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# HETEROPOLYANIONS AS OXIDATION CATALYSTS IN A 2-PHASE SYSTEM

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Summary: Described is a system using heteropoly-11-tungstates as homogeneous catalysts for the oxidation of cyclohexene with hydrogen peroxide. The catalyst is dissolved in an organic solvent while the oxidant resides in the aqueous phase. The oxidation efficiency is high.

Heteropolyanions (HPA's) can be used as catalysts for gas-phase oxidation reactions (1). Examples include the dehydrogenation of isobutyric acid (2) and the oxidation of isobutene (3), both to methacrylic acid. The HPA's used in these reactions are mostly of the "mixed" molybdenum-vanadium type (4). Gazarov et al. (5) were the first to show that HPA's of the so-called substituted-lacunary type (6,7) have a quite high oxidation activity despite the use of tungsten instead of molybdenum. Until recently the liquid-phase oxidation potential of the HPA's has attracted less interest. When Corigliano and DiPasquale (8) introduced the use of tetraalkylammonium salts to dissolve polyvanadates in water-immiscible organic solvents it became possible to use lacunary and substituted-lacunary type HPA's in liquid-phase reactions while avoiding dissociation of the catalyst. Other workers have reported on epoxidation reactions with iodosylbenzene catalyzed by HPA's (9) and on the change in the coordination chemistry of HPA's (10), both with the HPA's as tetraalkylammonium salts in an organic solvent. Recently, Venturello et al. (11) performed the epoxidations of alkenes using a related system of lower molecular weight, i.c. tetraalkylammonium$_3$-$PW_4O_{24}$ with hydrogen peroxide as the oxidant.

In this paper we report on the catalytic oxidation of alkenes using tetraalkylammonium-HPA's in a two-phase system. The oxidizing agent used is hydrogen peroxide.

The catalysts used are tungsten-HPA's, both with complete Keggin structure (12) and with a lacunary and substituted-lacunary structure (see Figure 1). In aqueous solution pH dependent dissociation equilibria occur (13). For example tetraButylAmmonium$_3$-$PW_{12}O_{40}$ gave 0.03 %/h dissociation to water soluble tungsten species at pH 2, 0.31 %/h at pH 3 and 1.49 %/h at pH 4. $tBA_7$-$PW_{11}O_{39}$ (a lacunary-type HPA) even gave 27.3 %/h dissociation at pH 3 (14). In fact, oxidations performed with these HPA's in aqueous hydrogen peroxide were shown to be homogeneously catalyzed by dissociated tungsten species (15). The oxidation efficiency - defined as the % $H_2O_2$ effectively used for oxidation of the organic reactants - of this system was low. Dissociation can be prevented, however, by dissolving the catalyst in a water-immiscible second phase. Thus the catalytic oxidation efficiency proved to be greatly enhanced.

We have studied the oxidation of cyclohexene (as a model compound) with 30% hydrogen peroxide using 1,2-dichloroethane as the organic solvent. The initially formed epoxide is rapidly converted into trans-1,2-cyclohexanediol in the acidic aqueous phase. When using

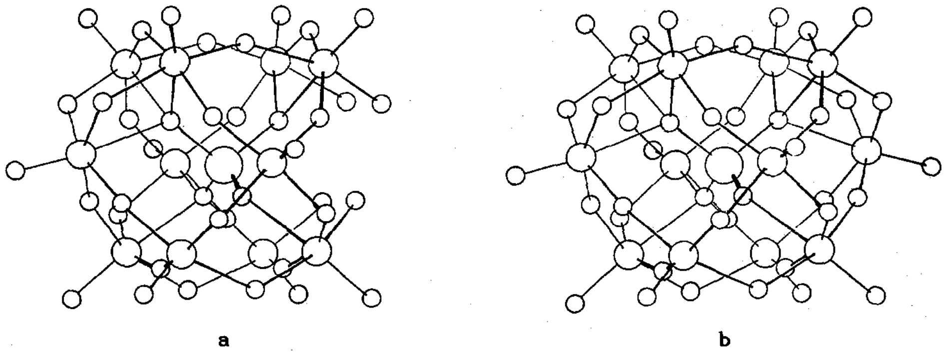
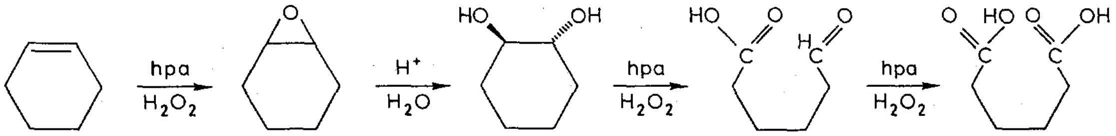


Fig. 1. Molecular structure of a 11- (a) and a 12-tungstosilicate (b).

the stoichiometric amount of hydrogen peroxide part of the diol is further oxidized to 6-oxohexanoic acid (adipaldehyde) and 1,6-hexanedioic acid (adipic acid).



The reaction was shown to take place in the organic phase by replacing this layer after 1 hour of reaction with fresh 1,2-dichloroethane and cyclohexene <u>without</u> catalyst; the reaction rate slowed down to zero (Fig. 2). Thus, catalysis does not take place in the aqueous phase nor are decomposition products of the HPA's involved.

During the reaction the conversion of hydrogen peroxide was monitored by iodometric titration. Some typical conversion plots are shown in Fig. 3.

Hydrogen peroxide partially decomposes to oxygen and water, the oxygen thus formed was measured.

The results of the experiments are shown in Table 1. HPA catalysts with a lacunary, and some systems with a filled-lacunary structure, proved to be active and highly efficient for this type of oxidation. The 12-tungstophosphate is inactive. This difference in activity between the complete and the lacunary HPA indicates that the place where the tungsten has been removed is the active site. Gazarov and Gordeeva (5) consider the HPA's as model compounds for larger crystal lattices, and it is widely accepted that catalysis often takes place at <u>faults</u> in a crystal lattice. We assume that the vacancy activates the surrounding tungsten atoms for transformation into peroxo structures by reaction with hydrogen peroxide. The precise mechanism remains to be elucidated however.

The product selectivities are dependent on the HPA used. The selectivities to adipaldehyde in the consecutive reaction are noteworthy. The iron-containing HPA is less selective for cyclohexanediol formation than the lacunary or the nickel-containing HPA and gives 34% of an as yet unidentified product. The central atom also has influence on the selectivity. The efficiency for oxidation of organic reactants seems to be correlated to the

Table 1. Results of cyclohexene oxidation[a].

| Catalyst | $H_2O_2$ Conversion[b] | $H_2O_2$ Decomposed[c] | Products[d] CH-diol | adipic acid | adipaldehyde | other |
|---|---|---|---|---|---|---|
| | % | % | % | % | % | % |
| $PW_{12}O_{40}^{3-}$ | 5 | 5 | – | – | – | – |
| $PW_{11}O_{39}^{7-}$ | 100 | 7 | 68 | 7 | 25 | – |
| $PNiW_{11}O_{39}^{5-}$ | 94 | 5 | 70 | 7 | 22 | 1 |
| $PCoW_{11}O_{39}^{5-}$ | 100 | 100 | – | – | – | – |
| $PCuW_{11}O_{39}^{5-}$ | 100 | 100 | – | – | – | – |
| $PFeW_{11}O_{39}^{4-}$ | 80 | 5 | 56 | 5 | 5 | 34 |
| $SiW_{11}O_{39}^{8-}$ | 69 | 3 | 54 | 7 | 38 | 1 |

a Tetrahexylammonium HPA (.14 mmole), cyclohexene (100 mmole), $H_2O_2$(30%, 100 mmole, pH 2) and 24 g of 1,2-dichloroethane were vigorously stirred at 340 K.

b Conversion of $H_2O_2$ after 5 hours.

c Oxygen monitored as % of total $H_2O_2$.

d Products in mole % of total products. Analysis was performed with HPLC on a BIORAD HPX-87 column.

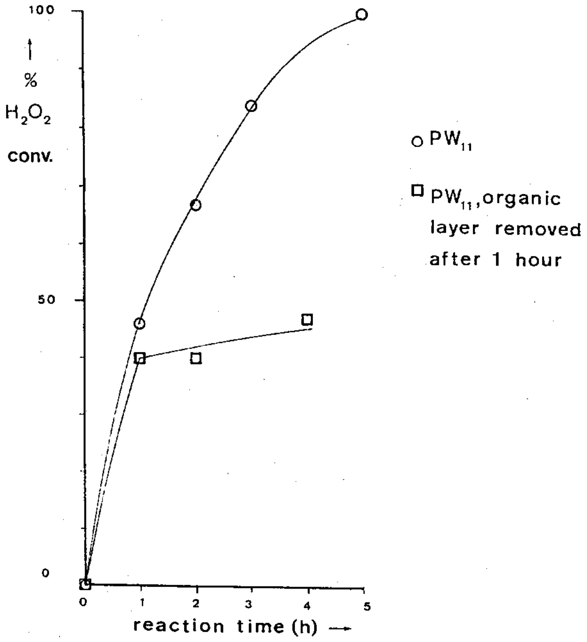


Fig. 2. Reaction with and without exchanging the organic layer.

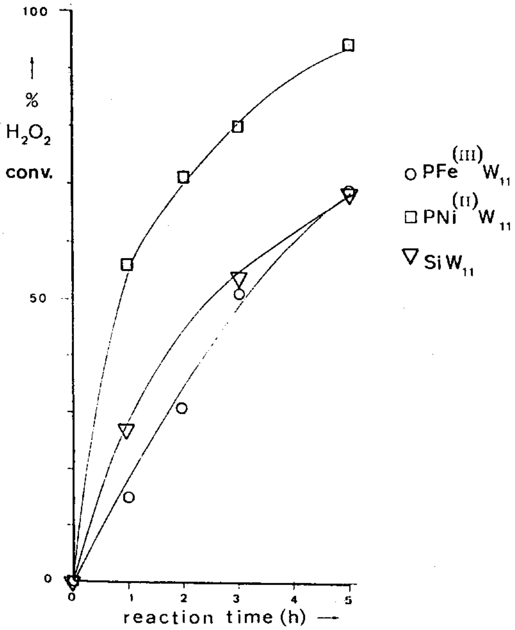


Fig. 3. Some typical conversion plots.

possibility of the substituted metal-ion to participate in one-electron redox-cycles. Cobalt(II) is oxidized in the environment used and the system produces only oxygen. The same holds for copper(II) which might be oxidized to copper(III). In contrast, iron(III) and nickel(II), both difficult to oxidize, give good oxidation efficiencies.

The system described here is the first which uses lacunary HPA's in organic solution as oxidation catalysts while the oxidant resides in a different phase. The system is highly efficient and stable. Further research will be directed to the elucidation of the oxidation mechanism and the reaction kinetics.

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