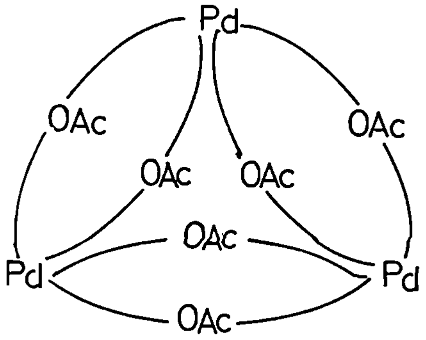




α-form

β-form

The structure of $Pd(OAc)_2$ is also known(15) and consists of three palladiums in a triangle doubly bridged by acetates.



However, the structure of $PdSO_4$ is unknown.

Many different reoxidation catalysts have been claimed. With the standard $PdCl_2$-$CuCl_2$ system used for ethene oxidation the reaction rates for butenes are much slower, but-1-ene reacting at 0.25 times the rate of ethene and but-2-ene at 0.07 times the rate of ethene. Also the longer chain olefin forms chlorinated side products much more readily and these can be as much as 25% of the total products.(16) Hence a chloride free system would be an advantage in eliminating chlorinated side products, as well as reducing problems of corrosion.

Two patents of interest claim chloride free systems; the first(17) uses a $PdSO_4/Fe_2(SO_4)_3$ system and the second(13) uses a mixed heteropolyacid as reoxidant. The $PdSO_4$- mixed heteropolyacid system was the one chosen for study after preliminary experiments had been tried with both systems. The $PdSO_4/Fe_2(SO_4)_3$ system was found to give slow rates which decreased with time.[1]

1.3 Heteropolyacids

1.3.1 A General Survey

Heteropolycompounds are a large class of salts and free acids containing complex anions, the structures of which are based on MO_6 octahedra. The MO_6 octahedra can be joined by sharing corners, edges or faces to form a co-ordination sphere around a central heteroatom. The central atom can either be tetrahedral, octahedral or icosahedral. While up to as many as forty elements have been claimed as central heteroatoms, only niobium, vanadium, molybdenum and tungsten are known to form the outer MO_6 octahedra, although some other transition elements can be substituted into the structures in a few cases. The range of heteropolymolybdate and heteropolytungstate compounds is much greater than that for the other two elements ,probably as a result of relative stabilities. Details of Mo and W compounds which are claimed to have been prepared are given in Table 1.1.

1.3.1.1 $X^{+} \; M_{12}O_{40} \; (8-n)^{-}$ (12-Heteropolyanions - Series A)

The basic structure of this series was first proposed by Keggin in 1934(18) and was later confirmed by X-ray structure studies.(19) The so called Keggin structure consists of a tetrahedrally co-ordinated

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[1] Work done by Dr. A. Keasey, B.P. Chemicals Ltd.

Table 1.1

		Elements Claimed	
Formulae	Central Group	M = W	M = Mo
$X^{+}M_{12}O_{40}{}^{(8-n)-}$	XO_4	B^{III}, Si^{IV}, Ge^{IV}, P^{V} As^{V}, Al^{III}, Fe^{III}, Co^{II} Co^{III}, Cu^{I}, Cu^{II}, Zn^{II} Cr^{III}, Mn^{IV}, Te^{IV}, Ga^{III}	Si^{IV}, Ge^{IV}, P^{V}, As^{V} Ti^{IV}, Zr^{IV}
$X_2{}^{+}M_{18}O_{62}{}^{(16-n)-}$	XO_4	P^{V}, As^{V}	P^{V}, As^{V}
$X_2{}^{+n}Z_4{}^{+m}M_{18}O_{70}H_4{}^{(28-2n-4m)-}$	XO_4	P^{V}, As^{V} ($Z=Mn^{II}$, Co^{II}, Ni^{II} Cu^{II}, Zn^{II})	
$X_2{}^{+}M_5O_{23}{}^{(16-2n)-}$	XO_4	P^{V}	P^{V}
$X^{+}M_9O_{32}{}^{(10-n)-}$	XO_6		Mn^{IV}, Ni^{IV}
$X^{+}M_6O_{24}{}^{(12-n)-}$	XO_6	Ni^{IV}, Te^{IV}, I^{VII}	Te^{VI}, I^{VII}
$X^{+}M_6O_{24}H_6{}^{(6-n)-}$	XO_6	Ni^{II}	Al^{III}, Cr^{III}, Co^{III}, Fe^{III} Ga^{III}, Rh^{III}, Mn^{II}, Co^{II} Ni^{II}, Cu^{II}, Zn^{II}
$X_2{}^{+}M_{10}O_{38}H_4{}^{(12-n)-}$	XO_6		Co^{III}
$X^{+}M_{12}O_{42}{}^{(12-n)-}$	XO_{12}		Ce^{IV}, Th^{IV}, U^{IV}

Table to show the range of heteropolyanions found for Mo and W heteroatom surrounded by four sets of 3 MO_6 octahedra which share edges and share a single oxygen with the XO_4 group joined together by corner sharing. See Figure 1b.

It has later been found that isomerisation can occur giving an α and a β-form in some cases. The α-form (Figure 1b) is the most common and most stable. The β-form (Figure 1c), which may be represented by rotating one of the edge sharing sets of MO_6 octahedra through 60°, is less stable. The presence of the β-form for $[SiW_{12}O_{40}]^{4-}$ has been confirmed by an X-ray structure analysis,(20) while the presence of the more labile β-$[SiMo_{12}O_{40}]^{4-}$ has been deduced from polarographic and spectrophotometric studies. The β-forms are stabilised in mixed solvent systems.(21)

In aqueous solution 12-heteropolyacids are degraded by treatment with alkali,(22) initially to compounds of the form $[X^{+n}M_{11}O_{39}]^{(12-n)-}$ and then to polyanions with less than six metal atoms (see Section 1.3.2.2). Generally members of the tungsten series are more resistant than those of the molybdenum series to such degradation. The stability to increasing pH also depends on the central heteroatom, the order of increasing stability is as follows:

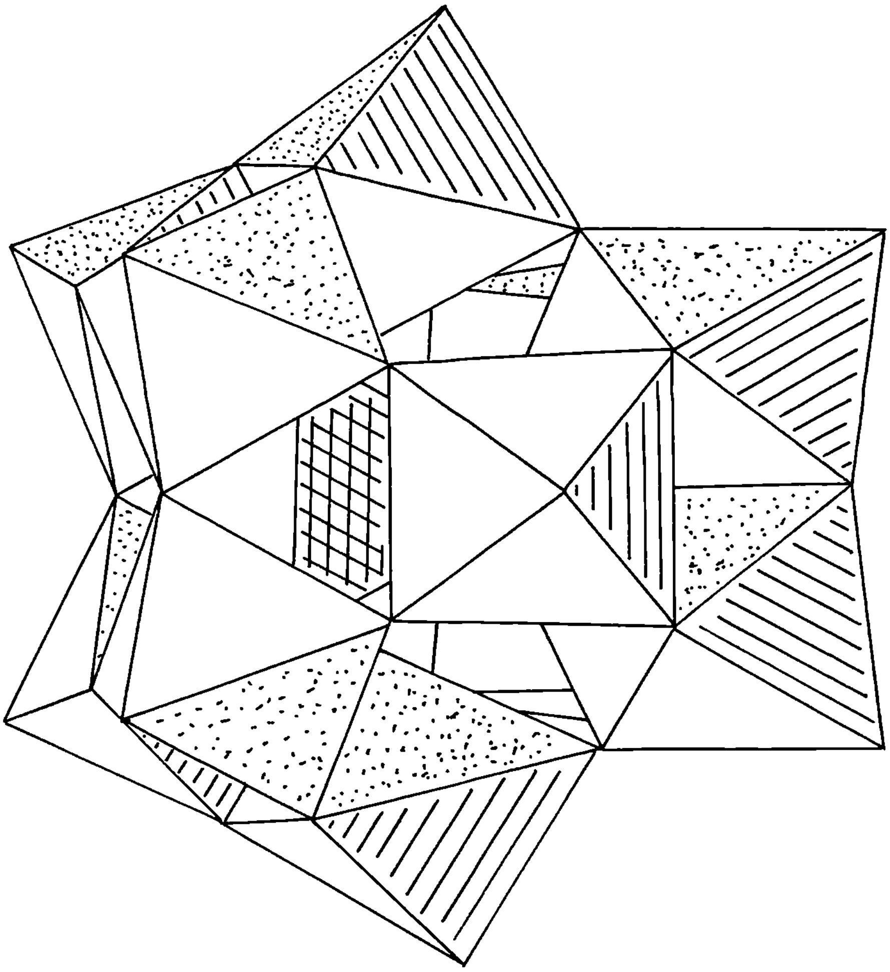
$$As < P < Ge < (Ti, Zr) < Si .$$

Compounds of this series are strong oxidising agents and under mild reducing conditions form mixed-valence species without change of structure, as shown by the fact that reoxidation can occur rapidly to give the original forms. These reduced species are often deep blue in colour and are known as heteropolyblues.

1.3.1.2 $X_2^{+n}M_{18}O_{62}^{(16-2n)-}$ Dimeric 9-Heteropolyanions

These compounds have a structure which can be explained as

The KEGGIN Structure



$X^{+n}M_{12}O_{40}{}^{(8-n)-}$ Figure 1b, follows. Three adjacent corner linked octahedra are removed from the Keggin anion, one from each of three edge sharing groups to give a half anion (Figure 1d). Two such half anions are joined so that those vertices which were originally shared are again shared and lie in the mirror plane of the anion. This is the so called β-form (Figure 1e). An α-form in which one half anion is rotated about the principal axis by 60^o is also proposed.

In aqueous solution the $X_2^{+n}M_{18}O_{62}{}^{(16-2n)-}$ anions also undergo degradation by base, firstly to a $[X_2M_{17}O_{61}]^{(20-2n)-}$ species, followed by complete decomposition. In acid they are converted to the 12-heteropolyanions.(22)

Similarly to the Keggin anions, anions of this series are reduced by mild reducing agents to heteropolyblues. The anions in this series are stronger oxidising agents than those in the Keggin series.

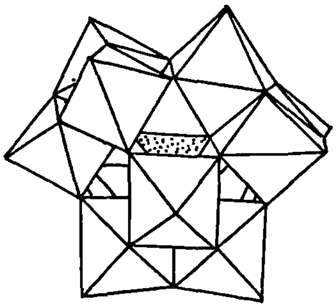
1.3.1.3 $X_2^{+n}Z_4^{m+}M_{18}O_{70}H_4{}^{(28-2n-4m)-}$

Anions of this type are prepared by prolonged action at 90^o-100^oC of an aqueous mixture containing H^+: HXO_4^{2-}: Z^{m+}: WO_4^{2-} (see Table 1.1) in the ratio 11:2:4:18.(23) The structure is shown in Figure 1f. The twelve octahedra adjacent to each XO_4 tetrahedron are linked in the manner of the β-Keggin anion (see Section 1.3.1.1). This minimises crowding of the unshared ZO_6 vertices.

1.3.1.4 $X_2^{+n}M_5O_{23}{}^{6-}$ 2:5 series

In this series of compounds the molybdenum analogues are the more readily prepared and a crystal structure of $Na_6P_2Mo_5O_{23}.13H_2O$ was determined in 1973.(24) This compound is prepared from HPO_4^{2-} and MoO_4^{2-} at 25^oC in near neutral solution. The tungsten analogue has

HETEROPOLYANIONS



$X^{+n}M_{12}O_{40}^{(8-n)-}$ -Figure 1c

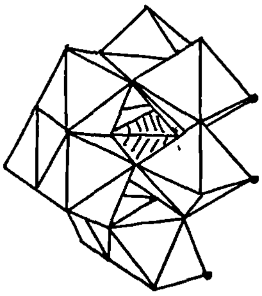
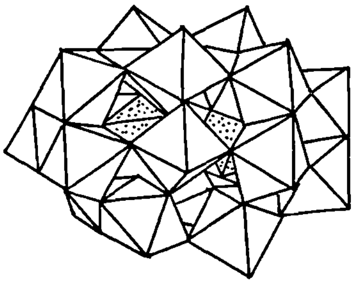
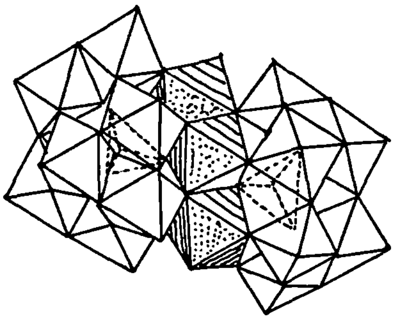


Figure 1d

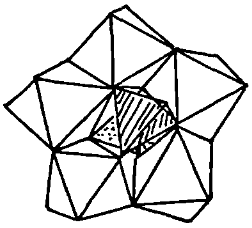


$X_2^{+n}M_{18}O_{62}^{(16-2n)-}$ - Figure 1e



$X_2^{+n}Z_4^{m+}M_{18}O_{70}H_4^{(28-2n-4m)-}$

Figure 1f



$X_2^{+n}M_5O_{23}^{6-}$

Figure 1g

only been recently reported as the cesium salt.(25)

The structure of this series consists of a ring of five distorted octahedra sharing edges except for one pair which share corners. Two PO_4 tetrahedra lie on either side of this ring and each shares three of its corners with the ring (Figure 1g). Analogous compounds containing organic groups have also been prepared by replacing phosphoric acid with aryl or alkyl phosphonic acids.(26,27)

1.3.1.5 $X^{+n}Mo_9O_{32}^{(10-n)-}$

The proposed structure for this series is shown in Figure 1h. These compounds are prepared by oxidising a solution of the salt of the divalent central atom and paramolybdate with persulphate, peroxide or bromine water.(22) They are readily degraded by excess acid or base.

1.3.1.6 $X^{+n}M_6O_{24}^{(12-n)-}$ and $XM_6O_{24}H_6^{(6-n)-}$

The structure of these types of heteropolyanion is shown in Figure 1i.(28) Both forms are degraded at high or low pH to compounds of lower ratio or to simple salts.

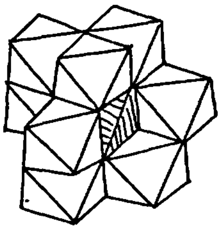
1.3.1.7 $X_2^{+n}M_{10}O_{38}H_4^{6-}$

$Co_2^{III}Mo_{10}O_{38}H_4^{6-}$ is prepared by the reaction of H_2O_2, Co^{2+} and $Mo_7O_{24}^{2-}$ in hot solution in the presence of activated charcoal.(29)

1.3.1.8 $X^{+n}M_{12}O_{42}^{(12-n)-}$

The ammonium salts are prepared by adding the ammonium hexanitrato salt of the central ion to a boiling solution of paramolybdate. The acids can be isolated by ion exchange.(30) The structure is shown in Figure 1j. The MoO_6 octahedra form six face sharing pairs; corners are shared between octahedra in different pairs and each octahedron

HETEROPOLYANIONS



$X^{+n}M_9O_{32}^{(10-n)-}$ -Figure 1h

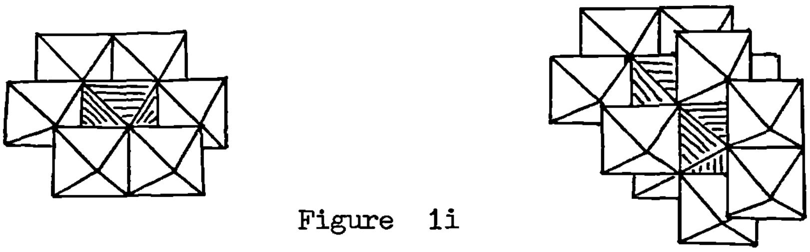
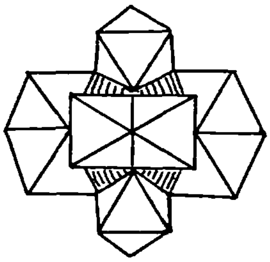


Figure 1i

$X^{+n}M_6O_{24}^{(12-n)-}$

$X^{+n}M_6O_{24}H_6^{(6-n)-}$



$X^{+n}M_{12}O_{42}^{(12-n)-}$ -Figure 1j shares a face with the central icosahedron.

More detailed reviews of the structure and properties of heteropoly compounds can be found in references (19), (21)and (31).

1.3.2 $H_3PMo_{12}O_{40}$ Dodecamolybdophosphoric acid

1.3.2.1 Properties of the Solid

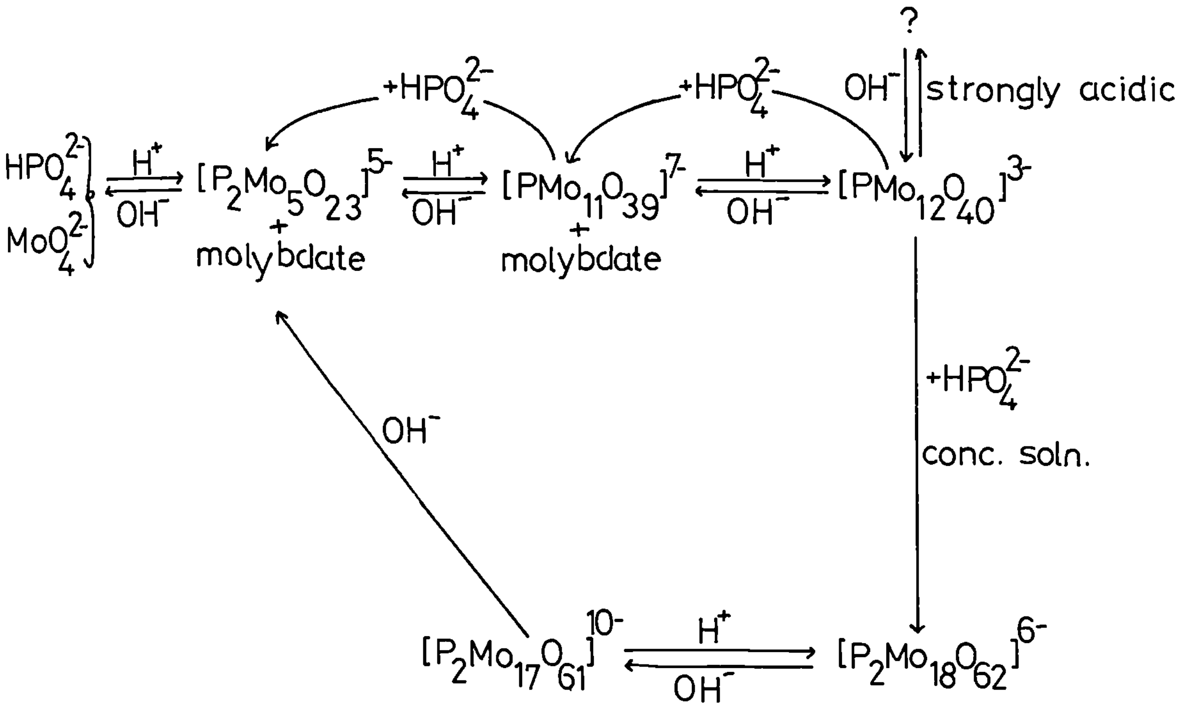
This compound is a member of the 12-A series of heteropolyanions and has the Keggin structure (see Figure 1b). The compound can be prepared as a yellow crystalline solid by boiling molybdenum trioxide in phosphoric acid. The crude product is obtained after crystallisation from water at room temperature. Alternatively it can be prepared by ether extraction of acidified solutions of Na_2MoO_4 and phosphate;(32) again the product must be recrystallised from water.

Dodecamolybdophosphoric acid is very soluble in water (solutions containing 85% of the acid by weight can be obtained) and in oxygen containing organic solvents (e.g. methanol, acetone, DMF), but is insoluble in non oxygen containing organics such as toluene.

The crystalline acid contains waters of hydration (the number depends on the conditions of formation);these can be removed by heating at 180°C. $H_3PMo_{12}O_{40}$ is stable up to temperatures of 350°C.

1.3.2.2 Properties in Aqueous Solution

Many studies of dodecamolybdophosphoric acid have been confused by a lack of appreciation of the instability of this acid even in acidic solutions. As previously mentioned,$[PMo_{12}O_{40}]^{3-}$ is very susceptible to degradation by base. The behaviour of $[PMo_{12}O_{40}]^{3-}$ with variation in pH has been extensively studied. The present knowledge of the equilibria occurring is summarised in the following reaction scheme.(22)



$H_3PMo_{12}O_{40}$ is a tribasic acid but many studies have concluded it to be heptabasic.(33) These results arise as dodecamolybdophosphoric acid is extensively hydrolysed in aqueous solution giving H^+, especially when the solutions are dilute.(21b,34) However it has been found that addition of certain oxygen containing organic solvents stabilises the $[PMo_{12}O_{40}]^{3-}$ anion to hydrolytic degradation. Dioxan was found to be particularly good.

1.3.2.3 Reduction

As previously stated, heteropolyanions of the 12-A series and dimeric 9 series (X_2M_{18}) are strong oxidising reagents and are reduced by mild reducing agents to give the so called "heteropolyblues". The formation of heteropolyblues involves the step-wise reduction of the d^o M atoms to the d^1 oxidation state without a change in structure of the anion.

It has been proposed(35) that only anions containing metals in octahedra with a single terminal unshared oxygen can form heteropolyblues. To date only polyanions with this structure have been shown to undergo reversible step-wise reductions to form heteropolyblues, e.g. $Mo_6O_{18}^{2-}$, $PMo_{12}O_{40}^{3-}$, $P_2Mo_{18}O_{62}^{6-}$. Other polyanions which have two cis terminally unshared oxygens are not reduced in this way.

It is generally thought(36) that the first electrons added are weakly trapped on individual metal atoms. Electron delocalisation is seen as a combination of two effects, a thermally-activated hopping process between metal atoms and a ground state delocalisation involving π-bonding through bridging oxygens from the reduced metal atom to its neighbour.

The reduction of $H_3PMo_{12}O_{40}$ in aqueous solutions by electrochemical(37-40,21) and chemical(41) means has been studied by several groups of workers. Some of the earlier work is not very useful as the hydrolytic instability of the polyacid and its ability to oxidise mercury in some of the polarographic experiments were not recognised. The reliable results can be summarised as follows.

In acidic solution stabilised with dioxan, $H_3PMo_{12}O_{40}$ gives three reversible waves when studied by cyclic voltametry;(38) each wave corresponds to a 2 electron reduction step. The half wave potentials occur at +0.31, +0.175, -0.065 volts. A wave also occurs at -0.218v, very close to H_2 evolution. It has been found that the half wave potentials vary with pH and generally the anion is a stronger oxidising agent at lower pH.(37,38) The reduced species formed are found to be more stable to hydrolytic degradation (i.e. they are stable over a wider pH range) than the oxidised form. The reduction usually proceeds in steps of 2 electrons but one electron reduction can be observed at higher pH(37) or in aprotic solvents.(39) Although no description of the isolation of a β-form of $H_3PMo_{12}O_{40}$ is given, half wave potentials are quoted for this compound;(37) +0.55, +0.37, -0.07 volts, which indicate that it is a more powerful oxidising agent than the more stable α-form. It was suggested that, at low pH, the α-form reduced by four electrons rapidly transforms to the four electron reduced β-form, but that increasing the pH retards this reaction.

Results of chemical reduction by $SnCl_2$,(41) ascorbic acid(42) etc. are confusing. The reductions have usually been monitored by following the visible spectrum since reduced $[PMo_{12}O_{40}]^{(3+e)-}$ has an intense absorption in the red. It has been found that the exact position of this peak varies with the reducing agent and the conditions of reduction.(43) El-Shamey(41) found that reduction with $SnCl_2$ in water gave absorption at 700 nm, while in acidic solution the main absorbance was at 820 nm. However, these studies were carried out without consideration of the hydrolytic instability of $H_3PMo_{12}O_{40}$.

1.3.3 $H_{3+n}PMo_{12-n}V_nO_{40}$

1.3.3.1 Structure and Preparation

These compounds have the same structure as $H_3PMo_{12}O_{40}$ but some of the Mo(VI) atoms are replaced by V(V).(19) Only the compounds where n =1, 2 or 3 have been successfully isolated in crystalline form,(44) but even the complex n=3 was only claimed in very low yields. These compounds are prepared by mixing Na_2HPO_4 and $NaVO_3$ in hot water and adding it when cool to a solution of Na_2MoO_4 in water. The PO_4^{3-} and MoO_4^{2-} are used in stoichiometric quantities, but V(V) is used in excess. The solutions are acidified and extracted with ether. The ether is removed with air and the solid remaining is crystallised from water.

1.3.3.2 Properties in Aqueous Solution

In aqueous solution the mixed heteropolyacids of molybdenum and vanadium seem to be more stable to degradation by base than the parent compound $H_3PMo_{12}O_{40}$. Titration with base removes the acidic protons between pH2 and 4 when 4, 5 and 6, molar equivalents of the base have been added to the $H_4PMo_{11}VO_{40}$, $H_5PMo_{10}V_2O_{40}$ and $H_6PMo_9V_3O_{40}$ acids respectively.(44) They do not seem to be degraded until pH8.5 when degradation is rapidly complete, for example,

$$[PMo_{11}VO_{40}]^{4-} + 22OH^- \longrightarrow HPO_4^{2-} + 11MoO_4^{2-} + HVO_4^{2-} + 10H_2O$$

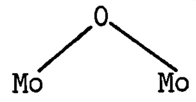
As with dodecamolybdophosphoric acid the vanadium containing species are unstable to hydrolytic degradation by acid, the $H_6PMo_9V_3O_{40}$(44) species is particularly sensitive. $H_5PMo_{10}V_2O_{40}$ is thought to be decomposed to $H_4PMo_{11}VO_{40}$ by acid; the $H_4PMo_{11}VO_{40}$ being the most stable in acidic media. These compounds can be stabilised by dioxan similarly to $H_3PMo_{12}O_{40}$.

Studying the nature of these compounds in solution has proved difficult as many of the more usual techniques give little in the way of useful information. However, NMR spectroscopy has given some interesting results. ^{31}P, ^{51}V and ^{17}O NMR spectroscopy have all been studied.(45-50) Generally it has been found difficult to produce pure samples of the molybdovanadophosphoric acids and NMR has revealed that most of the preparations result in samples containing both compounds with lower and higher vanadium contents as well as the intended compound.

A series of exchange, disproportionation and dissociation equilibria in aqueous solution were proposed by Matveev(51) et al. in 1980.

$$\begin{aligned}
H_5PMo_{10}V_2O_{40} + MoO_4^{2-} + 3H^+ &\rightleftharpoons H_4PMo_{11}VO_{40} + VO_2^+ + 2H_2O \\
2H_4PMo_{11}VO_{40} &\rightleftharpoons H_5PMo_{10}V_2O_{40} + H_3PMo_{12}O_{40} \\
10H_6PMo_9V_3O_{40} &\rightleftharpoons 9H_5PMo_{10}V_2O_{40} + 12VO_2^+ + H_3PO_4 + 12OH^- \\
H_{(3+n)}PMo_{12-n}V_nO_{40} + H_3\overset{+}{O} &\rightleftharpoons VO_2^+ + H_{(6+n)}PMo_{(12-n)}V_{n-1}O_{39} \qquad (1) \\
H_{(3+n)}PMo_{12-n}V_nO_{40} &\rightleftharpoons mH^+ + [H_{(3+n-m)}PMo_{(12-n)}V_nO_{40}]^{m-}
\end{aligned}$$

Theoretically molybdovanadophosphoric acids containing more than one vanadium atom can give rise to isomers depending on the mutual orientation of the vanadium atoms.(48) Both ^{51}V and ^{31}P n.m.r. give some evidence for the presence of such isomers(45,47,48,50) although any assignment of peaks to specific isomers must be tenuous.

Studies of the variation of ^{51}V chemical shifts with pH and the ^{17}O NMR(50) spectra have led to a proposal that Mo-O-Mo bonds bridging molybdenum atoms within a single Mo_3O_{10} unit of the Keggin structure are the first to be protonated in acidic media, and that protonation is by $H_3\overset{+}{O}$ which adds to a Mo_3O_{10} unit on three  bridges simultaneously.

1.3.3.3 Reduction

Many studies have been carried out on the reduction of the mixed heteropolyacids of P, Mo, V.(21,38,52-57) Cyclic voltametry carried out on $H_4PMo_{11}VO_{40}$ and $H_5PMo_{10}V_2O_{40}$ in acidic, aqueous/dioxan media gave the following half wave potentials for $H_4PMo_{11}VO_{40}$, +0.47, +0.22, +0.12, -0.15 and for $H_5PMo_{10}V_2O_{40}$; +0.40, +0.13, -0.24. In both cases the waves were ill-defined but showed evidence of reversibility. The second and third waves of $H_5PMo_{10}V_2O_{40}$ are completely overlapping. By comparison with results for $H_3PMo_{12}O_{40}$, the vanadium containing samples seem to be more strongly oxidising than the parent α- compound, with $H_4PMo_{11}VO_{40}$ being more oxidising than $H_5PMo_{10}V_2O_{40}$. However, β-$H_3PMo_{12}O_{40}$ is the strongest oxidising agent. It was concluded that once reduced the polyacids decay to different species.

Reduction by chemical agents has led to the following concensus of opinion. It is generally thought that initial reduction occurs at the vanadium atoms and that molybdenum(VI) is only reduced when all the vanadium(V) has been converted to vanadium(IV). The reduced vanadium can be dissociated from the polyacid structure and exist in the solution as $VO(H_2O)_5^{2+}$. More of the dissociated vanadyl is present at lower pH, cf. equilibria proposed for oxidised forms. See Section 1.3.3.2 equation (1). At pH 1, for example, half the vanadium is proposed to dissociate from the reduced $PMo_{11}VO_{40}$ species. The form of the heteropolyanion once the vanadium has dissociated is not known. The following equations summarise the above.

$$\begin{tikzcd}
{[PMo_{12-n}V_nO_{40}]^{(3+n)-}} \arrow[r, "e"] & {[PMo_{12-n}V^{V}_{n-1}V^{IV}O_{40}]^{(4+n)-}} \arrow[d, shift right, "H^+"'] \\
& {[PMo_{12-n}V_{n-1}O_{39}]^{(6+n)-} + VO(H_2O)_5^{2+}} \arrow[u, shift right]
\end{tikzcd}$$

Recent work(55) has shown that VO^{2+} in the form of $VOSO_4$ will reduce molybdovanadophosphate anions to their blues and the following is suggested

$$[PMo_{(12-n)}V_nO_{40}]^{(3+n)-} + VO^{2+} \rightleftarrows \text{heteropolyblue} + V(V) \text{ or } Mo(VI) \qquad (2)$$

1.3.3.4 Use in Homogeneous Catalysis

Heteropolyacids of P, Mo and V are used as reoxidation catalysts for Pd(0) in the Wacker type process.(13,51,58,59) Their important feature in this connection is that, unlike VO^{2+} or reduced free molybdate, their heteropolyblues can be reoxidised by oxygen in air to give the original heteropolyacid at low pH. This is frequently the limiting stage in such reactions.

A mechanism similar to that for the p-benzoquinone system is suggested (see Section 1.2.2). The reoxidation of Pd(0) is proposed to occur by the reduction of only the vanadium in the heteropolyacid, any free VO_2^+ in solution being reduced due to exchange with the heteropolyacid (equation 1 Section 1.3.3.2). The reoxidation by O_2 is said to take place by the formation of an intermediate between the heteropolyblue and a $O_2^{\dot{-}}$ radical. The free VO^{2+} being oxidised by exchanging into the heteropolyacid, (equation 2 Section 1.3.3.3).

CHAPTER 2

Preparation, Analysis and NMR Spectroscopy Studies of Heteropolyacids of the $H_{3+n}PMo_{(12-n)}V_nO_{40}$ Series

2.1 Introduction

As no detailed investigation of these compounds had been reported in the literature, n.m.r. spectroscopic investigations of solution properties were carried out before work on the activity of heteropoly acids for reoxidation of Pd(0) in Wacker type catalytic reactions was started.

2.2 Preparation and Analysis

Preparations of heteropolyacids with 1, 2 or 3 vanadiums were carried out by the literature method.(44) This involved the mixing of an acidified aqueous solution of sodium vanadate, always in excess, and sodium hydrogen phosphate with an aqueous solution of sodium molybdate. The polyacid was separated as an ether complex and was then recrystallised from water.

Where $n \geqslant 4$, the method used was a modified form of that described in a patent,(16) and involved boiling the components in acidified aqueous solution. The product was again separated as an etherate and recrystallised from water. Details of the methods are given in Experimental 2.7.

The analysis results[1] for the compounds prepared are given in Table 2.1. The water of crystallisation was calculated by determining

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[1] These were carried out by E. Longbottom of B.P. Chemicals Ltd.

Table 2.1

		% WEIGHTS			RATIO
COMPOUND (a)	Found Calculated	P	Mo	V	P : Mo : V
$H_4PMo_{11}VO_{40}34H_2O$	Found	1.27	45.1	3.40	1 : 11.5 : 1.6
	Calculated	1.29	44.1	2.13	1 : 11 : 1
$H_5PMo_{10}V_2O_{40}35H_2O$	Found	1.32	40.4	6.96	1 : 9.9 : 3.3
	Calculated	1.31	40.5	4.31	1 : 10 : 2
$H_6PMo_9V_3O_{40}43H_2O$	Found	1.26	35.2	8.5	1 : 9 : 4.1
	Calculated	1.26	35.1	6.2	1 : 9 : 3
$H_7PMo_8V_4O_{40}26H_2O$	Found	1.46	32.6	9.95	1 : 7.2 : 4.1
	Calculated	1.46	36.3	9.63	1 : 8 : 4
$H_8PMo_7V_5O_{40}9H_2O$	Found	1.75	42.6	14.2	1 : 7.9 : 4.9
	Calculated	1.75	38.0	14.4	1 : 7 : 5
$H_9PMo_6V_6O_{40}11H_2O$	Found	1.76	39.6	15.8	1 : 7.3 : 5.5
	Calculated	1.76	32.7	17.4	1 : 6 : 6
$H_{10}PMo_5V_7O_{40}16H_2O$	Found	1.74	28.8	18.9	1 : 5.3 : 6.3
	Calculated	1.72	26.5	19.8	1 : 5 : 7
$H_{11}PMo_4V_8O_{40}14H_2O$	Found	1.79	23.0	21.5	1 : 4.1 : 7.3
	Calculated	1.80	22.3	23.6	1 : 4 : 8

(a) Water of crystallisation calculated by difference (see text)

Table to show the results of analysis of crystalline samples of $H_{3+n}PMo_{12-n}V_nO_{40}$ prepared by the methods described the difference between the calculated anhydrous molecular weights and the molecular weights indicated by the best fit to the analysis results.

In general the analyses indicate that the purity of these compounds leaves something to be desired. Even when standard literature preparations were used for n=1, 2 or 3, the vanadium content was always high,indicating contamination by either higher vanadium content heteropolyacids or free vanadate. As the value of n increased the vanadium content became lower than expected, indicating some contamination by lower vanadium content heteropolyacids.

Numerous variations on the method of preparation were tried but no better results were obtained.

2.3 NMR Spectroscopy in Aqueous Solution

2.3.1 ^{31}P NMR Spectroscopy

^{31}P n.m.r. spectroscopy yielded the results shown in Table 2.2. As can be seen,a general pattern of chemical shifts is present. This pattern and the overall trend of the results is clearly shown in Figures 2a and 2b. $H_4PMo_{11}VO_{40}$ shows a single peak at -4.17 ppm, indicating that, despite its high vanadium analysis, it is essentially a single material. This peak occurs in all the spectra except the n=5 case and becomes progressively smaller as n increases. The three peaks at -3.95, -3.85 and -3.65 ppm are always in about the same intensity ratio of 3:4:2 and occur in all spectra where $n \geqslant 2$. Peaks at lower field, although less well defined, have the same overall pattern in all cases and increase in relative intensity as n increases.

To further clarify peak assignments an experiment was carried out in which the ^{31}P n.m.r. spectra of the various heteropolyacids were recorded together with additional $H_4PMo_{11}VO_{40}$. The results in Table 2.3

Table 2.2

Compound(a)	Chemical Shift (ppm)(b)
$H_4PMo_{11}VO_{40}$	-4.17
$H_5PMo_{10}V_2O_{40}$	-4.21 -3.96, -3.87, -3.69 -3.29, -3.08, -2.63
$H_6PMo_9V_3O_{40}$	-4.15 -3.93, -3.85, -3.69 -3.44, -3.39, -3.24
$H_7PMo_8V_4O_{40}$	-4.15 -3.90, -3.81, -3.60 -3.23, -3.02, -2.47, -2.35
$H_8PMo_7V_5O_{40}$	-3.92, -3.83, -3.65 -3.24, -3.03, -2.51, -2.38

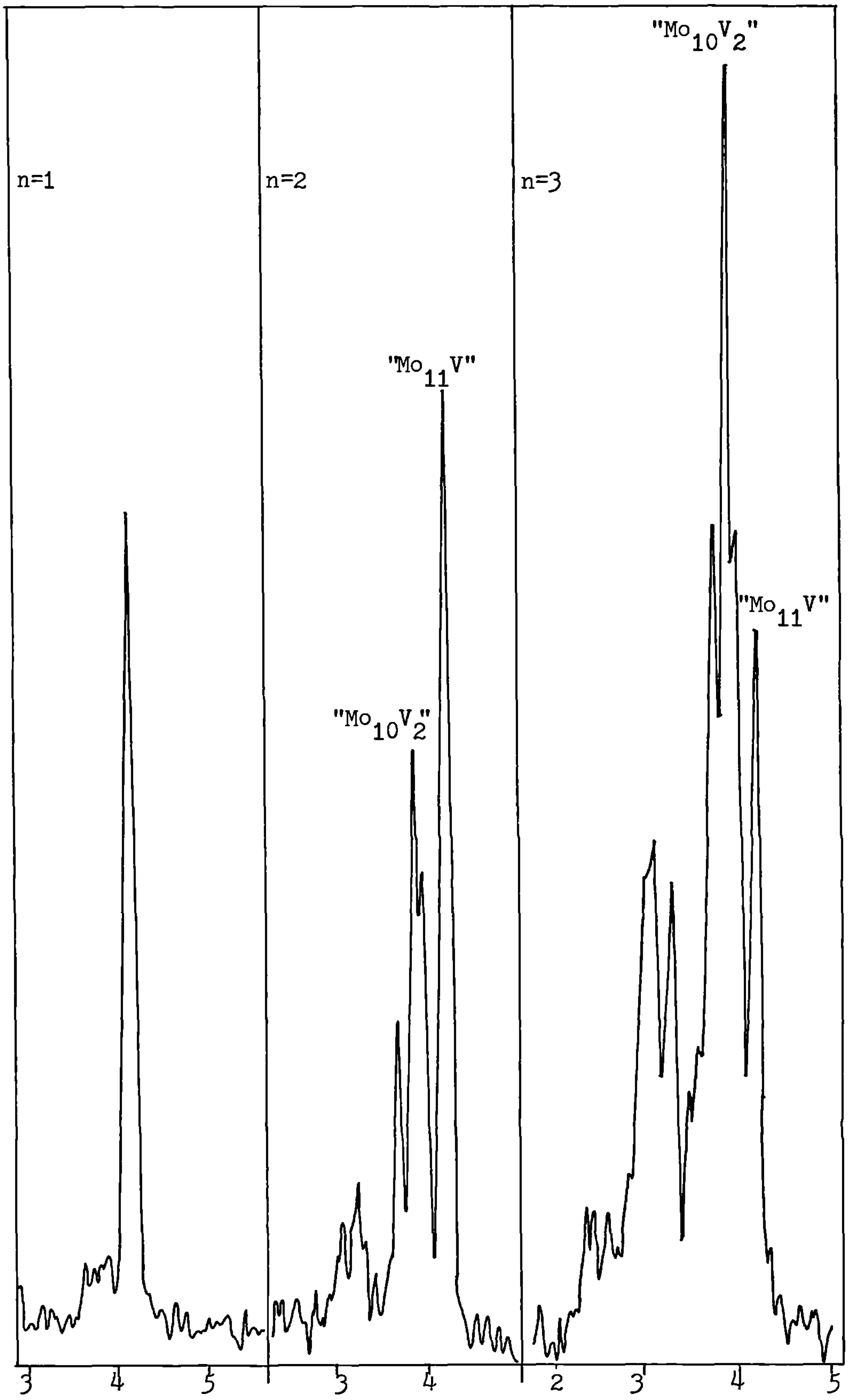
(a) Dissolved in D_2O

(b) Shifts quoted with respect to external 85% H_3PO_4

^{31}P NMR of $H_{3+n}PMo_{12-n}V_nO_{40}$ n=1-5

Figure 2a

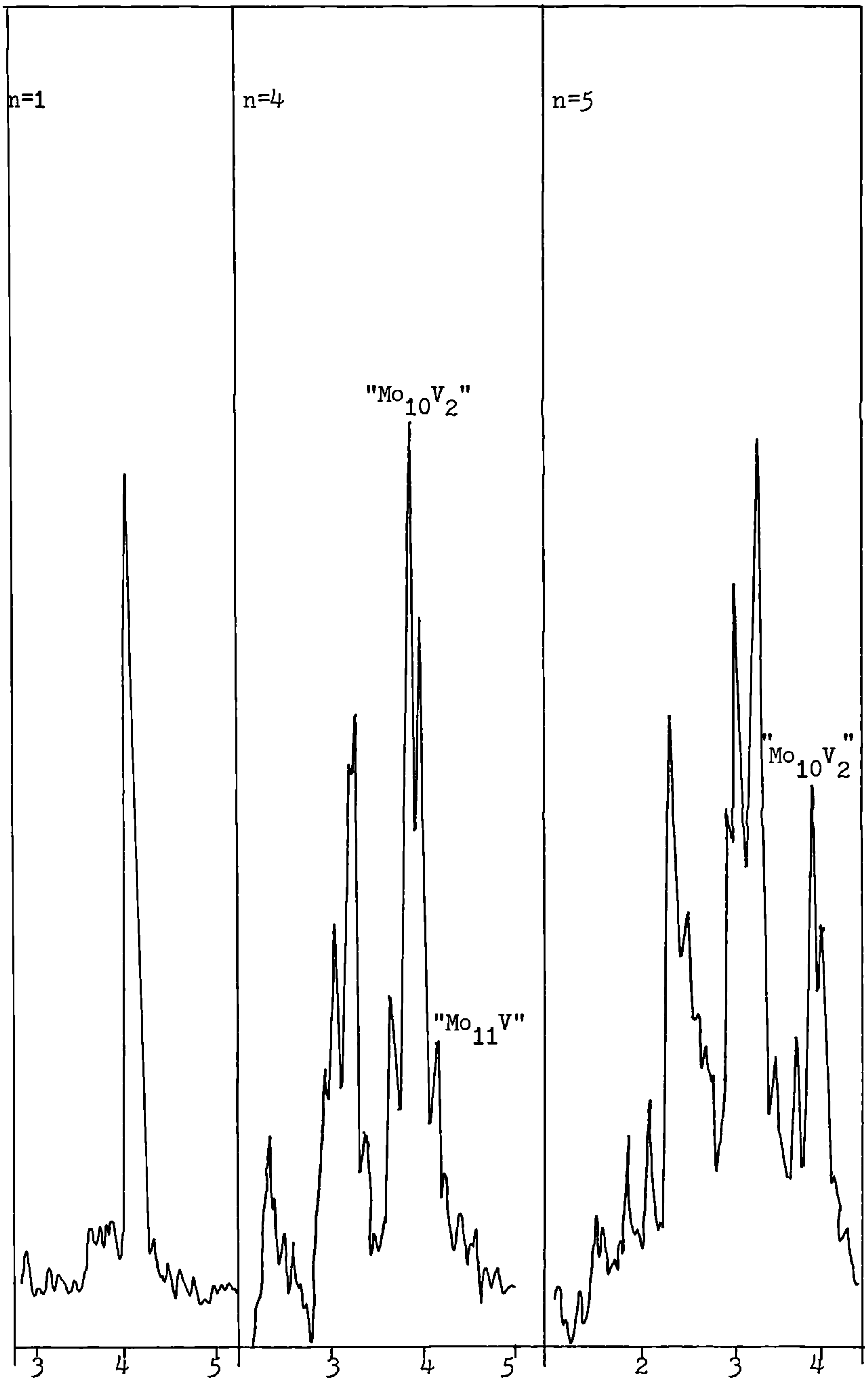
^{31}P NMR Spectra of Heteropolyacids of the $H_{3+n}PMo_{12-n}V_nO_{40}$ series



Chemical Shifts (ppm) with respect to 85% H_3PO_4

Figure 2b

^{31}P NMR Spectra of Heteropolyacids of the $H_{3+n}PMo_{12-n}V_nO_{40}$ Series



Chemical Shifts (ppm) with respect to 85% H_3PO_4

Table 2.3

Sample[(a)]	Chemical Shifts ppm[(b)] (relative intensities)			
$H_5PMo_{10}V_2O_{40}$	-6.61(1),	-6.41 -6.32 -6.15	(2.5)[(c)]	
$H_5PMo_{10}V_2O_{40}$ + $H_4PMo_{11}VO_{40}$	-6.62(1),	-6.38 -6.29 -6.12	(1.1)	
$H_6PMo_9V_3O_{40}$	-6.66(1)	-6.45 -6.36 -6.20	(5.4)	-5.74, -5.56, -5.46
$H_6PMo_9V_3O_{40}$ + $H_4PMo_{11}VO_{40}$	-6.59(1),	-6.38 -6.30 6.12	(2)	-5.72, -5.67, -5.50
$H_7PMo_8V_4O_{40}$	-6.67(1),	-6.44 -6.36 -6.18	(6)	-5.93, -5.76, -5.73 -5.56, -4.91
$H_7PMo_8V_4O_{40}$ + $H_4PMo_{11}VO_{40}$	-6.61(1),	-6.38 -6.30 -6.12	(2)	-5.87, -5.72, -5.68 -5.50, -5.38, -4.85

(a) Dissolved in water

(b) Referenced with respect to external $(MeO)_3PO$ dissolved in $CDCl_3$ (50 mg/cm^3) $CDCl_3$ used for ^2D lock. (NB. Shift of $(MeO)_3PO$ with respect to H_3PO_4 = 2.55 ppm.)

(c) Relative peak intensities in brackets

^{31}P NMR Spectroscopy to Confirm Peak Assingments

show no additional peaks and the relative intensity of the peak at -6.62 ppm increases in all examples. Hence it is clear that the peak at -6.62 ppm with respect to $(MeO)_3PO$ (-4.2 ppm with respect to 85% H_3PO_4) is due to the $H_4PMo_{11}VO_{40}$ species in solution. It also seems reasonable to assign the next group of three signals to the $H_5PMo_{10}V_2O_{40}$ species. (see Discussion)

The same general conclusion can be drawn from these spectra as from the analysis. Only where n=1 is the material a pure compound; all the others are mixtures, the intended compounds being contaminated by both higher and lower vanadium content heteropolyacids.

2.3.2 ^{51}V NMR Spectroscopy

The ^{51}V n.m.r. spectra are shown in Table 2.4 and in Figures 2c, 2d and 2e. The same general trend is apparent as was seen in the ^{31}P n.m.r. spectra. A peak at -536.2 ppm occurs in all samples and can be assigned to $H_4PMo_{11}VO_{40}$. Four further peaks between -541 and -545 ppm recur through all the spectra. All other peaks are broad and are superimposed on a very broad signal. This very broad signal was shown to be due to VO_2^+ by adding V_2O_5 dissolved in $2MH_2SO_4$ (i.e.VO_2^+ solution) to samples of the phosphomolybdovanadic acids. This caused the relative intensity of this broad signal to increase. It was found that as the vanadium content of the polyacids increased, the amount of free VO_2^+ also increased.

The peaks narrowed and sharpened as the temperature at which the spectra were run was increased, due to a reduction in the relaxation time brought about by the increased rate of molecular tumbling and the decrease in viscosity of water at higher temperature. This narrowing is more pronounced for quadrupolar nuclei such as ^{51}V since they give

Table 2.4

Sample(a)	Chemical Shifts (ppm)(b)
$H_4PMo_{11}VO_{40}$	-536.2
$H_5PMo_{10}V_2O_{40}$	-536.2 -541.6, -542.4, -543.1, -543.6 -551.7 (vb)
$H_6PMo_9V_3O_{40}$	-536.2 -541.3, -542.4, -542.9, -545.4 -546.4(b), -548.5(b), -551.6(vb)
$H_7PMo_8V_4O_{40}$	-536.2 -540.9, -542.3, -542.8, -545.2 -546.3(b), -548.5(b), -551.4(vb)
$H_8PMo_7V_5O_{40}$	-536.2 -539.1 -541.6, -542.0, -542.3 -548.2(b), -549.9(b), -551.6(b), -553.7(vb), 556.7(vb)

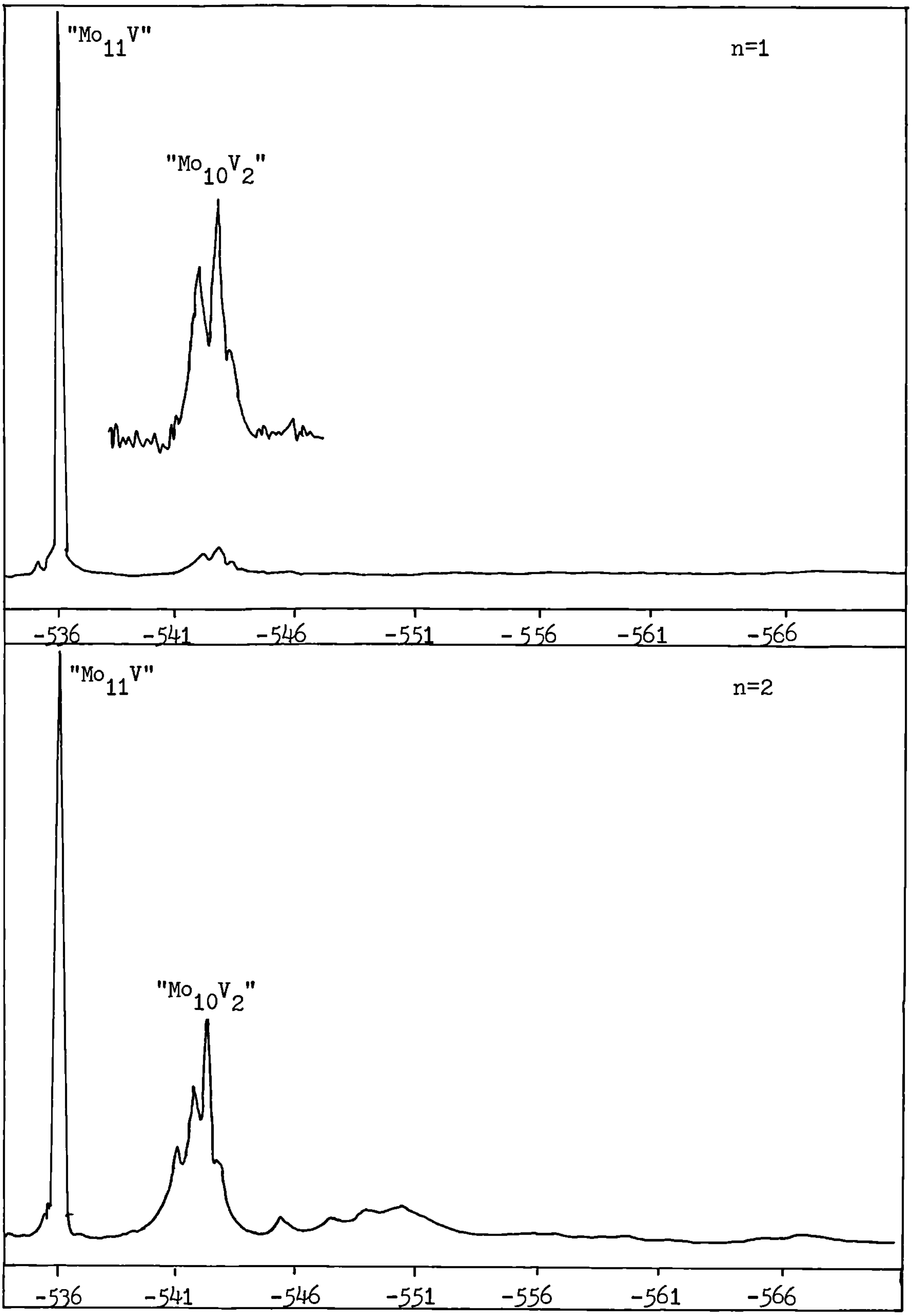
(a) Dissolved in water/20% D_2O

(b) Shifts with respect to $VOCl_3$ external (calculated from fixed frequency point)

^{51}V NMR of $H_{3+n}PMo_{12-n}V_nO_{40}$ $1 \geqslant n \geqslant 5$

Figure 2c

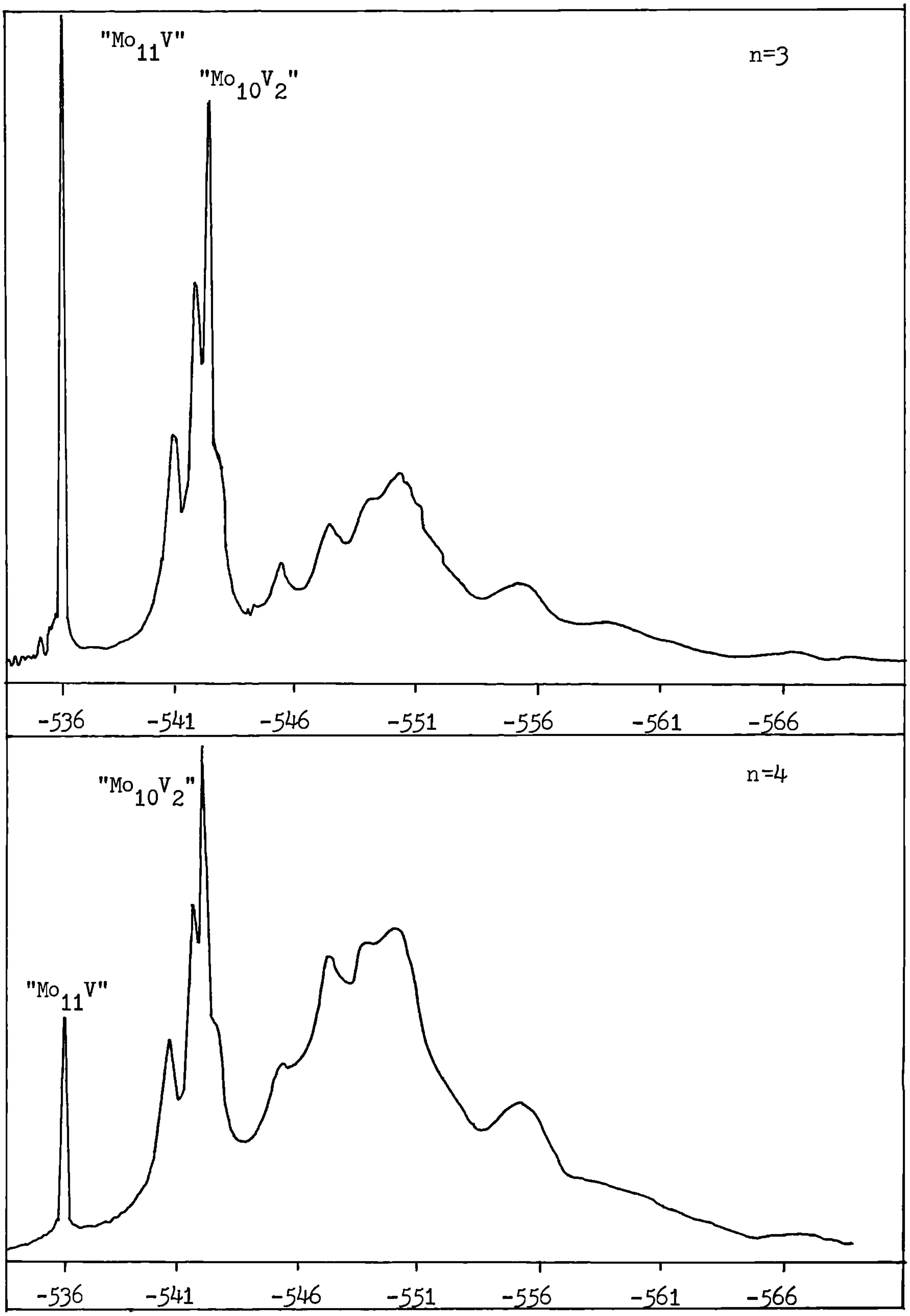
^{51}V NMR Spectra of Heteropolyacids of the $H_{3+n}PMo_{12-n}V_nO_{40}$ Series



Chemical Shifts (ppm) with respect to $VOCl_3$

Figure 2d

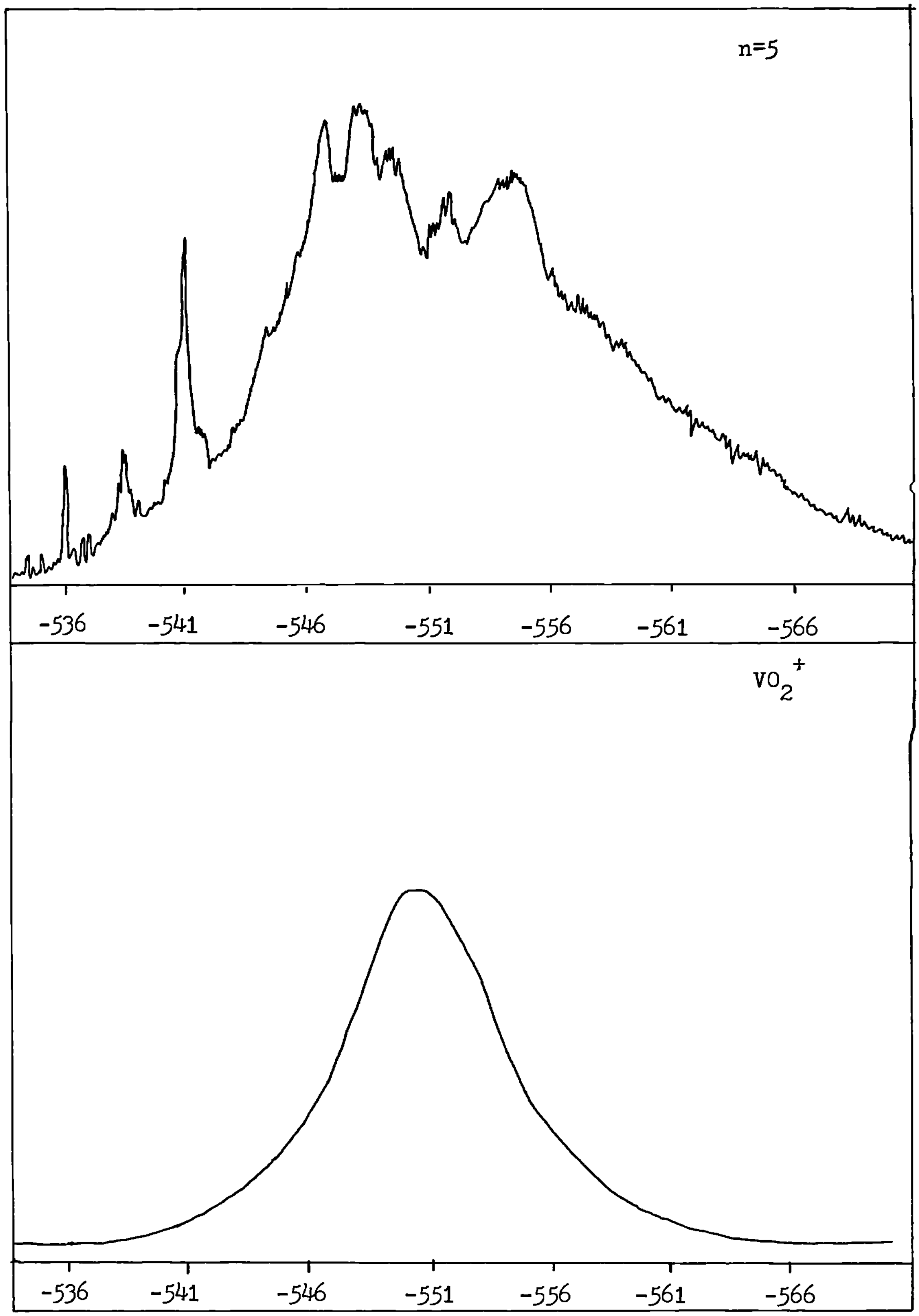
^{51}V NMR Spectra of Heteropolyacids in the $H_{3+n}PMo_{12-n}V_nO_{40}$ Series



Chemical Shifts (ppm) with respect to $VOCl_3$

Figure 2e

^{51}V NMR Spectra of Heteropolyacids of the $H_{3+n}PMo_{12-n}V_nO_{40}$ Series



Chemical Shifts (ppm) with respect to $VOCl_3$

relatively broad signals at room temperature.

The results for $H_5PMo_{10}V_2O_{40}$ and $H_7PMo_8V_4O_{40}$ are shown in Table 2.5 and Figures 2f and 2g respectively. The general pattern of the spectra seem , at first sight, to be changed. The peak due to the $H_4PMo_{11}VO_{40}$ species is clear, occurring at -531.3 and -532.7 ppm respectively. A separate broad signal now arises among the sharp ones. This is assigned to VO_2^+ by comparison with VO_2^+ spectra run at these temperatures. One of the original set of four peaks has been shifted considerably more than the other three; on this basis it is proposed that this signal is due to a different species, probably an isovanadate since no similar effect is seen in the ^{31}P n.m.r. spectra. The remaining three peaks are clearly in the intensity ratio 3:4:2 and are assigned to the $H_5PMo_{10}V_2O_{40}$ species. In the $H_7PMo_8V_4O_{40}$ spectrum the peaks, previously ill-defined, lying on top of the broad VO_2^+ signal, are now sharper. They are probably due to higher $H_{3+n}PMo_{(12-n)}V_nO_{40}$ species with $n \geqslant 3$.

2.3.3 Discussion

2.3.3.1 Mixtures

It was not found possible to produce totally pure samples of the individual heteropolyacids described here; the best results were for $H_4PMo_{11}VO_{40}$ and $H_5PMo_{10}V_2O_{40}$ which, from n.m.r. spectroscopy results, were approximately 80% and 70% pure respectively. Even when the analysis gives good results the n.m.r. spectra clearly show that when $n>1$ the samples are mixtures. Peak assignments were only possible for $n=1$ and 2 and it was not possible to draw many conclusions about those acids with higher vanadium content, except that they were mixtures and also heavily contaminated with VO_2^+. The n.m.r.

Table 2.5

Sample(a)	Temperature	Chemical Shifts(b) (ppm)	Assignment
$H_5PMo_{10}V_2O_{40}$	333K	-531.3	$H_4PMo_{11}VO_{40}$
		-535.0(b)	VO_2^+
		-536.8	?
		-539.8, -540.5, 540.8(c) (3) (4) (2)	$H_5PMo_{10}V_2O_{40}$
$H_7PMo_8V_4O_{40}$	353K	-532.7	$H_4PMo_{11}VO_{40}$
		-537.3	?
		-538.8(b)	VO_2^+
		-540.3, -540.8, -541.1 (3) (4) (2)(c)	$H_5PMo_{10}V_2O_{40}$
		-543.6, -544.3, -545.7 -547.3, -548.5, -548.8 -550.5, -551.3, -553.4	?

(a) Dissolved in water with 20% D_2O

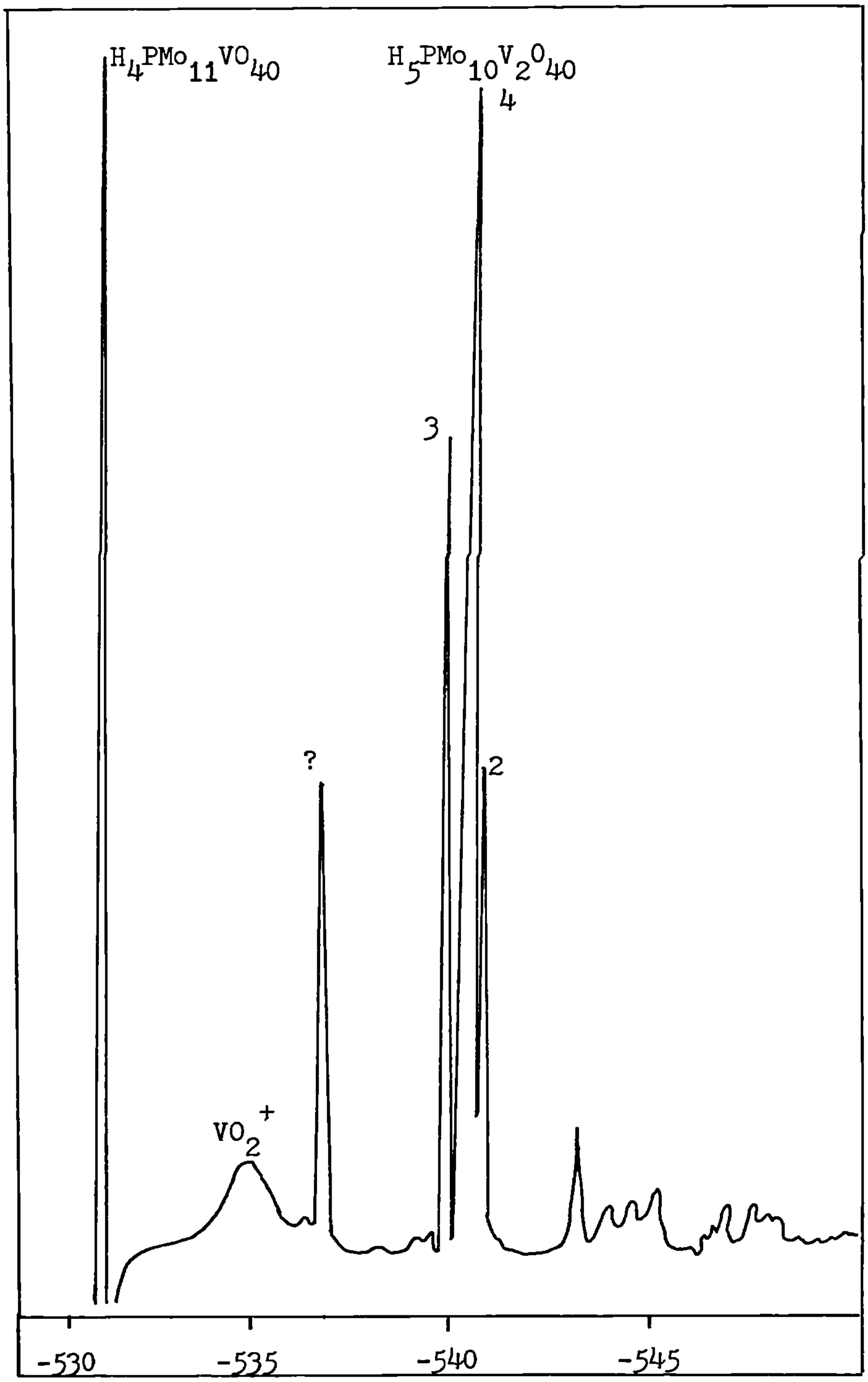
(b) Shifts with respect to $VOCl_3$

(c) Relative peak intensities

^{51}V NMR Spectra at High Temperature

Figure 2f

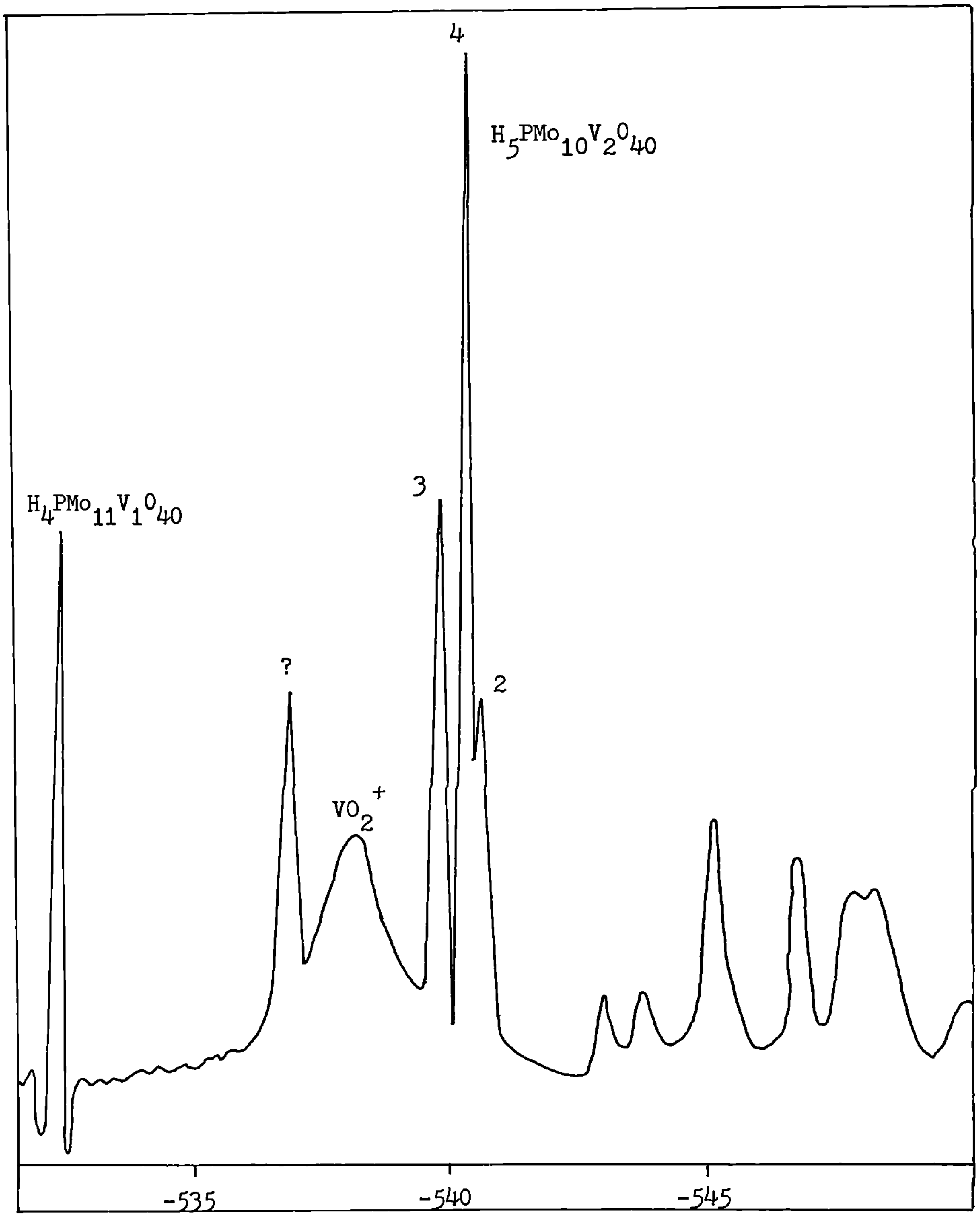
Bruker WH 400 ^{51}V NMR Spectrum of $H_5PMo_{10}V_2O_{40}$ at 333K



Chemical Shift (ppm) with respect to $VOCl_3$

Figure 2g

Bruker WH 400 ^{51}V NMR Spectrum of $H_7PMo_8V_4O_{40}$ at 353K



Chemical Shift (ppm) with respect to $VOCl_3$

spectroscopy results are in general agreement with those found by Matveev et al(50) with some variation in chemical shift due to pH and temperature differences. However, the use of more sensitive instrumentation has yielded more detailed and extensive results which in turn have made peak assignments easier and allowed more detailed analysis.

An explanation for the difficulty in preparing pure samples has recently been offered by Matveev(51) on the basis of his own work(60) with reduced heteropolyacids and earlier studies by French workers.(61,62) It is suggested that the following equilibria take place in acidic aqueous media.

$$H_5PMo_{10}V_2O_{40} + MoO_4^{2-} + 3H^+ \rightleftharpoons H_4PMo_{11}VO_{40} + VO_2^+ + 2H_2O$$

$$2H_4PMo_{11}VO_{40} \rightleftharpoons H_5PMo_{10}V_2O_{40} + H_3PMo_{12}O_{40}$$

$$10H_6PMo_9V_3O_{40} \rightleftharpoons 9H_5PMo_{10}V_2O_{40} + 12VO_2^+ + H_3PO_4 + 12OH^-$$

$$H_{3+n}PMo_{12-n}V_nO_{40} + H_3\overset{+}{O} \rightleftharpoons VO_2^+ + H_{6+n}PMo_{12-n}V_{n-1}O_{39}$$

$$H_{3+n}PMo_{12-n}V_nO_{40} \rightleftharpoons mH^+ + [H_{3+n-m}PMo_{12-n}V_nO_{40}]^{m-}$$

Although this would explain the results reported here, no evidence for such equilbria, in the form of line broadening, was found in our n.m.r. spectra run at high temperature. However, ^{51}V n.m.r. spectra of mixtures of $H_3PMo_{12}O_{40}$ and VO_2^+ in $1MH_2SO_4$ clearly showed that after 4h the sole product was $H_4PMo_{11}VO_{40}$. It was also found that ^{51}V n.m.r. spectra of $H_4PMo_{11}VO_{40}$ with added VO_2^+ in $1MH_2SO_4$ showed an increase in the relative amount of $H_5PMo_{10}V_2O_{40}$ in the sample. Thus we do have evidence for

$$2H_2O + VO_2^+ + H_3PMo_{12}O_{40} \rightleftharpoons H_4PMo_{11}VO_{40} + MoO_4^{2-} + 3H^+$$

and

$$2H_2O + VO_2^+ + H_4PMo_{11}VO_{40} \rightleftharpoons H_5PMo_{10}V_2O_{40} + MoO_4^{2-} + 3H^+$$

In using these compounds as catalysts, the important points to note are that, unless very great precautions are taken, they are always present as complex mixtures and that they contain large amounts of free VO_2^+, the amount increasing with the proposed value of n. The results in fact make it probable that if these higher vanadium content mixed heteropolyacids ($n \geqslant 3$) exist at all in aqueous solution as discrete Keggin anions, they are only ever present in a very low concentration and cannot be isolated. In support of this, reliable reports of synthesis of only up to n=3 have been made.

The instability of the higher vanadium containing heteropolyanions can be rationalised in the following way; as more Mo(VI) are substituted for by V(V) the overall negative charge of the anion increases. Eventually the Keggin structure will be unable to support more. Clearly this effect will depend on pH. In addition to this, V^{5+} is slightly smaller than Mo^{6+} (0.59Å compared with 0.62Å (Pauling radius));(63) this will cause the Keggin structure to be more distorted when it contains more vanadium and therefore more unstable.

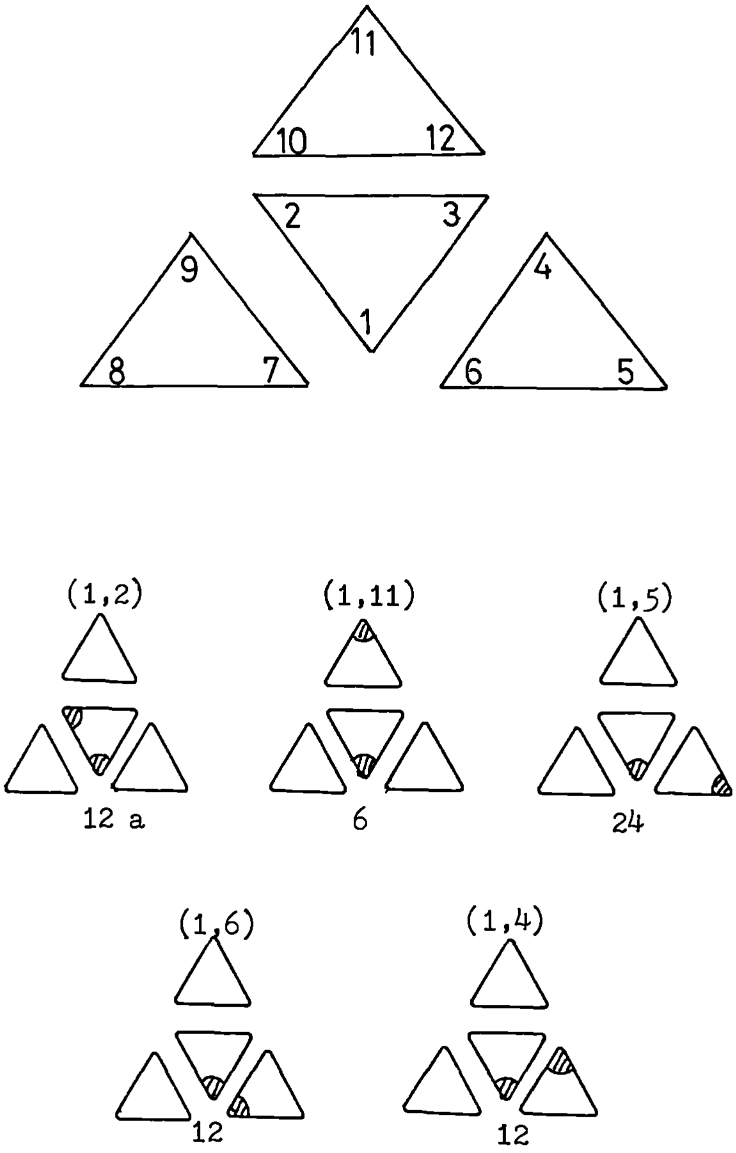
2.3.3.2 Isomers of $H_5PMo_{10}V_2O_{40}$

Where n>1, a variety of isomers is possible depending on the relative positions of the vanadium atoms in the Keggin structure.(48) Figure 2h shows the possibilities for the $H_5PMo_{10}V_2O_{40}$ case.

Both ^{31}P (Figure 2i) and ^{51}V (Figure 2f) n.m.r. spectra of $H_5PMo_{10}V_2O_{40}$ reported here show three signals due to this compound in the intensity ratio 3:4:2. Addition of equimolar amounts of the shift reagent $Eu(NO_3)_3$ to the samples produced a shift to higher field of all these signals in the ^{31}P n.m.r. spectrum. In the ^{51}V n.m.r. addition of $Eu(NO_3)_3$ caused movement of the peaks relative to each other, resulting in a single signal at -536.5 ppm. See Table 2.6.

Figure 2h

Diagram to Show Possible Isomers of $H_5PMo_{10}V_2O_{40}$



a, Statistical abundance

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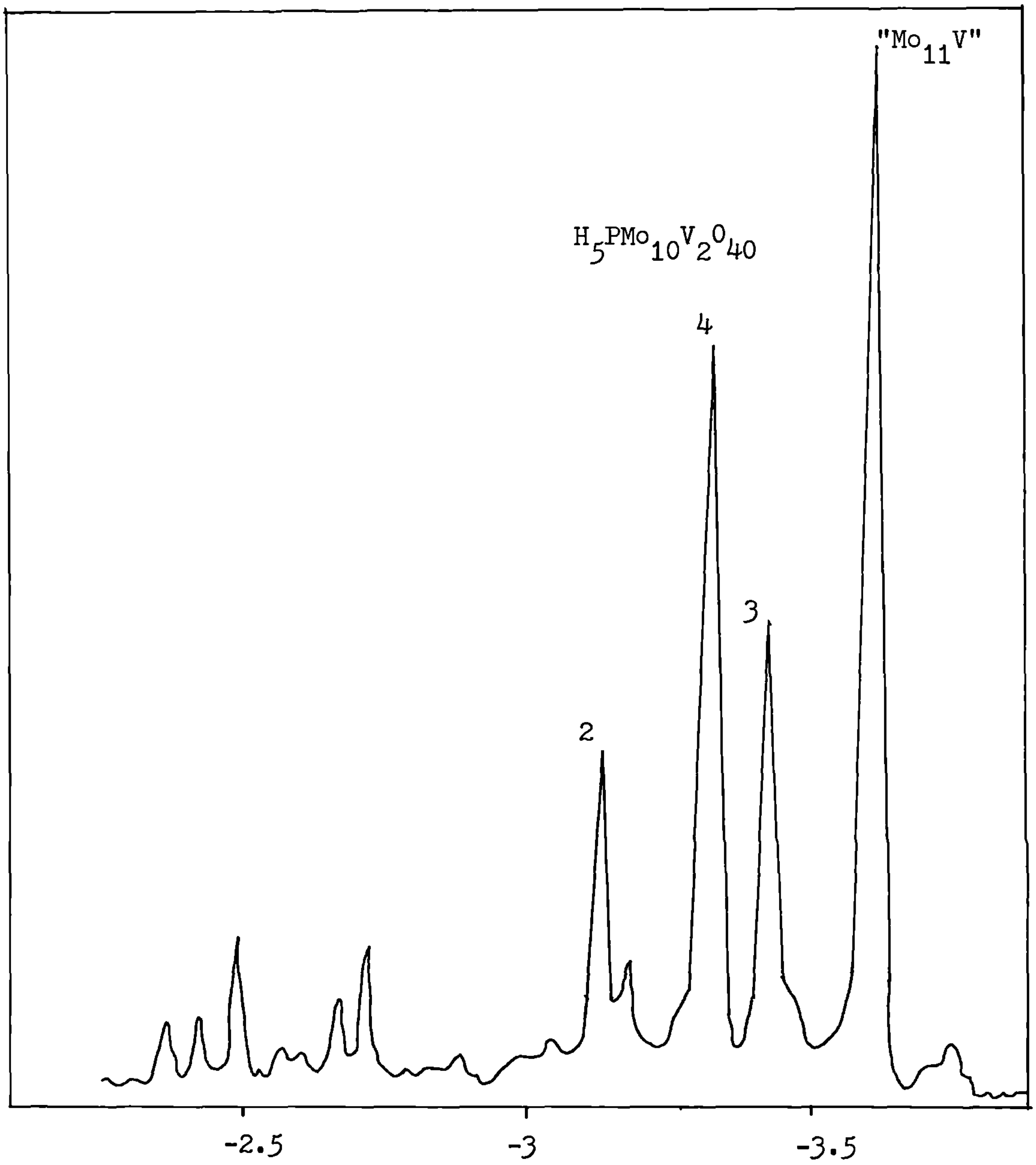
Figure 2i

Bruker WH 400 ^{31}P NMR Spectrum of $H_5PMo_{10}V_2O_{40}$



Chemical Shift (ppm) with respect to H_3PO_4

Table 2.6

$[Eu(NO_3)_3]$	^{51}V Chemical Shifts (ppm)$^{(a)}$
0	-537.2, -537.5, -537.7 (3) (4) (2) (b)
1×10^{-4}M	-536.7, -537.0 (3) (6)
2×10^{-4}M	-536.5

(a) Referenced with respect to $VOCl_2$

(b) Relative intensities

Table to Show the Effect of Shift Reagent on the ^{51}V NMR Spectrum of $H_5PMo_{10}V_2O_{40}$

It is difficult to explain the observed ratios in terms of the statistical abundances. However, the following might be considered reasonable. The isomer where both vanadium ions lie in the same group of three edge sharing octahedra can be considered more unlikely due to steric and electrostatic effects and we therefore propose that this isomer does not occur to significant degrees. We then propose that the (1, 4) and (1, 11) isomers have the same chemical shift in both ^{31}P and ^{51}V n.m.r. spectra and correspond to the peak with intensity 3. This leaves the (1, 6) and (1, 5) isomers corresponding to signals of intensity 2 and 4 respectively. The fact that the peak with intensity 2 is the most affected by the shift reagent is consistent with this being the (1, 6) isomer since the adjacent vanadiums are likely to generate excess negative charge in a specific area which will lead to Eu^{3+} being bound more closely to these vanadiums. [1]

This proposal differs from that given by Pope,(48) who reported only two peaks at 3.09 ppm and 3.79 ppm in the ^{31}P n.m.r. spectrum (with respect to H_3PO_4) with intensities 3 and 8 respectively. He then assigned the peaks to the five isomers with relative abundances (6+12):(24+12+12). However, it is likely that the 3.09 ppm signal is, in fact, due to higher vanadium content impurities and that poor resolution led to the observation of only a single resonance for the $H_5PMo_{10}V_2O_{40}$ species.

---

[1] This argument is predicted on the assumption that the Keggin structure is retained from the PMo_{12} to at least the lower members of the P-Mo-V series. This seems likely for $H_4PMo_{11}VO_{40}$ which has been reasonably well-defined analytically by others and which our n.m.r. data shows to be largely a single compound, but this may not be so for the higher members.

2.4 Results of NMR Spectroscopy in Organic Solvents

2.4.1 ^{31}P NMR Spectroscopy

^{31}P n.m.r. spectra of the two compounds which have the best understood spectra in water, that is $H_4PMo_{11}VO_{40}$ and $H_5PMo_{10}V_2O_{40}$, were recorded in acetic acid, T.H.F. and acetonitrile. The results are given in Table 2.7. To give a clearer picture, the spectra of $H_5PMo_{10}V_2O_{40}$ in these three solvents and in water are shown in Figure 2j. As can be seen, the same groups of peaks occur in all the solvents with some small variations in chemical shifts. For example, the resolution of peaks due to the isomers of $H_5PMo_{10}V_2O_{40}$ is lower than in aqueous solution.

2.4.2 ^{51}V NMR Spectroscopy

The results of the ^{51}V n.m.r. spectroscopy in different solvents are shown in Table 2.8. In all cases the signals are very broad. (see Discussion).

2.4.3 Discussion

The ^{31}P n.m.r. spectra show the same general patterns for various solvents as were found in aqueous solution, except that the different isomers of $H_5PMo_{10}V_2O_{40}$ can no longer be seen in T.H.F. and acetic acid. Also other small, previously unresolved, peaks have appeared and chemical shifts are found to vary between solvents. On the whole there are no major changes in the spectra and these results suggest that the aqueous solution structure of the polyacids is retained in these organic solvents.

In contrast to the ^{31}P n.m.r. spectra, the ^{51}V n.m.r. spectra are markedly different to those in water when recorded in the organic

Table 2.7

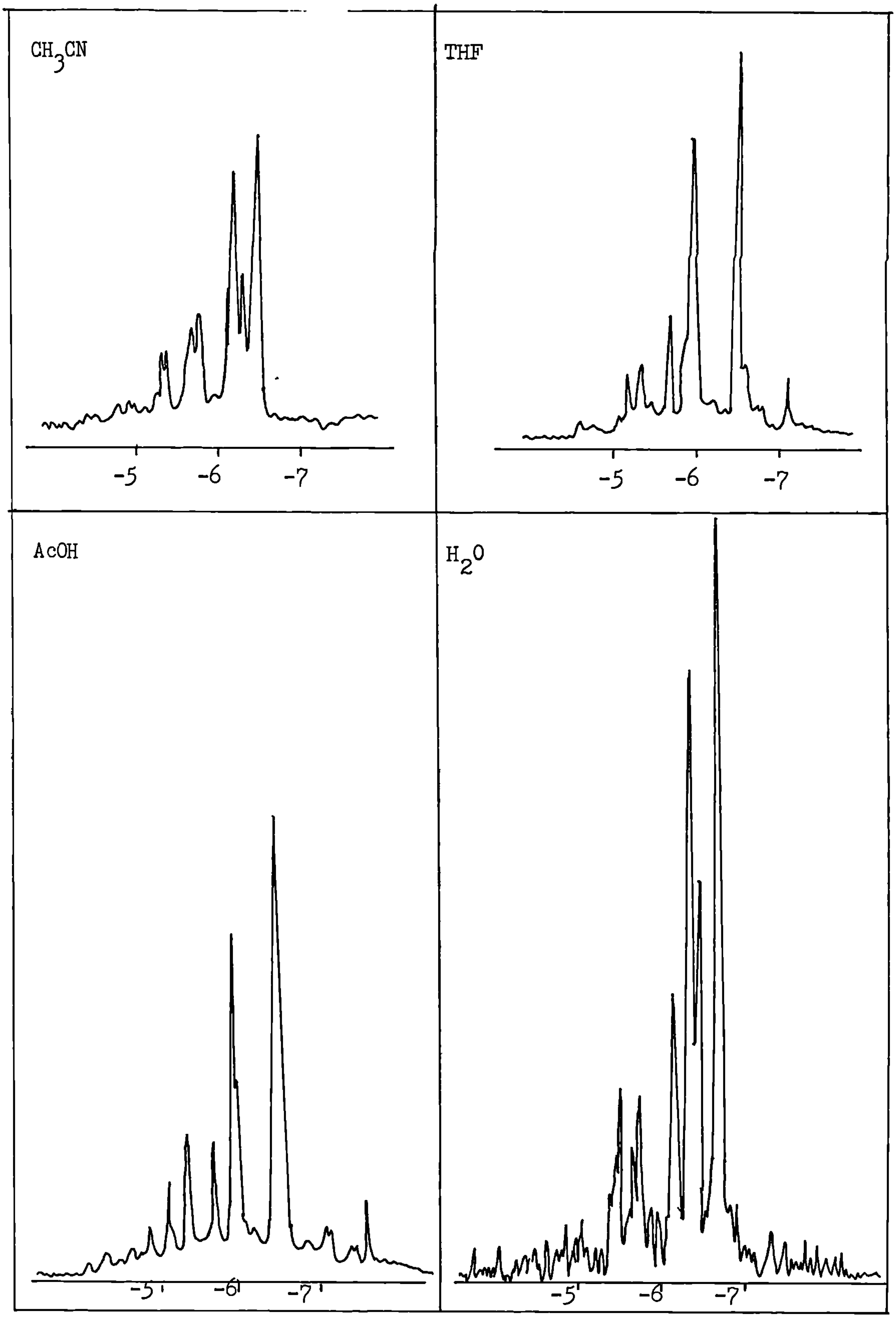
Compound	Solvent	Chemical Shifts (ppm)$^{(a)}$
$H_4PMo_{11}VO_{40}$	AcOH	-6.43 (+ some small peaks at base)
	THF	-6.32 (main peak) -7.33, -6.83, -5.83, -5.58, -5.30
	CH_3CN	-6.50 (main peak) -7.60, -6.31, -6.21, -5.80, -5.35
$H_4PMo_{10}V_2O_{40}$	AcOH	-6.40 -5.95, -5.91 } main peaks -5.66, -5.34, -5.12, -7.43
	THF	-6.36 -5.85 } main peaks -6.24, -5.63, -5.21, -5.14 -7.30, -6.81
	CH_3CN	-6.50 -6.42, -6.34, -6.23 } main peaks -5.83, -5.69, -5.67, -5.51 -5.40, -5.35, -5.27

(a) Shifts with respect to $(MeO)_3PO$ in $CDCl_3$ (50 mgs/cm^3) $CDCl_3$ lock

^{31}P NMR in Organic Solvents

Figure 2j

^{31}P NMR Spectra of $H_5PMo_{10}V_2O_{40}$ in Organic Solvents



Chemical Shifts (ppm) with respect to $(MeO)_3PO$ in $CDCl_3$

Table 2.8

Compound	Solvent	Chemical Shift (ppm)$^{(a)}$ (width at ½ height)
$H_4PMo_{11}VO_{40}$	THF	-549.7 (288 Hz) main peak
		-588.1 (300 Hz)
		-556.5 (1440 Hz)
	CH_3CN	-551.2 (134 Hz) main peak
		-550.0 (140 Hz)
		-562.5 (210 Hz)
	$(CH_3)_2CO$	-549.3 (192 Hz) main peak
		-553.0 (very small)
		-554.8 (200 Hz)
		-562.2 (200 Hz)
$H_5PMo_{10}V_2O_{40}$	THF	-548.4 (250 Hz)
		-557.8 (290 Hz)
		-561.7 (800 Hz)
	CH_3CN	-550.7 (135 Hz)
		-552.7 (100 Hz)
		-555.2 (200 Hz)
		-563.6 (200 Hz)
		-569.3 (330 Hz)

(a) With respect to $VOCl_3$

^{51}V NMR in Organic Solvents

solvents. All the signals are now very broad. However, it is still possible to recognise patterns, for example, a peak at approximately -550 ppm recurs in all spectra and can be assigned to $H_4PMo_{11}VO_{40}$.

The ^{51}V nucleus has a quadrupole moment of $0.3x10^{-28}cm^2$ (64) putting it in the medium quadrupole catagory where signal widths are very sensitive to the electric field gradient at the nucleus. Thus it is proposed that the electric field gradients at the ^{51}V nuclei are increased, thus giving the broad signals observed as a result of a decrease in symmetry at the nucleus, brought about by the co-ordination of the organic solvent at the polyanion, probably via hydrogen bonds. This argument is prefered to one involving an increase in relaxation times due to the increased size of the molecule, as the Keggin anions are already large molecules.

Thus the two types of n.m.r. spectroscopy complement each other; the ^{31}P n.m.r. spectra showing that the Keggin structure is retained while the ^{51}V spectra clearly show that organic solvents co-ordinate to this structure.

2.5 pH Dependence

2.5.1 Results of ^{31}P NMR Spectroscopy

Experiments were carried out in which heteropolyacids dissolved in water were titrated with sodium acetate, the n.m.r. spectra being recorded at various pH intervals. The results are shown in Tables 2.9 and 2.10 and a pictorial representation for the $H_5PMo_{10}V_2O_{40}$ case is given in Figure 2k.

2.5.2 Discussion

As has been mentioned previously, mixed heteropolyacids are known

Table 2.9

pH[(a)]	Chemical Shift (ppm)[(b)]
0.8	-6.57 -6.45, -6.40, -6.25 -5.80, -5.77, -5.62, -5.58
1	-6.60 -6.57, -6.54, -6.43 -5.94, -5.89, -5.75, -5.65
1-1.2	-6.57 -5.81, -5.96, -6.00
1.8	-6.62 -6.47, -6.09, -5.90
returned to[(c)] 0.7	-6.57 -6.47, -6.42, -6.28 -5.81, -5.60
0.1[(c)]	-6.53 -6.25, -6.16, -6.01 -2.58

(a) Dissolved in water

(b) With respect to $(MeO)_3PO$ in $CDCl_3$ (50 mgs/cm^3) $CDCl_3$ lock

(c) By addition of dilute H_2SO_4

pH Dependence of ^{31}P NMR Spectrum for $H_5PMo_{10}V_2O_{40}$

Figure 2k - ^{31}P NMR Spectra to Show pH Dependence of $H_5PMo_{10}V_2O_{40}$

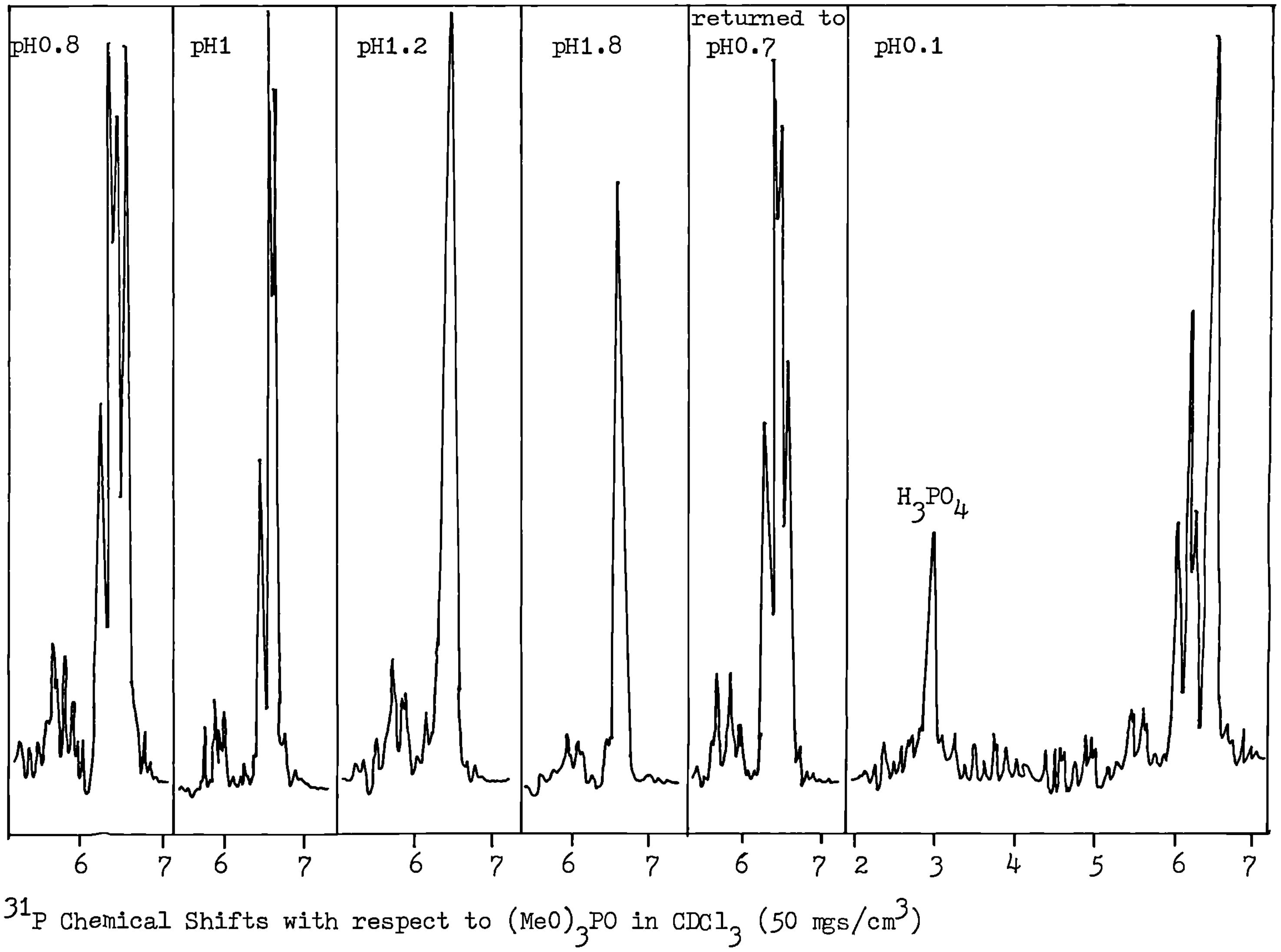


Table 2.10

pH[a]	Chemical Shifts (ppm)[b]
0.8	-6.51, -6.46, -6.33 -5.86, -5.80, -6.64 -4.98
1	-6.55, -6.45 -5.95, -5.89, -5.75 -5.05
1.6	-6.62 -6.10, -6.04, -5.91 -5.22
3	-6.67 -6.31, -6.19 -5.63
4	-6.67 -6.58, -6.52 -6.03
4.6	-6.69 -6.63, -6.58 -6.16
5	-6.63 -6.22

(a) Dissolved in water

(b) Shifts with respect to $(MeO)_3PO$ in $CDCl_3$/50 mgs/cm^3) $CDCl_3$ lock, only main peaks listed for clarity.

pH Dependence of ^{31}P NMR Spectrum for $H_7PMo_8V_4O_{40}$

to be unstable to degradation by base (see Chapter 1). The results shown here confirm this. First, for $H_5PMo_{10}V_2O_{40}$, as the pH is increased the signals move to higher field and slowly coalesce, by pH 1.2 the signals due to the $H_4PMo_{11}VO_{40}$ impurity (-6.60 ppm) and the different isomers of $H_5PMo_{10}V_2O_{40}$ have collapsed to give a single peak at -6.57 ppm. The higher vanadium containing species, however, seem to be more resistent and the signals at lower field assigned to these species are still clear at pH 1.8. Reacidification causes a return to the original pattern, while further acidification gives rise to some acid degradation, the peak at -2.58 ppm being due to H_3PO_4. It can also be seen that the $PMo_{11}V_1O_{40}{}^{4-}$ signal has a greater intensity than before, whilst the $PMo_{10}V_2O_{40}{}^{5-}$ signals are smaller. This indicates some degradation of $H_5PMo_{10}V_2O_{40}$ to $H_4PMo_{11}VO_{40}$. The results for $H_7PMo_8V_4O_{40}$ mirror those for $H_5PMo_{10}V_2O_{40}$ and here it is possible to see that the higher vanadium containing species are beginning to collapse at pH 3.

Although it is not possible to say definitely what the species is to which these systems are degraded at higher pH, it is likely that it is some form of heteropolyacid since the original spectrum is obtained on reacidification. It seems reasonable to suggest, by correlation of chemical shifts, that it is the $[PMo_{11}VO_{40}]^{4-}$ species.

Titration to pH 7.5 indicates the beginnings of complete degradation by the occurrence of a phosphoric acid signal.

2.5.3 Degradation in Acid of $H_5PMo_{10}V_2O_{40}$

Samples of $H_5PMo_{10}V_2O_{40}$ had their ^{51}V and ^{31}P n.m.r. spectra recorded in distilled water and $1M\,H_2SO_4$ (containing 20% D_2O) at 60°C. It was found that in $1M\,H_2SO_4$ the signals due to the $H_5PMo_{10}V_2O_{40}$ species had greatly reduced intensity whilst the signal for the $[PMo_{11}VO_{40}]^{4-}$ species was enhanced. This result shows that in acidic solution $[PMo_{10}V_2O_{40}]^{5-}$ decomposes to $[PMo_{11}VO_{40}]^{4-}$ as was previously proposed (see Chapter 1). A signal due to H_3PO_4 also came up in the ^{31}P n.m.r. spectrum of $H_5PMo_{10}V_2O_{40}$ in acid.

The peaks shifted to higher field in $1MH_2SO_4$ for both ^{51}V and ^{31}P n.m.r. spectra.

2.6 ^{17}O NMR Spectroscopy

^{17}O n.m.r. spectroscopy was carried out on $H_3PMo_{12}O_{40}$ on the Bruker WH400. It was possible to detect the different types of oxygen present at natural abundance. Two types of bridging oxygen atoms were detected at 555 ppm and 572 ppm. One set of bridging oxygens joins molybdenums from the same group of edge sharing octahedra. A third resonance occurs at 943 ppm and can be assigned to terminally bound Mo=0 (See Figure 21). This is in agreement with the data published by Klemperer.(65,66)

^{17}O n.m.r. spectra of $H_4PMo_{11}VO_{40}$ and $H_5PMo_{10}V_2O_{40}$ which had been enriched with ^{17}O from $H_2{}^{17}O$ were also recorded. (Figures 2m and 2n). The assignments of peaks are shown on the spectra and are in agreement with those given by Matveev et al.(50)

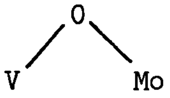
For $H_4PMo_{11}VO_{40}$, the peaks in the 900 ppm region are assigned to the terminal Mo=0; there are four peaks here, three of which are clearly resolved and one of which forms a shoulder on the largest of the group. The four signals are in the approximate intensity ratios of 2:3:4:2. This is in agreement with the expected statistical abundances of the different types of Mo=0 (1:2:2:2:2:2) if we have the Keggin structure. The peaks in the 600 ppm region due to 

Figure 21 - ^{17}O NMR Spectrum of $H_3PMo_{12}O_{40}$

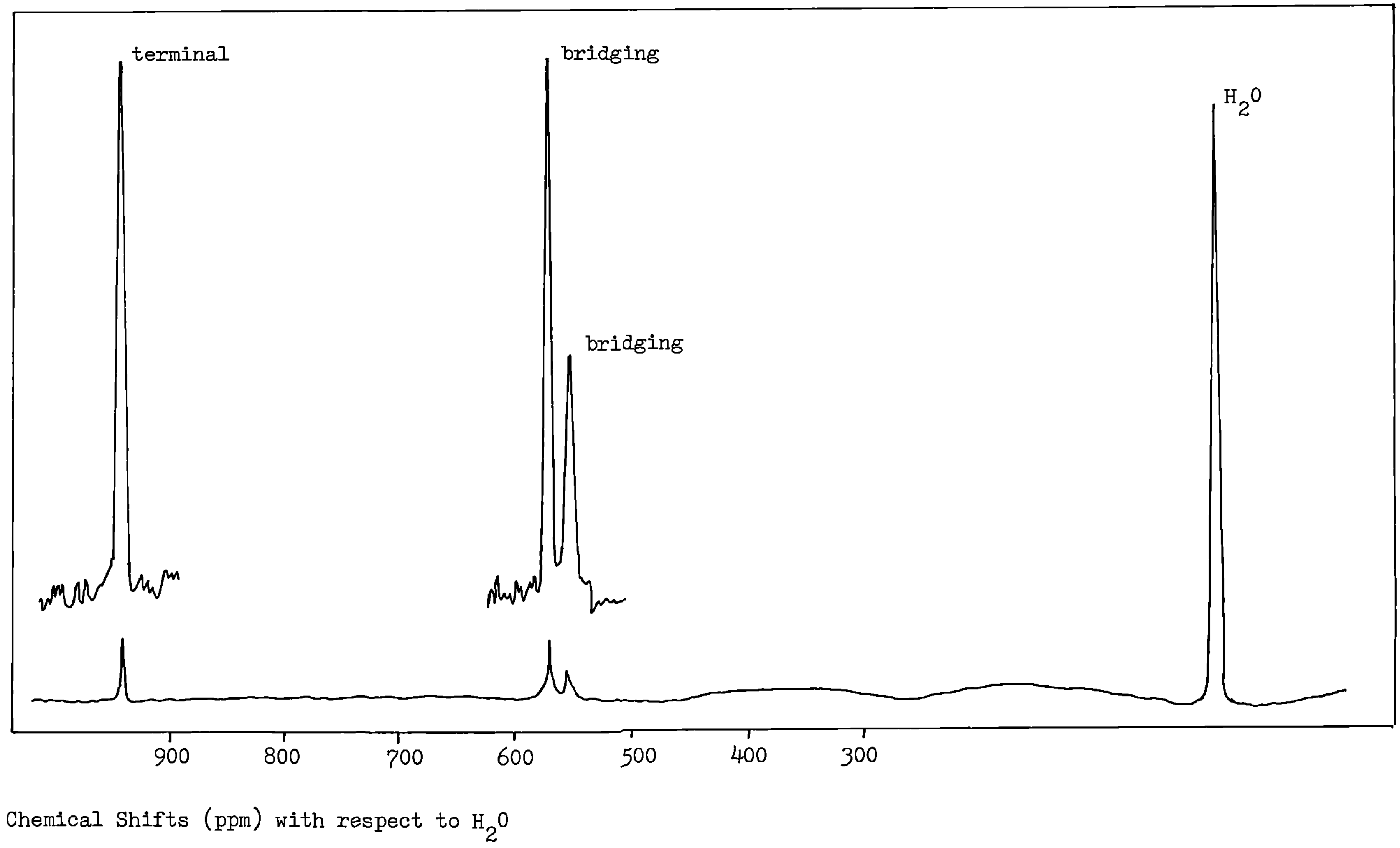
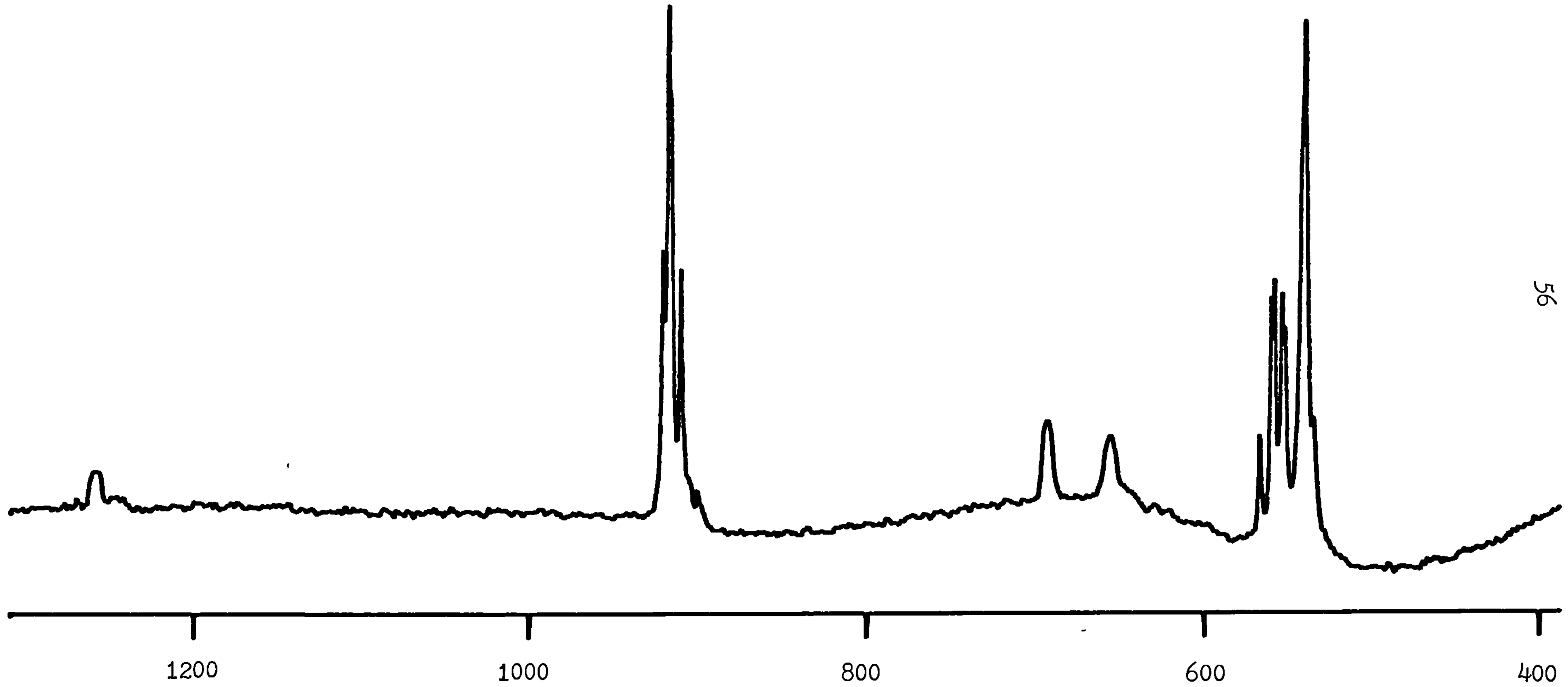
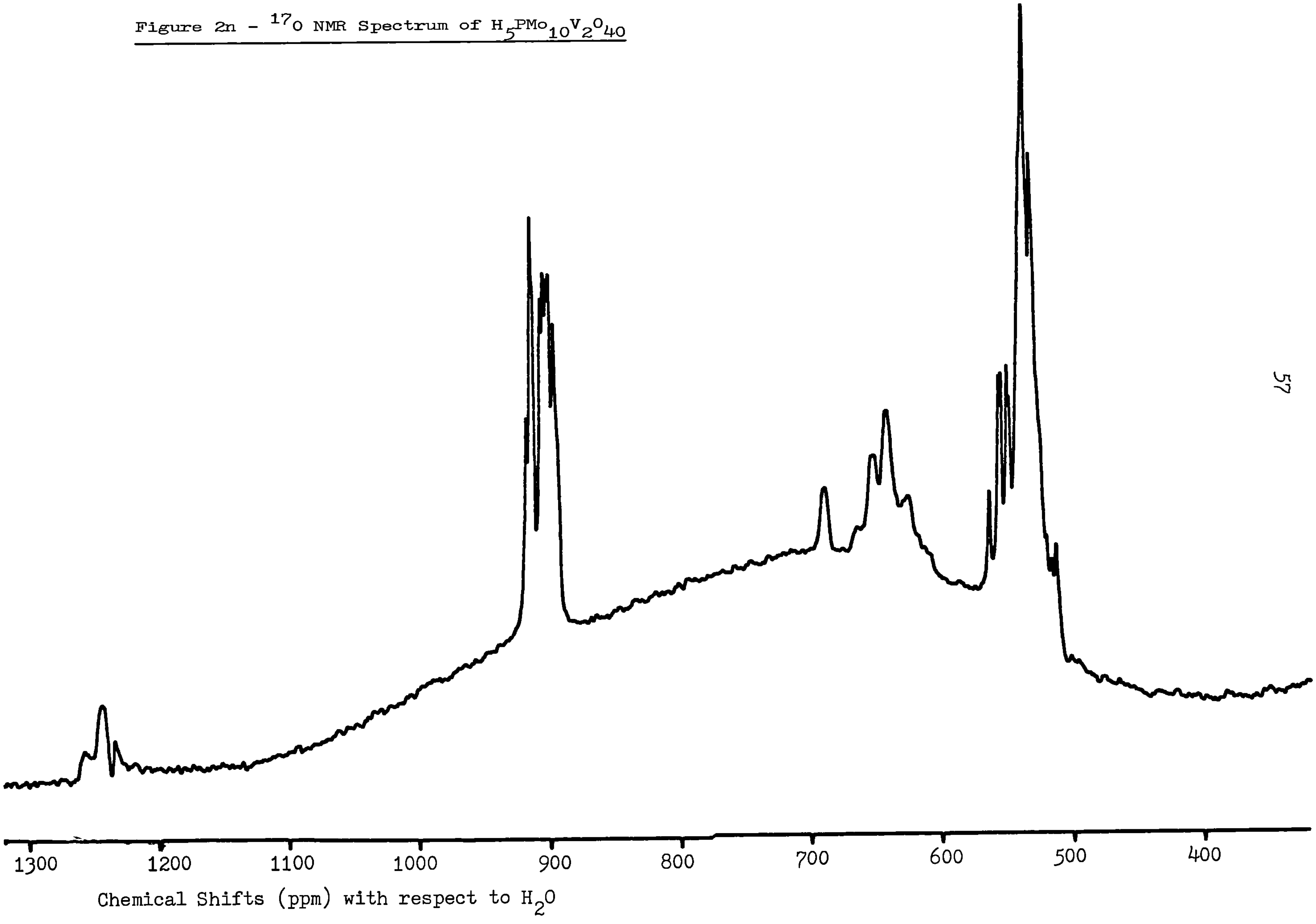


Figure 2m - ^{17}O NMR Spectrum of $H_4PMo_{11}VO_{40}$



Chemical Shifts with respect to H_2O

Figure 2n - ^{17}O NMR Spectrum of $H_5PMo_{10}V_2O_{40}$



oxygen are also in the expected intensity ratio for the Keggin anion of 2:2. Thus it is reasonable to say that $H_4PMo_{11}VO_{40}$ retains the Keggin structure in aqueous solution.

(It should be noted that integrated intensities are not usually a reliable measure of the number of symmetry equivalent nuclei in ^{17}O n.m.r. spectroscopy because relaxation times for oxygen nuclei in chemically non-equivalent sites are generally different and the degree of isotopic enrichment may be different for each set of sites.)

As expected the spectrum of $H_5PMo_{10}V_2O_{40}$ is more complex due to the greater number of possible isomers and to contamination with $H_4PMo_{11}VO_{40}$. As a result of this it is not possible to draw many conclusions from this example, however, it is interesting to note that there are no signals around 850 ppm where resonances due to an oxygen bridging two vanadiums would be expected.(67)

2.7 Experimental

2.7.1 Preparation of Mixed Heteropolyacids of the $H_{3+n}PMo_{12-n}V_nO_{40}$ Series

2.7.1.1 Heteropolyacids with n=1, 2, 3

These were prepared according to the method of Tsigdinos and Hallada.(44)

A hot solution of $NaVO_3$ in distilled water was mixed with a solution of $Na_2HPO_4 12H_2O$ in distilled water. The solution was acidified with concentrated H_2SO_4 to give a red colour. A solution of Na_2MoO_4 in water was added to this red solution and the total was treated by slow addition with vigorous stirring with a second quantity of concentrated H_2SO_4. The solution was cooled before being extracted into an almost equal volume of ether. The etherate-polyacid formed a central oily layer which was separated and the ether was removed in a stream of air to leave an oily solid. The solid was dissolved in a minimum volume of water and the resulting solution was evaporated over silica gel to give large orange crystals. (For quantities and yields, see Table 2.11).

7.7.1.2 Heteropolyacids with n=4-8

$Na_3PO_4 12H_2O$, V_2O_5, MoO_3 and Na_2CO_3 (anhydrous) were refluxed in 75 cm^3 water for approximately one hour. The resulting red solution was filtered hot to remove undissolved residues. After cooling the volume of the solution was reduced to a minimum on a rotary evaporator. The resulting dense solution was extracted by the method of Drechsel.(68) The solution was treated with a volume of ether equal to $\frac{1}{3}$ of its volume. The mixture was shaken vigorously until the aqueous layer was saturated with ether. Concentrated HCl was then added. As the acid was added the ether layer diminished and a third dense lower layer of mixed heteropoly-etherate formed. More ether and acid were added with careful shaking (emulsions were readily formed) until the etherate no longer separated from the ether layer. (For details of individual preparations see Table 2.12).

2.7.2 NMR Spectroscopy

^{31}P n.m.r. spectra were recorded on Jeol JMN-PS-100 at 40 MHz using a deuterium lock. The referencing system used varied and is described for each experiment with results.

^{51}V n.m.r. spectra were recorded on a Bruker WH 400 at 105 MHz using a deuterium lock. The referencing was initially to a fixed frequency point and was then calculated to give chemical shifts with

PRODUCT	QUANTITIES OF STARTING MATERIALS USED (VOLUME OF WATER)			VOLUME OF H_2SO_4 conc.		YIELD	%[a]
	$Na_2HPO_4 12H_2O$	$NaVO_3$	$Na_2MoO_4 2H_2O$	1st ADDT	2nd ADDT		
$H_4PMo_{11}VO_{40}$	4.48g,12.5mmol ($25cm^3$)	1.52g,12.5mmol ($25cm^3$)	33.2g,137mmol ($50cm^3$)	$1.2cm^3$	$21.2cm^3$	8.32g,3.47mmol	(27%)
$H_5PMo_{10}V_2O_{40}$	3.58g,10mmol ($20cm^3$)	4.88g,40mmol ($20cm^3$)	24.2g,100mmol ($40cm^3$)	1 cm^3	17 cm^3	8.26g,3.48mmol	(35%)
$H_6PMo_9V_3O_{40}$	8.89g,24.8mmol ($25cm^3$)	18.3g,150mmol ($100cm^3$)	27.3g,113mmol ($75cm^3$)	$2.5cm^3$	42 cm^3	3.73g,1.51mmol	(21%)

[a] Yield based on phosphorus

Table 2.11

PRODUCT	QUANTITIES OF STARTING MATERIALS				YIELD	%[a]
	$Na_3PO_4 12H_2O$	MoO_3	V_2O_5	Na_2CO_3		
$H_7PMo_8V_4O_{40}$	5.7g (15mmol)	17.25g (120mmol)	6.3g (34.6mmol)	2.41g (23mmol)	9.75g (4.6mmol)	31%
$H_8PMo_7V_5O_{40}$	5.7g (15mmol)	15.12g (105mmol)	8.19g (45mmol)	2.41g (23mmol)	7.5g (4.24mmol)	28%
$H_9PMo_6V_6O_{40}$	2.85g(7.5mmol)	6.33g (44mmol)	5.12g (28.1mmol)	1.21g (11.5mmol)	8.1g (4.6mmol)	61%
$H_{10}PMo_5V_7O_{40}$	5.7g (15mmol)	10.7g (74.3mmol)	12.4g (68mmol)	2.41g (23mmol)	very low yield	
$H_{11}PMo_4V_8O_{40}$	5.7g (15mmol)	8.64g (60mmol)	14.74g (81mmol)	2.41g (23mmol)	very low yield	

[a] Percentage yield based on phosphorus

Table 2.12

respect to $VOCl_3$ by measuring the chemical shift of $VOCl_3$ using the same fixed frequency point.

^{17}O n.m.r. spectra were also recorded on a Bruker WH 400 at 54 MHz using a deuterium lock and were referenced to internal water. Samples were ^{17}O enriched by being dissolved in water which was 2% enriched with ^{17}O and then incubated overnight at 50°C.

CHAPTER 3

$PdSO_4$ Catalysed But-1-ene Oxidation with Heteropolyacids as Co-catalysts

3.1 Introduction

In order to better understand, and with the aim of improving on, the action of heteropolyacids of the $H_{3+n}PMo_{12-n}V_nO_{40}$ series as reoxidation catalysts in the palladium catalysed oxidation of but-1-ene, a systematic series of catalytic reactions with different members of the series was carried out. Some reactions with isopolyacids containing either molybdenum or vanadium,as well as a small number using the $H_{3+n}PW_{12-n}V_nO_{40}$ series,were investigated for comparison.

The NMR spectroscopy results (Chapter 2) showed that even crystalline heteropolyacids were, for the most part, not pure but contained complex mixtures of heteropolyanions and some isopolyanions. Furthermore,all the patents involving the use of these systems as reoxidants in fact utilise not the pure or even the crystalline heteropolyacids, but simply the mixtures of V_2O_5, MoO_3, Na_2HPO_4 used to make them, in the appropriate ratios. It was therefore decided that solutions prepared by boiling together the appropriate starting materials could be used for the reoxidation catalysts without further purification (see Section 3.4.1). ^{31}P n.m.r. and ^{51}V n.m.r. spectra of these solutions showed them to be essentially the same as the crystalline samples previously described. (Chapter 2).

As it is clearly misleading to refer to these solutions in terms of defined formulae, they will be designated simply by the ratios of P, Mo, V. Thus the solution prepared to contain P:Mo:V in the ratio 1:10:2 will be written $PMo_{10}V_2$ in subsequent discussions.

It has been commonly assumed that, when vanadium containing heteropolyacids are used as reoxidants, the redox processes actually occur at the V(V) centres.(51,59) For this reason the catalytic reactions were standardised by fixing the initial Pd(II):V(V) ratio at 1:10. As a result of the method of preparation and the dilutions required to give a Pd:V ratio of 1:10, the acidities in terms of the concentration of H_2SO_4 in the final solutions varied between 0.2 M and 0.03M for $PMo_{11}V$ and PMo_5V_7 respectively. The values for each solution are given in Section 3.4.2, Table 3.3.

The reactions were first carried out in the absence of oxygen to compare the abilities of the heteropolyacids to reoxidise Pd(0). The reactions were then done in the presence of oxygen to compare the ease of reoxidation of the heteropolyacids by oxygen.

3.2 Results and Discussion

3.2.1 In the Absence of Oxygen

The results of the experiments carried out in the absence of oxygen are shown in Figures 3a and 3b in a graphical form. Gas,liquid chromatography analysis showed the presence of only one product which was identified as butan-2-one. In each case the solutions changed colour from orange-red through green to deep blue, and metal was deposited.

As can be seen, apart from small differences which are within experimental error, all the heteropolyacids in this series gave an identical result. In each case the final turnover number based on palladium is about 5 drifting up to 6 or 7. The reactions were fast and virtually complete within the first ten minutes. Similar results were also found for the members of the tungsten series studied. See

Graphs to Show the Ability of the $H_{3+n}PMo_{12-n}V_nO_{40}$ Series to Reoxidise Pd(0) during But-1-ene Oxidation

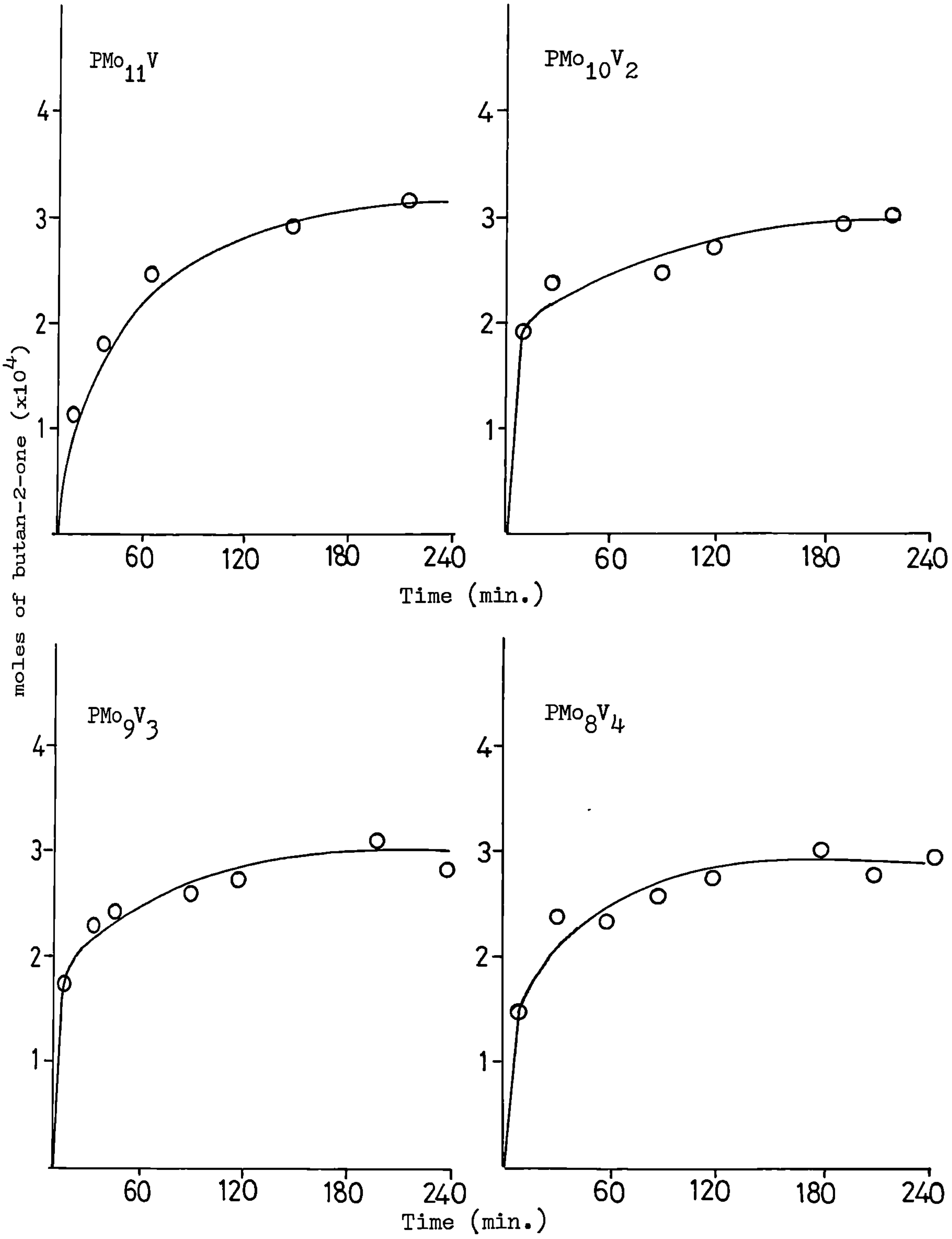


Figure 3a

Graphs to Show the Ability of the $H_{3+n}PMo_{12-n}V_nO_{40}$ Series to Reoxidise Pd(0) during But-1-ene Oxidation

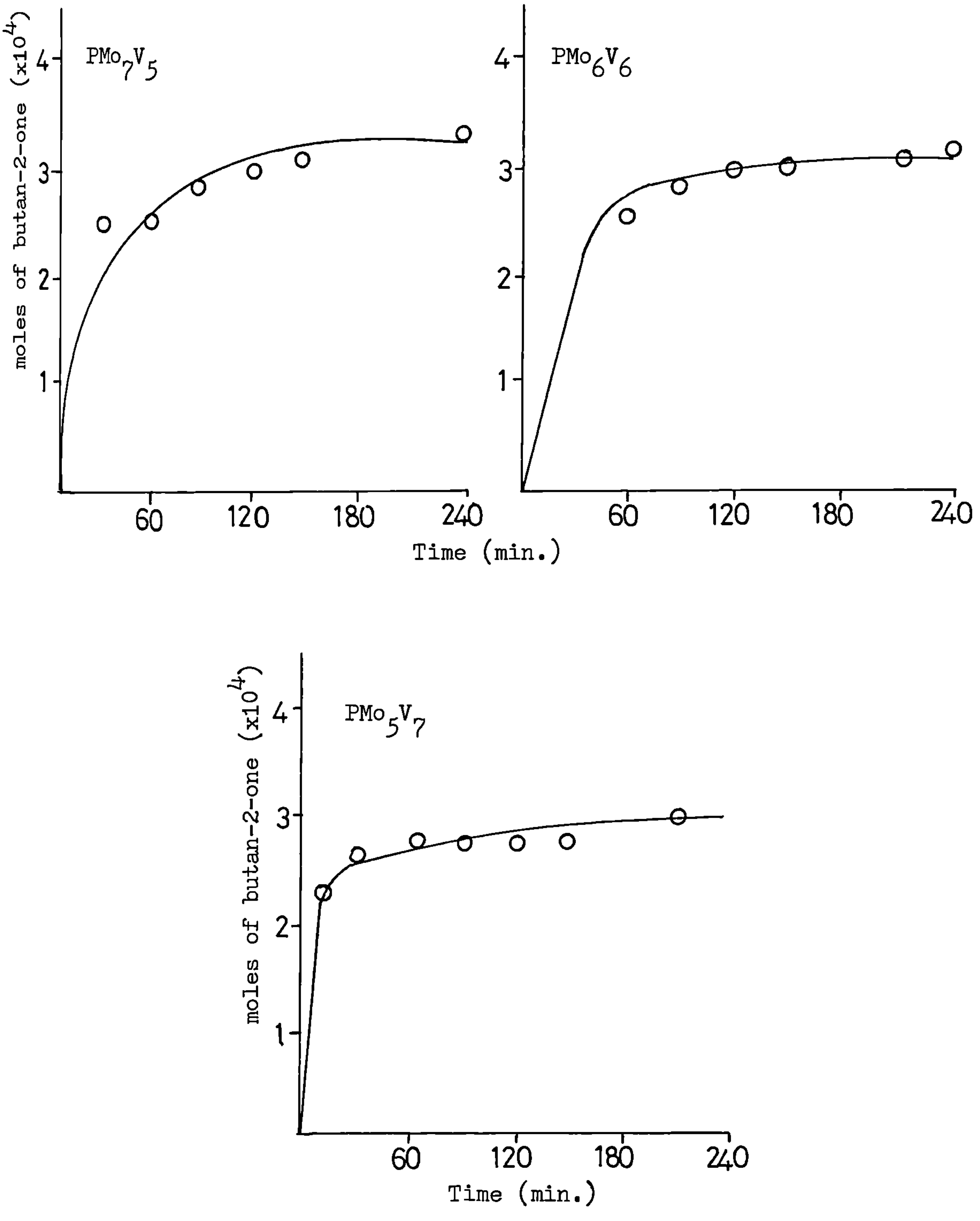


Figure 3b

Figure 3c.

A turnover number of 5 on palladium is equivalent to a turnover of 0.5 on vanadium (Pd:V=1:10) and is readily explained if we consider that only V(V) has been reduced by Pd(0). This confirms the assumption that Mo(VI) or W(VI) have taken no part in the reoxidation process of palladium. Thus we have

$$Pd^{o} + 2V^{V} \longrightarrow Pd^{II} + 2V^{IV}$$

With ten times as many V(V)'s present as g .ions of Pd(0) this process can occur five times before V(V) is exhausted. This theory was further reinforced by the fact that when the Pd:V ratio was increased from 1:10 to 1:20 for the $PMo_{10}V_2$ experiment the turnover on palladium increased to 10 drifting to 12,hence leaving the turnover based on V(V) as 0.5.

However, from the above, it might be expected that the phosphomolybdic acid $H_3PMo_{12}O_{40}$, which does not contain vanadium, would be inactive. This was found not to be the case. When the Pd:Mo ratio was 1:10, with 10 mgs $PdSO_4$ and 0.0931 g $H_3PMo_{12}O_{40}.24H_2O$ dissolved in 10 cm^3 degassed water, the solution changed colour from yellow to deep blue in the presence of but-1-ene, but turnover numbers on palladium approaching only 1 were achieved. However, if the Pd:Mo ratio was 1:100, turnovers of 4.9 on palladium were found. The reaction occurred over a longer time period than that found for the vanadium containing reoxidisers (about thirty minutes).

This result shows that the redox system of heteropolyacids is much more complex than has been believed. It appears that when vanadium(V) is present it is the species primarily involved in the reoxidation of Pd(0), but in its absence Mo(VI) can take over some of this role. This would explain the drift to turnover numbers exceeding 5; when all the V(V) has been reduced Mo(VI) will reoxidise Pd(0), but it does so much more

Graphs to Show the Ability of the $H_{3+n}PW_{12-n}V_nO_{40}$ Series to Reoxidise Pd(0) during But-1-ene Oxidation

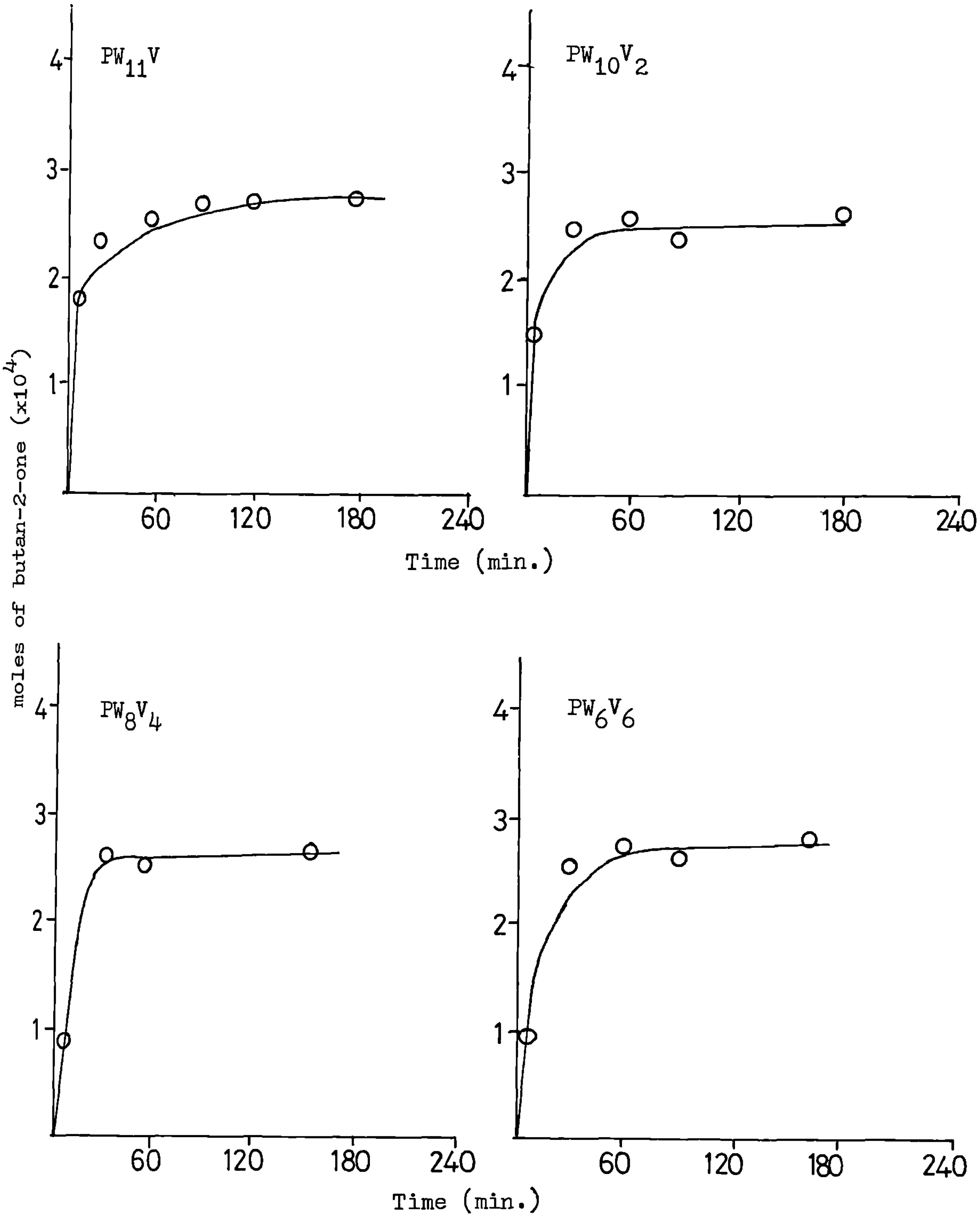


Figure 3c

slowly.

It was also found that a solution of VO_2^+ used in place of a heteropolyacid, but still at a concentration such that Pd:V ratio was 1:10, gave a turnover number of 5.2 on palladium or 0.52 on vanadium. Bearing in mind the results of the ^{51}V n.m.r. spectra which showed that the heteropolyacids always contain excess VO_2^+, it seemed possible that this was in fact the form in which V(V) was active as an oxidiser.

3.2.1.1 Using Other Transition Metal Salts.

Experiments were also carried out using other transition metal compounds in place of $PdSO_4$. The results are summarised in Table 3.1. To enable direct comparison these were all carried out using $PMo_{10}V_2$ as the reoxidation catalyst and the transition metal to vanadium ratio was fixed at 1:10 with a vanadium concentration of 4.95×10^{-4} g ions in 10 cm^3 of solution and at an acidity in terms of H_2SO_4 of 0.1M.

$PdCl_2$ has similar reactivity to $PdSO_4$ and the reactions go rapidly to completion. As might be expected, K_2PtCl_4 is also an active catalyst but reacts much more slowly than the Pd^{II} salts. As the turnover on Pt^{II} is ~ 5 at the end of the reaction the $PMo_{10}V_2$ must also be capable of reoxidising Pt(0) to Pt(II). $RuCl_3.3H_2O$ and $RhCl_3.3H_2O$ react slowly whilst Cr(II) and Ni(II) salts are inactive.

3.2.2 In the Presence of O_2.

Various ratios of but-1-ene to oxygen, either mixed with nitrogen or pure, were tried and the most suitable (on the grounds of the speed of but-1-ene oxidation and the reoxidation) was found to be a 1:1 mixture of but-1-ene and oxygen. Again the only detected product was butan-2-one.

The results are shown in Figure 3d. In each example the Pd:V

Table 3.1

Metal Salt	Yield at 2h of butan-2-one (moles)	Reaction time when metal deposited (mins)	Yield of butan-2-one when metal deposited (moles)
$PdSO_4$	2.66×10^{-4}	30	2.66×10^{-4}
$PdCl_2$	3.05×10^{-4}	20	3.05×10^{-4}
K_2PtCl_4	5.04×10^{-5}	overnight	2.37×10^{-4}
$RuCl_3 3H_2O$	1.69×10^{-6}	-	-
$RhCl_3 3H_2O$	1.79×10^{-6}	-	-
$CrCl_3 6H_2O$	0	-	-
$NiSO_4 5H_2O$	0	-	-

Table to compare activities for butene oxidation of different transition metals

Comparison of Heteropolyacids as Reoxidation Catalysts for the Reaction Between But-1-ene and $PdSO_4$ using a But-1-ene:O_2 ratio of 1:1

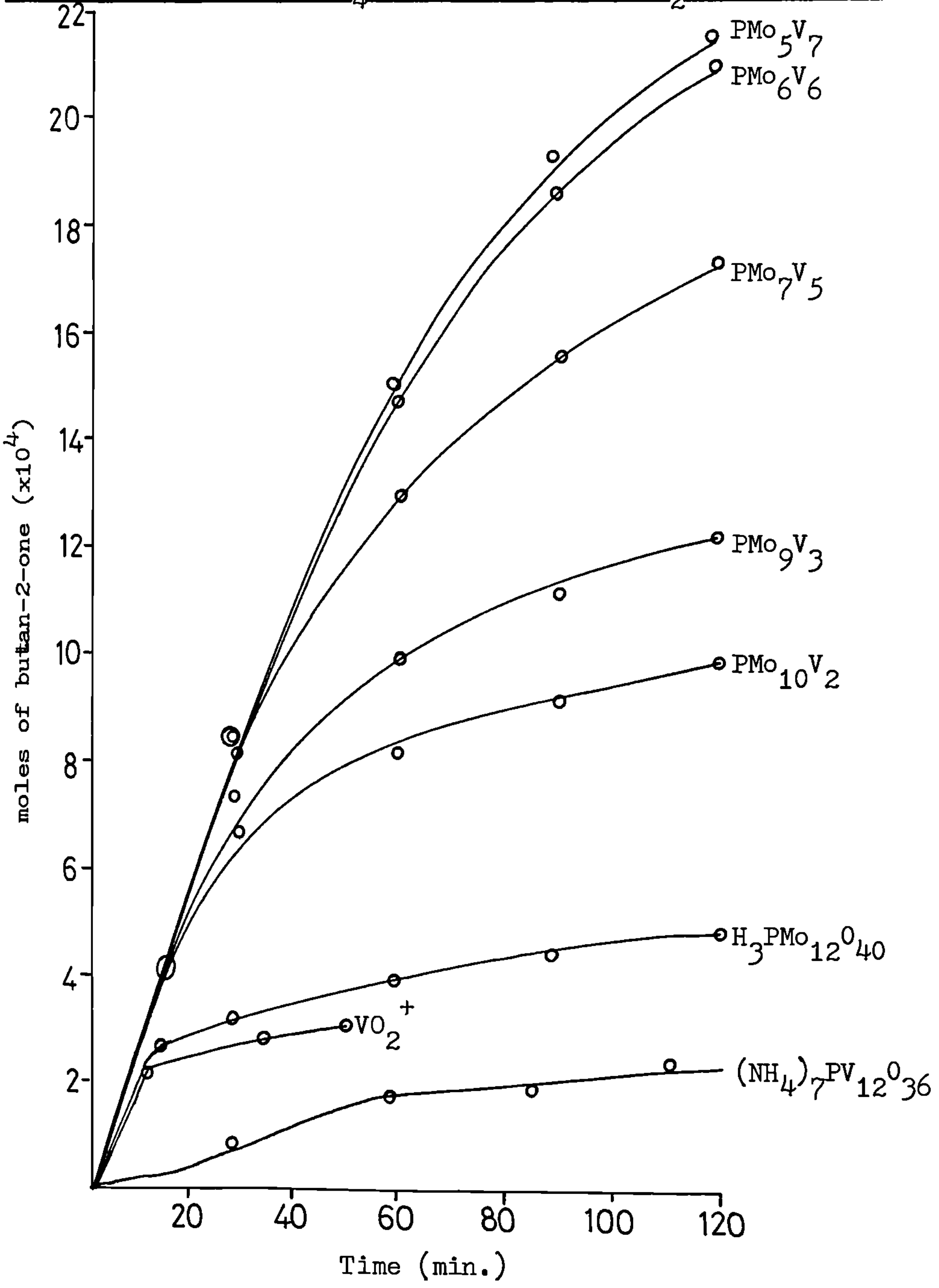


Figure 3d

ratio was 1:10 except for the $H_3PMo_{12}O_{40}$ case where the Pd:Mo ratio was 1:10. The concentration of Pd(II) was constant (see Experimental 3.3.2b).

For the P-Mo-V systems a striking trend is seen; as the percentage vanadium content of the heteropolyanion increases the catalysis improves. The initial rates of all these reactions are identical and the only differences are the points at which the reactions begin to slow down. This is expected as we have already shown that all the mixed heteropolyacids in this series have equal activity for the reoxidation of Pd(0), therefore any differences must be due to the ease with which the reduced heterpolyanions are reoxidised by oxygen. Thus it appears that, even when pH variations are taken into consideration,[1] the higher the percentage vanadium content of the heteropolyacid the more readily it is oxidised by O_2. The slowing down in the rates of reaction is thus thought to be due to a miss-match in the rate of the reduction of the heteropolyacid by Pd(0) and the oxidation of the heteropolyacid by oxygen; this miss-match being more pronounced at low vanadium contents.

As the NMR spectroscopy results indicated that the higher the percentage vanadium the heteropolyacids contained the more free VO_2^+ there was in the samples, it was thought possible that this was the active redox species. However, a most noticeable result is that VO_2^+ is not a good reoxidation catalyst. While it readily reoxidises Pd(0) to give a blue solution of VO^{2+}, VO^{2+} is not reoxidised by oxygen to VO_2^+ under these conditions, and palladium is rapidly precipitated

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[1] It can be seen that pH is not the overriding factor by consulting results shown in Chapter 4, Figure 4c, where it can be seen that increasing the acidity from 0.038M to 0.87M in terms of H_2SO_4 for the PMo_6V_6 case causes only a relatively small fall in the yields of butan-2-one achieved after 2h

(see also Section 4.2.1). Thus VO_2^+ alone cannot be the active species.

In contrast to the V(V) only systems, $H_3PMo_{12}O_{40}$, although nowhere near as effective as the P-Mo-V systems, does give turnovers in excess of 5 on palladium, indicating that it can undergo reoxidation by O_2, albeit at a much slower rate (for a detailed study of $H_3PMo_{12}O_{40}$, see Chapter 4 and Chapter 5).

For comparison a classical Wacker type experiment was carried out using $PdCl_2$ (4.95×10^{-5} moles) and $CuCl_2$ (4.95×10^{-3} moles) in 10 cm^3 water. Butan-2-one was the only detected product, but this reaction was much slower than the $PdSO_4$- heteropolyacid system and a turnover number of only 1.29 on Pd was achieved in two hours at room temperature (18^oC).

3.2.2.1 Using Mixed Solvent Systems

Reactions in mixed aqueous/organic media were tried, with the aim of increasing the reaction rates, using one of the best heteropolyacid systems - PMo_6V_6. Mixed solvent systems had been found useful in previous studies.(69,70)

The solvents tried were acetic acid, dimethyl formamide (DMF), dimethyl sulphoxide (DMSO) and diglyme. The results are shown in Figure 3e.

[N.B. These experiments were carried out before the stirring rates had been optimised to remove the gas/liquid mixing effects (see Section 3.4.2b), therefore the rates are slower than those shown in other results. However, a valid comparison of the solvent mixes can still be undertaken as all these experiments were done under identical conditions.]

Effect of Organic Solvents on the Reoxidation Ability of PMo_6V_6

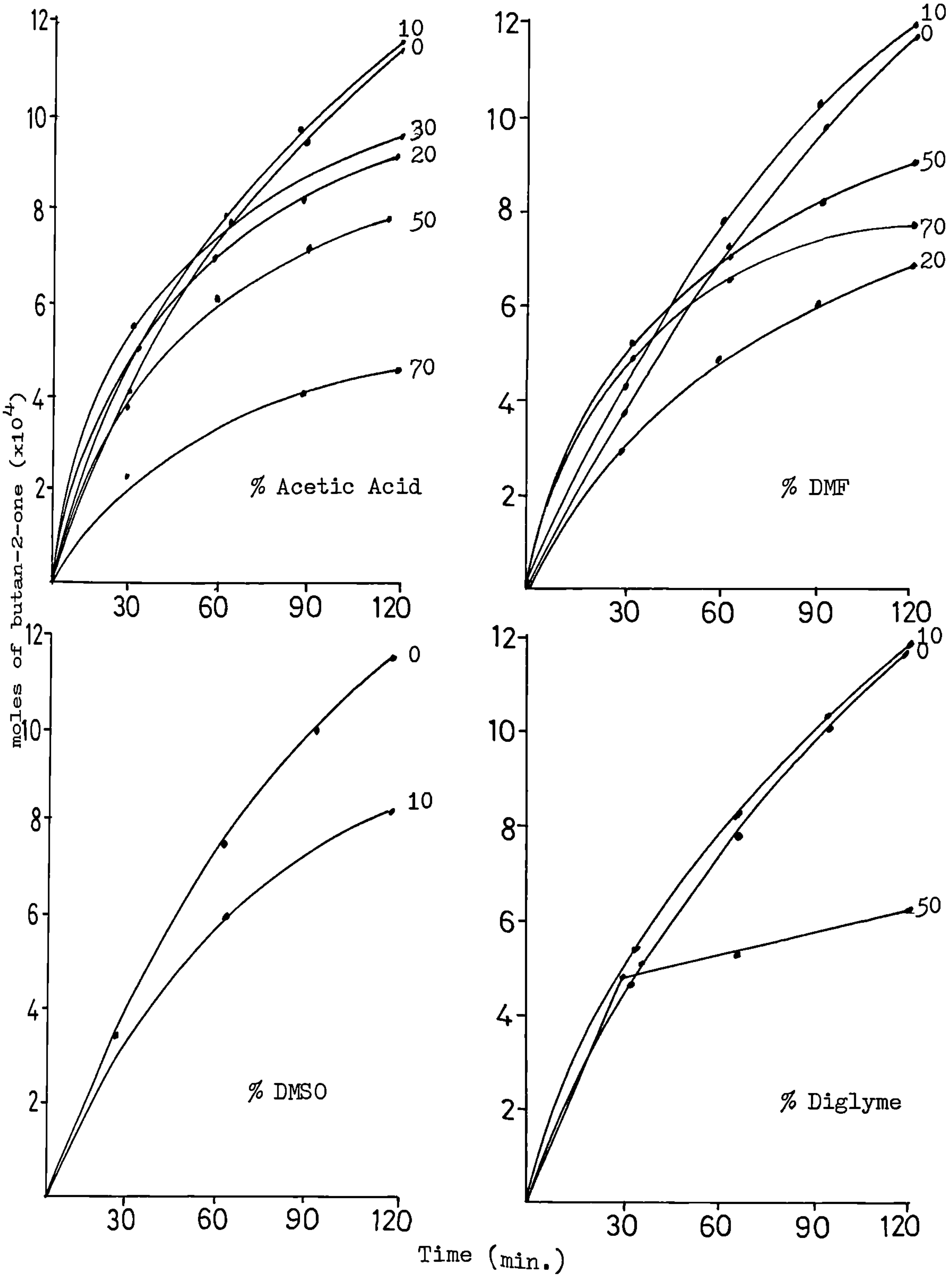

Figure 3e

3.2.2.1.1 Acetic Acid

A level of 10% acetic acid in water has little effect. At 20, 30 and 50% the initial rates are increased, due to increased olefin solubility, but the reactions slow down faster than the equivalent 100% water system. At 70% acetic acid the reaction is clearly impeded. Since the ^{31}P n.m.r. spectra indicated (Chapter 2) that heteropolyanions are intact in this solvent, the effect of acetic acid on the reaction could be due to differences in pH or to co-ordination of acetic acid to the outer oxygens of the heteropolyacid structure via H-bonding (see also Chapter 5).

3.2.2.1.2 Dimethyl Formamide

Again 10% DMF has little effect. At 20% DMF an insoluble orange material is formed, at 50% and 70% this solid is soluble. As DMF is known to act as a base forming a $(DMF)_2H^+$ cation(71) and heteropolyacids are known to form etherates(68), it is proposed that PMo_6V_6 forms a salt with DMF, which is insoluble in water but soluble in DMF, and which is less reactive than the free heteropolyacid as a reoxidation catalyst. Thus at 20% DMF some heteropolyacid is removed from solution as a DMF salt; hence the low activity.. At 50% DMF it is resolubilised but is less active than free heteropolyacid; at 70% nearly all the heteropolyacid is in the less active DMF salt form.

3.2.2.1.3 Dimethyl Sulphoxide

This is of little use as a solvent as it is itself oxidised by the catalyst.

3.2.2.1.4 Diglyme

10% diglyme increases the rate slightly, probably by increasing the solubility of butene in the solution. However, at 50% diglyme the reaction is completely stopped. This can also be explained in terms of the formation of a complex between the polyacid and the solvent, which is inactive to reoxidation.

3.2.2.2 Discussion of the Effects of Organic Solvents

Heteropolyacids are susceptible to complex formation with oxygen containing organic solvents, probably by co-ordination between outer oxygens of the heteropolyanion structure and the oxygen of the solvent via hydrogen-bonding (see ^{51}V NMR Chapter 2). Since such complexation reduces the ability of the heteropolyanion to be reoxidised, this indicates that O_2 needs free access to these outer oxygens in order to capture electrons and reoxidise the heteropolyacid.

3.3 Conclusion

The conclusions can be summarised as follows. Firstly, under the conditions investigated, all the P-Mo-V systems readily reoxidise Pd^0 and they do so with equal efficiency. However, the power to be reoxidised by O_2 varies and increases with the number of vanadiums in the system; but VO_2^+ alone in $1M H_2SO_4$ is not reoxidised by O_2. Although the ability of $H_3PMo_{12}O_{40}$ as a reoxidation catalyst is inferior to that of the P-Mo-V systems under the conditions investigated, these results show that the desired redox reaction can be achieved in the absence of V(V), and hence, imply that the Mo(VI) in the P-Mo-V systems has an active role and that V(V) is not the sole participant in the redox process. One might even speculate that the chief role of the vanadium is not a redox-active one but that it helps the P-Mo systems to form a catalytically more active PMo_x species.

3.4 Experimental

3.4.1 Preparation of Solutions of $H_{3+n}PMo_{12-n}V_nO_{40}$ n=1 to 7

The solutions were prepared by a method similar to that used by Matveev et al.(16) except that stoichiometric amounts of V_2O_5(not excess) were used so that the total amount of each component in the solution was known.

V_2O_5, MoO_3(see Table 3.2), $Na_3PO_4.12H_2O$, 1.505 g (3.96mmol) and Na_2CO_3 anhyd., 0.636 g (6mmol) were refluxed with vigorous stirring in distilled water (20 cm^3) for forty minutes. After the solution had been allowed to cool the pH was adjusted to 1 by the addition of concentrated H_2SO_4(approximately 1 cm^3). The solution was refluxed with stirring for a further twenty minutes, and allowed to cool before being made up to a volume of 80 cm^3 with distilled water. A small amount (20mgs) of green solid (analysed as 50% V^V) was removed by filteration

Table 3.2

Solution Product	V_2O_5	MoO_3
$PMo_{11}V$	0.36g,1.98mmol	6.27g, 43.7mmol
$PMo_{10}V_2$	0.72g,3.96mmol	5.70g, 39.6mmol
PMo_9V_3	1.08g,5.93mmol	5.13g, 35.6mmol
PMo_8V_4	1.44g,7.91mmol	4.56g, 31.6mmol
PMo_7V_5	1.80g,9.89mmol	3.99g, 27.7mmol
PMo_6V_6	2.16g,11.9mmol	3.42g, 23.7mmol
PMo_5V_7	2.52g,13.8mmol	2.85g, 19.8mmol

Quantities of starting materials used in preparations of $H_{3+n}PMo_{12-n}V_nO_{40}$ solutions

3.4.2 Oxidation of But-1-ene with $PdSO_4$ using $H_{3+n}PMo_{12-n}V_nO_{40}$ as Reoxidation Catalysts

a, In the absence of O_2

The solutions were refluxed under N_2 to remove dissolved O_2. A volume of the solution such that it contained $4.95x10^{-4}$ g ions V(V) was added to 10 mgs ($4.95x10^{-5}$ moles) $PdSO_4$ [1] in a 2 neck, round bottom flask. The volume was made up to a total of 10 cm^3 with distilled water which had been degassed under N_2. (The volumes of each heteropolyacid solution used are shown in Table 3.3). The flask was kept under N_2 before being attached via neoprene tubing to a burette containing but-1-ene. The flask was flushed through with but-1-ene and then shaken vigorously under but-1-ene. The gas uptake was monitored on the burette and samples of solution were analysed for volatiles by gas liquid chromatography (see Section 3.4.7) at regular intervals. All reactions were carried out at 20°C and atmospheric pressure.

The apparatus used is as shown in Figure 3f except that a longer length of flexible tubing connected the reaction flask to the gas manifold and mixing was achieved by shaking rather than stirring.

b, In the presence of O_2

The reactions were carried out as in a, but the exclusion of air was unnecessary. The mixing was achieved by stirring at the gas liquid interface. In order to ensure that the gas liquid mixing was efficient, several different methods of mixing were tried, including a vibromix and a magnetic stirrer with a teflon paddle. However, a standard magnetic stirrer orientated so that it broke the surface at each rotation was found to be as good as any of these methods. The efficiency was tested

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[1] $PdSO_4$ was replaced by other transition metal compounds in some examples.

APPARATUS FOR BUTENE OXIDATION

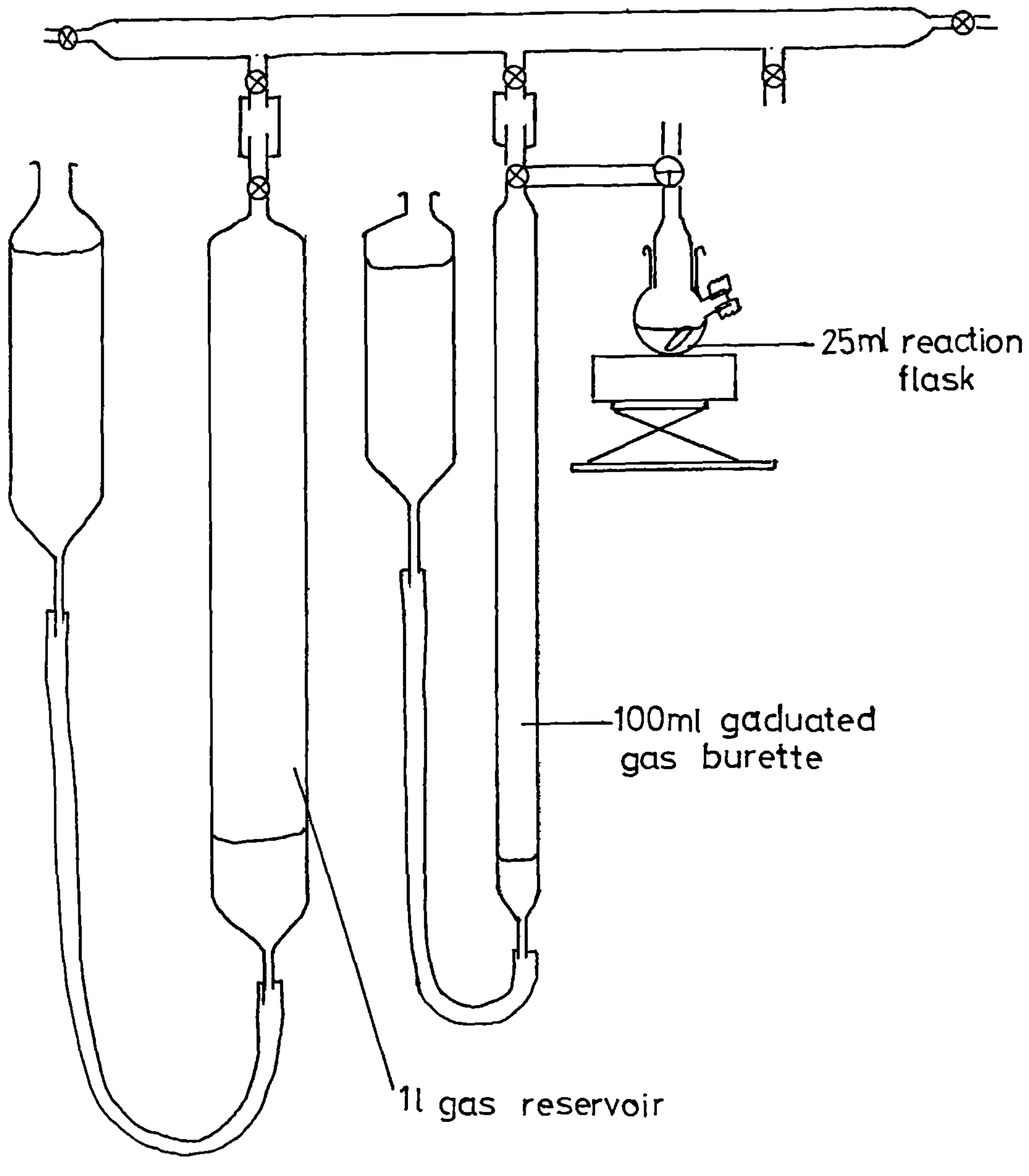


Figure 3f

by doubling the concentration of Pd(II) and reoxidation catalyst and measuring the rate of reaction; as expected the rate doubled indicating that it was not limited by gas liquid mixing effects. The apparatus is shown in Figure 3f. A mixture of but-1-ene and O_2 in the ratio 1:1 was found to be the most useful. In the case of mixed solvent systems some of the water added to make the total volume 10 cm^3 was replaced by the appropriate amount of organic solvent.

Table 3.3

Solution	Volume containing 4.95×10^{-4}g ions V(V)	Acidity in[(a)] terms of H_2SO_4	Calculated[(a)] pH
$PMo_{11}V$	10 cm^3	0.20 M	0.7
$PMo_{10}V_2$	5 cm^3	0.10 M	1
PMo_9V_3	3.33 cm^3	0.07 M	1.2
PMo_8V_4	2.5 cm^3	0.05 M	1.3
PMo_7V_5	2 cm^3	0.04 M	1.4
PMo_6V_6	1.67 cm^3	0.03 M	1.5
PMo_5V_7	1.42 cm^3	0.03 M	1.6

(a) Values for final solutions made up to 10 cm^3 with distilled water

Volumes of Standard Solutions Used in Catalyst Preparation

3.4.4 Preparation of $(NH_4)_7PV_{12}O_{36}.11H_2O$

This was carried out according to the method of Rosenhiem and Pieck.(72)

85% H_3PO_4, 4.8 g (41mmol) was added to a white suspension of NH_4VO_3 28 g (0.24mmol), in water (50 cm^3). The suspension became orange in colour. Addition of 1MHCl (50 cm^3) caused the colour to darken. The solution, which was now orange-red, was warmed with stirring to 50-60°C on a water bath. The solution became dark purple in colour and the suspension was deep red. The suspension was removed by filtering and the remaining solution deposited purple crystals. Washing the red solid with water gave more purple solution from which a further batch of purple crystals was formed. The total yield of purple crystals was 4.02 g (64%).

Analysis: Found P, 1.98% $^w/w$, V, 40.2% $^w/w$, $(NH_4)_7PV_{12}O_{36}.11H_2O$ requires P, 2.01%$^w/w$, V, 39.66%$^w/w$.

The compound gave a single peak in the ^{31}P n.m.r. spectrum at -0.84 ppm with respect to 85% H_3PO_4, when dissolved in water.

3.4.5 Preparation of VO_2^+

V_2O_5, 0.451 g (2.48mmol) was dissolved with heating in 1MH_2SO_4 (50 cm^3). The resulting yellow solution contained vanadium in the form VO_2^+.(73) 5 cm^3 of stock solution contained 4.95×10^{-4} g ionsV(V).

3.4.6 $H_3PMo_{12}O_{40}.24H_2O$

Commercially available, analytical grade $H_3PMo_{12}O_{40}.24H_2O$ was used. The sample was reanalysed and gave the following results: P, 1.39%$^w/w$, Mo, 50.74%$^w/w$. (Values required for $H_3PMo_{12}O_{40}.24H_2O$ P, 1.37%$^w/w$, Mo, 51.02%$^w/w$). Solutions for catalysis were prepared by dissolving an appropriate weight of $H_3PMo_{12}O_{40}$ in 10 cm^3 of water (degassed for O_2 free experiments) with 10 mgs $PdSO_4$.

3.4.7 Gas Liquid Chromatography

A Pye 104 chromatograph fitted with a packed SP1200 column was used with a flame ionisation detector. Initial samples were run with a temperature programme from 60°C to 180°C at 4°C/minute. Once the product had been determined as exclusively butan-2-one samples were run isothermally at 80°C.

CHAPTER 4

Investigations to Determine the Active Species in the Redox Reactions of Heteropolyacids

4.1 Introduction

The initial results of the catalysis described in Chapter 3, while producing some information as to the nature of these reactions, do not give any direct insight about the active species in the heteropolyacid solutions. In order to pin this down more closely a study of the different components, VO_2^+, MoO_4^{2-} and PO_4^{3-}, of the heteropolyanions was carried out.

Since the view held by Russian workers is that VO_2^+ is the active species and that VO^{2+} is reoxidised to VO_2^+ in the co-ordination sphere of the heteropolyacid by a series of complex equilibria (see Chapter 1), the reoxidation of VO^{2+} under a variety of conditions was investigated.

Oxidations of but-1-ene have been carried out using individual heteropolyacid components and combinations of components to show which are active as reoxidation catalysts and in what proportions.

4.2 Results and Discussion

4.2.1 Oxidation of VO^{2+}

Attempts were made to oxidise VO^{2+}, from $VOSO_4$, with O_2 in the presence of Na_2MoO_4 in water and $1MH_2SO_4$. The results were monitored by observing the intensity of the characteristic VO^{2+} band at 768 nm in the visible spectra. See Table 4.1.

The results show that VO^{2+} is readily oxidised in neutral solution but is not oxidised in the presence of MoO_4^{2-} in $1MH_2SO_4$.

Table 4.1

A In Water

Sample	Absorbance at 768nm[a]	Solution Concentration
$VOSO_4$	0.67	0.052M
$Na_2MoO_4 2H_2O$	0.00	0.052M
$VOSO_4 + Na_2MoO_4 . 2H_2O$	$>$1.47	0.052M (in each)
$VOSO_4 + Na_2MoO_4 . 2H_2O$	0.58	$4.3 x 10^{-3}M$ (in each)
$VOSO_4 + Na_2MoO_4 2H_2O$ O_2 bubbled for 1 h.	0.01	$4.3 x 10^{-3}M$ (in each)

B In $1M H_2SO_4$

Sample	Absorbance at 768nm[a]	Solution Concentration
$VOSO_4$	0.63	0.052M
$Na_2MoO_4 . 2H_2O$	0.00	0.052M
$VOSO_4 + Na_2MoO_4 . 2H_2O$	0.68	0.052M (in each)
$VOSO_4 + Na_2MoO_4 . 2H_2O$ $+ O_2$ for 1 h.	0.73	0.052M (in each)

[a] In 1 cm quartz cells

Table to Show the Results of Attempted Oxidation of VO^{2+}

Similarly, the oxidation of $VOSO_4$ in the presence of PMo_6V_6 with O_2 was attempted. The results of the visible spectroscopy are shown in Table 4.2.

Under these conditions VO^{2+} was not oxidised by O_2 in the presence of a heteropolyacid. The experiment was repeated with the addition of $PdSO_4$, but again no oxidation of VO^{2+} was detected.

Table 4.2

Sample	Absorbance at 786nm[a]	Solution Concentration
$VOSO_4$ (in water)	0.67	0.052M
PMo_6V_6 (pH 1.5)	0.03	0.052g ions $l^{-1}V(V)$
$VOSO_4$ PMo_6V_6 (pH 1.5)	1.47	0.052M 0.052g ions $l^{-1}V(V)$
$VOSO_4$ PMo_6V_6 + O_2 for 1.5h (pH 1.5)	1.47	0.052M 0.52g ions $l^{-1}V(V)$

[a] In 1 cm quartz cells

Table to Show the Results of Attempted Oxidation of VO^{2+} in the Presence of PMo_6V_6 Solution

It could be argued that the concentrations used to give useful visible spectra were very different from those used in catalysis, therefore an e.s.r. experiment using concentrations the same as those used in the catalysis (i.e. 4.95×10^{-4} g ions V/10 cm^3) was done. The e.s.r. signal due to V^{4+} in VO^{2+} gives seven peaks since V(IV) has a nuclear spin of 5/2 and one unpaired electron. The signal intensity is directly proportional to the concentration of V(IV) in solution.

The signal intensity did not change when VO^{2+} was mixed with PMo_6V_6 solution of equal vanadium concentration (pH 1.5), nor when O_2 had been bubbled through the sample (The amount of VO^{2+} from $VOSO_4$ was constant in each sample). This result shows no evidence for the oxidation of VO^{2+} by O_2 in acid in the presence of the heteropolyacid.

To show that vanadyl sulphate is a good model for VO^{2+} in general, experiments were also carried out on VO_2^+ solutions (in $1MH_2SO_4$) which had been reduced with $NaBH_4$ in situ, again reoxidation by O_2 in the presence of heteropolyacids was not detected by visible spectroscopy. Similarly adding H_3PO_4 to the Na_2MoO_4 examples had no effect on the reoxidation of VO^{2+} even at catalyst concentrations.

Hence we were unable to find any evidence to support the suggestion that VO^{2+} can be oxidised by O_2 in the presence of MoO_4^{2-} or heteropolyacids. VO^{2+} can be oxidised in neutral or basic media, but the solutions in which heteropolyacids are used as reoxidation catalysts are strongly ($pH<1.6$) acidic; under which conditions it is not appreciably oxidised over times equivalent to or greater than those used in butene oxidation reactions.

The main evidence (51,58,59) for such a reoxidation system seems to be work done by Matveev and Kuznetsova (74) on the oxidation of V(IV) in the presence of Na_2MoO_4. However, here it is clearly stated that no oxidation of V(IV) is observed below pH 2.5.

4.2.2 Investigations of the Activity as Oxidation Catalysts of the Components of Heteropolyacids

Oxidations of but-1-ene with $PdSO_4$ in the presence of O_2 using mixtures of the components of heteropolyacids were carried out in $1MH_2SO_4$. The details are given in Experimental 4.3.3 . The results are depicted graphically in Figure 4a.

As expected, VO_2^+ is a poor reoxidation catalyst and hence the overall rate of reaction decays very rapidly indeed, (see also Chapter 3). Addition of phosphate to VO_2^+ had little overall effect.

Na_2MoO_4 is slightly better, but the rate of the reaction also decays quite rapidly; this indicates that, similarly to VO_2^+, MoO_4^{2-} in acid solution (nature of species is uncertain)(73) can reoxidise Pd(0) to Pd(II) but its reduced form is not readily reoxidised by O_2 in acidic media. Mixtures of MoO_4^{2-} and VO_2^+ in acid show no better ability to be reoxidised, the result simply being the sum of those found for the separate species.

However, addition of phosphoric acid to Na_2MoO_4 greatly improves the reoxidation activity, further, levels of phosphate such that the P:Mo ratio is 1:12 are sufficient. Increasing the P:Mo ratio to 10:12 does not improve the reoxidation to any greater extent. Somewhat surprisingly, addition of V_2O_5 in $1MH_2SO_4$ (VO_2^+) to mixtures of Na_2MoO_4 and H_3PO_4 in $1MH_2SO_4$ does not improve on the catalyst.

The differences in the reactions were also highlighted by the colour changes observed. Reduction of VO_2^+ in acid during but-1-ene oxidation with $PdSO_4$ gave a pale turquoise blue. Reduction of Na_2MoO_4 under the same conditions gave no colour change (that reduction occurred is shown by the fact that turnover numbers greater than one on palladium were achieved; therefore MoO_4^{2-} must have reoxidised Pd(0) and itself been reduced), but in the presence of small amounts of phosphate gave a deep blue associated with "heteropolyblues" (see Chapter 1). This shows that a different species is present in the reduced solution when small amounts of phosphate are added.

In summary, in the P-Mo-V system, molybdate and phosphate seem

But-1-ene Oxidation using $PdSO_4$ with Heteropolyacid Components

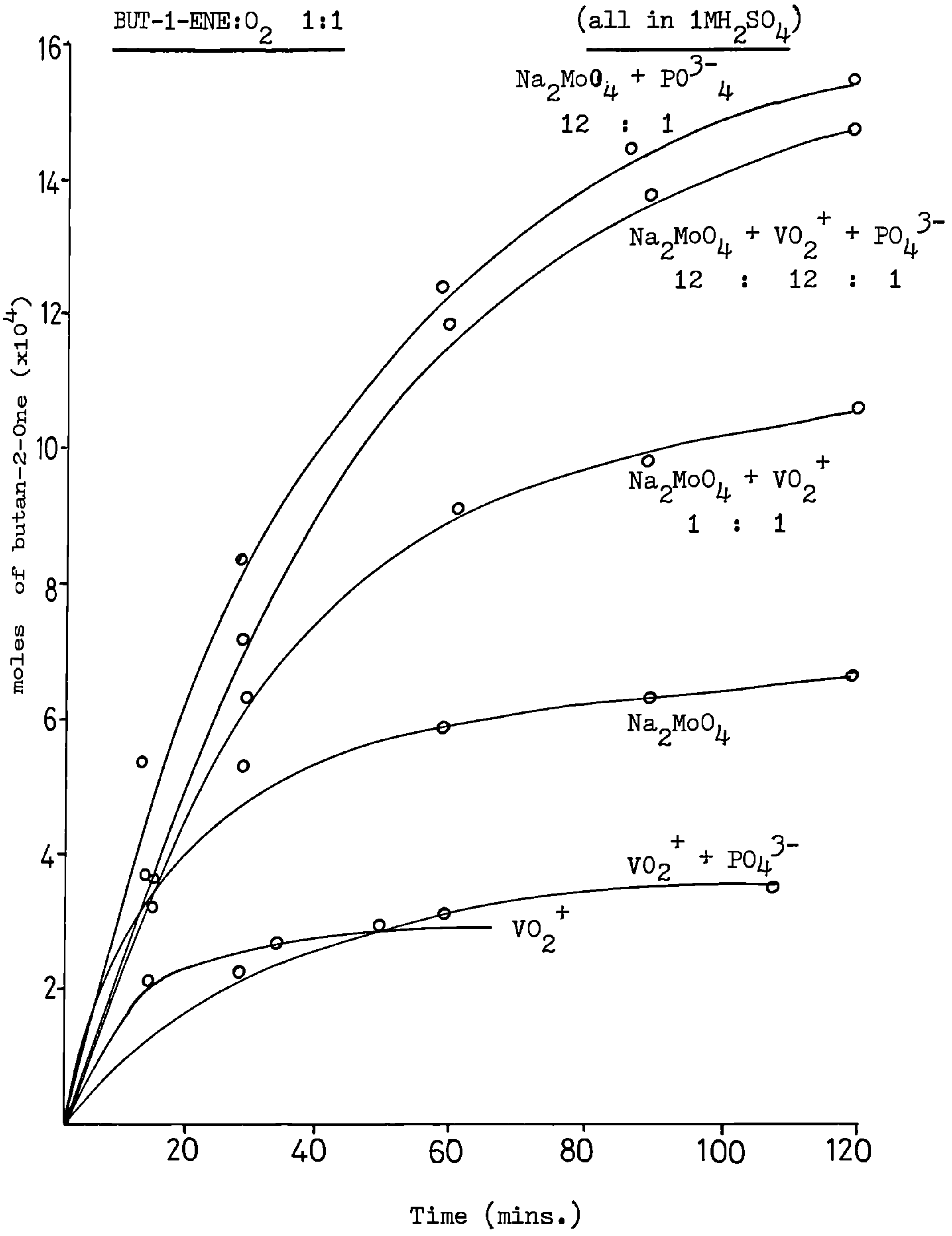


Figure 4a

to be the components most essential to give a good reoxidation catalyst for Pd(0) in acidic media. V(V) in the form of VO_2^+ seems to play little part in the reaction under acidic conditions. The levels of PO_4^{3-} necessary are discussed in more detail in Section 4.2.4.

4.2.3 A Comparison Between PMo_6V_6 Solution and $H_3PMo_{12}O_{40}$

A comparison of the result for mixtures of Na_2MoO_4 and H_3PO_4 in $1MH_2SO_4$ with that for $H_3PMo_{12}O_{40}$ (Chapter 3) is at first sight surprising. However, it is important to note that experiments described earlier were carried out in distilled water while those reported here were in $1MH_2SO_4$. Further experiments with $H_3PMo_{12}O_{40}$ gave results identical to those found for mixtures of MoO_4^{2-} and PO_4^{3-} in the same medium. By contrast with earlier results, $H_3PMo_{12}O_{40}$ in $1MH_2SO_4$ is now a reasonably good reoxidation catalyst for Pd(0) in this reaction. A direct comparison with PMo_6V_6 is shown in Figure 4b.

It should be noted that whereas reactions using PMo_6V_6 showed only a trace deposit of palladium metal even after a five hour run, relatively large amounts of metal could be detected in the $H_3PMo_{12}O_{40}$ reaction after fifteen minutes. As can be seen, $H_3PMo_{12}O_{40}$ in $1MH_2SO_4$ is still not as good as the best vanadium containing heteropolyacids (e.g. PMo_6V_6) for this reaction, as reactions using $H_3PMo_{12}O_{40}$ tend to slow down more rapidly than those using PMo_6V_6.

Since the addition of acid to $H_3PMo_{12}O_{40}$ enhanced its activity, acid was also added to PMo_6V_6 (volume made up to 10 cm^3 with $1MH_2SO_4$ in place of water). However, in this case extra acid was slightly detrimental, see Figure 4c.

Adding excess phosphate to these reactions had no effect.

Comparison of $H_3PMo_{12}O_{40}$ in ($1M H_2SO_4$) and PMo_6V_6 as Reoxidation Catalysts

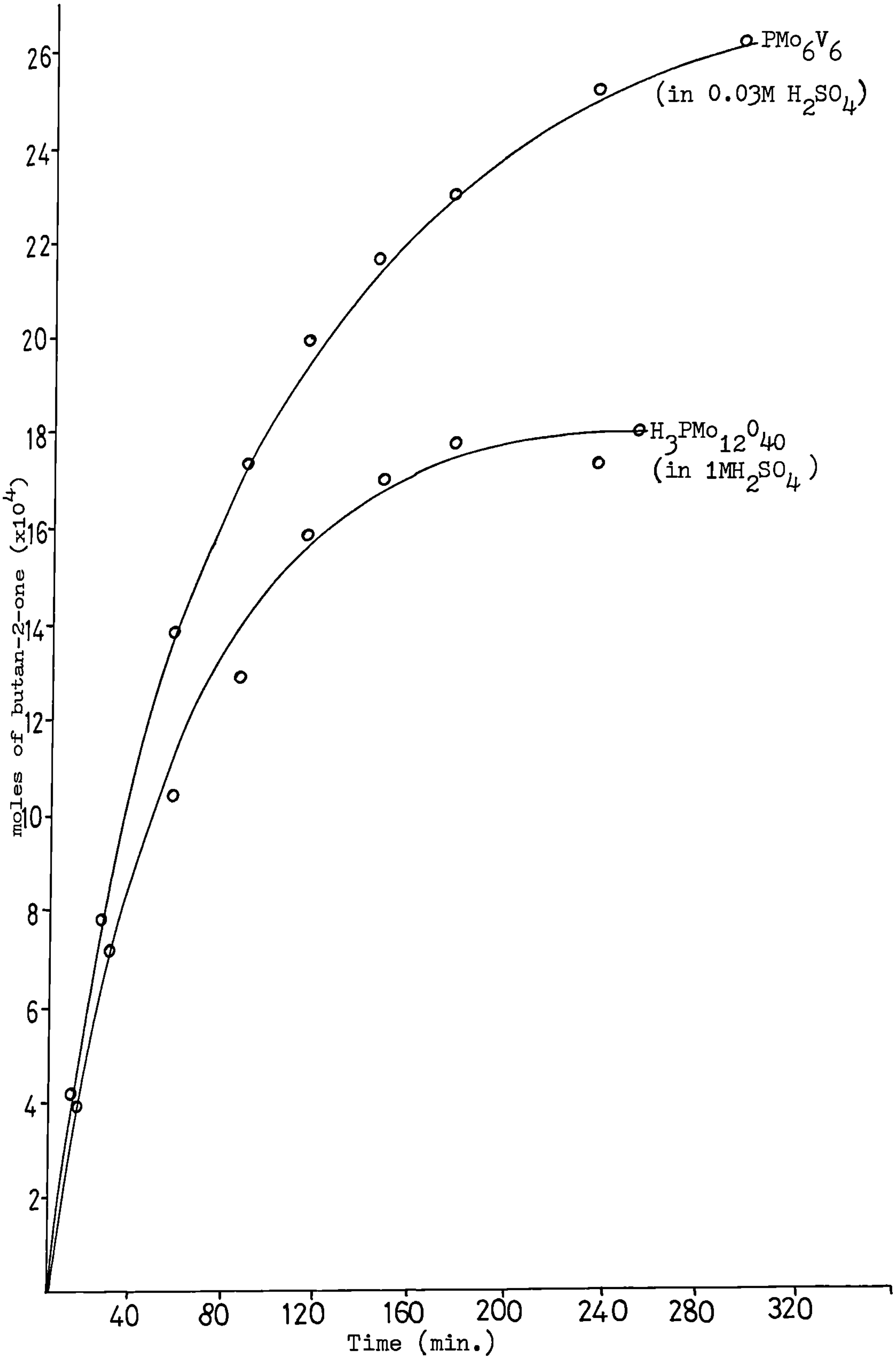


Figure 4b

Comparative Effects of Extra Acid on $H_3PMo_{12}O_{40}$ and PMo_6V_6

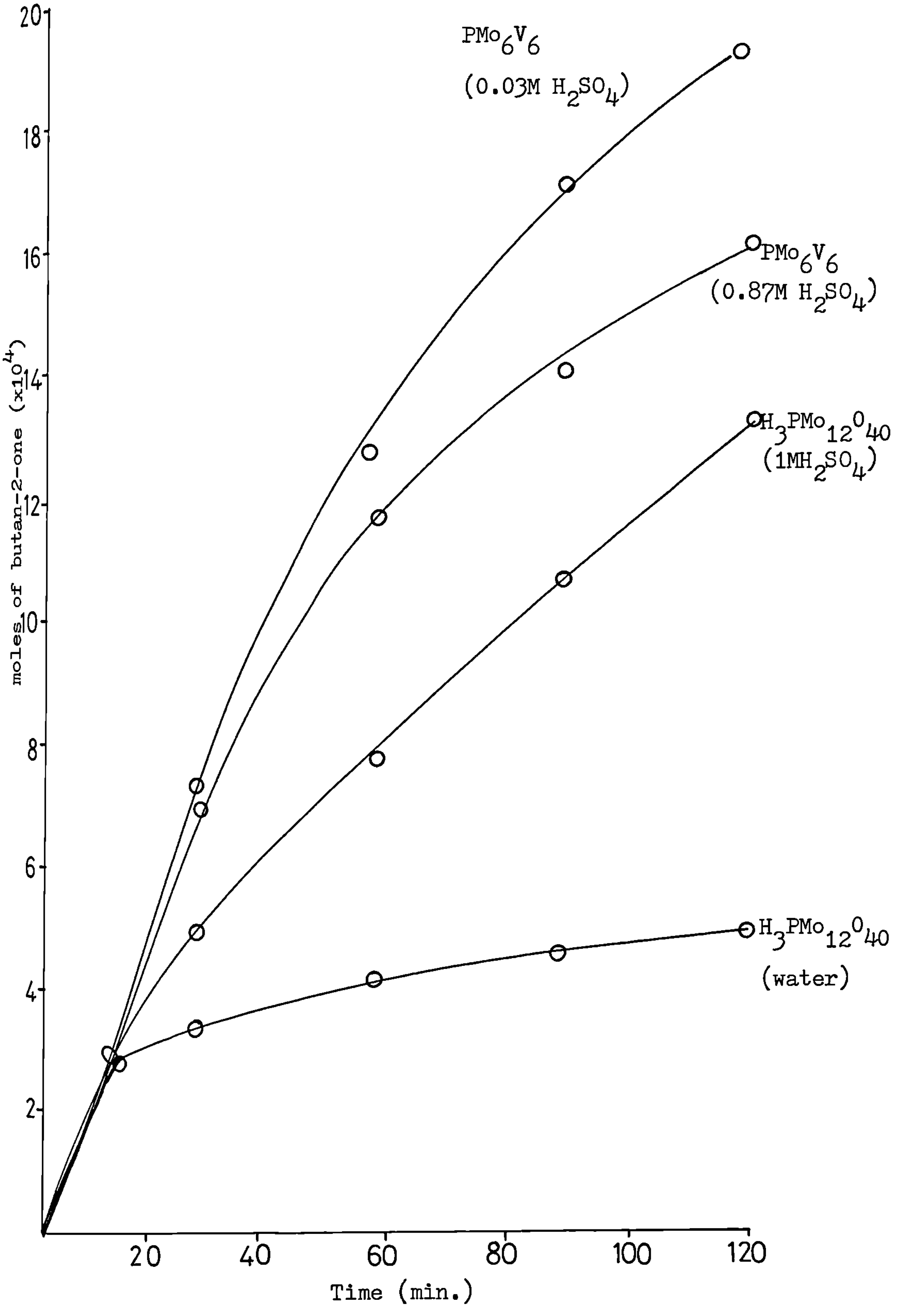


Figure 4c

4.2.4 Optimising PO_4^{3-} in Reactions using Molybdate in Acid

The results are presented in Figure 4d. With no phosphorus, the turnover on palladium achieved before the reaction started to slow down (folded over) was 20. Where the P:Mo ratio was 1:24 the fold over point occurred at a turnover number of 32 based on palladium, but where the P:Mo ratio was greater or equal to 1:12 the fold over occurred around turnover numbers of 40 based on palladium. It is clear that an optimum ratio of $PO_4^{3-}:MoO_4^{2-}$ is reached at 1:12. Further quantities of PO_4^{3-} have no effect. The relationship is, however, not a simple one; the yields achieved at P:Mo= 1:12, are not twice those achieved at a ratio of 1:24.

The optimum ratio of 1:12 at first sight seems to indicate that the active species is $[PMo_{12}O_{40}]^{3-}$. However, the complex nature of the relationship points to an equilibrium between free phosphate and some catalytically active phosphomolybdate species, and could also involve isopolymolybdates.

One might speculate that the dominant species at P:Mo ratio of 1:12 and above would be a PMo_x species where $x > 12$, since if $x < 12$ initial P:Mo ratios of greater than 1:12 would be expected to push the equilibrium to give more of such a species. However, no increased activity is observed at higher P:Mo ratios indicating no increase in the concentration of the active form.

4.3 Experimental

4.3.1 Visible Spectroscopy to Investigate Reoxidation of VO^{2+}

Spectra were recorded on a Perkin Elmer 402 U.V.-visible spectrometer using 1cm^3 quartz cells with $1M H_2SO_4$ or water as appropriate in the reference cell. $VOSO_4$ and Na_2MoO_4 were commercially available

Graphs to Show the Optimisation of the P:Mo Ratio in 1MH_2SO_4

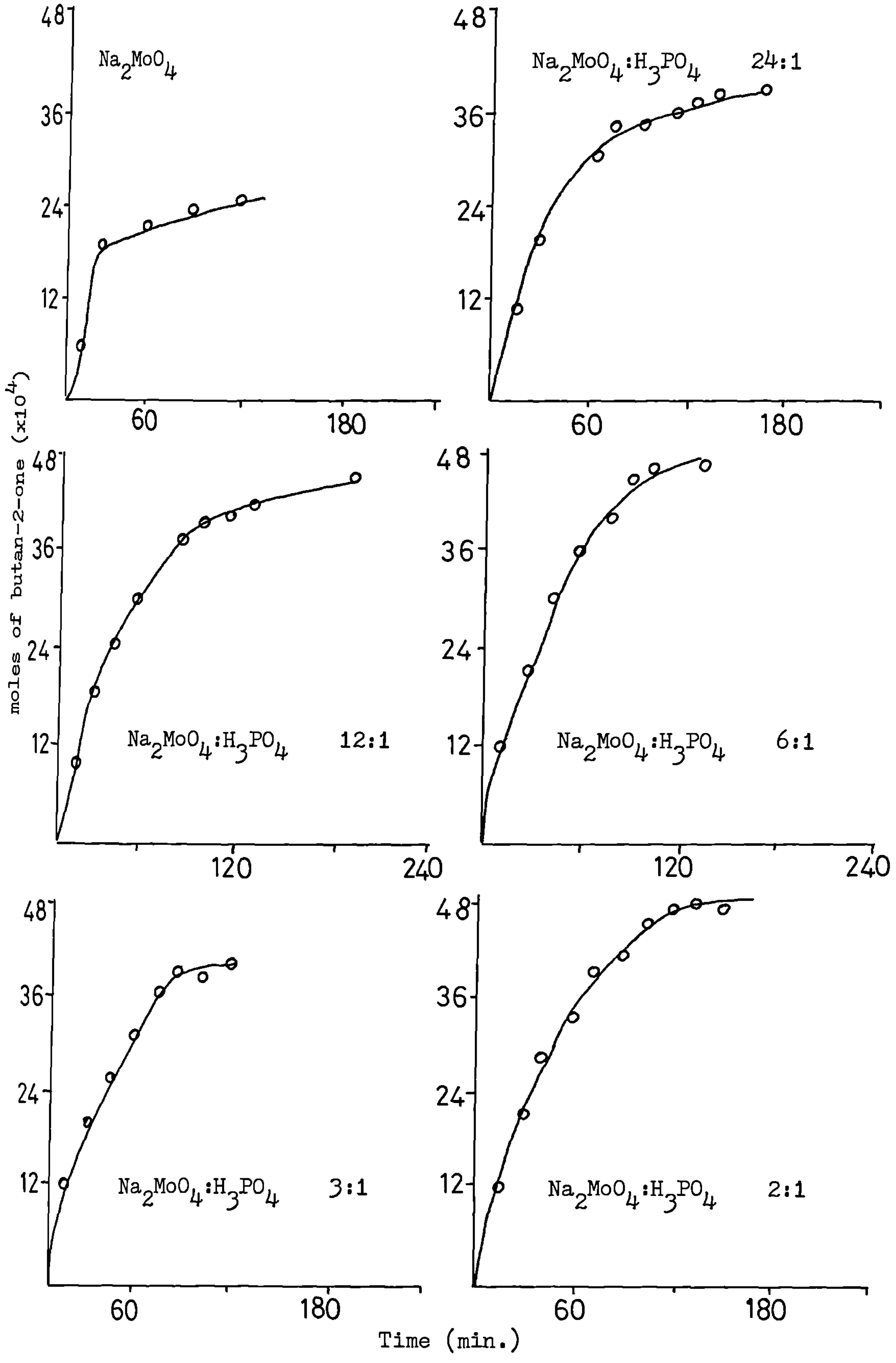


Figure 4d

Analar grade. PMo_6V_6 solutions were prepared as described in Chapter 3.

VO^{2+} absorbs in the visible spectrum at 768 nm whereas its oxidation product VO_2^+ does not. The intensity of this absorbance was used to monitor the amount of VO^{2+} present.

4.3.2 ESR Experiments

ESR experiments were done with the following settings. Scan range 1000G. Field set 3440G. Modulation amplitude 1g. Modulation frequency 100 K c.p.s. Receiver gain 6.3×10^{-5}. Microwave power 5mW. The samples were run in sealed glass capillaries.

4.3.3 Investigation of Components

As in previous experiments the concentration of $PdSO_4$ used was 4.95×10^{-3}M and the total volume of the solution was 10 cm^3 (10 mgs $PdSO_4$ in 10 cm^3). The Pd(II) to Mo(VI) ratio was fixed at 1:10.

The quantities of starting materials mixed to give the stated component ratios are given in Table 4.3.

The solutions were made up to total volumes of 10 cm^3 with $1MH_2SO_4$ in order to solubilise $PdSO_4$. The solutions were stirred for four hours before reaction. The solutions were then stirred under butene: O_2 in the ratio 1:1 in the apparatus shown in Figure 3f. The reactions were monitored by gas uptake and g.l.c. as before.

4.3.4 Comparisons Between $H_3PMo_{12}O_{40}$ and $H_9PMo_6V_6O_{40}$

$H_3PMo_{12}O_{40}$ solutions were prepared as follows. $H_3PMo_{12}O_{40}24H_2O$ (0.0931g) and $PdSO_4$ (10 mgs) were stirred in 10 cm^3 solvent for about four hours. The solvent was either water or aqueous $1MH_2SO_4$.

PMo_6V_6 solutions were prepared as described in Chapter 3. Where

Table 4.3

Component Ratio Pd:Mo:V : P	$PdSO_4$	$Na_2MoO_4 2H_2O$	VO_2^+ soln.(a)	H_3PO_4 soln.(b)
1 :10 - -	0.01g	0.1198g	-	-
1 : - :10 -	0.01g	-	5 cm^3	-
1 :10:10 -	0.01g	0.1198g	5 cm^3	-
1.2:12:- :1	0.01g	0.1198g	-	0.413 cm^3 (0.1M)
1.2:12:- :10	0.01g	0.1198g	-	0.413 cm^3 (1 M)
1.2:12:12:1	0.01g	0.1198g	5 cm^3	0.413 cm^3 (0.1M)
1.2:12:12:10	0.01g	0.1198g	5 cm^3	0.413 cm^3 (1 M)
1.2:- :12:2	0.01g	-	5 cm^3	0.826 cm^3 (0.1M)

(a) VO_2^+ stock solution was prepared as described in Chapter 3.

(b) H_3PO_4 solutions prepared by dissolving 85% H_3PO_4 in appropriate volumes of water.

Quantities of Heteropolyacid Components Used

$1MH_2SO_4$ was the required medium it replaced water in making up the total volume of 10 cm^3.

Excess phosphate was added as measured quantities of dilute H_3PO_4.

4.3.5 Optimising levels of PO_4^{3-}

These experiments were carried out in a reaction vessel of 50 cm^3 volume, therefore the volume of the solution used was increased to 20 cm^3 but the concentrations were the same as previously used. The stirring had been checked for efficiency (see Section 3.4.2b). A stock solution of $Na_2MoO_4 2H_2O$ and $PdSO_4$ in $1MH_2SO_4$ was prepared such that it was $4.95x10^{-3}M$ in $PdSO_4$ and $4.95x10^{-2}M$ in Na_2MoO_4. To 20 cm^3 portions of this solution were added appropriate quantities of H_3PO_4 to give the desired Mo:P ratio. The solutions were then stirred under butene:O_2 1:1. The reaction being monitored by gas uptake and g.l.c. analysis.

Ratio Mo:P	Quantity of H_3PO_4 added
24:1	41.3 μl (1M)
12:1	82.5 μl (1M)
6:1	165 μl (1M)
3:1	330 μl (1M)
2:1	247 μl (2M)

CHAPTER 5

A Study of $H_3PMo_{12}O_{40}$ as a Reoxidation Co-Catalyst

5.1 Introduction

Since $H_3PMo_{12}O_{40}$ proved to be a reasonable reoxidation catalyst in the palladium catalysed oxidation of butene a more detailed study of this compound was undertaken. It was hoped that a study of this compound, which is a defined single substance, would prove to be less complicated than the corresponding vanadium containing species and that a clearer understanding of its nature and mode of activity would lead to a better comprehension of the more complex vanadium containing analogues.

Initial experiments were concentrated on optimising the activity of $H_3PMo_{12}O_{40}$ in this type of reaction. A detailed spectroscopic study was then carried out in an attempt to determine the active species in solution in the oxidised and reduced forms.

5.2 Results and Discussion

5.2.1 Optimisation Experiments

Results of experiments to optimise the Pd:Mo ratio are shown in Figure 5a. As can be seen, in $1MH_2SO_4$ the optimum Pd:Mo ratio is 1:10. When the Pd:Mo ratio was fixed at 1:10 and the total concentration of the reactants was varied, the optimum was found to occur at $4.95x10^{-5}$ g ions Pd^{II} in a 10 cm^3 sample (See Figure 5b). At this concentration and a ratio of Pd:Mo of 1:10 the level of acidity was varied. The results are shown in Figure 5c. Figure 5d shows the results of a similar experiment for a Pd:Mo ratio of 1:5. In the case of Pd:Mo=1:10

Experiment to optimise Pd:Mo ratio in 1MH_2SO_4 with $PdSO_4$ ($4.95x10^{-5}$g ions/10 cm^3

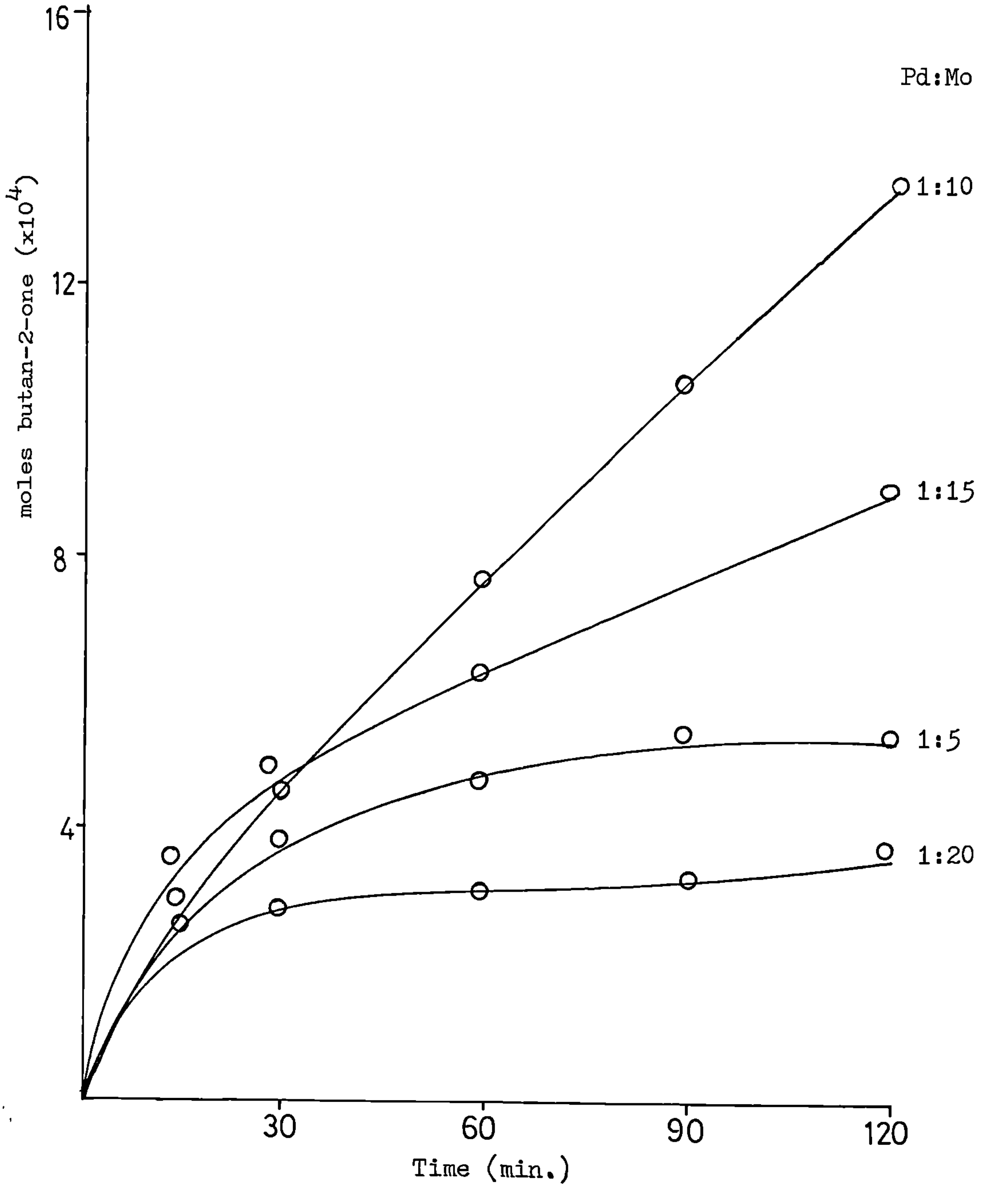


Figure 5a

Experiment to optimise catalyst concentration at Pd:Mo Ratio of 1:10 in $1M H_2SO_4$

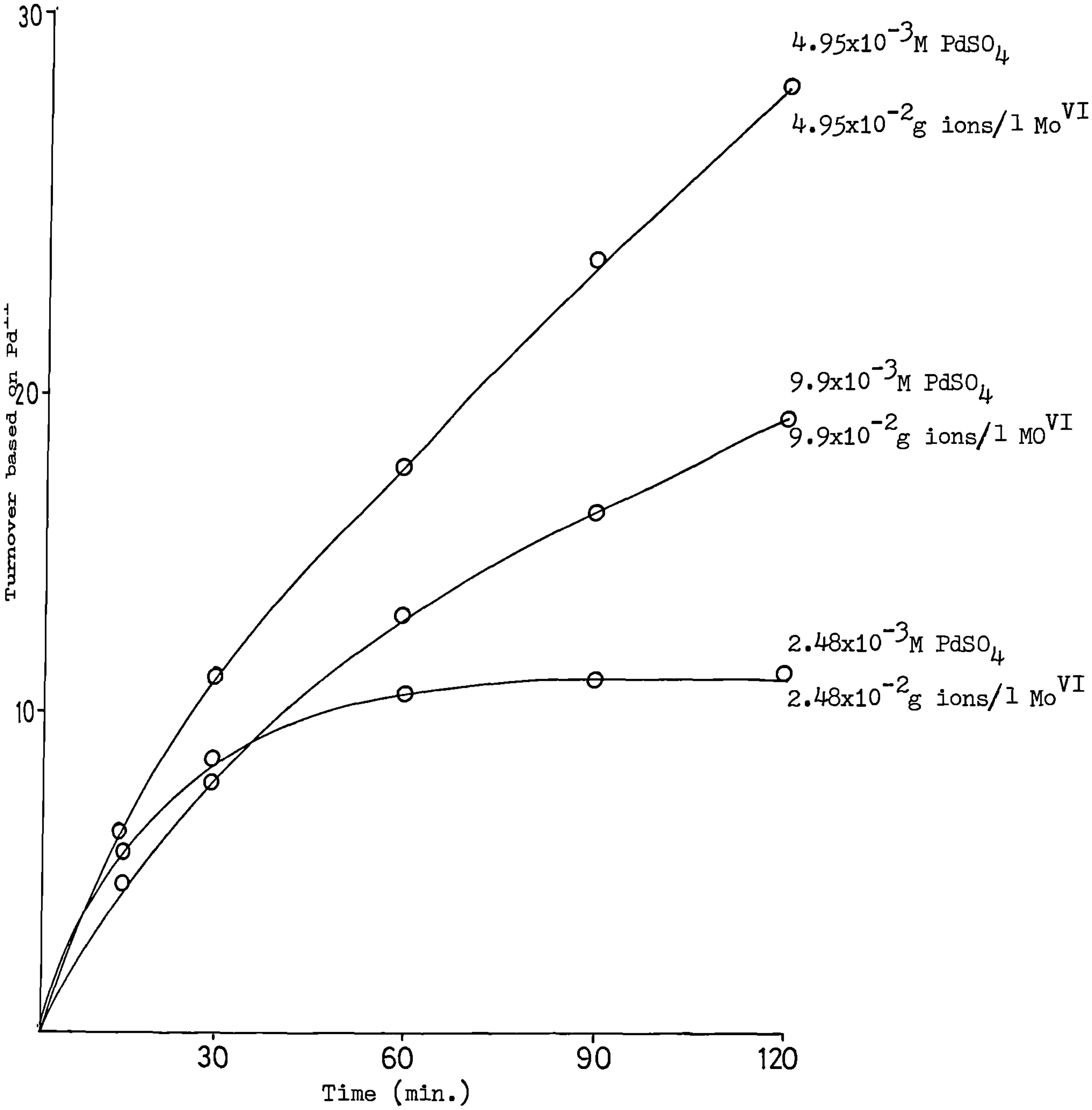


Figure 5b

Effect of Acid Concentration on:- 1, $PdSO_4$ ($4.95x10^{-3}M$) $H_3PMo_{12}O_{40}$ ($4.13x10^{-3}M$)

Pd:Mo 1:10

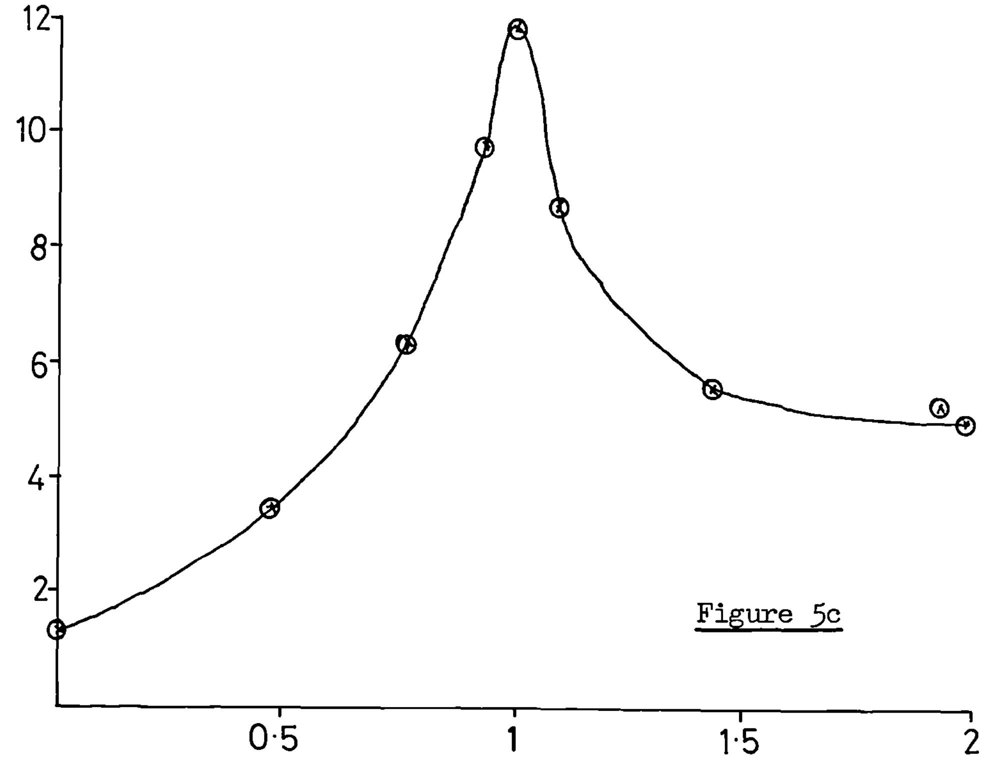


Figure 5c

2, $PdSO_4$ ($4.95x10^{-3}M$) $H_3PMo_{12}O_{40}$ ($2.06x10^{-3}M$)

Pd:Mo 1:5

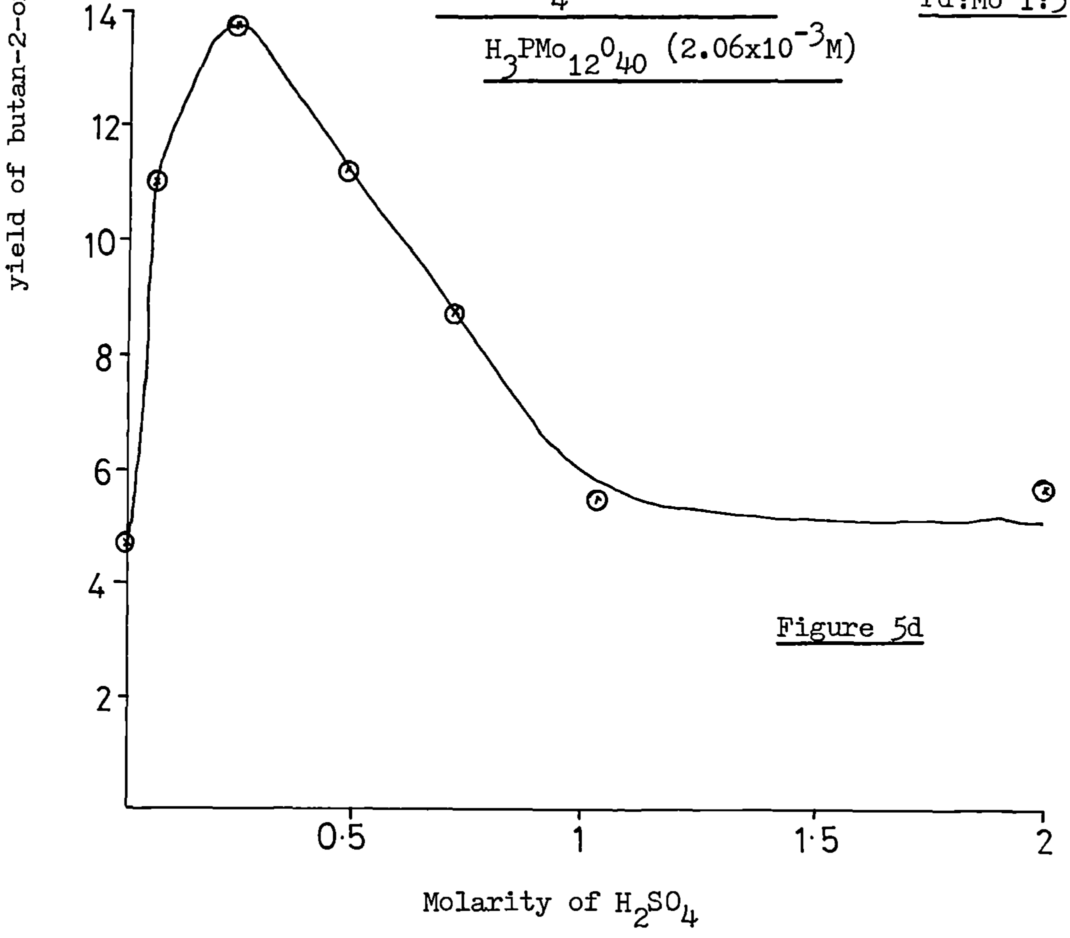


Figure 5d

the optimum acidity is $1MH_2SO_4$,but for Pd:Mo=1.5 the optimum is 0.25M H_2SO_4. When orthophosphoric acid was used in place of sulphuric acid the improvement over distilled water was small, even at high concentrations; this is probably due to the weaker nature of the H_3PO_4 acid.

Clearly, as might be expected, the different variables in this reaction are closely entwined and it is very difficult to draw any decisive information from these results. However, the following might be considered reasonable.

If the reoxidation of $H_3PMo_{12}O_{40}$ by oxygen follows the equation,

$$[H_3PMo_{12}O_{40}]^{2-} + \tfrac{1}{2}O_2 + 2H^+ \rightleftharpoons H_3PMo_{12}O_{40} + H_2O$$

the rate of reoxidation should be proportional to $[H^+]^2$ and should increase rapidly with increasing acidity.

As the measurements were recorded in terms of final yields of butan-2-one at two hours, it is not possible to determine accurately whether or not this is the case, but it is interesting to note that when the concentration of $H_3PMo_{12}O_{40}$ was halved (Pd:Mo=1:5) the acid concentration which gave the optimum butan-2-one yield was a quarter of that previously required (0.25M as compared with 1M for Pd:Mo=1:10). Thus up to the optimum acidity it seems likely that the rate of reoxidation of $H_3PMo_{12}O_{40}$ is the limiting factor and that it depends on $[H^+]^2$.

Two explanations are possible for the fall of the yields at $[H^+]$ greater than optimum, either the rate limiting step in the reaction changes to become inversely proportional to $[H^+]$ (see Section 1.2.1) as in the Wacker reaction; or the excess acid causes the breakdown of the active reoxidation species. The later is more likely since the fall in the yield in this region of acidity is caused more by the reaction coming to an end, than by a decrease in rate.

5.2.2 NMR Spectroscopic Studies (oxidised species)

^{31}P n.m.r. spectroscopic studies were initiated to determine the nature of $H_3PMo_{12}O_{40}$ in acid solutions. The data are shown in Table 5.1.

Table 5.1

Conditions	References (Chemical Shifts (ppm))		
	$85\%H_3PO_4$	PPh_3 in $(CD_3)_2CO$	$(MeO)_3PO$ in $CDCl_3$
$4.13x10^{-3}M$ in water	-1.31	4.69	-3.81
$4.13x10^{-3}M$ in $1MH_2SO_4$	-0.11	5.89	-2.5
$4.13x10^{-3}M$ in $1MH_2SO_4$, 50% dioxan	-0.11	5.89	-2.5
	-3.61	2.39	-6.11
$1.68x10^{-2}M$ in water	-1.31	4.69	-3.81
	-3.5	2.50	-6.0
$1g/cm^3$ in water	-3.77	2.23	-6.27
Literature(49)	-3.9	2.1	-6.4

Table of Chemical Shifts Recorded for $H_3PMo_{12}O_{40}$ in solution

Under the conditions most suitable for catalysis, i.e. $4.13x10^{-3}M$ $H_3PMo_{12}O_{40}$ in $1MH_2SO_4$, only one peak arises at -0.11 ppm with respect to 85% H_3PO_4. It seemed likely that this peak was due to free phosphoric acid, but this would not explain the fact that the presence of phosphate is essential for good reoxidation (see Chapter 4). Hence a rigorous test was applied to prove whether or not this peak could be assigned to H_3PO_4.

First, a series of spectra at different concentrations of H_2SO_4 were run using catalytic concentrations of $H_3PMo_{12}O_{40}$ ($4x10^{-3}M$). Table 5.2. This showed one peak at about 4.7 ppm at low acidities and a different one at 5.8 ppm at higher $[H^+]$, with respect to PPh_3. Both were present between 0.3M and 0.4M H_2SO_4 (Table 5.2).

Due to difficulties in accumulating spectra at such low concentrations the measurements were repeated using four times the concentration of $H_3PMo_{12}O_{40}$, Table 5.3. These spectra showed an extra peak at about 2.4 ppm, but the peaks of interest were still present so further work was done at this higher concentration in 0.75M H_2SO_4.

Table 5.2

Solvent	Shifts with respect to PPh_3 in $(CD_3)_2CO$ (ppm)	
water	4.69	
0.1MH_2SO_4	4.83	
0.2MH_2SO_4	4.80	
0.3MH_2SO_4	4.81 ,	5.95
0.4MH_2SO_4	4.79 ,	5.86
0.5MH_2SO_4		6.07
0.6MH_2SO_4		5.96
0.7MH_2SO_4		5.89
0.75MH_2SO_4		5.85
0.95MH_2SO_4		5.73
1MH_2SO_4		5.96

^{31}P Chemicals Shifts of $H_3PMo_{12}O_{40}$ (4.13×10^{-3}M) at different acidities

Table 5.3

Solvent	Shifts with respect to PPh_3 in $(CD_3)_2CO$ (ppm)		
water	2.50 ,	4.70	
0.5MH_2SO_4	2.41 ,	4.70	
0.75MH_2SO_4	2.41 ,	4.72 ,	5.89
1MH_2SO_4			5.73

^{31}P Chemical Shifts of $H_3PMo_{12}O_{40}$ (1.68×10^{-2}M) at different acidities

Increasing quantities of shift reagents were added to the solutions and the new positions of the peaks recorded. At maximum shift free phosphoric acid was then added to the samples. The results are shown in Tables 5.4 and 5.5 and Figure 5e.

Table 5.4

[$Eu(NO_3)_3$]	[H_3PO_4]	Shifts with respect to PPh_3 in $(CD_3)_2CO$ (ppm)		
0	0	2.23,	4.49,	5.59
$4.2\mathrm{x}10^{-3}$M	0	2.27,	4.53,	5.01
$8.4\mathrm{x}10^{-3}$M	0	2.21,	4.48,	4.34
$1.26\mathrm{x}10^{-2}$M	0	2.20,	4.49,	3.78
$1.68\mathrm{x}10^{-2}$M	0	2.01,	4.29,	3.01
$1.68\mathrm{x}10^{-2}$M	$1.65\mathrm{x}10^{-3}$M	2.06,	4.38,	2.97
$1.68\mathrm{x}10^{-2}$M	$6.4\ \mathrm{x}10^{-3}$M	2.07,	4.39,	3.07
$1.68\mathrm{x}10^{-2}$M	$1.65\mathrm{x}10^{-2}$M	2.22,	4.52,	3.31

^{31}P Chemical Shifts of $H_3PMo_{12}O_{40}$ ($1.68\mathrm{x}10^{-2}$M) in $0.75MH_2SO_4$ with $Eu(NO_3)_3$ Shift Reagent

Table 5.5

[$Pr(NO_3)_3$]	[H_3PO_4]	Shifts with respect to PPh_3 in $(CD_3)_2CO$(ppm)		
0	0	2.23,	4.49,	5.59
$4.2\mathrm{X}10^{-3}$M	0	2.19,	4.45,	5.77
$8.4\mathrm{x}10^{-3}$M	0	2.13,	4.39,	6.03
$1.26\mathrm{x}10^{-2}$M	0	2.08,	4.35,	6.19
$1.68\mathrm{x}10^{-2}$M	0	2.16,	4.41,	6.42
$1.68\mathrm{x}10^{-2}$M	$1.65\mathrm{x}10^{-3}$M	2.13,	4.37,	6.44
$1.68\mathrm{x}10^{-2}$M	$1.4\ \mathrm{x}10^{-3}$M	2.13,	4.39,	6.49
$1.68\mathrm{x}10^{-2}$M	$1.65\mathrm{x}10^{-2}$M	2.21,	4.46,	6.55

^{31}P Chemical Shifts of $H_3PMo_{12}O_{40}$ ($1.68\mathrm{x}10^{-2}$M) in $0.75MH_2SO_4$ with $Pr(NO_3)_3$ Shift Reagent

Graphs to Show Variation of ^{31}P Chemical Shift of H_3PO_4 with Concentration of Shift Reagents

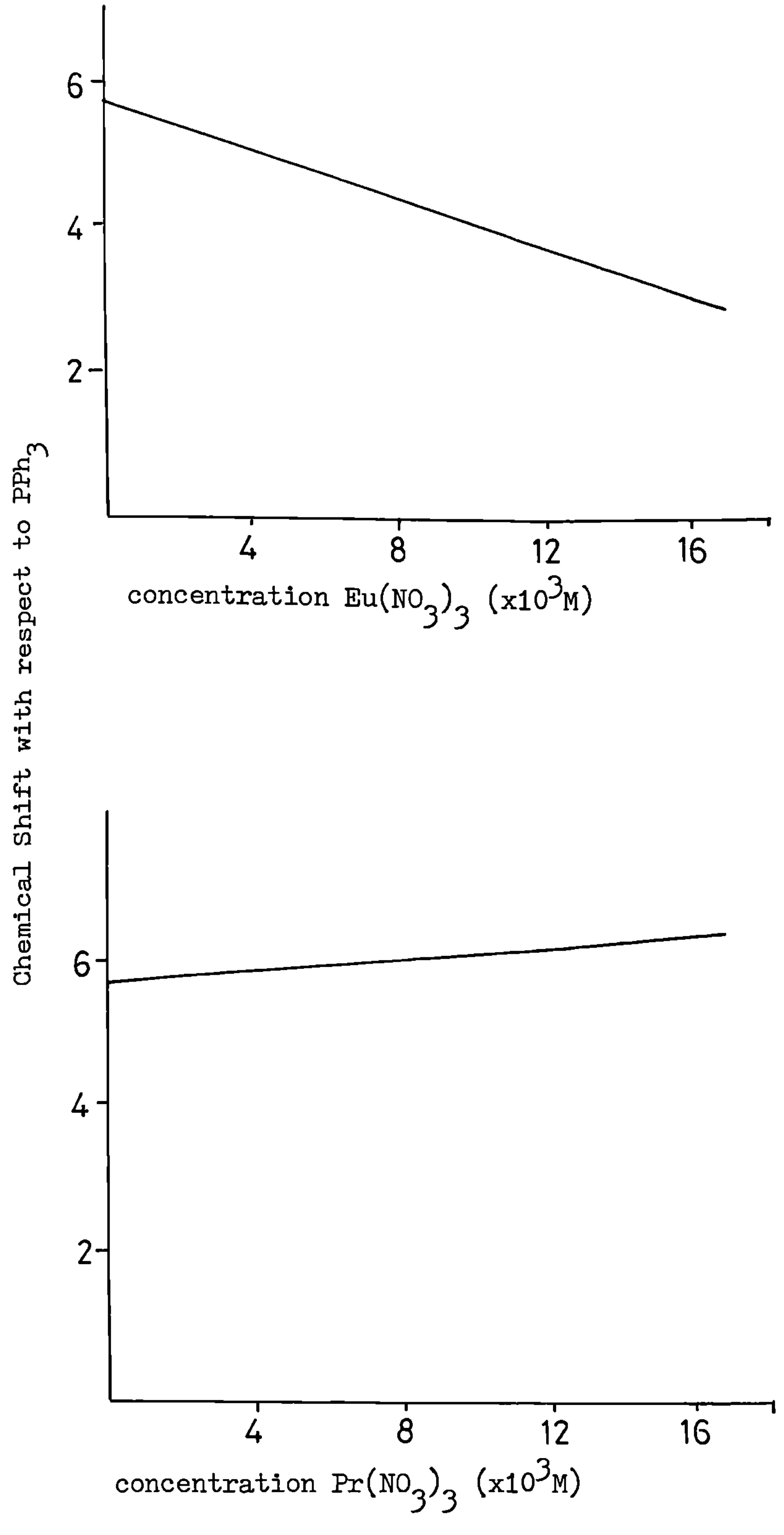


Figure 5e

As can be seen, in both cases the peak at 5.6 ppm is shifted much more than the other two peaks, indicating that the phosphorus is more exposed to the influence of the shift reagents in solution for this signal than the other two. This would be expected if the peaks at 2.2 ppm and 4.5 ppm are due to polyacid forms in which the phosphorus is encased, while the peak at 5.6 ppm is free phosphate. Also, addition of orthophosphoric acid to the shifted samples does not give rise to an additional peak in either the $Eu(NO_3)_3$ or $Pr(NO_3)_3$ shifted examples, but an increase in the intensity of the peak at 3 ppm (Eu^{3+}) and the corresponding peak at 6.4 ppm (Pr^{3+}) is observed. While it might have been possible for a compound to have the same chemical shift as phosphoric acid under one set of conditions, it is very unlikely for it to do so under three sets of conditions. Hence the peak at 5.59 ppm with respect to PPh_3 is due to free phosphoric acid.

On the basis of literature results$^{(49)}$ and the fact that $H_3PMo_{12}O_{40}$ is more unstable to degradation in dilute solutions (see Chapter 1) but can be stabilised in the presence of dioxan,$^{(38)}$ the peak at -3.7 ppm (Table 5.1) with respect to 85% H_3PO_4 (2.23 ppm with respect to PPh_3) is assigned to $H_3PMo_{12}O_{40}$, whilst the peak at -1.31 ppm with respect to 85% H_3PO_4 (4.69 ppm with respect to PPh_3) is assigned to an unknown, intermediate degradation product.

If the phosphorus in $H_3PMo_{12}O_{40}$ exists as free phosphoric acid in the solutions in which the compound is most active as an oxidising catalyst, the role of the phosphorus in these reactions is far from obvious. One possibility is that phosphate acts as a template allowing the molybdenums to form some structure which they could not form in its absence. This theory was tested by ^{95}Mo n.m.r. spectroscopy. The results show (Table 5.6) that a template effect is unlikely to be the explanation,since the same species that is generated by $H_3PMo_{12}O_{40}$ in $1MH_2SO_4$ is also observed when Na_2MoO_4 is dissolved in the same medium.

Table 5.6

Sample	Chemical Shift with respect to $2MNa_2MoO_4$ pH11 (ppm)
$H_3PMo_{12}O_{40}$ $1.65\times10^{-2}M$ in water	-2.87 (very broad)
$H_3PMo_{12}O_{40}$ $4.13\times10^{-3}M$ in $1MH_2SO_4$	-66.53 (broad)
Na_2MoO_4 $4.95\times10^{-2}M$ in $1MH_2SO_4$	-66.53 (broad)

^{95}Mo n.m.r. to Determine Species in Solution

Thus we have,

$$\begin{tikzcd}
H_3PMo_{12}O_{40} \arrow[r, "1MH_2SO_4"] & H_3PO_4 + \text{"Molybdate"} \\
& Na_2MoO_4 \arrow[u, "1MH_2SO_4"']
\end{tikzcd}$$

However it is possible that a small amount of phosphorus forms a PMo species in an amount which is undetected by n.m.r. spectroscopy.

5.2.3 NMR Spectroscopy Studies (Reduced Species)

From the previous results,phosphate seems not to participate to a significant degree in oxidised heteropolyacid formation in $1MH_2SO_4$; the alternative possibility is that the phosphate becomes reassociated with the molybdate once the system has been reduced. In order to investigate this, ^{31}P n.m.r. spectroscopy was carried out using solutions which had been theoretically reduced by 2e per $H_3PMo_{12}O_{40}$ (see Experimental 5.3.3.2). These experiments were done on a Bruker WH 400 in which the magnetic field is parallel to the axis of the sample tube, hence, since external referencing was used,the chemical shifts recorded are different from those

Table 5.7

Sample	Chemical Shifts with respect to PPh_3 in $(CD_3)_2CO$ (ppm)[(a)]		
1) Oxidised samples			
$H_3PMo_{12}O_{40}$ $4.13 \times 10^{-3}M$ in water	0.94,	3.20,	4.29
$0.3M H_2SO_4$	0.66,	2.96,	4.04
$1M H_2SO_4$			4.41
2) Reduced samples			
$H_3PMo_{12}O_{40}$ $4.13 \times 10^{-3}M$ in $1M H_2SO_4$			4.41
$H_3PMo_{12}O_{40}$ $4.13 \times 10^{-3}M$ + $Pr(NO_3)_3$ ($3 mgs/cm^3$) in $1M H_2SO_4$		4.87	
$H_3PMo_{12}O_{40}$ $4.13 \times 10^{-3}M$ + $Pr(NO_3)_3$ ($3 mgs/cm^3$) + H_3PO_4 $4.13 \times 10^{-3}M$ in $1M H_2SO_4$		4.91	
$H_3PMo_{12}O_{40}$ $4.13 \times 10^{-3}M$ + $Eu(NO_3)_3$ ($2 mgs/cm^3$) in $1M H_2SO_4$		3.71	
$H_3PMo_{12}O_{40}$ $4.13 \times 10^{-3}M$ + $Eu(NO_3)_3$ ($2 mgs/cm^3$) + H_3PO_4 $4.13 \times 10^{-3}M$ in $1M H_2SO_4$		3.71	

(a) 50 mgs/cm^3

^{31}P Chemical Shifts of $H_3PMo_{12}O_{40}$ recorded on Bruker WH 400 on the Jeol JNM-PS 100 which has the field perpendicular to the sample. However, as with the oxidised form, at catalyst concentrations (4.95×10^{-3}M $PdSO_4$, 4.13×10^{-3}M $H_3PMo_{12}O_{40}$) in 1MH_2SO_4 only one peak was detected at 4.41 ppm (with respect to PPh_3). The results, including those of an experiment with shift reagents, are shown in Table 5.7.

The coincidence of this peak and the phosphoric acid peak, even after shifts had been induced, showed that the signal at 4.41 ppm was again due to phosphoric acid.

In order to determine how much of the phosphorus in $H_3PMo_{12}O_{40}$ is released as free phosphoric acid in 1MH_2SO_4, a quantitative experiment was carried out in which samples of free phosphoric acid, oxidised $H_3PMo_{12}O_{40}$ and reduced $H_3PMo_{12}O_{40}$ in 1MH_2SO_4 were run for equal numbers of scans using PPh_3 (50 mgs/ml) in $(CD_3)_2CO$ as an external reference (shift and quantitative reference). A relatively large amount of time was allowed between each pulse so that equilibrium could be reattained after each scan. Using this method the integrals of the peak at 4.41 ppm should be accurate to ±10%. The results are shown in Table 5.8.

Table 5.8

Sample	Concentration	Integral[(a)]	Concentrated H_3PO_4
H_3PO_4	2.32×10^{-3}M	2.26	2.32×10^{-3}M
$H_3PMo_{12}O_{40}$	4.13×10^{-3}M	2.12	2.18×10^{-3}M
$H_3PMo_{12}O_{40}$ reduced by 2e	4.13×10^{-3}M	2.27	2.33×10^{-3}M

(a) Adjusted in proportion with the integral of PPh_3 Peak

Table to Show Amounts of Free H_3PO_4 in Samples of $H_3PMo_{12}O_{40}$ (4.13×10^{-3}M)

About 45% of the phosphorus present in the $H_3PMo_{12}O_{40}$ is not observed in the spectra. The difference between the oxidised and the reduced forms is within experimental error. The most plausible explanation of the undetected phosphorus is the existence of an equilibrium of intermediate speed, which does not involve phosphoric acid,and gives rise to very broad signals which are not detected in the presence of the sharp H_3PO_4 signal.

A detailed variable temperature study should give more information about such an equilibrium. Only preliminary experiments have been carried out here.

The results are shown in Table 5.9.

Table 5.9

Temperature	Chemical Shifts with respect to PPh_3 in DMSO d_6 (ppm)
20°C	6.03
50°C	5.05
80°C	3.9 (7),$^{(a)}$ 5.3 (2)

(a) Relative Intensities

Table to Show the Effect of Variable Temperature on ^{31}P n.m.r. Spectra of $H_3PMo_{12}O_{40}$ (4.13×10^{-3}M in $1MH_2SO_4$)

In order to accommodate the higher temperatures,the method of referencing was changed to external PPh_3 (50 mgs/cm^3 in DMSO d_6).

It can be seen that the reference and phosphoric acid signals move closer together at higher temperatures, but the most interesting result is the occurrence of a second small peak at 80°C,providing evidence for the existence of an equilibrium involving previously undetected species.

This, together with previously described results, implies that the species which is active for the reoxidation reaction under the optimum conditions found for $H_3PMo_{12}O_{40}$ is only a minor component of a mixture of species present, and that it is some form of phosphomolybdate.

Only speculation as to the nature of this species is possible. It has already been suggested that the optimum P:Mo ratio of 1:12 (see Chapter 4) indicates that the active PMo_x species has a larger number of molybdenums per phosphorus than 12 to 1. The fact that this species is very difficult to detect by n.m.r. spectroscopy supports this, since a large cluster would give a very broad signal in the ^{95}Mo n.m.r. spectrum which would not be detected in the presence of a sharper resonance. Also, phosphorus at the centre of a larger cluster would be more difficult to detect in the ^{31}P n.m.r. spectrum.

However, it is generally believed (see Chapter 1) that $H_3PMo_{12}O_{40}$ at low concentrations in acidic solution is degraded to smaller polyanions, and our n.m.r. spectroscopy data show that more than half of the phosphomolybdic acid is dissociated to give H_3PO_4 and some isomolybdate. Hence, it might be expected that any undetected species are more likely to be transitionary stages in this degradation.

5.2.4 Visible Spectroscopy Investigations of reduced $H_3PMo_{12}O_{40}$

$H_3PMo_{12}O_{40}$ changes colour from yellow in water or clear in $1MH_2SO_4$ to deep blue once it is reduced. This intense absorbance in the red was used to monitor some properties of the reduced species. This colour change does not occur on reduction of Na_2MoO_4 in $1MH_2SO_4$. This gives further evidence for interaction between phosphorus and molybdenum in solutions of $H_3PMo_{12}O_{40}$ in $1MH_2SO_4$,although this was not detected readily by n.m.r. spectroscopy.

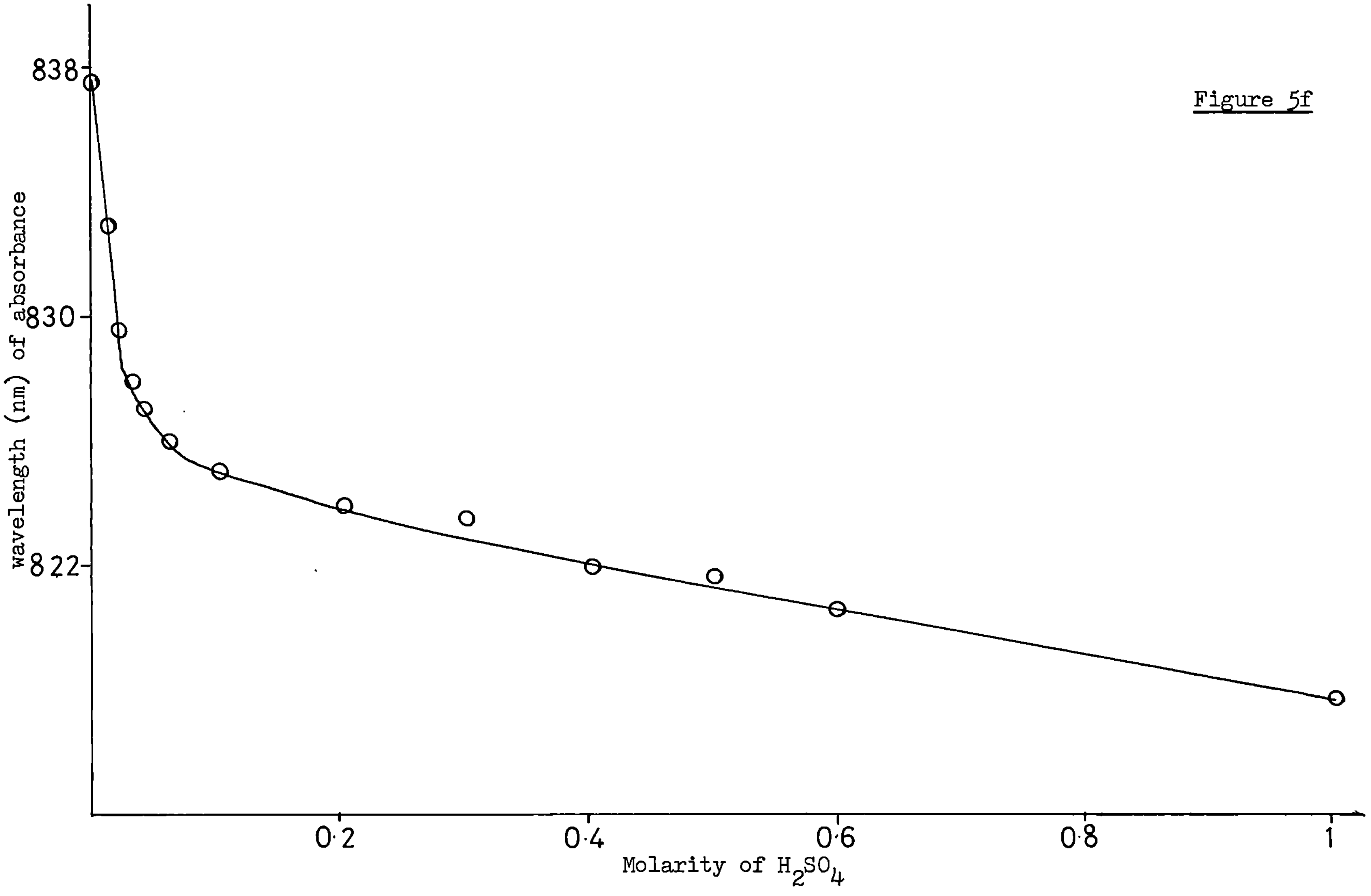
Initial experiments were carried out using ascorbic acid as the reducing agent. Reductions were carried out in water and $1MH_2SO_4$. While the position of the absorbance was found to depend on the acidity of the medium,the absorbance was independent of the theoretical degree of reduction. The dependence on acidity is depicted in Figure 5f. This result can be explained in two ways. Either in terms of two species, one which exists at molarities of H_2SO_4 below 0.05 and is very sensitive to pH and one which exists at H_2SO_4 molarities above 0.05 and is less pH sensitive; or in terms of a single species whose first protonation sphere is complete at $0.05MH_2SO_4$, hence any further protons have little effect.

Although the position of the absorbance was independent of the degree of reduction, the intensity of absorbance was roughly proportional to the degree of reduction, up to 4e in water, but only up to 2e in $1MH_2SO_4$. It was found that exposure to O_2 had no effect on the final results,and in fact the $H_3PMo_{12}O_{40}$ once reduced by ascorbic acid, could not be reoxidised by O_2.

Since ascorbic acid appeared not to be a very good mimic for the reductant in the catalyst system, as no reoxidation of the $H_3PMo_{12}O_{40}$ could be achieved, the reduced species was generated by palladium and an olefin. The liquid olefin hex-1-ene was found to be the most convenient, with $PdSO_4$ as the Pd(II) salt. Again the position of absorbance in the visible spectrum of the reduced $H_3PMo_{12}O_{40}$ was independent of the degree of reduction. It occurred at 818 nm in $1MH_2SO_4$ as before, but it was found that reoxidation occurred slowly in water and rapidly in

Variation of absorbance maximum with acidity for $H_3PMo_{12}O_{40}$, 4.13×10^{-3}M reduced by 2e with ascorbic acid

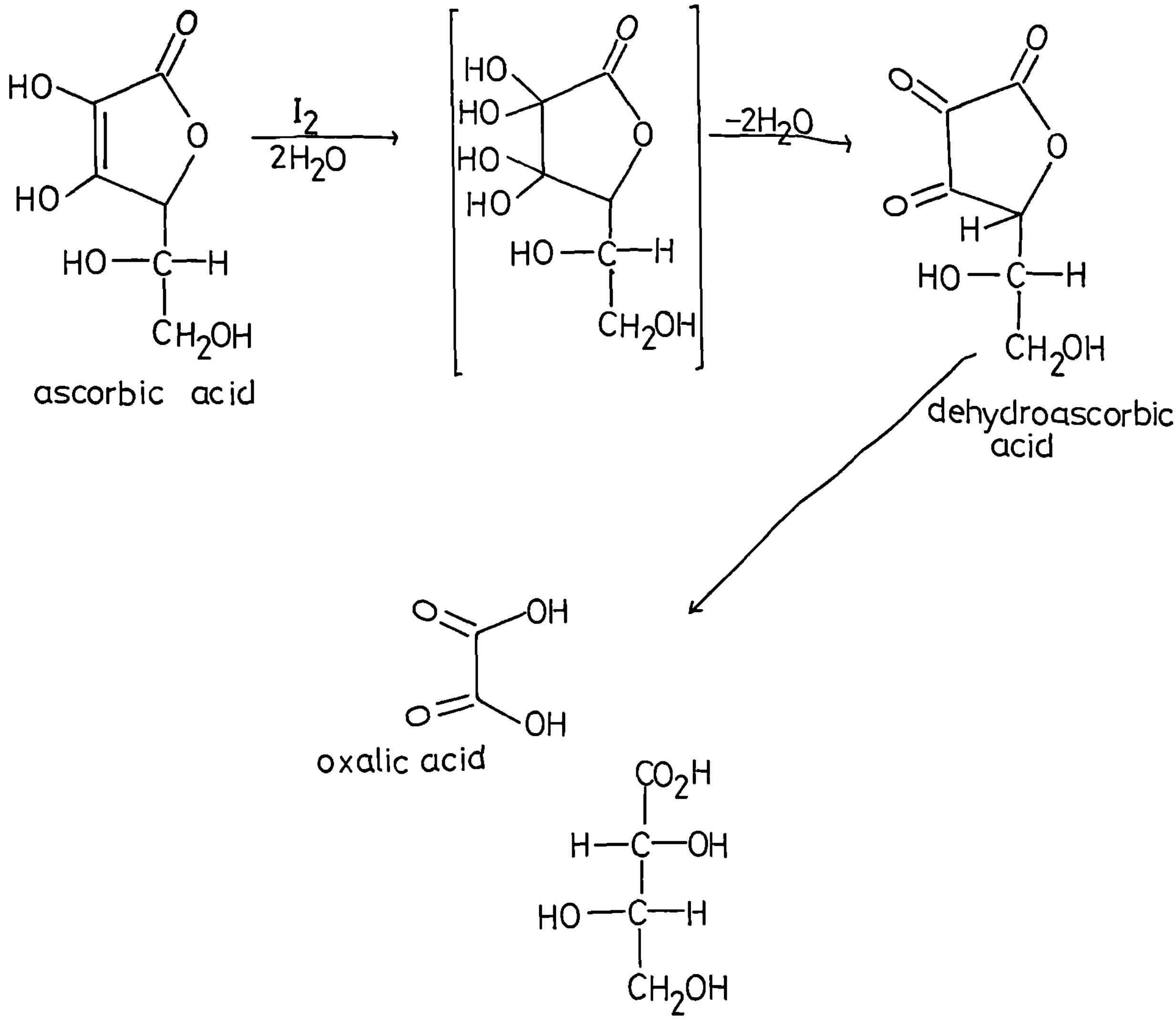
Figure 5f



1MH_2SO_4 with O_2 under these conditions. The extent of oxidation was measured in terms of the increase in the intensity of the absorbance at 818 nm.

To check that the absence of $PdSO_4$ in the ascorbic acid reactions was not the deciding factor, the ascorbic acid experiment was repeated using a catalyst solution containing $PdSO_4$ (4.95×10^{-3}M), but reoxidation still did not occur. Hence ascorbic acid or its' oxidation products were inhibiting the reoxidation process.

The oxidation of ascorbic acid proceeds as follows(75)



5.2.5 Inhibition of Reoxidation

The experiments using hex-1-ene in the presence of $PdSO_4$ as a reducing agent for $H_3PMo_{12}O_{40}$ ($4.13\times10^{-3}M$) in $1MH_2SO_4$ were now repeated with the addition of a selection of organic compounds at concentrations of $4.95\times10^{-3}M$. The results of attempts to reoxidise these samples are shown in Table 5.10.

Table 5.10

Substances which inhibited the reoxidation(b) of $H_3PMo_{12}O_{40}$	Substances which did not inhibit the reoxidation(b) of $H_3PMo_{12}O_{40}$
dehydroascorbic acid(a)	oxalic acid
butyraldehyde	butan-2-one
acetaldehyde	butyric acid
formaldehyde	

(a) Generated by treating ascorbic acid with 1 equivalent of I_2.

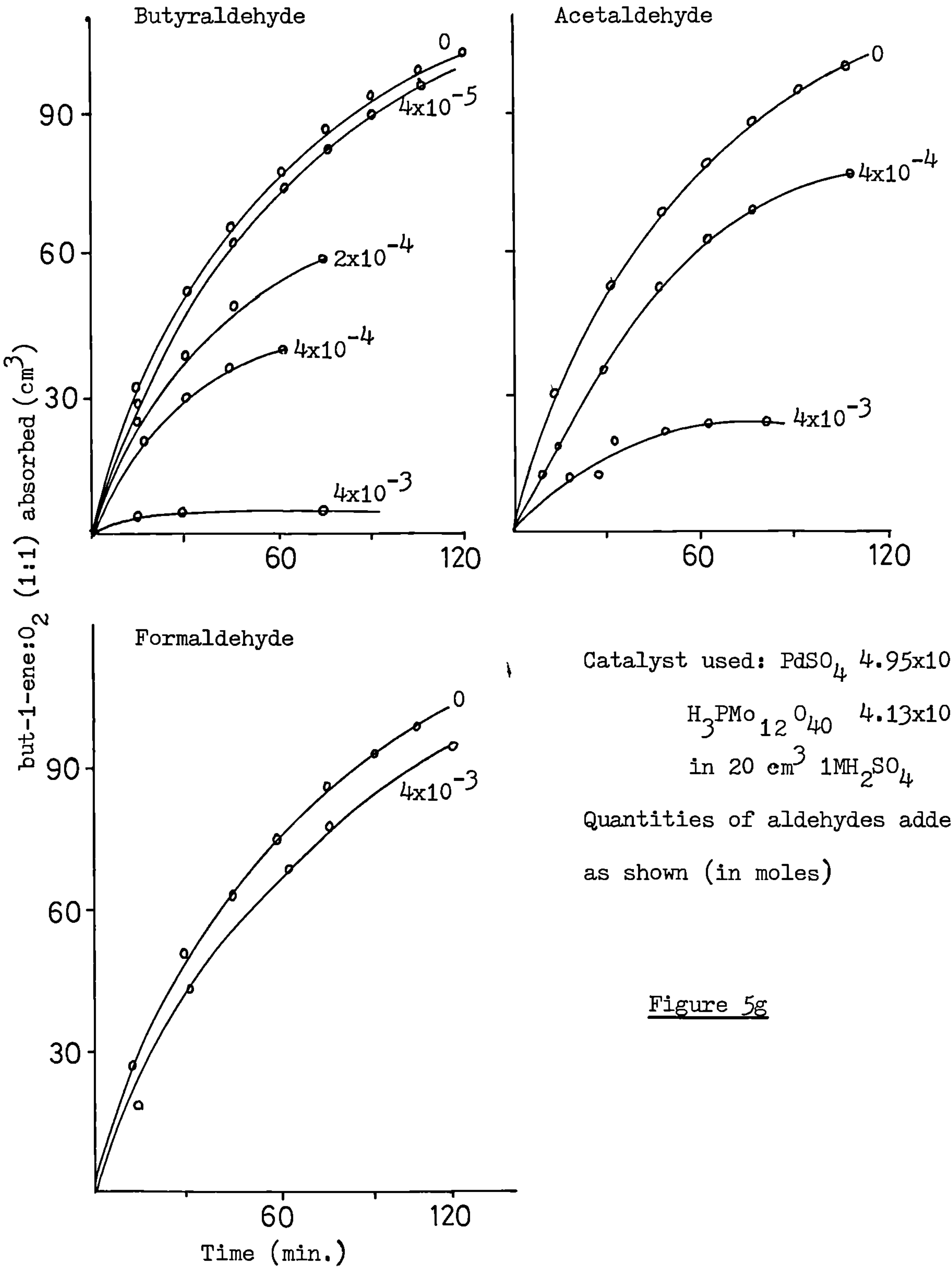
(b) Followed by measuring absorbance of 818 nm.

Results of Experiments to Check Inhibitory Effects of Some Organic Compounds on the Reoxidation of Reduced $H_3PMo_{12}O_{40}$

Several of these substances were found to inhibit reoxidation. In the ascorbic acid system dehydroascorbic acid seems to be the inhibitor. From the other results it can be seen that aldehydes inhibit reoxidation, while ketones and acids do not.

The inhibitory effects of aldehydes were also tested in catalytic runs ($PdSO_4$ $4.95\times10^{-3}M$, $H_3PMo_{12}O_{40}$ $4.13\times10^{-3}M$ in $1MH_2SO_4$ (20 cm^3) stirred under butene:O_2 1:1). The results which were monitored by g.l.c. are shown in Figure 5g. The result for PMo_6V_6 (solution prepared as in

Graphs to Show the Inhibitory effects of Aldehydes on the Oxidation of but-1-ene



Catalyst used: $PdSO_4$ $4.95x10^{-3}$ M

$H_3PMo_{12}O_{40}$ $4.13x10^{-3}$ M

in 20 cm^3 1MH_2SO_4

Quantities of aldehydes added as shown (in moles)

Figure 5g

Chapter 3) with added butyraldehyde is also shown in Figure 5h.

The order of inhibition by aldehydes is

$$CH_3CH_2CH_2CHO > CH_3CHO > HCHO$$

$H_3PMo_{12}O_{40}$ systems are more readily inhibited than PMo_6V_6, systems.

How the aldehydes act to inhibit oxidation is not clear. Initially an adduct such as that identified by Klemperer and Shum (76-78) (Figure 5i) was favoured,

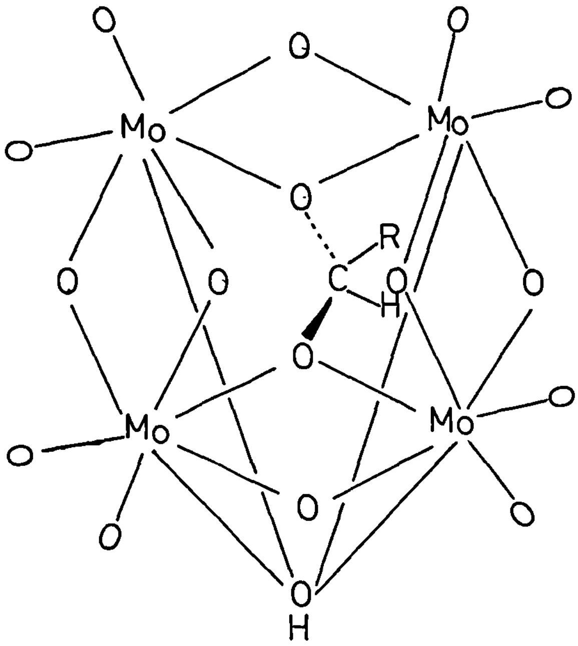
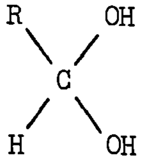


Figure 5i

but the aldehydes with a larger proportion of the hydrated form



would be expected to form this adduct more readily. However, the order of inhibition is the reverse to that of increasing hydration.

(HCHO > MeCHO > PrCHO)

Production of the corresponding acids either as a competing reaction or as inhibitory agents can also be ruled out since no acid production was

Graph to Show the Effect of Butyraldehyde on the $PdSO_4 - H_9PMo_6V_6O_{40}$ system

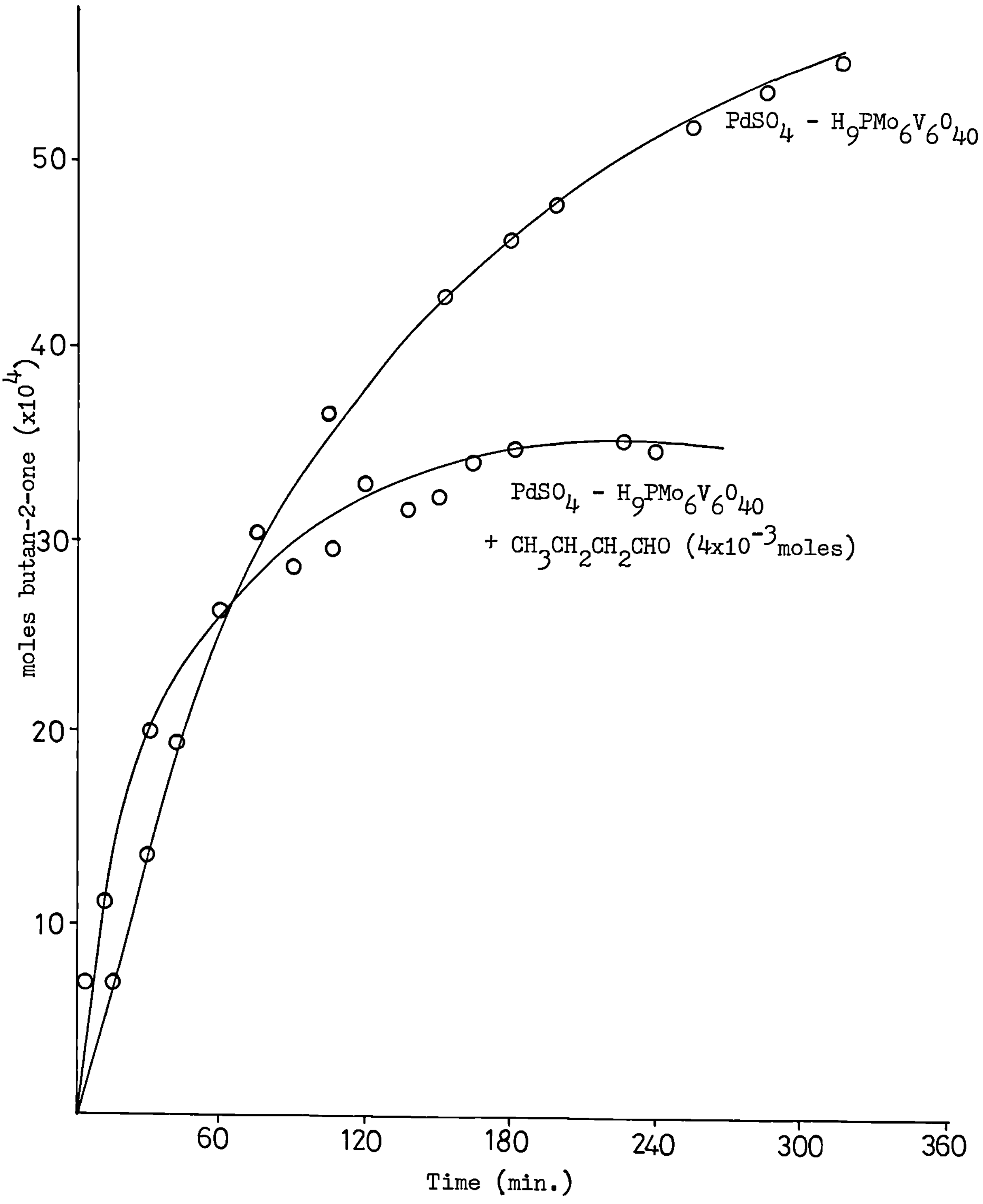


Figure 5h

detected by g.l.c., and acids do not seem to be oxidation inhibitors. It seems most likely that the aldehydes do co-ordinate in some way to the outer oxygens of the polyacid via H-bridges, and inhibit the oxidation by preventing interaction with O_2 in the same way as other organic solvents (see Chapter 2).

A butyraldehyde adduct of the $(Ph_4As)_3PMo_{12}O_{40}$ has been prepared for both the oxidised and reduced forms. The presence of butyraldehyde has been confirmed by i.r., Figures 5j and 5k. The peaks in the 3000 to 2850 cm^{-1} region are due to the alkyl stretches of butyraldehyde and can be clearly seen superimposed on the $(Ph_4As)_3PMo_{12}O_{40}$ spectra (Figure 5l). The peak at 1820 - 30 cm^{-1} in the butyraldehyde adducts is due to the carbonyl stretch of butyraldehyde. A spectrum of butyraldehyde is given for comparison in Figure 5m.

Production of butyraldehyde is not a significant factor in the oxidation of but-1-ene with $PdSO_4$- heteropolyacids. No butyraldehyde was detected in these reactions. (Concentrations of 1% butyraldehyde of the butan-2-one concentration would be detected by the g.l.c. method used).

5.3 Experimental

5.3.1 Reactions to Optimise $H_3PMo_{12}O_{40}$ as a Redox Catalyst

5.3.1.1 Varying the Pd:Mo Ratio

Solutions were prepared by stirring $PdSO_4$, 10 mgs (4.95×10^{-5} moles) with varying amounts of $H_3PMo_{12}O_{40}24H_2O$ in 10 cm^3. 1MH_2SO_4.

Amount of $H_3PMo_{12}O_{40}$	Pd:Mo
0.1862g (8.26×10^{-5} moles)	1:20
0.1396g (7.43×10^{-5} moles)	1:15
0.0931g (4.13×10^{-5} moles)	1:10
0.0465g (2.06×10^{-5} moles)	1:5

Infrared Spectra of "$(PH_4As)_3PMo_{12}O_{40}$" (Oxidised) Precipitated from solutions with and without Butyraldehyde

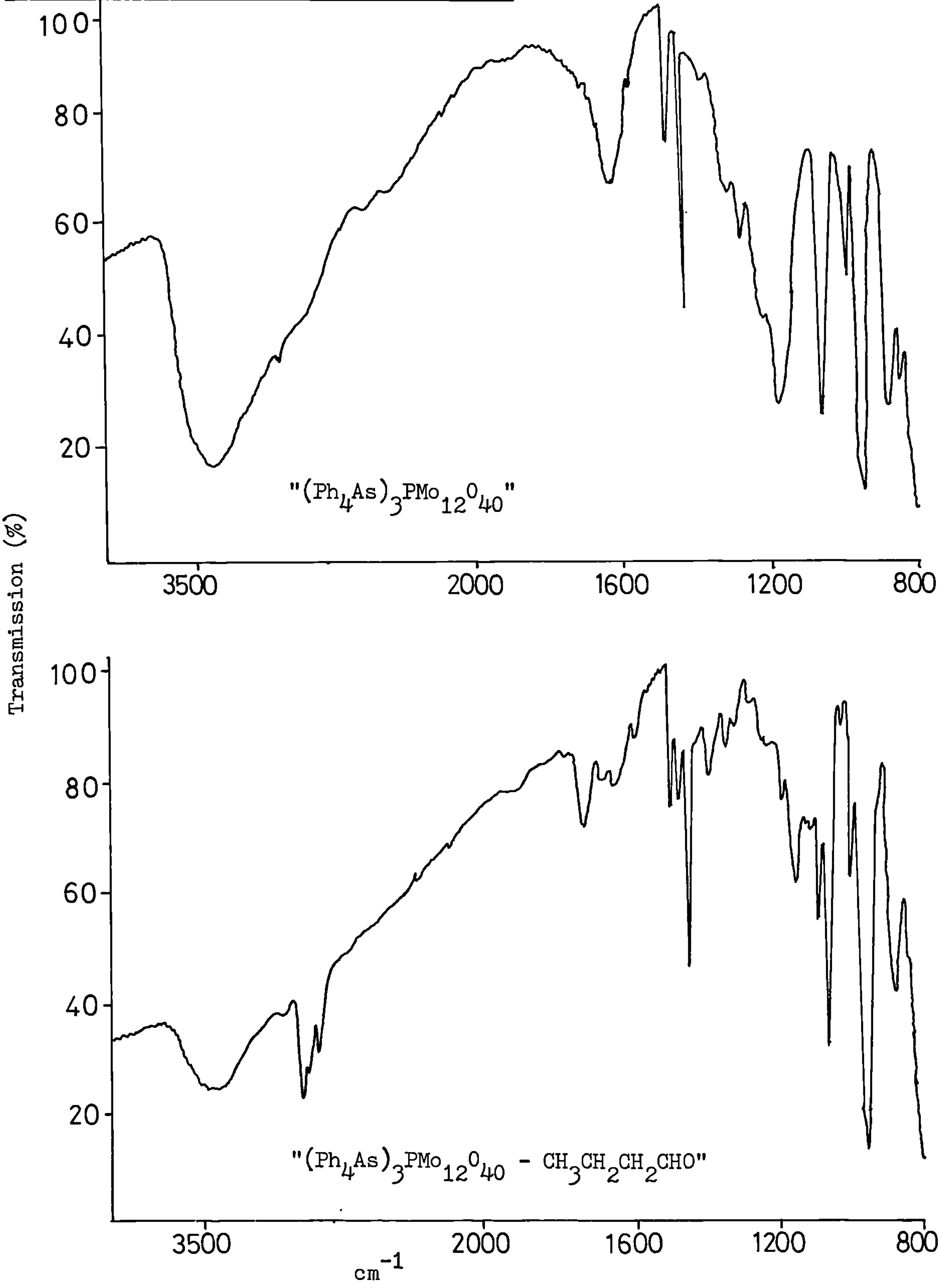


Figure 5j

Infrared Spectra of "$(Ph_4As)_3PMo_{12}O_{40}$" (Reduced) Precipitated from Solutions with and without Butyraldehyde

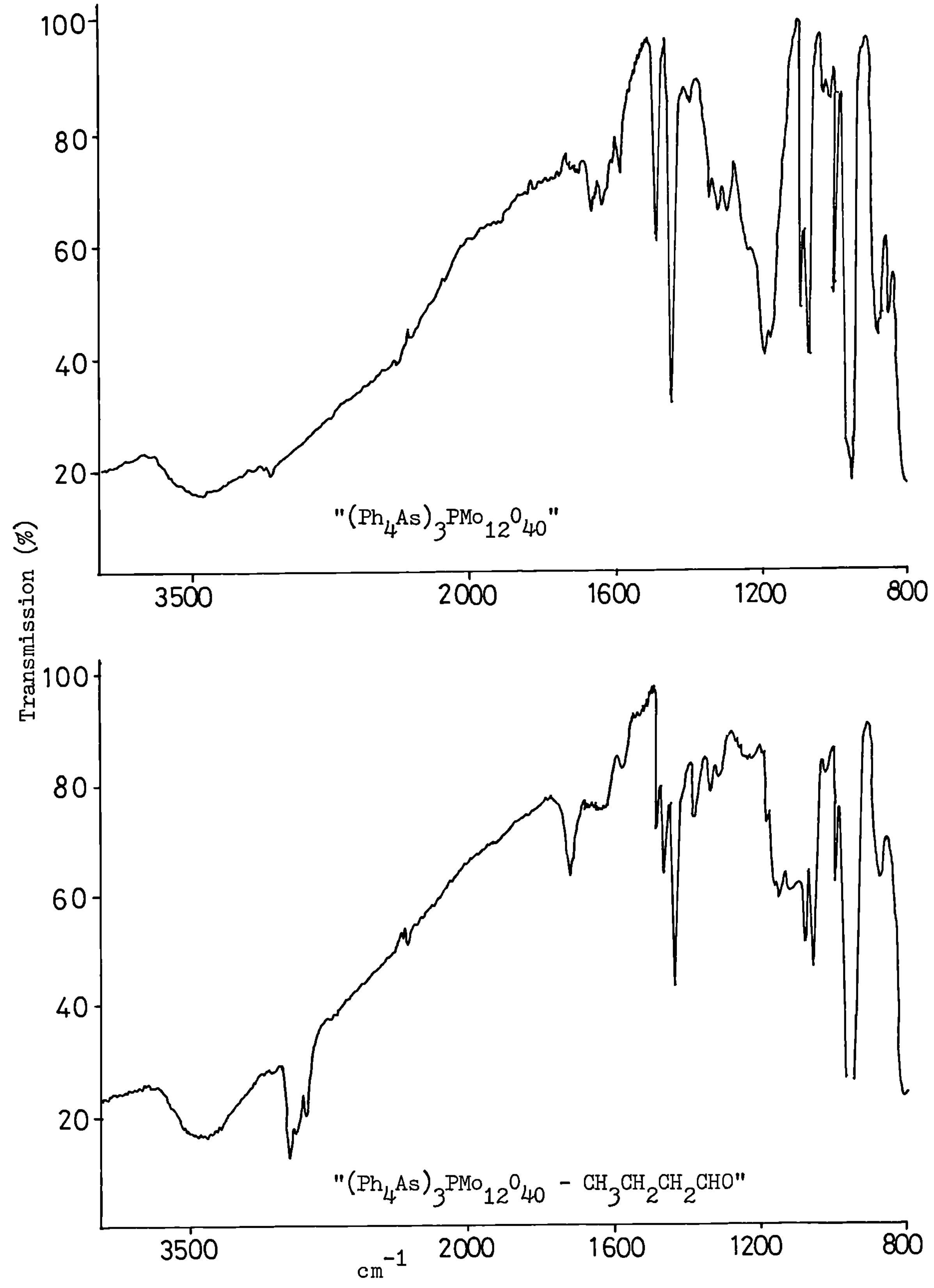


Figure 5k

Expanded Infrared Spectra of "$(Ph_4As)_3PMo_{12}O_{40}$" to Show Alkyl bands in Butyraldehyde containing samples a, Without butyraldehyde

b, With butyraldehyde

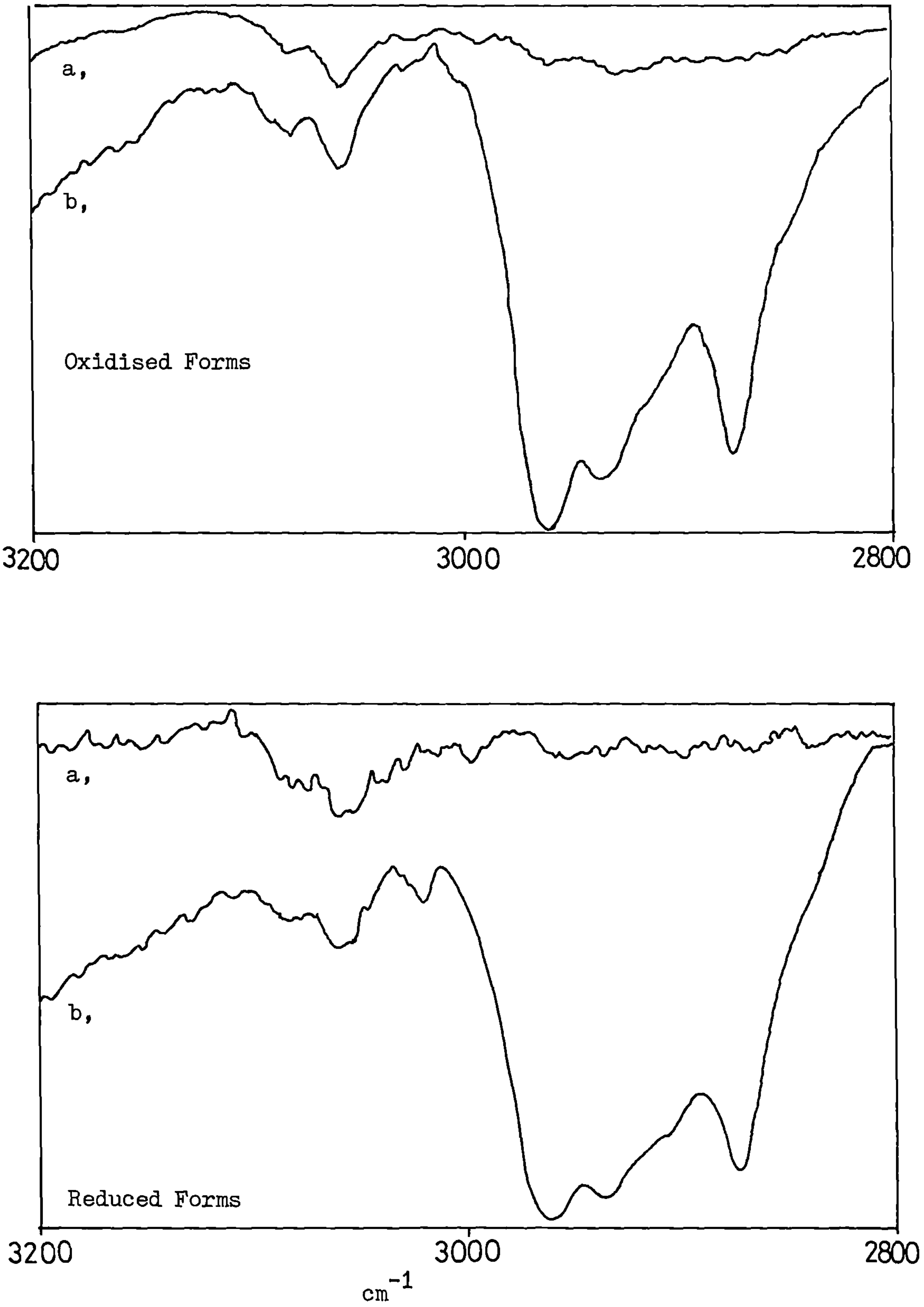


Figure 51

Infrared Spectrum of n-Butyraldehyde

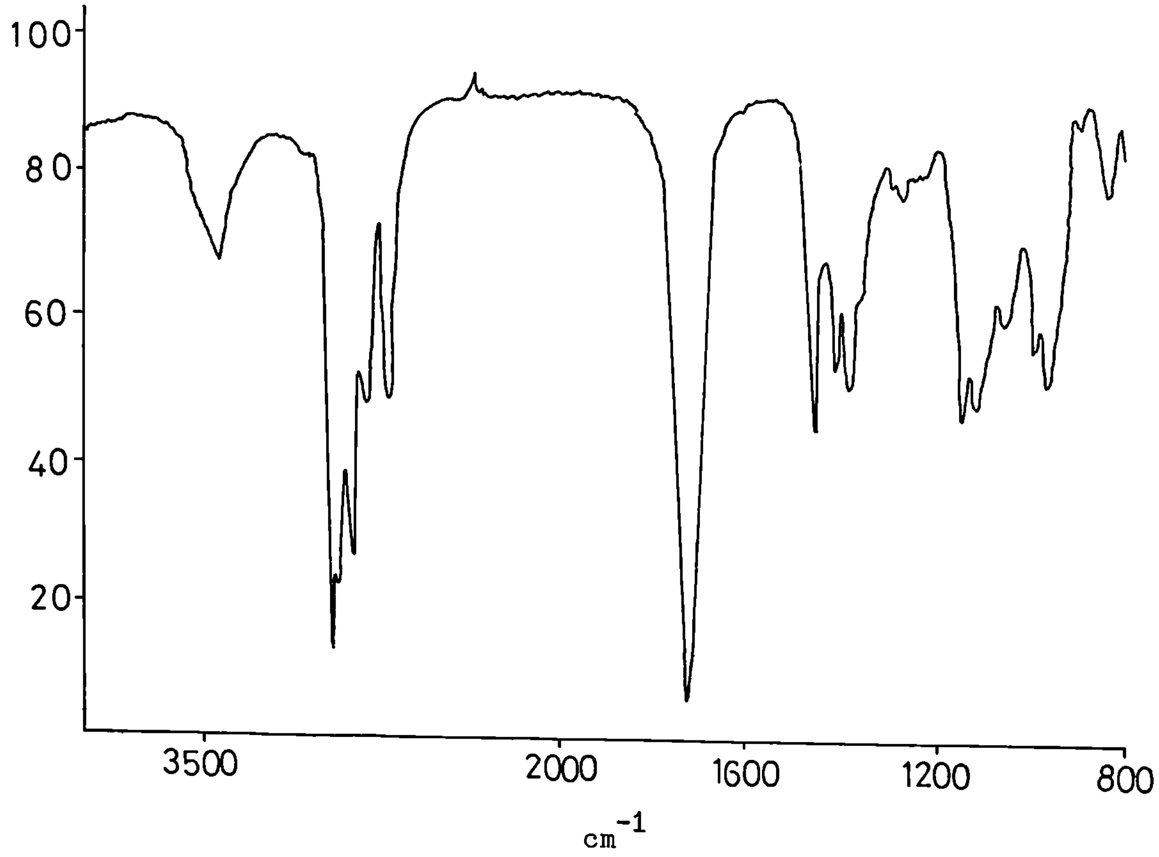


Figure 5m

The solutions were then stirred under an atmosphere of but-1-ene:O_2 1:1 as before. The results were monitored by g.l.c. (see Chapter 3).

5.3.1.2 Variation of the Catalyst Concentration

Solutions were prepared by stirring $PdSO_4$ and $H_3PMo_{12}O_{40}$ in quantities such that the Pd:Mo ratio was 1:10 in 10 cm^3 1MH_2SO_4.

$H_3PMo_{12}O_{40}.24H_2O$	$PdSO_4$
0.1862g ($8.26x10^{-5}$moles)	20 mgs ($9.9x10^{-5}$moles)
0.0931g ($4.13x10^{-5}$moles)	10 mgs ($4.95x10^{-5}$moles)
0.0465g ($2.06x10^{-5}$moles)	5 mgs ($2.48x10^{-5}$moles)

The solutions were then stirred under but-1-ene:O_2 as before.

5.3.1.3 Varying the Acidity of the Medium

i, 0.0931g ($4.13x10^{-5}$moles) $H_3PMo_{12}O_{40}24H_2O$ and 10 mgs ($4.95x10^{-5}$moles) $PdSO_4$ were dissolved in 10 cm^3 dilute H_2SO_4 and stirred under butene:O_2 1:1. The concentrations of acid used were 0, 0.5, 0.75, 0.8, 0.9, 1, 1.1, 1.2, 1.5, 1.9 and 2M.

ii, Repeat of (i) using 0.0465g $H_3PMo_{12}O_{40}24H_2O$ and 10 mgs $PdSO_4$ and the following acid concentrations; 0, 0.1, 0.25, 0.4, 0.5, 0.75, 1 and 2M.

iii, Repeat of (i) using H_3PO_4 in place of H_2SO_4 at the following concentrations; 0, 0.5, 0.66, 1, 1.5 and 2M.

5.3.2 Nuclear Magnetic Resonance Spectroscopy

5.3.2.1 ^{31}P NMR Spectroscopy

(i) Experiments on the oxidised form

These were run on a Jeol JNM-PS 100 NMR Spectrometer. The samples were run in 10 mm n.m.r. tubes with the reference in an inner 5 mm tube.

The reference sample was dissolved in a deuterated solvent which was used for a lock. Most of the samples were run using PPh_3 (50 mgs/cm^3) in $(CD_3)_2CO$ as the reference with a few using $(MeO)_3PO$ (50 mgs/cm^3) in $CDCl_3$.

A small number of samples (Table 5.7) were run on a Bruker WH 400. The samples were prepared in the same way and PPh_3 in $(CD_3)_2CO$ was used as reference.

(ii) Experiments on the reduced form

These were all done on the Bruker WH 400 with external referencing to PPh_3 in $(CD_3)_2CO$ as before.

5.3.2.2 ^{95}Mo NMR Spectroscopy

These samples were run on a Bruker WH 400. The referencing was to external $2MNa_2MoO_4$ at pH 11 by the use of fixed frequencies. The samples were run in 8 mm tubes which were inserted into 10 mm tubes containing $(CD_3)_2CO$ which was used for the lock.

5.3.3 Reductions

5.3.3.1 With Ascorbic Acid

Catalyst solutions were prepared by dissolving $H_3PMo_{12}O_{40}24H_2O$ in water or $1MH_2SO_4$ as required to give the appropriate concentrations (usually $1.38x10^{-3}M$). 3 cm^3 aliquots of this were then degassed and put under N_2. A solution of ascorbic acid in $1MH_2SO_4$ was also prepared (0.619M). This solution was also degassed and put under N_2. Small volumes of the ascorbic acid were then added by syringe to the $H_3PMo_{12}O_{40}$ solutions to give the required level of reduction (e.g. $H_3PMo_{12}O_{40}$ $1.38x10^{-3}M$, 6.7μl ascorbic acid solution gives 2e/$H_3PMo_{12}O_{40}$). The flasks were shaken to give a deep blue colour. The samples were transferred under N_2 to 1 mm quartz cells.

5.3.4.2 With $PdSO_4$ / hex-1-ene

Catalyst solutions were prepared by dissolving $H_3PMo_{12}O_{40}$ (4.13×10^{-3}M) and $PdSO_4$ (4.95×10^{-3}M) in water or 1MH_2SO_4 as required. 5 cm^3 aliquots of this solution were then degassed and put under N_2. Appropriate volumes of hex-1-ene, to give the required level of reduction, were then added by syringe (2.6 μl hex-1-ene=2e reduction). The flasks were shaken for one hour before samples were transferred, with filtering to remove metal, under N_2 to either 10 mm NMR tubes or 1 mm quartz cells.

5.3.5 Visible Spectroscopy

Spectra were recorded between 400 and 900 nm on a Perkin Elmer 559 UV-visible spectrometer in 1 mm quartz cells.

5.3.6 Preparation of $(Ph_4As)_3PMo_{12}O_{40}$ and its Butyraldehyde Adducts

(i) Oxidised forms

A solution containing $H_3PMo_{12}O_{40}.24H_2O$, (0.3724g in 10 cm^3 1MH_2SO_4) was prepared and to this was added 1.2mmol $(Ph_4As)Cl$ dissolved in warm 1MH_2SO_4. The resulting yellow precipitate was filtered, washed and air dried.

The butyraldehyde adduct was prepared in the same manner but butyraldehyde (slight excess) was added to the polyacid solution before precipitation.

(ii) Reduced forms

5 cm^3 of catalyst solution (4.95×10^{-3}M $PdSO_4$, 4.13×10^{-3}M $H_3PMo_{12}O_{40}$ in 1MH_2SO_4) was degassed and placed under N_2 and then reduced with

2.6µl hex-1-ene. The solution was shaken for half an hour and filtered under N_2 before 0.51mmol of $(Ph_4As)Cl$ in warm $1MH_2SO_4$ was added. A pale blue precipitate formed which was filtered, washed and air dried.

The butyraldehyde adduct was prepared in the same way but butyraldehyde (excess) was added before reduction.

(iii) Infrared

Run on a Perkin Elmer 684 infrared spectrometer with a data base facility, as KBr discs.

CHAPTER 6

Continuous Reactor Reactions

6.1 Introduction

The original problem around which the work was based was to find a useful new route to butan-2-one from butenes. Whilst the small batch reactions already discussed have shown that the reactions studied do in fact achieve this, they bear little resemblance to the kind of reactor systems used industrially. To test the heteropolyacid - $PdSO_4$ system under more realistic conditions a continuous reactor was designed (Figure 6d).

6.2 Results and Discussion

The results under a variety of conditions are shown in Table 6.1. At first sight it is difficult to see any trends in this information. The following useful comparisons can be made. Firstly, it can be seen that by gradually changing the reaction conditions the catalyst lifetime can be improved (Figure 6a).

By comparing runs 4 and 5 it can be seen that a temperature of about 19°C in the oxidising column is preferred over one of 55°C. It was found that Pd^o was deposited more rapidly at increased temperatures. Runs 7 and 8 show that the reaction is improved by increasing the amount (flow rate) of oxygen used. Comparison of run 14 with run 8 indicates that mixtures of phosphoric acid and sodium molybdate give slightly better results than the corresponding $H_3PMo_{12}O_{40}$ system. The reaction could be further improved by allowing the reactor contents to foam.(run 15)

In general,gas liquid mixing was very important. Foaming in the

Table of Results with Continuous Reactor

Table 6.1

Type of Heteropolyacid	Catalyst cycle rate lh^{-1}	N_2, AIR, O_2 flow rate lh^{-1} (reactor)	O_2 flow rate lh^{-1} (oxidiser)	Temp. ^{o}C (oxidiser)	Time reaction complete	Turnover on Pd^{II}
RUN 1 $H_3PMo_{12}O_{40}$	0.81	N_2 1.6	10	55	$1\frac{1}{4}$h	3.07
RUN 2 $H_3PMo_{12}O_{40}$	4.1	AIR 1.8	5.5	54	$\frac{3}{4}$h	3.49
RUN 3 PMo_6V_6	4.1	1.8	5.5	55	3 h	16.02
RUN 4 a, $H_3PMo_{12}O_{40}$	4.1	1.8	5.5	55	$\frac{3}{4}$h	3.1
RUN 5 a, $H_3PMo_{12}O_{40}$	4.1	1.8	5.5	19	$1\frac{1}{2}$h	4.48
RUN 6 $H_3PMo_{12}O_{40}$	4.1	1.8	5.5	19	2h b, $3\frac{1}{2}$h	4.83 b, 7.42
RUN 7 $H_3PMo_{12}O_{40}$	4.1	O_2 1.8	5.5	19	$1\frac{1}{4}$h	5.83
RUN 8 $H_3PMo_{12}O_{40}$	4.1	5	9.6	20	$2\frac{1}{4}$h	8.01
RUN 9 $H_3PW_{12}O_{40}$	4.1	5	9.6	19	2 h	10.87
RUN 10 $H_3SiW_{12}O_{40}$	4.1	5	9.6	19	$\frac{3}{4}$h	1.94

Table of Results with Continuous Reactor (continued)

Table 6.1

Type of Heteropolyacid		Catalyst cycle rate lh^{-1}	N_2, AIR, O_2 flow rate lh^{-1} (reactor)	O_2 flow rate lh^{-1} (oxidiser)	Temp. $^{\circ}C$ (oxidiser)	Time reaction complete	Turnover on Pd^{II}
RUN 11	Na_2Mo_4 12 H_3PO_4 1	4.1	5	9.6	19	2½h	7.93
RUN 12 PMo_6V_6		4.1	5	9.6	21	3½h	11.02
RUN 13 c, d,	Na_2MoO_4 12 H_3PO_4 1	4.1	5	9.6	21	6 h	19.90
RUN 14	Na_2MoO_4 12 H_3PO_4 1	4.1	5	9.6	19	6 h	10.81
RUN 15 d,	Na_2MoO_4 12 H_3PO_4 1	4.1	5	9.6	20	3½h	19.84

Concentration of catalysts - 7.43×10^{-3}g ions Mo(VI) or W(VI), all in $1MH_2SO_4$ except PMo_6V_6.

But-1-ene flow rate - 1.6 lh^{-1}. Reactor temperature - $20^{\circ}C$.

a, Concentration 0.371 g ions Mo(VI) l^{-1}.

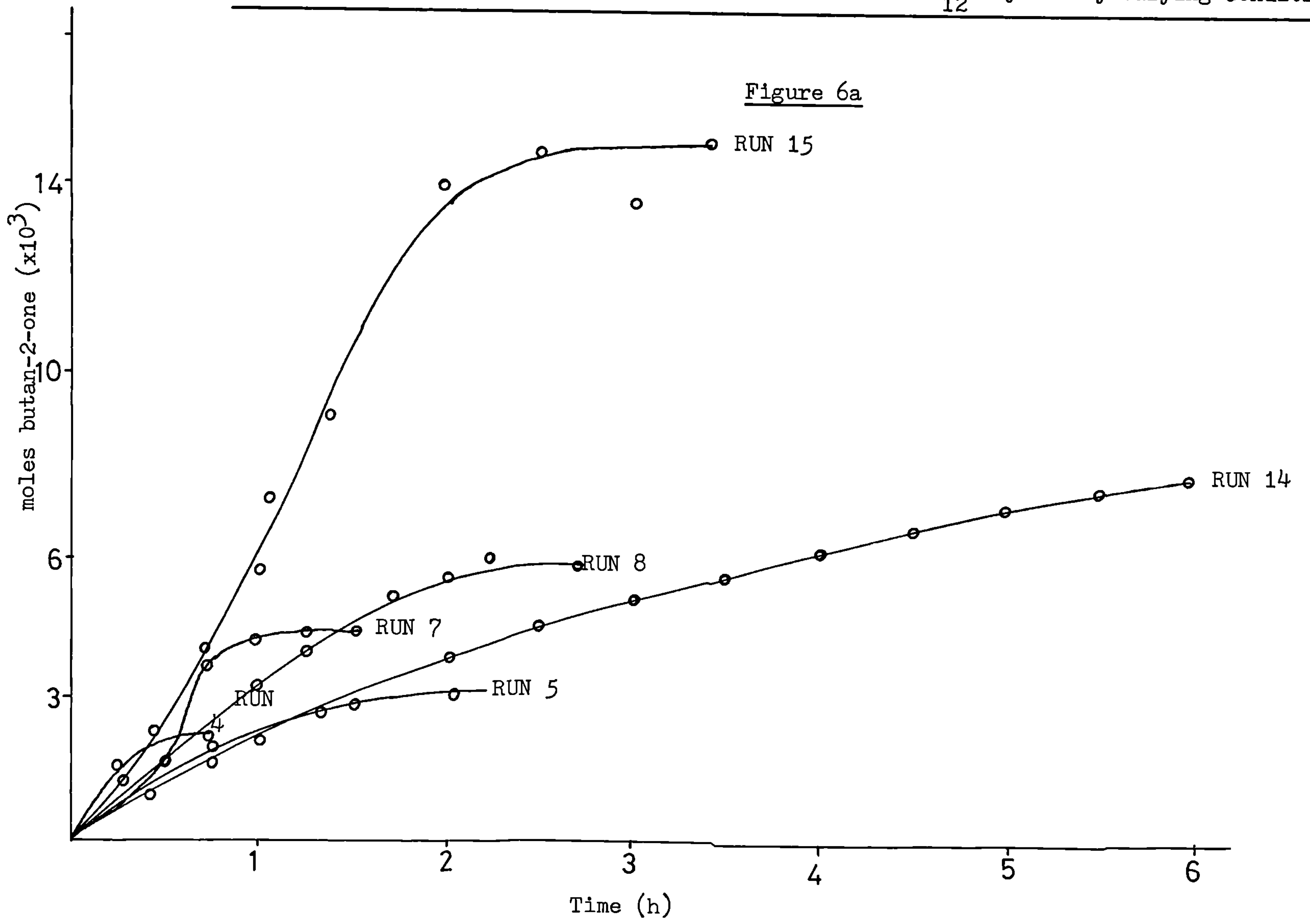
b, 0.675 g V_2O_5 (7.43 g ions V^V) added as a suspension in 30 mls $1MH_2SO_4$

c, 0.394 g carbowax 20M added in 20 mls $1MH_2SO_4$ at start of reaction.

d, Foaming in reactor.

Graphs to Show Improvement of Final Yields for the "PMo_{12}" System by Varying Conditions

Figure 6a



reactor greatly increased the reaction rates. Run 13 shows the effect of adding a foaming agent (carbowax 20M).

An attempt to revive the $H_3PMo_{12}O_{40}$ system by the addition of V_2O_5 was made, however this caused only a temporary improvement in the reaction (run 6 - Figure 6b).

Figure 6c shows a comparison of different reoxidation systems. Again the $H_9PMo_6V_6O_{40}$ system seemed to be the best (run 12). For the tungsten compounds phosphorus is the preferred heteroatom over silicon (runs 9 and 10). The molybdate - phosphate system was better than the comparable tungsten system (run 14 and run 9).

6.3 Experimental

A diagram of the reactor is shown in Figure 6d. Pre prepared solutions (see Chapter 3) (150 cm^3 containing $7.43 x 10^{-4}$ g ions Pd^{II})[1] were added to, and circulated around the reactor and oxidiser with a peristaltic pump which had been precalibrated. The gases were introduced at the bottom of the reactors, the flow being controlled by needle valves and measured on calibrated rotaflows. The butan-2-one product was collected in the scrubber and bubbler systems. The total product was calculated by sampling all the reactors, scrubbers and bubblers onto a g.l.c. unit (see Chapter 3).

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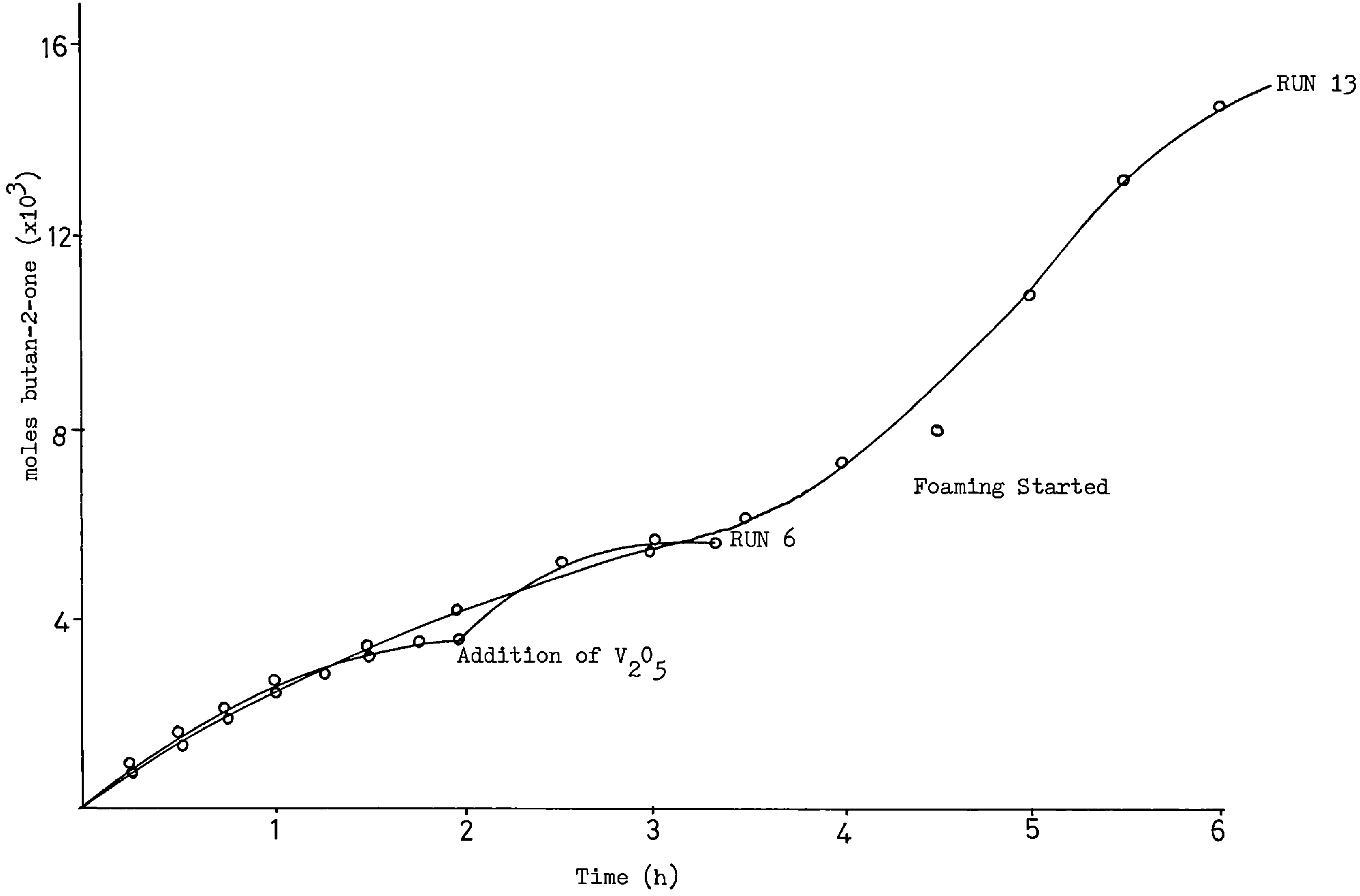
[1] $1M H_2SO_4$ was the solvent in all examples except PMo_6O_6 where the solvent was distilled water. (see Chapter 3).

Graph to Show the Effects of Some Additives on the "PMo_{12}" System

Figure 6b



[illegible] heteropolyacid systems under the same reaction conditions

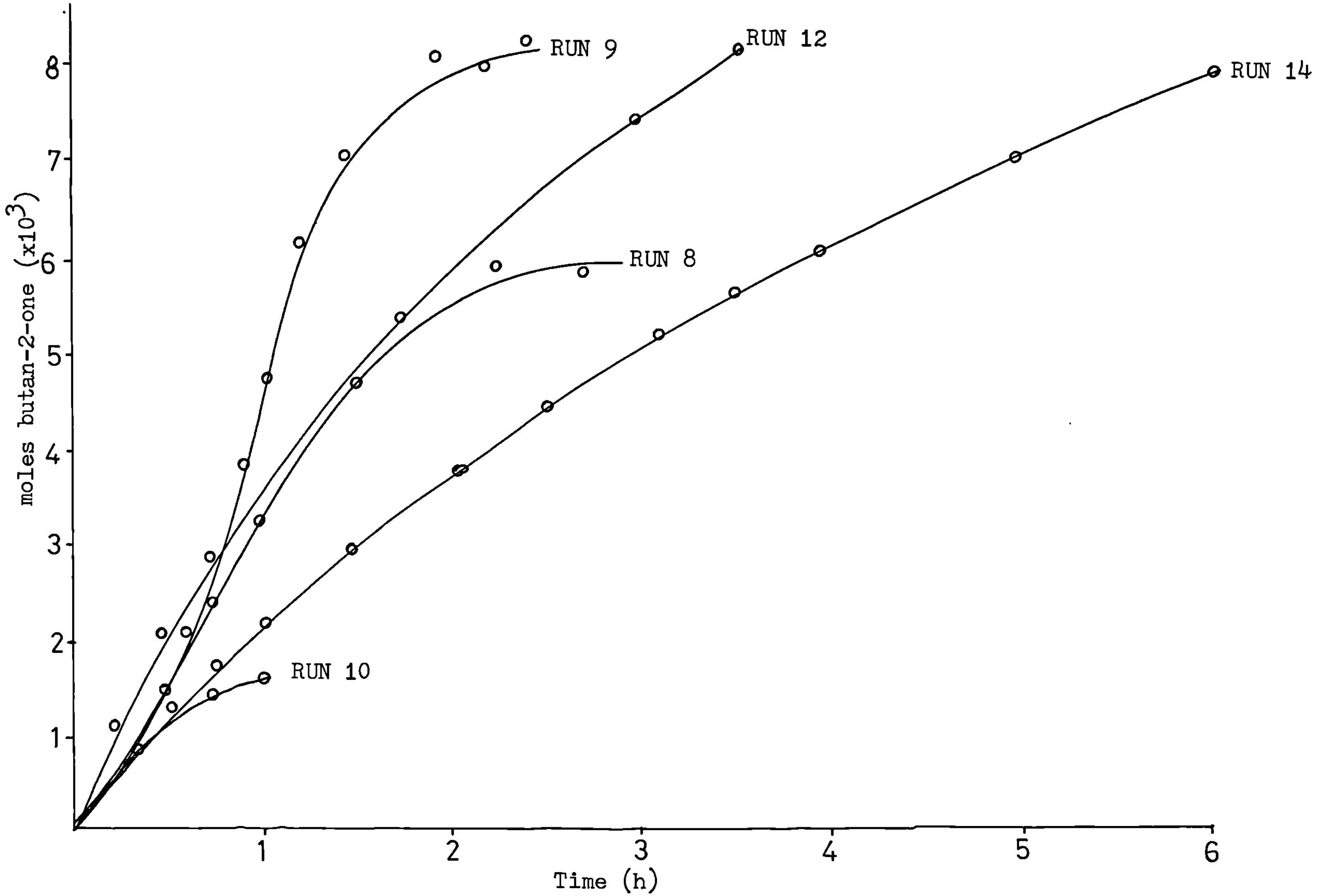


Figure 6c

Continuous Reactor System for Butene Oxidation

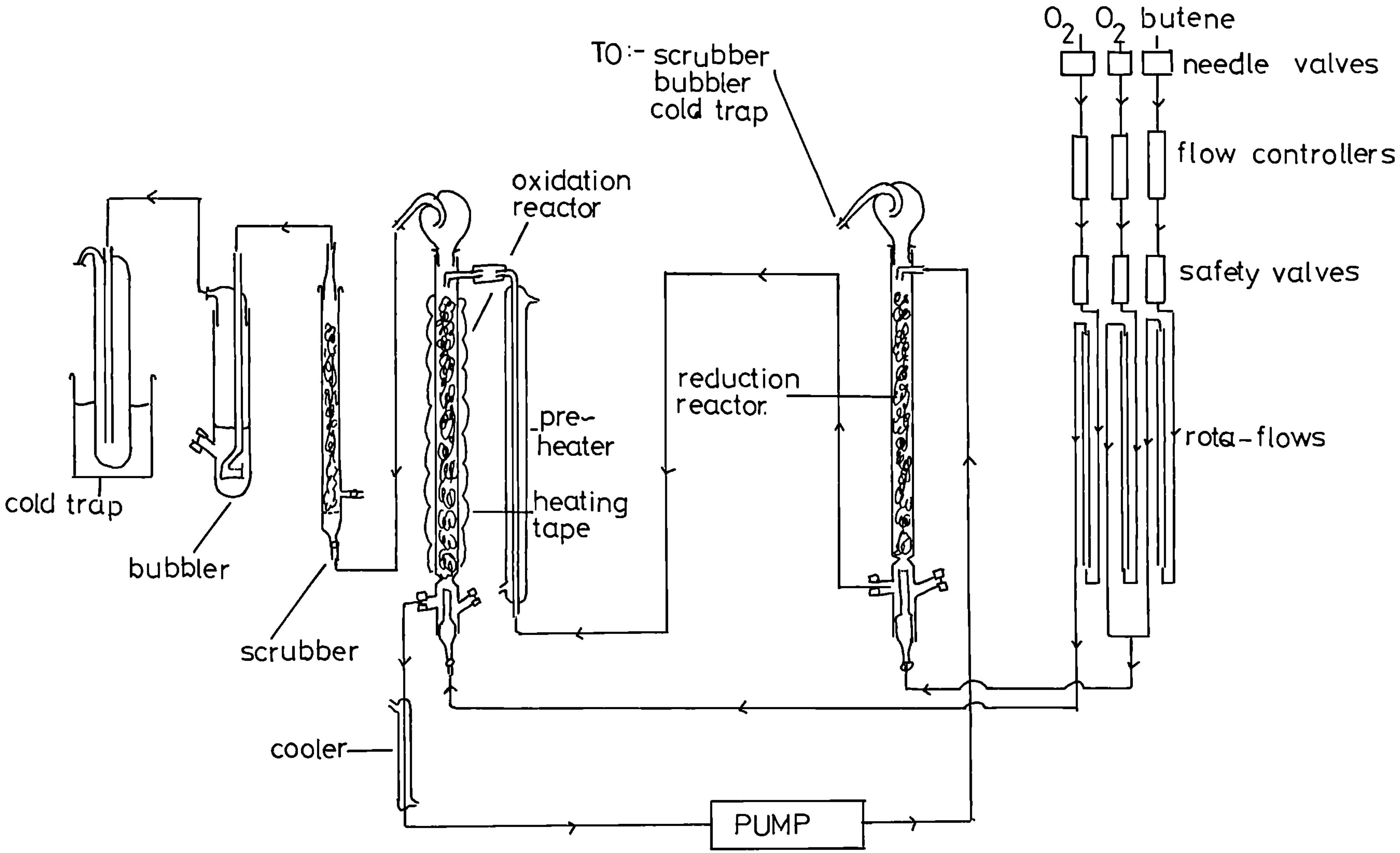


Figure 6d

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