Phosphomolybdic Acid † as a Reoxidant in the Palladium(II)-catalysed Oxidation of But-1-ene to Butan-2-one

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Phosphomolybdic and a variety of phosphomolybdovanadic acids were examined as reoxidants for the palladium sulphate-catalysed oxidation of but-1-ene to butan-2-one both in the absence and the presence of oxygen. All of these co-oxidants were approximately equally effective in reoxidising Pd^0 to Pd^{II} but they varied substantially in their ability to be reoxidised themselves by air under the optimum reaction conditions in aqueous acid. Phosphomolybdovanadate systems were the most effective at a pH > 0, but V^{IV} by itself could not be reoxidised by air under these conditions and therefore the molybdenum must play a vital role. Phosphomolybdic acid, $H_3[PMo_{12}O_{40}]$, itself was quite a good co-oxidant under more acid conditions (1 mol dm^{-3} sulphuric), but ^{31}P n.m.r. spectroscopy showed that in dilute solution it was largely dissociated into phosphoric acid; evidence for the presence under some conditions of other phosphomolybdic acids, which may be related to the active species, is presented.

Patents to Eastman Kodak in the 1960s described the use of phosphomolybdic acid, $H_3[PMo_{12}O_{40}]$, and palladium chloride supported on various oxides as catalysts for olefin oxidation.[1] It was also mentioned that the reactions could be carried out using aqueous solutions of phosphomolybdic acid and palladium chloride. Especially interesting was the report that under such conditions but-1-ene was oxidised to butan-2-one (methyl ethyl ketone, mek), free of impurities. The normal oxidation system developed by Wackerchemie for oxidising ethylene to acetaldehyde ($PdCl_2 + CuCl_2 + HCl + H_2O + O_2$)[2] is, in practice, not suitable for oxidation of higher olefins to methyl ketones since large amounts of chlorinated organics are produced as by-products.[3] For this reason considerable effort has been expended in the search for alternative oxidising systems which do not require high chloride levels. A further advantage of a low-chloride process is that it would be less corrosive, thus reducing plant costs.

Later, other workers noted that addition of vanadium(V) to the homogeneous $PdCl_2$ + phosphomolybdic acid system (which produces phosphomolybdovanadates *in situ*) gave a further substantial improvement of the rate of oxidation.[4–6] More recently phosphomolybdotungstic acids have been used in such oxidation systems.[7,8] However, as we [9] and others [10,11] have found, the phosphomolybdo-vanadic and -tungstic acids as normally prepared (and as used in the oxidation catalysts) are extremely complex mixtures of compounds of the type $[PMo_{12-x}V_xO_{40}]^{(3+x)-}$ (P–Mo–V) or $[PMo_{12-x}W_xO_{40}]^{3-}$ (P–Mo–W), where x = 1—12. A simpler system should be more amenable to a mechanistic study; we here discuss one such system, Pd^{II} + $[PMo_{12}O_{40}]^{3-}$, and compare it to the Pd^{II} + P–Mo–V catalysts previously reported.

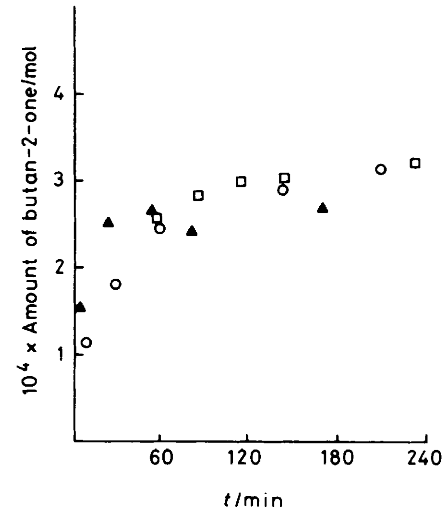

Figure 1. Moles of butan-2-one formed during typical reactions of but-1-ene with $PdSO_4$ (10 mg, 4.95 × 10^{-5} mol) in water (10 cm^3) containing the appropriate heteropolyacid such that each solution contained 4.95 × 10^{-4} g ions V^V; no oxygen was present (see Experimental section). ▲, '$H_5[PW_{10}V_2O_{40}]$'; ○, '$H_4[PMo_{11}VO_{40}]$'; and □, '$H_9[PMo_6V_6O_{40}]$'

Results and Discussion

Reactions in the Absence of Oxygen.—Our initial experiments (under standard conditions: no oxygen, 1 atm but-1-ene, 20 °C) showed that for the catalyst system $PdSO_4$ + $[PM_{12-x}V_xO_{40}]^{(3+x)-}$ in dilute sulphuric acid (0.03—0.2 mol dm^{-3}) using a Pd : V ratio of 1 : 10 and constant [Pd^{II}] and [V^V], the initial rates of reaction were very similar (Figure 1) for M = Mo, x = 1—7 and for M = W, x = 1, 2, 4, and 6. In each case the reactions were essentially complete within *ca.* 30 min and gave a turnover of about 5 on Pd; over longer periods this increased slowly to 6—7. The only organic product detected in any of these reactions was butan-2-one.

Previous work [5] which indicated that in Pd^{II} + P–Mo–V (or P–W–V) catalyst systems reoxidation occurred at V implied that the V : Pd ratio should be rate (*i.e.* yield) determining. Our observation that a V : Pd ratio of 10 : 1 gave an initial turnover of butene to butanone of *ca.* 5 agrees with this proposal and indicates the overall stoicheiometry (1). In other

$$5EtCH{=}CH_2 + 10V^V + 5H_2O \longrightarrow 5EtCOCH_3 + 10V^{IV} + 10H^+ \quad (1)$$

words, for every molecule of butanone produced, two V^V are reduced to V^{IV}. A variety of palladium salts were successful in these reactions, but since they were carried out in dilute sulphuric acid and since the intention was to minimise the chloride content, most reactions were carried out using com-

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† Dodecamolybdophosphoric acid.

Non-S.I. unit employed: atm = 101 325 Pa.

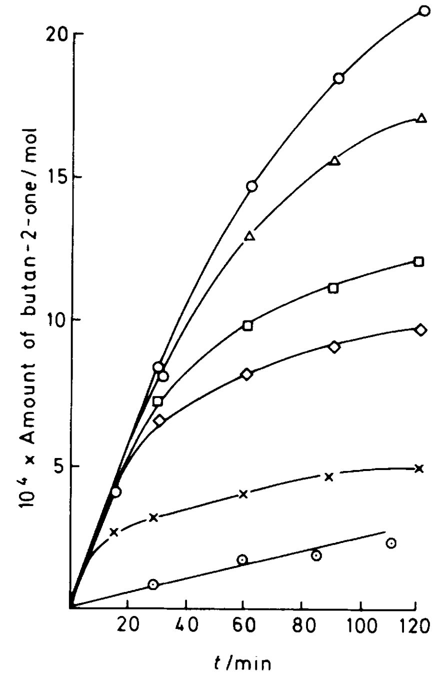

Figure 2. Moles of butan-2-one formed during the reaction of but-1-ene and oxygen (1 : 1) with $PdSO_4$ and the heteropolyacid in water (conditions as for Figure 1). ⊙, '$[NH_4]_9[PV_{14}O_{42}]$'; ×, '$H_3[PMo_{12}O_{40}]$'; ◇, '$H_5[PMo_{10}V_2O_{40}]$'; □, '$H_6[PMo_9V_3O_{40}]$'; △, '$H_8[PMo_7V_5O_{40}]$'; and ○, '$H_9[PMo_6V_6O_{40}]$'

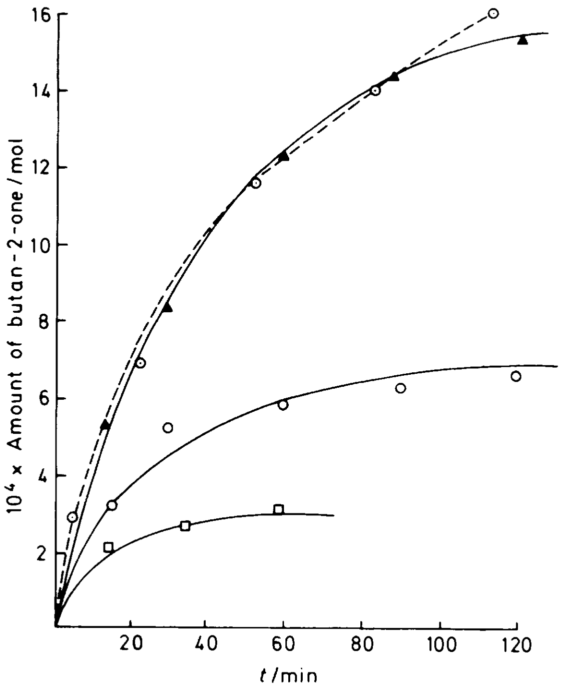

Figure 3. Moles of butan-2-one formed during the reaction of but-1-ene and oxygen (1 : 1) with the heteropolyacid (V or Mo : Pd = 10 : 1) in sulphuric acid (10 cm^3, 1 mol dm^{-3}) (conditions otherwise as for Figure 1). □, V_2O_5 ('VO_2^+'); ○, MoO_4^{2-} ('$H_2[MoO_4]$'); ▲, MoO_4^{2-} + PO_4^{3-} (12 : 1); and ⊙, '$H_9[PMo_6V_6O_{40}]$'

mercial palladium sulphate, which our analyses indicated to be anhydrous $PdSO_4$.

However, we also found that phosphomolybdic acid, $H_3[PMo_{12}O_{40}]$, even in the absence of V^V, functioned as a reoxidant for Pd^0 to Pd^{II} and was itself reduced to a heteropoly-blue, probably by taking up two electrons per cage to give $H_5[PMo_{12}O_{40}]$.[10,12] This reaction was much slower and also gave a turnover of only 1 at a Mo : Pd ratio of 10 : 1, although this increased to *ca.* 5 (on Pd) over 30 min when a ratio of 100 : 1 was used.

Thus we may define two reoxidation processes for Pd^0 to Pd^{II}, one fast, involving reduction of V^V to V^{IV}, the other slow and involving the take-up of electrons by phosphomolybdic acid itself. (Under the conditions used there was no butene oxidation in the absence of palladium.) The latter reaction probably explains the slow drift to higher turnovers observed when the various P–Mo–V co-catalysts were used; reoxidation occurs first at V^V and then more slowly at Mo^{VI}. The presence of V^{IV} in the reduced solutions of the P–Mo–V catalysts was confirmed by e.s.r. spectroscopy, which showed the eight peaks characteristic of V^{IV} ($I = \frac{7}{2}$).

Reactions in the Presence of Oxygen.—The reactions were then repeated using an atmosphere of butene and oxygen (1 : 1; separate trials showed that this ratio of gases gave the optimum rates under the conditions used), but with the same reagents and keeping the concentrations of Pd^{II} and V^V (ratio 1 : 10) constant. Again, only butan-2-one was formed.

A series of experiments was carried out in the pH range 1—2 (Figure 2) and in 1 mol dm^{-3} sulphuric acid (pH *ca.* −0.3, Figure 3). In the less acidic regime the various P–Mo–V co-catalysts were much longer lasting but, interestingly enough, the *initial rates* of all the co-catalysts were very similar. We interpret this to mean that the ease of reoxidation of Pd^0 by all the co-catalysts is similar but that they differ markedly in the ease with which their reduction products are in turn reoxidised by oxygen.

An alternative way to express the results of Figures 2 and 3 is that the systems with the smallest contents of molybdenum are reoxidised fastest. However catalysts containing only vanadium as reoxidant (for example,[13] $[PV_{14}O_{42}]^{9-}$) are quite ineffective as reoxidants. Similarly, although we have established that VO_2^+ is a significant component of all the P–Mo–V heteropolyacids [9] (and must therefore be present in the catalytic systems), it is a poor co-catalyst. Although it is easily reduced to blue VO^{2+} by Pd^0, at a pH < 2 VO^{2+} cannot be reoxidised at all by oxygen. Palladium metal therefore precipitated out quickly from such catalytic systems.

In 1 mol dm^{-3} sulphuric acid the P–Mo–V systems are slightly less active, but in contrast phosphomolybdic acid (or acid solutions containing molybdate and phosphate in a 12 : 1 ratio) is much more active and now almost equal to the best P–Mo–V system 'PMo_6V_6.' Molybdate by itself has only very low activity under these conditions.

Optimisation of the Palladium(II) *and Phosphomolybdic Acid Catalyst System in the Presence of Oxygen.*—In order to explore the activity of the Pd^{II} and phosphomolybdic acid catalyst system and to obtain some information on the active entity, a series of optimisation experiments were carried out. These showed that in 1 mol dm^{-3} sulphuric acid the optimum Pd : Mo ratio is 1 : 10. Figure 4 shows the variation of yield of butanone with variation of acidity using this ratio and a concentration of Pd^{II} of 4.95×10^{-5} g ions in 10 cm^3. It indicates that when the ratio of Pd : Mo is 1 : 5, the optimum acidity is lowered to 0.25 mol dm^{-3} sulphuric acid. When phosphoric acid was used in place of sulphuric the improvement over distilled water was small; this was probably due to phosphoric acid being a weaker acid than sulphuric.

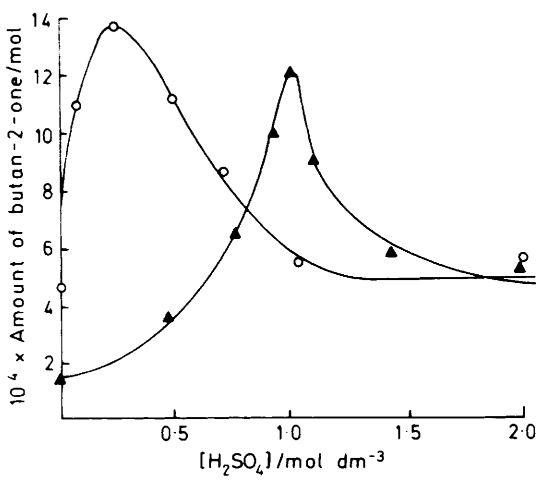

Figure 4. Moles of butan-2-one formed (after 2 h) from the reaction of but-1-ene and oxygen (1 : 1) with $PdSO_4$ (4.95×10^{-3} mol dm^{-3}) and $H_3[PMo_{12}O_{40}]$ (▲, 4.13×10^{-3}; ○,, 2.06×10^{-3} mol dm^{-3}) in sulphuric acid (10 cm^3)

One possible interpretation of this marked effect of the acid concentration on the rate of reoxidation of the heteropoly-blue is that it follows the equation (2). If this is so then

$$[PMo_{12}O_{40}]^{5-} + \tfrac{1}{2}O_2 + 2H^+ \longrightarrow [PMo_{12}O_{40}]^{3-} + H_2O \quad (2)$$

the rate of reoxidation should be proportional to $[H^+]^2$ and should increase rapidly with increasing acidity. Although our experiments suggest that $H_3[PMo_{12}O_{40}]$ is itself largely absent at the acidities and concentrations used here (see below), this argument holds good for any other species undergoing such two-electron redox processes. The decrease in yield at higher acidities may be due to a change in the rate-determining step or to the breakdown of the active reoxidation species. Since the fall in yield is caused more by the reaction coming to an end rather than by a decrease of rate, we favour the latter explanation.

In 1 mol dm^{-3} sulphuric acid VO_2^+ is a poor reoxidation catalyst and hence the overall rate of reaction decays very rapidly; addition of phosphate had little overall effect and $[PV_{14}O_{42}]^{9-}$ behaved similarly. Molybdate in acid was slightly better but the rate of reaction also decayed quite rapidly. This indicates that, similarly to VO_2^+, MoO_4^{2-} (the nature of the species present when molybdate is dissolved in acid is unknown [14,15]) can reoxidise palladium, but that its reduced form is not easily reoxidised by oxygen in an acidic medium. Mixtures of molybdate and VO_2^+ in acid show no better ability to be reoxidised, the result being simply the sum of those found for the separate species.

However, addition of phosphate to molybdate solutions greatly improved the reoxidation activity. Further, levels of phosphate such that the P : Mo ratio is 1 : 12 were sufficient (Figure 5) and higher ratios did not improve the rate of reoxidation. We caution against interpreting this observation as indicating that the active species is indeed $H_3[PMo_{12}O_{40}]$ since a variety of complex equilibria are clearly operating in such solutions. However this observation suggests that the active species has a Mo : P ratio of 12 : 1 *or more*.

The differences in the reactions were also highlighted by the colour changes observed. Reduction of VO_2^+ in acid during butene oxidation with palladium sulphate gave a pale blue-turquoise solution. Reduction of molybdate under the same conditions gave no colour change even though reduction occurred since turnover numbers greater than one on palladium were achieved; this means that molybdate must have reoxidised palladium and itself been reduced. On addition of small amounts of phosphate the typical deep blue colour associated with the formation of the heteropoly-blues was observed, indicating that different species are present in the reduced solutions in the presence and absence of phosphate.

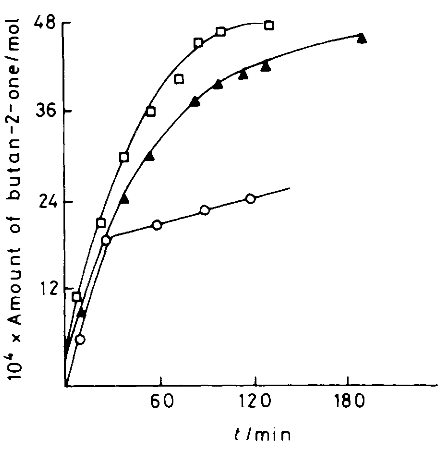

Figure 5. Moles of butan-2-one formed from the reaction of but-1-ene and oxygen (1 : 1) with $PdSO_4$ in sulphuric acid (1 mol dm^{-3}) (Pd : Mo = 1 : 12). ○, MoO_4^{2-}; ▲, MoO_4^{2-} + PO_4^{3-} (12 : 1); and □, MoO_4^{2-} + PO_4^{3-} (12 : 2)

In summary, molybdate and phosphate seem to be the essential components of a good reoxidation catalyst in the P–Mo–V system, and V^V in the form of VO_2^+ seems to play little *direct* part in the reoxidation under acidic conditions.

Experiments with phosphomolybdic acid gave results identical to those found for mixtures of molybdate and phosphate in the same medium and this is now a reasonably good reoxidation catalyst in 1 mol dm^{-3} sulphuric acid, although it does deactivate rather more quickly than the best of the P–Mo–V catalysts, 'PMo_6V_6.' In fact whereas continuous reactions carried out with 'PMo_6V_6' reoxidation showed only trace deposits of metal after a 5-h run, relatively large amounts of metal appeared after 15 min when phosphomolybdic acid was used as co-oxidant. Addition of further acid to the 'PMo_6V_6' catalyst system was slightly detrimental. In all cases the addition of excess of phosphate had no effect.

Studies were next undertaken with the aim of identifying more closely the species present in solution which were active in the co-oxidation catalysis. We noticed that although phosphomolybdic acid is yellow ($\lambda_{max.}$ 280 nm) both in the solid and in aqueous solution, in sulphuric acid under catalytic conditions the solutions are colourless. This is consistent with a breakdown of the structure in acid. In fact the u.v.–visible spectra of the various species are very similar [16] and this technique does not provide a useful means for investigating the solutions; our attempts to obtain useful data from Raman spectra were also unsuccessful. However the n.m.r. spectra, in particular using the sensitive ^{31}P nucleus as probe, promised to give more helpful results.

N.M.R. Spectroscopic Studies.—A solution of phosphomolybdic acid (4.13×10^{-3} mol dm^{-3}) in sulphuric acid (1 mol dm^{-3}, pH *ca.* −0.3) showed only one peak in the ^{31}P n.m.r. spectrum (−0.11 p.p.m. with respect to 85% H_3PO_4 as external standard, 5.9 p.p.m. with respect to external triphenylphosphine in hexadeuterioacetone). This peak, due to phosphoric acid, was the only detectable species present.

Table. ^{31}P chemical shifts of $H_3[PMo_{12}O_{40}]$ (1.68×10^{-2} mol dm^{-3}) in 0.75 mol dm^{-3} H_2SO_4

(*a*) Shift reagent $Eu(NO_3)_3$

$[Eu(NO_3)_3]$	$[H_3PO_4]$	Shifts (p.p.m.) with respect to PPh_3 in $(CD_3)_2CO$		
mol dm^{-3}				
0	0	2.23	4.49	5.59
4.20×10^{-3}	0	2.27	4.53	5.01
8.40×10^{-3}	0	2.21	4.48	4.34
1.26×10^{-2}	0	2.20	4.49	3.78
1.68×10^{-2}	0	2.01	4.29	3.01
1.68×10^{-2}	1.65×10^{-3}	2.06	4.38	2.97
1.68×10^{-2}	6.40×10^{-3}	2.07	4.39	3.07
1.68×10^{-2}	1.65×10^{-2}	2.22	4.52	3.31

(*b*) Shift reagent $Pr(NO_3)_3$

$[Pr(NO_3)_3]$	$[H_3PO_4]$	Shifts (p.p.m.) with respect to PPh_3 in $(CD_3)_2CO$		
mol dm^{-3}				
0	0	2.23	4.49	5.59
4.20×10^{-3}	0	2.19	4.45	5.77
8.40×10^{-3}	0	2.13	4.39	6.03
1.26×10^{-2}	0	2.08	4.35	6.19
1.68×10^{-2}	0	2.16	4.41	6.42
1.68×10^{-2}	1.65×10^{-3}	2.13	4.37	6.44
1.68×10^{-2}	1.40×10^{-3}	2.13	4.39	6.49
1.68×10^{-2}	1.65×10^{-2}	2.21	4.46	6.55

At lower acidity (0.1 mol dm^{-3} sulphuric, pH *ca.* 0.7), another peak was observed [-1.31 (phosphoric acid), 4.7 p.p.m. (triphenylphosphine)], and at intermediate acidities (0.3—0.4 mol dm^{-3} sulphuric, pH *ca.* 0.1) both signals were present. At higher concentrations of phosphomolybdic acid (1.68×10^{-2} mol dm^{-3} in 0.75 mol dm^{-3} sulphuric acid, pH *ca.* -0.2), in addition to the two resonances noted in the more dilute solutions, now at 5.6 and 4.5 p.p.m., a third resonance was observed [$+2.2$ p.p.m. (reference triphenylphosphine)] the position of which agreed with that of phosphomolybdic acid itself.[17]

In order to confirm these assignments varying amounts of two shift reagents, europium and praseodymium nitrates, were added to the solutions. The $+2.2$ and $+4.5$ p.p.m. resonances were hardly affected but the resonance originally at 5.9 p.p.m. showed a large shift to lower frequencies on addition of europium nitrate and a corresponding change to higher frequencies on addition of praseodymium nitrate (Table). This is the behaviour expected when the phosphorus is comparatively unshielded by substituents, as in phosphate, and can interact directly with the shift metal ion. Final proof that this resonance was indeed due to phosphoric acid came from the increase in intensity which it underwent when phosphoric acid was added to solutions showing the maximum shifts.

Both the chemical shift and the lack of any significant change on the addition of shift reagent indicate that the $+2.2$ p.p.m. resonance is due to phosphomolybdic acid, where the phosphorus is indeed deeply buried and well shielded from interaction with shift metal ions. The fact that it is not present to any significant degree in dilute acid solutions agrees with other reports of its instability unless dioxane or analogous oxy-compounds are present.[14,18]

This then leaves just one resonance, at 4.5 p.p.m. (reference triphenylphosphine), unassigned; it occurs in dilute solutions at acidities down to pH *ca.* 0.3 and in more concentrated solutions even at higher acidities. In the dilute solutions phosphomolybdic acid is not observed and at higher acidity the only detectable species is phosphoric acid. Since the species giving rise to the resonance at 4.5 p.p.m. is relatively unaffected by shift reagent we may conclude that the phosphorus there is well buried and that it is therefore in a phosphomolybdic acid. The range of acidity and concentration in which it occurs suggests that it is an intermediate in the acid-promoted hydrolysis of phosphomolybdic to phosphoric acid. The appearance of phosphoric acid implies that a great deal of molybdate must also be formed in the hydrolysis. This could be present as some type of isomolybdate, *e.g.* $[Mo_{36}O_{112}(H_2O)_{16}]^{8-}$.[19] One may also speculate that some of it combines with phosphate to give a phosphomolybdate with a Mo : P ratio greater than 12 and that this is the species giving rise to the resonance at 4.5 p.p.m.

These results show further that at the acidity where phosphomolybdic acid acts best as a co-catalyst (*ca.* 1 mol dm^{-3} sulphuric acid) it has already broken down, apparently entirely from the n.m.r. measurements (but see below), to phosphoric acid. This contrasts with the observation (Figure 4) that phosphate improves the co-catalytic character of molybdate dramatically.

One possible way to resolve this anomaly is if the phosphate were acting as a template for the molybdates to organise themselves into a shape particularly effective for co-catalysis. However, the ^{95}Mo n.m.r. spectrum of a 4×10^{-3} mol dm^{-3} solution of phosphomolybdic acid in 1 mol dm^{-3} sulphuric acid showed a broad resonance at -66.5 p.p.m. [with respect to an external reference of sodium molybdate (2 mol dm^{-3}) at pH 11], and was identical to that of a sample of sodium molybdate itself at the same acidity and concentration. By contrast, a concentrated solution of phosphomolybdic acid itself showed an extremely broad resonance (-2.9 p.p.m.) in water. Thus the major Mo-containing species in sulphuric acid seems to be the same whether or not phosphate is present and the template hypothesis is therefore unable to explain the data.

An alternative possibility is that although phosphate seems not to participate to a significant degree in the oxidised form, such an association could be important in the reduced blue. In order to investigate this, the ^{31}P n.m.r. spectra (at 105 MHz, Bruker WH-400) of solutions of the reduced $[PMo_{12}O_{40}]^{5-}$ were investigated using an actual working catalyst solution in sulphuric acid (1 mol dm^{-3}). This again only showed one peak at 5.9 p.p.m. (reference triphenylphosphine), which was again shown to be due to phosphoric acid by addition of shift reagent.

In order to determine how much of the phosphorus in phosphomolybdic acid was converted into free phosphoric acid in sulphuric acid (1 mol dm^{-3}), comparative spectra (at 105 MHz) were run of solutions of phosphoric, phosphomolybdic, and reduced phosphomolybdic acids using equal numbers of scans against a reference of triphenylphosphine in deuterioacetone (external, 0.05 g cm^{-3}). A relatively long time was allowed between each pulse so that equilibrium could be re-attained after each scan, and we estimate that the integrals of the 5.9 p.p.m. peak should be accurate to $\pm 10\%$. The integral of a standard sample of phosphoric acid (2.3×10^{-3} mol dm^{-3}) under these conditions was 2.26, compared to those of samples of phosphomolybdic acid (4.1×10^{-3} mol dm^{-3}), integral 2.12, and reduced phosphomolybdic acid (4.1×10^{-3} mol dm^{-3}), integral 2.27. Thus as much as 45% of the phosphorus present in phosphomolybdic acid in sulphuric acid is not observed, the difference between the oxidised and reduced forms being within experimental error. This suggests the presence of an equilibrium of intermediate rate, which does not involve the phosphoric acid, and which gives rise to very broad and undetected signals. Some evidence supporting this is that when the spectrum of phosphomolybdic acid in sulphuric acid (1 mol dm^{-3}) is run at 80 °C a small peak (in addition to the phosphoric acid peak, here at 3.9 p.p.m.

with respect to triphenylphosphine in hexadeuteriodimethyl sulphoxide) is seen at 5.3 p.p.m. in the approximate intensity ratio of 7 : 2.

It is tempting to suggest that the species responsible for the observed co-oxidation and the species giving this resonance are the same. Only speculation as to its nature is possible, but it could again be a phosphomolybdic acid with a Mo : P ratio of greater than 12. This would be consistent with the absence of a detectable ^{95}Mo resonance; it would also be more difficult to detect a phosphorus in the centre of such a molecule. The observation that for the co-catalysis an excess of phosphate does not give any improvement is also consistent with this suggestion.

Conclusions

We have shown that in the oxidation of butene to butanone catalysed by Pd^{II} in the absence of chloride, heteropolyacids are active co-catalysts. Their role is to reoxidise Pd^0 to Pd^{II} and to be themselves reoxidised from their 'blue' reduced state to the fully oxidised state by oxygen (air). Phosphate is a necessary ingredient of all the catalysts. Both V^V and Mo^{VI} will reoxidise Pd^0 with about equal efficiency, but the P–Mo–V co-catalysts are themselves more easily reoxidised than formulations without V^V. However, V^{IV}, the reduction product of V^V in these reactions, is not reoxidised by oxygen at all under even mildly acidic conditions. This highlights the role of the molybdate. Acid is necessary for these reactions; the P–Mo–V systems proceed well in more dilute acid (pH > 0), but $H_3[PMo_{12}O_{40}]$, which is itself as good a co-catalyst for the Pd^0/Pd^{II} reoxidation as are the P–Mo–V catalysts, has optimal activity in 1 mol dm^{-3} sulphuric acid.

N.m.r. studies show that $H_3[PMo_{12}O_{40}]$ is highly dissociated in acid solution, largely to phosphoric acid, although at least one intermediate species is detectable in more concentrated and less acidic solutions. Careful quantitative n.m.r. studies show that a significant proportion of the ^{31}P in catalytic (hydrolysed) solutions of $H_3[PMo_{12}O_{40}]$ is not detectable under ambient conditions. The appearance of a peak at higher temperature suggests that the undetectable species may be undergoing some intermediate-rate exchange processes. By implication, these species may well (*a*) be present in rather low concentration, (*b*) be phosphomolybdic acids with Mo : P greater than 12, and (*c*) be the actual active catalysts for Pd^0/Pd^{II} reoxidation. It is even possible that such species are the active ones in the P–Mo–V catalysts.

Experimental

^{31}P N.m.r. spectra were recorded on a JEOL JMN-PS-100 spectrometer at 40 MHz and in some cases also at 105 MHz on a Bruker WH 400 spectrometer; a deuterium lock was used in all cases. The referencing was to external triphenylphosphine dissolved in hexadeuterioacetone for ambient-temperature experiments and in hexadeuteriodimethyl sulphoxide for the higher-temperature experiments. The magnetic field is parallel to the axis of the n.m.r. sample tube on the WH-400, while it is perpendicular on the JMN-PS-100 spectrometer. As a consequence, since external references were used, there are chemical shift differences between spectra run on the two spectrometers. For example, a solution of $H_3[PMo_{12}O_{40}]$ (4.1×10^{-3} mol dm^{-3}) in sulphuric acid (1 mol dm^{-3}) showed the phosphoric acid peak at 5.9 (JEOL) and at 4.41 p.p.m. (Bruker), with respect to the same external standard, triphenylphosphine in acetone. There were also some small changes in chemical shifts with changes in acidity. To make comparison easier the shifts quoted have all been normalised to those quoted in the Table.

The solutions were analysed by gas–liquid chromatography (Pye 104 chromatograph with packed SP 1200 column; flame ionization detection). Samples were initially run on a temperature program from 60 to 180 °C at 4 °C/min; once the product had been determined as exclusively butan-2-one, samples (for quantitative analysis) were run isothermally at 80 °C.

Palladium sulphate (Aldrich) and analytical grade phosphomolybdic acid (B.D.H.) were purchased; solutions for catalysis were prepared (see below) by dissolving the appropriate weight of phosphomolybdic acid and palladium sulphate (10 mg) in water (10 cm^3). Vanadium pentoxide (analytical grade; 0.45 g, 2.48 mmol) was dissolved with heating in sulphuric acid (1 mol dm^{-3}, 50 cm^3); the resulting stock solution contained 10^{-4} g ions V^V per cm^3 as VO_2^+. The crystalline phosphomolybdovanadic acids, $H_{3+n}[PMo_{12-n}V_nO_{40}]$, n = 1—3, were prepared by the method of Tsigdinos and Hallada.[20] However, in view of our observation [9] that even these heteropolyacids were mixtures which disproportionated still further in the acidic media used in the catalysis, in many cases solution were prepared by the method of Matveev *et al.*[4] A solution of the P–Mo$_6$–V$_6$ acid was made as follows. Vanadium pentoxide (2.16 g, 11.9 mmol), molybdenum trioxide (3.42 g, 23.7 mmol), sodium phosphate hydrate (1.51 g, 4.0 mmol), and anhydrous sodium carbonate (0.64 g, 6 mmol) were refluxed in distilled water (20 cm^3) for 40 min. The solution was cooled and the pH adjusted to 1 by addition of concentrated sulphuric acid (*ca.* 1 cm^3); it was then refluxed with stirring (20 min), cooled, and made up to a total volume of 80 cm^3 with distilled water. A small amount of greenish solid (*ca.* 20 mg) was filtered off; analysis showed this to contain 50% V^V. The filtered orange-brown stock solution, containing known amounts of P, Mo, and V, was then used in the oxidation experiments.

Butene Oxidation in the Absence of Oxygen.—The solution containing the reoxidant was refluxed under nitrogen to remove all dissolved oxygen. A volume containing 4.95×10^{-4} g ions V^V was then added to palladium sulphate (10 mg, 4.95×10^{-5} mol) under nitrogen in a two-necked round-bottomed flask (25 cm^3), fitted with a rubber septum on one neck. The volume was made up to 10 cm^3 with degassed distilled water. The flask was then attached by a wide neoprene tube to a burette containing but-1-ene; it was flushed with butene and then shaken vigorously on a mechanical shaker under butene. Gas uptake was monitored on the burette (corrected to 1 atm and 20° C) and samples of the solution were removed by syringe through the rubber septum and analysed by gas–liquid chromatography at regular intervals.

Butene Oxidation under Oxygen.—The reactions were carried out using the apparatus and materials described above, except that exclusion of air was not needed. In this case mixing was accomplished by use of a magnetic stirrer oriented so that it broke the gas-liquid interface at each rotation. (Checks were carried out which showed that this was as efficient as other methods, *e.g.* a Vibromix, and it was shown that on doubling the palladium sulphate and reoxidation catalyst concentrations the rates were doubled; thus the measured rate was not limited by gas-liquid mixing effects.) A 1 : 1 mixture of butene and oxygen was found to give optimum rates.

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