

Heterogeneously catalysed cleavage of carbon–carbon double bonds with hydrogen peroxide using calcined heteropolyacids on oxide supports

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Reaction of an alkene with aqueous hydrogen peroxide and a catalytic quantity of a heteropolyacid adsorbed onto magnesium, aluminium or zinc oxide leads to complete, rapid cleavage of the alkene to give carbonyl compounds.

Oxidative cleavage of alkenes to ketones, aldehydes or carboxylic acids is useful synthetically. Reagents for effecting this reaction include ozone and lead tetraacetate, although the latter often gives only small yields of cleavage products.¹ Alkenes are often cleaved indirectly through intentional or incidental prior formation of 1,2-diols, followed by further oxidation. There are many reagents for effecting this last cleavage, as with sodium bismuthate, osmium tetroxide, chromium compounds, permanganates and ruthenium oxides.¹ All of these reactions are carried out in homogeneous solution and are generally stoichiometric, or they use expensive oxidants to recycle precious metal catalysts. Here, oxidative cleavage of alkenes has been attained through the use of heterogeneous calcined heteropolyacid catalysts supported on zinc, magnesium or aluminium oxide, with hydrogen peroxide as a cheap, environmentally benign oxidant.

Heteropolyacids are easy to prepare from readily available tungstates, molybdates and phosphates and are soluble in organic solvents.² Those based on molybdenum and/or tungsten have been used as catalysts for effecting epoxidation of alkenes³ and for ring-opening of epoxides.⁴ Small yields (5–7%) of adipic acid have been reported during homogeneous conversion of cyclohexene to its *trans*-1,2-diol.^{3a} Similar homogeneous oxidation of cyclopentene gave a fair to modest yield of glutaraldehyde.^{3c} In homogeneous two-phase transfer systems, 12-tungstophosphoric acid and hydrogen peroxide have been reported to give epoxides and 1,2-diols from alkenes. On extended reaction, some complete cleavage of alkene was observed.^{3b}

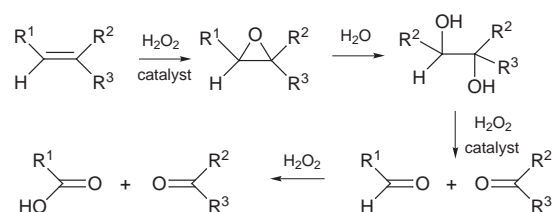
In the present work, 12-molybdophosphoric (PMA), 12-tungstophosphoric (PWA) or 6-molybdo-6-tungstophosphoric acid (PMWA) were deposited onto aluminium, zinc or magnesium oxide or hydroxide and then calcined to give heterogeneous catalysts. The alkenes shown in Table 1 were oxidatively cleaved to give acids, ketones or keto acids in high yields. In the presence of aqueous hydrogen peroxide and 2-methylpropan-2-ol as solvent, these catalysts gave very poor and often only fleeting yields of epoxides and 1,2-diols, unlike analogous oxidations reported for homogeneous heteropolyacid systems, from which high yields of epoxide can be obtained.³ As revealed by gas chromatographic monitoring of the reactions, the initial alkene disappeared completely from the reaction medium, but final percentage yields of oxidation products such as epoxides and 1,2-diols did not remotely match the percentage disappearance of starting material. Although the formation of 1,2-diols suggested that epoxides were being formed and were then being ring-opened solvolytically, no significant amounts of 1,2-diols were found at the end of reaction when all the alkene had disappeared. However, when MeOH was used as solvent, considerable quantities of 1-hydroxy-2-methoxy derivatives were found; such solvolysis products are typical of ring-opening of epoxides by nucleophilic solvents. Unlike the 1,2-diols, the 1-hydroxy-2-alkoxy compounds appear to be stable towards cleavage under the present reaction conditions and can form

significant proportions of the final reaction product. In the poorly nucleophilic solvent, 2-methylpropan-2-ol, no 1-hydroxy-2-butoxy derivatives were found and the very small quantities of 1,2-diol observed as intermediate products presumably arose from water in the hydrogen peroxide. Although in MeOH, yields of 1-hydroxy-2-methoxy derivatives reached a steady value towards the end of reaction, any 1,2-diols produced at the same time first increased in amount during the early stages of reaction and then decreased to zero towards the end. For example, during oxidation of cyclohexene with a PWA catalyst, maximum intermediate yields of some 7% epoxide and 15% cyclohexane-1,2-diol were observed during the course of oxidation, in which 100% of the alkene was converted to other products; at the end of reaction almost all of the epoxide and 1,2-diol had disappeared. Work-up of this reaction mixture for non-volatile components showed that the alkene double bond had been completely cleaved to give adipic acid in high yield and selectivity (Table 1), which had not been observed by GC monitoring. Other alkenes behaved similarly (Table 1). It is clear that these supported heteropolyacids (or their anions on the supporting oxides and hydroxides) split alkenes efficiently so as to give complete double-bond cleavage (Scheme 1). Any

Table 1 Oxidative cleavage of alkenes with supported heteropolyacids and hydrogen peroxide

Alkene	Heteropolyacid ^a	<i>t/h</i> ^b	Product (% yield)
2,3-Dimethyl-2-butene	PMWA:Mg:C:150/0.5	8	acetone ^c (91)
Cyclohexene	PMA:Al:C:150/0.5	24	adipic acid ^d (90)
1-Methylcyclohexene	PWA:Al:C:150/0.5	24	6-ketoheptanoic acid ^d (96)
Oct-1-ene	PMWA:Mg:C:150/0.5	4	heptanoic acid ^d (100)
Cyclooctene	PMWA:Al:A:150/0.5	10	epoxide ^e
Styrene	PWA:Al:C:500/4	24	benzoic acid (90)
<i>trans</i> -Stilbene	PWA:Al:C:500/4	24	benzoic acid (92)
<i>trans</i> -Stilbene	PWA:Al:C:500/4	24	<i>f</i>

^a See text for code. ^b All reactions were carried out at 60 °C in 2-methylpropan-2-ol as solvent, except for entry *f*. ^c Isolated as its 2,4-dinitrophenylhydrazone. ^d Isolated and identified by comparison with authentic material for mp, ¹H NMR and mass spectrum. ^e The epoxide of cyclooctanone is well-known for its resistance to nucleophilic attack. In this instance, after about 50% conversion of alkene, its epoxide was isolated in 30% yield along with some suberic acid (7% yield). ^f This example is included to show the effect of MeOH as solvent. The bulk of the product consisted of equal amounts of the enantiomeric pair of 1-hydroxy-2-methoxy-1,2-diphenylethanes, together with surprisingly only a little of the *meso* derivative.



Scheme 1

final oxidation of aldehyde to carboxylic acid may or may not be catalysed.

Where the carbonyl formed on cleavage is an aldehyde, further oxidation to carboxylic acid ensues rapidly, since intermediate aldehydes are rarely observed, one such exception occurring in the oxidation of styrene. The oxidation of aldehydes to acids by hydrogen peroxide is known.⁵ 1-Hydroxy-2-methoxy derivatives appear not to be oxidised further in these systems. For this reason, for optimum cleavage yields, either 2-methylpropan-2-ol or MeCN were used as solvent (Table 1).

For all oxidations, a blank reaction was carried out by omitting the catalyst from the reaction mixture. No oxidation was observed. To verify that leakage of catalyst from heterogeneously-supported materials to give homogeneous catalysts was not significant, parallel experiments were carried out by first refluxing the catalyst with the reaction mixture minus hydrogen peroxide and then filtering the mixture. The filtrate was used without more catalyst to determine its ability to effect oxidation of an alkene and the residue was used likewise. In all cases, the degree of oxidation observed with the filtrate as catalyst was very small but the solid residual catalysts were as efficient as the initial one. Finally, the longevity of the catalysts was examined by using the same catalyst for several successive oxidations. Generally, by the fourth cycle, the catalyst had lost most of its potency.

The catalysts were prepared in several ways to examine changes in their effectiveness with their pre-treatments. In some cases, the heteropolyacids were deposited onto preformed oxides (method A) or hydroxides (method B) but, in others, the catalyst was co-precipitated during formation of the hydroxide (method C). In all cases, the resulting solids were dried to 80 °C *in vacuo* and then calcined at either 150 or 500 °C. The catalysts are distinguished by a code. Thus, (PMA:Al:A:500/4) means 12-molybdophosphoric acid deposited onto aluminium oxide by method A and calcined at 500 °C for 4 h. Not all catalysts were equally effective for cleavage of alkenes. Generally, catalysts prepared by method B gave either inferior or no better yields than the corresponding catalysts prepared by method A or C.

In a typical catalyst preparation, 6-molybdo-6-tungstophosphoric acid (19.5 g)⁶ in water (20 ml) was added to an approximately equal weight of freshly prepared and washed aluminium hydroxide, prepared from aluminium ammonium sulfate and sodium hydroxide; the mixture was stirred for 1 h.

Excess of water was removed by centrifugation and the residue was washed with distilled water (3 × 20 ml). The solid product was dried at 80 °C *in vacuo* (20 mmHg) until its weight remained constant (about 2 days). The dried product was calcined by heating it either at 150° for 30 min or 500 °C for 4 h to give 45.3 g of the required catalyst, PMWA:Al:C:150/0.5.

In a typical oxidation, 1-methylcyclohexene (1.00 g; 10 mmol), dodecane (0.1 g, used as internal GC standard), hydrogen peroxide (70% w/w; 3–4 equiv. to alkene) and the catalyst (PWA:Al:C:150/0.5; 0.5 g) in 2-methylpropan-2-ol (25 ml) were stirred together at 60 °C. The progress of reaction was monitored by GC and the concentration of hydrogen peroxide was assessed with test strips (Merck). After complete conversion of the alkene or after a maximum of 24 h, the reaction was cooled, the catalyst filtered off and the filtrate was evaporated to dryness. The residue was distilled to give 6-oxoheptanoic acid, mp 33–34° (lit.,⁷ 34–35 °C), identified by ¹H NMR spectroscopy and mass spectrometry. The other alkenes were reacted similarly and the products were isolated (see Table 1).

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Notes and references

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