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High-valent manganese in polyoxotungstates. 4. Catalytic and stoichiometric alkene oxidation

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Abstract

Six manganese-containing heteropolytungstates, α - $[(XO_4)W_{11}MnO_{36}]^{n-}$ ($XW_{11}Mn$; $X = P, Si, B,$ and Zn), γ - $[(SiO_4)W_{10}Mn^{III}_2O_{36}H_6]^{4-}$ ($SiW_{10}Mn_2$), and $[Mn_4^II(H_2O)_2(PW_9O_{34})_2]^{10-}$ ($P_2W_{18}Mn_4$) have been compared as catalysts for the oxidation of cyclohexene and *cis*-stilbene by iodosylbenzene. The yield of epoxide and the *cis/trans* isomer ratio of stilbene epoxides are dependent upon the charge of the $XW_{11}Mn$ catalysts. In addition to the oxidation reactions, isomerization of *cis*-stilbene to *trans*-stilbene was observed when an oxidized derivative of $P_2W_{18}Mn_4$ was used as a catalyst. Stoichiometric oxidation of cyclohexene or *cis*-stilbene by high-oxidation-state manganese-substituted heteropolyanions was also examined. Product distributions from stoichiometric oxidation are different from those from the catalytic reactions for each heteropolyanion, suggesting that different reaction pathways may be involved in these two types of reactions.

Keywords: Heteropolytungstates; Manganese(III,IV); Dimanganese(III,III); Tetramanganese(II,III); Iodosylbenzene; Epoxidation; Cyclohexene; Stilbene; *cis/trans* isomerization

1. Introduction

The catalytic activity of polyoxometalates, especially transition-metal-substituted polyoxometalates, has attracted increased attention in recent years [1,2] (for recent reviews of this chemistry see contributions from several authors in Ref. [3]). Monosubstituted Keggin anions, $[(XO_4)ZW_{11}O_{36}]^{n-}$ (where Z^{z+} is a transition metal cation) display many reactive characteristics of metalloporphyrins, with the added advantage of an oxidatively inert 'ligand'. These

species are able to activate dioxygen and to catalyze oxo transfer reactions, processes highly analogous to those involving metalloporphyrins in rate and selectivity. Hill and coworkers [4–7] first reported the use of $[(PO_4)ZW_{11}O_{36}]^{n-}$ ($Z^{z+} = Mn^{2+}, Fe^{3+}, Co^{2+},$ and Cu^{2+}) as catalysts for the epoxidation of alkenes and for the hydroxylation of alkanes. Finke et al. [8,9] examined $[\alpha_2-P_2W_{17}O_{61}(M^{n+})]^{n-11}$ ($M^{n+} = Mn^{3+}, Fe^{3+}, Co^{2+}, Ni^{2+},$ and Cu^{2+}) as catalysts for oxidation of cyclohexene and *cis*-stilbene and noted that the manganese-substituted heteropolyanion showed the highest catalytic activity in this group of catalysts. Neumann and Gara [10] have recently demonstrated alkene oxidation catalyzed by other tungstoman-

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ganates, $[\text{WZnMn}_2(\text{ZnW}_9\text{O}_{34})_2]^{12-}$ and $[\text{WMn}_3(\text{ZnW}_9\text{O}_{34})_2]^{12-}$, and Liu [11] has reported that the trimanganese-substituted Keggin anion $[(\text{SiO}_4)\text{W}_9\text{O}_{33}\text{Mn}_3(\text{OH}_2)_3]^{10-}$ showed catalytic activity for epoxidation.

In earlier papers of this series [12–14] we have described several manganese-substituted polyoxotungstates in which the manganese is oxidizable to Mn^{III} and/or Mn^{IV} . Here we report a comparative study of the catalytic activity of these complexes with respect to oxidation of the exemplary substrates, cyclohexene and *cis*-stilbene, with iodosylbenzene.

Mono-, di-, and tetramanganese species were examined. It is of interest to learn how the accessibility of higher oxidation states might influence catalytic efficacy, and, for the Mn_2 and Mn_4 species, the consequences of more than one redox center. The mono-manganese-substituted Keggin anions can have different central atoms, which determine the total anion charge and influence Mn redox potentials [12,15].

2. Experimental

2.1. Reagents and catalysts

Acetonitrile (Aldrich) and dichloromethane (VWR) were 'glass distilled grade' and were used as received. Other organic chemicals were highest grades (Aldrich) and used without further purification.

Iodosylbenzene was prepared by the hydrolysis of iodobenzene diacetate (98%, Aldrich) with sodium hydroxide, washed with chloroform, carefully dried under vacuum, and stored at 4°C [16,17].

The preparation and characterization of the catalysts, $[(\text{C}_6\text{H}_{13})_4\text{N}]_7[(\text{ZnO}_4)\text{W}_{11}\text{Mn}^{\text{IV}}\text{O}_{36}\text{H}] \cdot 21\text{H}_2\text{O} \cdot \text{CH}_3\text{CN}$, (abbreviated as $\text{ZnW}_{11}\text{Mn}^{\text{IV}}$), $[(\text{C}_4\text{H}_9)_4\text{N}]_{5,3}[(\text{BO}_4)\text{W}_{11}\text{Mn}^{\text{IV}}\text{O}_{36}\text{H}_{0.7}] \cdot 10\text{H}_2\text{O} \cdot 0.5(\text{C}_6\text{H}_5)_3\text{CN}$, ($\text{BW}_{11}\text{Mn}^{\text{IV}}$), $[(\text{C}_4\text{H}_9)_4\text{N}]_5[(\text{SiO}_4)\text{W}_{11}\text{Mn}^{\text{IV}}\text{O}_{36}\text{H}] \cdot 18\text{H}_2\text{O} \cdot 0.5(\text{C}_6\text{H}_5)_3\text{CN}$, ($\text{SiW}_{11}\text{Mn}^{\text{IV}}$), and

$[(\text{C}_4\text{H}_9)_4\text{N}]_4[(\text{SiO}_4)\text{W}_{10}\text{Mn}^{\text{III}}\text{O}_{36}\text{H}_6] \cdot 1.5\text{CH}_3\text{CN} \cdot 2\text{H}_2\text{O}$ ($\text{SiW}_{10}\text{Mn}^{\text{III}}$) has been described elsewhere [12,13]. The tetra-*n*-butylammonium salt of $[(\text{PO}_4)\text{W}_{11}\text{O}_{35}\text{Mn}(\text{OH}_2)]^{5-}$ ($\text{PW}_{11}\text{Mn}^{\text{II}}$), was prepared by the addition of solid tetra-*n*-butylammonium bromide to a solution of $\text{K}_5[(\text{PO}_4)\text{W}_{11}\text{O}_{35}\text{Mn}(\text{OH}_2)] \cdot 15\text{H}_2\text{O}$. This afforded a yellow precipitate which was dissolved in acetonitrile and precipitated by dropwise addition of water [12]. The red Mn^{III} derivative, $[(\text{C}_4\text{H}_9)_4\text{N}]_4[(\text{PO}_4)\text{W}_{11}\text{O}_{35}\text{Mn}^{\text{III}}\text{OH}_2] \cdot 10\text{H}_2\text{O}$, ($\text{PW}_{11}\text{Mn}^{\text{III}}$), was obtained by aerial oxidation of an acetonitrile solution of $\text{PW}_{11}\text{Mn}^{\text{II}}$.

The tetrabutylammonium salt of $[\text{Mn}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2]^{10-}$ ($\text{P}_2\text{W}_{18}\text{Mn}_4^{\text{II}}$) was obtained as follows. A solution of the potassium salt [14,18] (10 g) in 100 ml water was heated to 50°C until all solids were dissolved. Addition of 15 g $[(\text{C}_4\text{H}_9)_4\text{N}]\text{NO}_3$ yielded an orange precipitate of a tetra-*n*-butylammonium–potassium salt of $\text{P}_2\text{W}_{18}\text{Mn}_4^{\text{II}}$. The precipitate was filtered off and redissolved in 20 ml acetonitrile. Traces of insoluble solids were filtered out and the salt was reprecipitated by addition of 20 ml water to the filtrate. The yield was about 15%. Anal. Found: W, 47.29; Mn, 2.90; P, 0.79; C, 21.44; N, 1.53; H, 4.08; $K < 0.1$. Calc. for $[(\text{C}_4\text{H}_9)_4\text{N}]_{7,8}\text{H}_{2,2}[\text{Mn}_4(\text{H}_2\text{O})_2(\text{PW}_9\text{O}_{34})_2] \cdot 22\text{H}_2\text{O}$: W, 47.28; Mn, 3.14; P, 0.89; C, 21.40; N, 1.56; H, 4.01.

2.2. Instrumentation

Gas chromatographic analyses were carried out with a Hewlett Packard 5890 gas chromatograph equipped with a hydrogen flame ionization detector and a Hewlett Packard Model 3396 II integrator. A cross-linked methylsilicone-coated capillary column (25 m; i.d. 0.32 mm, purchased from Hewlett Packard) was used for analyses of products from cyclohexene and *cis*-stilbene oxidations. Oxidation products were analyzed and identified by comparing their retention times with those of authentic samples and further confirmed by coinjection and GC-mass spectroscopy.

GC-MS were recorded on a Fisons MD 800 instrument equipped with a capillary column (10 m cross-linked methylsilicone-coated; i.d. 0.15 mm). In order to remove the heteropolyanion catalysts, samples were passed through a mini column of 60 mesh silica-gel (EM Science) before injection into the GC-MS.

2.3. Typical reactions and product analyses

All reactions were examined both in the presence of air and under argon. Substrates, catalysts, and standard were dissolved in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1 by volume).

In the presence of air, the reaction was carried out in a 7 ml vial equipped with an open screw top cap, a teflon–silicone septum, and a stirring bar. Solid PhIO (0.011 g, 0.05 mmol), and solutions of substrate (0.20 ml, 1.0 mmol), the internal standard (benzonitrile, 25 μl , 10 μmol), and catalyst (0.20 ml, 1.0 μmol) were placed in the vial and stirred for a given time.

For the reactions under argon, a two-lobed Schlenk flask was equipped with a septum and a stirring bar. Solid PhIO (0.011 g, 0.05 mmol) and substrate solution (0.20 ml, 1.0 μmol) were placed in one lobe. The internal standard (25 μl , 10 μmol) and catalyst (0.20 ml, 1.0 μmol) were placed in the other lobe. The solutions were degassed by three freeze–pump–thaw cycles and the reaction was started by mixing the two solutions.

Time-dependent experiments were performed in the same way but with 0.0220 g PhIO (0.10 mmol) and at 30°C controlled with a constant temperature water bath. Aliquots were withdrawn at appropriate time intervals and stored in liquid nitrogen. Quantitative analysis was performed on each aliquot which was thawed immediately before injection.

For the stoichiometric reactions the high-oxidation-state manganese-substituted polyanions were prepared using PhIO as described previously [12–14]. Typically, heteropolyanion (0.13 mmol) and PhIO (0.44 g, 2.0 mmol) in 1.0 ml solvent were stirred for ca. 10 min. Excess

PhIO was filtered off and washed with another 0.50 ml solvent. The filtrate and washings were evaporated to dryness under vacuum. The residue was redissolved in 1.0 ml fresh solvent for use in the reaction. A typical reaction was carried out with a solution of high-oxidation-state manganese-substituted polyanion (0.1 ml, 13 μmol), internal standard (25 μl , 10 μmol), and substrate (20 μl cyclohexene or 40 μl *cis*-stilbene).

Quantitative analysis was performed using benzonitrile as an internal standard. Yields for catalytic oxidation of alkenes by PhIO were calculated based on the consumption of the oxidant (PhIO), i.e. $\text{Yield} = 100 \times [\text{product component}]/[\text{PhI}]$. Oxidant conversion was calculated from moles of PhIO added, M_{PhIO} , and moles of PhI produced, M_{PhI} , i.e. yield for $\text{PhI}(\%) = 100 \times M_{\text{PhI}}/M_{\text{PhIO}}$.

For the non-catalytic (stoichiometric) oxidations with high-oxidation-state manganese-substituted polyanions, yields were not calculated for those reactions which only afforded a small amount of products (less than 2% based on the polyanion). For a reaction which afforded a significant amount of product, ‘yields’ are reported as $100 \times /M_p/M_h$, where M_p and M_h are the numbers of moles of the product and heteropolyanion, respectively. No attempts were made to correct for the different numbers of manganese atoms in the heteropolyanions and the different numbers of electrons transferred in the different products.

3. Results

3.1. Catalytic oxidation of cyclohexene

Oxidation of cyclohexene under argon afforded the epoxide as the main product as shown in Table 1. In every case, except when BW_{11}Mn was used as a catalyst, the reaction slurry had clarified within 3 h indicating total consumption of PhIO. Stirring the resulting solution for an

Table 1
Oxidation of cyclohexene by PhIO under argon^a

| Catalyst | Yield ^b | | | Conversion ^c |
|--|----------------------|---------|--------|-------------------------|
| | epoxide | alcohol | ketone | |
| None | — ^d | — | — | 8 |
| PW ₁₁ Mn ^{III} | 64 (69) ^e | — (—) | 1 (2) | 89 (90) |
| SiW ₁₁ Mn ^{IV} | 59 (55) | 10 (10) | 7 (7) | 82 (81) |
| BW ₁₁ Mn ^{IV} | 9 (46) | — (—) | — (6) | 70 (88) |
| ZnW ₁₁ Mn ^{IV} | 29 (34) | 9 (9) | 10 (7) | 72 (84) |
| SiW ₁₀ Mn ₂ ^{III} | 29 (25) | — (—) | — (—) | 87 (89) |
| P ₂ W ₁₈ Mn ₄ ^{II} | 48 (43) | 9 (—) | — (—) | 86 (83) |

^a 11 mg (0.05 mmol) PhIO, 1 mmol cyclohexene, 1 μmol catalyst, 0.4 ml CH₂Cl₂/CH₃CN (1:1 v:v), ambient temperature; see text for details.

^b % based on consumption of oxidant after 3 h.

^c % conversion of PhIO to PhI after 3 h.

^d < 1%.

^e Figures in parentheses are yields and conversions after 24 h.

additional 21 h had no further effect upon the product distribution.

The oxidation of cyclohexene by PhIO in the presence of air afforded relatively more allylic alcohol and ketone as shown in Table 2. The reactions proceeded faster than those under argon. All reactions finished within 2 h based on the solid PhIO consumption. The total yield of epoxide, allylic alcohol, and ketone were greater than 100% in most cases in terms of the PhIO consumption, indicating that oxidation by air also occurred. The yield of epoxide decreases as

Table 2
Oxidation of cyclohexene by PhIO in air^a

| Catalyst | Yield ^b | | | Conversion ^c |
|--|---------------------|---------|---------|-------------------------|
| | epoxide | alcohol | ketone | |
| None | 5 (11) ^d | 15 (20) | 19 (35) | 57 (100) |
| PW ₁₁ Mn ^{III} | 40 (38) | 34 (35) | 40 (44) | 89 (90) |
| SiW ₁₁ Mn ^{IV} | 42 (40) | 26 (38) | 33 (44) | 93 (92) |
| BW ₁₁ Mn ^{IV} | 13 (11) | 43 (52) | 53 (58) | 89 (90) |
| ZnW ₁₁ Mn ^{IV} | 28 (28) | 17 (27) | 39 (45) | 90 (90) |
| SiW ₁₀ Mn ₂ ^{III} | 15 (15) | 45 (49) | 55 (60) | 93 (94) |
| P ₂ W ₁₈ Mn ₄ ^{II} | 15 (15) | 46 (47) | 55 (59) | 93 (92) |

^a 11 mg (0.05 mmol) PhIO, 1 mmol cyclohexene, 1 μmol catalyst, 0.4 ml CH₂Cl₂/CH₃CN (1:1 v:v), ambient temperature; see text for details.

^b % based on consumption of oxidant after 2 h.

^c % conversion of PhIO to PhI after 2 h.

^d < 1%.

^e Figures in parentheses are yields and conversions after 24 h.

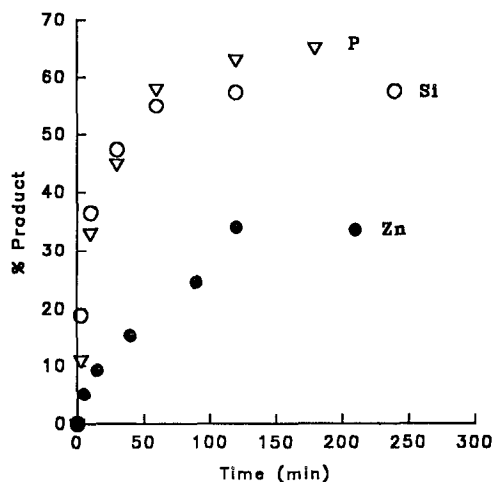


Fig. 1. Time course of cyclohexene epoxide production with PW₁₁Mn, SiW₁₁Mn, and ZnW₁₁Mn catalysts.

the Mn^{II}/Mn^{III} redox potential [12,15] decreases.

The yield of epoxide at different time intervals is shown in Fig. 1. When PW₁₁Mn or SiW₁₁Mn was used as a catalyst, about 85% epoxide production was achieved within 1 h, i.e. 58 and 55 turnovers ($M_{\text{epox}}/M_{\text{cat}}$, M_{epox} is moles of epoxide and M_{cat} is moles of catalyst). The reaction catalyzed by ZnW₁₁Mn is relatively slow and about 50% epoxidation is achieved in 1 h, e.g. 20 turnovers, which is comparable with the reaction catalyzed by P₂W₁₇Mn [16].

3.2. Catalytic reactions involving *cis*-stilbene

Oxidation of *cis*-stilbene under argon (Table 3) resulted in both *cis*- and *trans*-stilbene epoxides. The *cis/trans* isomer ratio and the total yield of epoxide decrease as the charge on the heteropolyanion catalyst increases. Although the yield of *cis*-stilbene epoxidation catalyzed by the tetra-manganese heteropolyanion, P₂W₁₈Mn₄, is not as high as that catalyzed by PW₁₁Mn, the selectivity is better. We also observed (see below) that P₂W₁₈Mn₄ catalyzed not only the epoxidation of *cis*-stilbene but also the isomerization of *cis*-stilbene to *trans*-stilbene.

Table 3
Epoxidation of *cis*-stilbene by PhIO under argon^a

| Catalyst | Yield ^b | | | Conversion ^c |
|--|--------------------|--------------|--------------------|-------------------------|
| | <i>cis</i> | <i>trans</i> | ratio ^d | |
| None | — ^e | — | | 4 |
| PW ₁₁ Mn ^{III} | 41 | 23 | 1.79 | 88 |
| SiW ₁₁ Mn ^{IV} | 22 | 18 | 1.22 | 85 |
| BW ₁₁ Mn ^{IV} | 27 | 28 | 0.96 | 86 |
| ZnW ₁₁ Mn ^{IV} | 13 | 21 | 0.62 | 81 |
| SiW ₁₀ Mn ₂ ^{III} | 19 | 16 | 1.19 | 74 |
| P ₂ W ₁₈ Mn ₄ ^{II} | 21 | 4 | 5.26 | 81 |

^a 11 mg (0.05 mmol) PhIO, 1 mmol *cis*-stilbene, 1 μmol catalyst, 0.4 ml CH₂Cl₂/CH₃CN (1:1 v:v), ambient temperature; see text for details.

^b % based on consumption of oxidant after 2 h.

^c % conversion of PhIO to PhI after 2 h.

^d [*cis* epoxide]/[*trans* epoxide].

^e < 1%.

The *trans* isomer, which is present in a small amount in *cis*-stilbene, does not appear to be involved in these oxidation experiments because the normalized area of the *trans*-stilbene peak remained unchanged after catalytic reactions except when the tetra-manganese polyanion was the catalyst.

The product distributions are listed in Table 4 for the catalytic oxidation of *cis*-stilbene by PhIO in the presence of air. In a separate experiment it was found that air (oxygen) did not

Table 4
Epoxidation of *cis*-stilbene by PhIO in air^a

| Catalyst | Yield ^b | | | Conversion ^c |
|--|--------------------|--------------------|--------------------|-------------------------|
| | <i>cis</i> | <i>trans</i> | ratio ^d | |
| None | 1 (4) ^e | — ^f (4) | | 11 (19) |
| PW ₁₁ Mn ^{III} | 54 (51) | 27 (28) | 2.00 | 89 (91) |
| SiW ₁₁ Mn ^{IV} | 40 (37) | 28 (29) | 1.43 | 90 (90) |
| BW ₁₁ Mn ^{IV} | 20 (26) | 19 (27) | 1.28 | 73 (89) |
| ZnW ₁₁ Mn ^{IV} | 13 (12) | 22 (23) | 0.59 | 88 (87) |
| SiW ₁₀ Mn ₂ ^{III} | 20 (18) | 18 (17) | 1.11 | 81 (87) |
| P ₂ W ₁₈ Mn ₄ ^{II} | 33 (31) | 11 (13) | 3.00 | 85 (85) |

^a 11 mg (0.05 mmol) PhIO, 1 mmol *cis*-stilbene, 1 μmol catalyst, 0.4 ml CH₂Cl₂/CH₃CN (1:1 v:v), ambient temperature; see text for details.

^b % based on consumption of oxidant after 2 h.

^c % conversion of PhIO to PhI after 2 h.

^d [*cis* epoxide]/[*trans* epoxide].

^e Figures in parentheses are yields and conversions after 24 h.

^f < 1%.

oxidize *cis*-stilbene in the presence of P₂W₁₈Mn₄^{II} over a period of 3 days. On the other hand the presence of air increases the total yields when PW₁₁Mn, SiW₁₁Mn, and P₂W₁₈Mn₄ were used as catalysts with PhIO as oxidant. The product distributions are similar to those obtained from reactions under argon.

3.3. Oxidation of cyclohexene and *cis*-stilbene by high-oxidation-state manganese-substituted polyoxotungstates

The high oxidation state complexes used for these reactions were prepared by oxidation with PhIO as described in Section 2. The concentrated solution of brown SiW₁₁Mn^{IV} prepared in this manner was not stable and evolved oxygen, leading to a pink–brown solution of the Mn(III) derivative. Upon reaction of this solution with cyclohexene for 3 h, at least eight products were observed in the presence of air, and six products were observed when the experiment was carried out under argon. In both cases the ‘yield’ of each product did not exceed 1% based on the heteropolyanion.

The results of reactions with the other heteropolyanions are summarized in Table 5. Under argon only SiW₁₀Mn₂ and P₂W₁₈Mn₄ yielded any significant oxidation products. For

Table 5
Product yields for oxidation of cyclohexene by high oxidation state polyoxoanions^a

| Oxidant | Yield ^b | | | |
|---|--------------------|--------------------|---------|---------------|
| | epoxide | alcohol | ketone | cyclohexanone |
| BW ₁₁ Mn ^{IV} | 0 (8) ^c | x ^d (x) | x (x) | 0 (0) |
| ZnW ₁₁ Mn ^{IV} | 0 (0) | 25 (X) | 10 (X) | 0 (0) |
| SiW ₁₀ Mn ₂ ^{III} | 2 (2) | 3 (33) | 5 (77) | 0 (0) |
| P ₂ W ₁₈ Mn ₄ ^{II,IV} | 24 (34) | < 1 (23) | 13 (37) | < 1 (11) |

^a 13 μmol oxidant in 0.1 ml CH₂Cl₂/CH₃CN (1:1 v:v), 20 μl (0.20 mmol) substrate, 25 μl benzonitrile (10 μmol) internal standard, argon atmosphere except where noted, ambient temperature, 3 h, see text for details.

^b 100(mol product/mol polyoxoanion).

^c Figures in parentheses give yields for reaction carried out in air.

^d X denotes a broad peak with retention time similar to those of the allylic alcohol and ketone (see text).

Table 6
Product yields for reaction of *cis*-stilbene with $P_2W_{18}Mn_4^{III,IV}$ ^a

| Conditions | Yields ^b | | |
|----------------|------------------------|---------------------|----------------------|
| | <i>trans</i> -stilbene | <i>cis</i> -epoxide | <i>trans</i> epoxide |
| 3 h (argon) | 38 | 0 | 0 |
| 3 days (argon) | 78 | 0 | 4 |
| 3 h (air) | 58 | 6 | 6 |
| 3 days (air) | 76 | 5 | 22 |

^a 13 μ mol oxidant in 0.1 ml CH_2Cl_2/CH_3CN (1:1 v:v), 40 μ l (0.22 mmol) substrate, 25 μ l benzonitrile (10 μ mol) internal standard, ambient temperature, see text for details.

^b 100(mol product/mol polyoxoanion).

the reactions carried out in air the possibility of catalytic behavior cannot be ruled out.

Oxidations of *cis*-stilbene with $SiW_{11}Mn^{III}$, $BW_{11}Mn^{IV}$, $ZnW_{11}Mn^{IV}$ and $SiW_{10}Mn_2^{III/IV}$ were carried under argon and in the presence of air for 3 h at room temperature. With the first three oxidants no epoxidation was observed under argon and only minor amounts (ca. 1%) were produced in air. The dimanganese oxidant yielded 1% *cis*- and 3% *trans*-epoxides under argon and 2% *cis* and 15% *trans* when the reaction was carried out in air.

The oxidation of *cis*-stilbene with high-oxidation-state $P_2W_{18}Mn_4$ is summarized in Table 6.

Reaction of the oxidized $P_2W_{18}Mn_4$ with *cis*-stilbene under argon produced only *trans*-stilbene. Three days later 4% *trans*-stilbene epoxide was detected. However, when air was present, 6% *cis*-stilbene epoxide was produced in 3 h and its amount did not increase after three days. The *trans*-stilbene epoxide production increased with time as shown in the reaction under argon. The isomerization product slowly increased with time. The color of the solution was still brown after 3 days and became orange after 5 days. The orange species was air-dried and its IR spectrum was found to be similar to that of $P_2W_{18}Mn_4^{II}$. When $P_2W_{18}Mn_4^{II}$ and *cis*-stilbene were mixed under the same conditions, no isomerization was observed after 3 days. Therefore, we conclude that the isomerization is

catalyzed by the high-oxidation-state-manganese polyanion, $P_2W_{18}Mn_4^{III,IV}$, instead of $P_2W_{18}Mn_4^{II}$.

4. Discussion

The oxidation of cyclohexene with PhIO catalyzed by the manganese-containing heteropolyanions selectively afforded cyclohexene epoxide under argon, a result which has been observed by others [2] using other transition metal substituted polyanions as catalysts. The yield of epoxide from catalysis with $PW_{11}Mn$ in our hands is comparable to that reported by Hill and Brown [4]. The present investigation shows that the yield of epoxide decreases in the order: $PW_{11}Mn > SiW_{11}Mn > BW_{11}Mn > ZnW_{11}Mn$. This order may reflect the variation in redox potential for manganese, which roughly tracks the overall anion charge (–5 to –8 for Mn^{II} derivatives).

When the reaction was carried out in the presence of air, the oxidation proceeded more quickly than under argon. Yields of allylic alcohol and ketone were dramatically increased. Because the total yield, except for the case catalyzed by $ZnW_{11}Mn$, is over 100% when PhIO is a limiting reagent, oxygen in the solvent must act as an oxidant.

As is well known, alkene epoxidation is catalyzed by a variety of transition metal complexes, and the redox properties of transition metals in these catalysts play an important role in determining catalytic activity. Usually, complexes containing first row transition metal cations, such as manganese or iron, sometimes chromium or cobalt, are catalytically active, while nickel-, zinc-, and silver-containing species are not [4,5,19,20]. Consequently, high oxidation states have generally been implicated in the catalytic process [4,5,16,20]. Thus, high-oxidation-state transition-metal heteropolyanions, e.g. manganese(IV)-polyoxotungstates, have been proposed as intermediate species [4]. The stability of high oxidation state intermediates depends on many factors. In some cases

such species cannot be observed, e.g. 'PW₁₁Mn^{IV}'. In other cases they are stable at low concentration, e.g. SiW₁₁Mn^{IV}. Stable high oxidation state intermediates usually do not attack substrates unless temperatures are elevated [6,7,10,21]. In the present work we noted that chromatograms of the products of anaerobic oxidation of cyclohexene with ZnW₁₁Mn^{IV} and BW₁₁Mn^{IV} showed a very broad elution peak (denoted as x in Table 5) between those of the allylic alcohol and ketone. This peak might result from the slow release of organic species associated with the Mn^{IV} complexes.¹

Oxidation of cyclohexene with high-oxidation-state P₂W₁₈Mn₄ under argon afforded mainly the epoxide. Thus, the high-oxidation-state P₂W₁₈Mn₄ is stable and is able to oxidize cyclohexene. It would be a good catalyst for studying the kinetics and mechanism of the catalytic reaction in the future.

Although product distributions from the oxidation of cyclohexene with high-oxidation-state manganese polyanions are different from those in the catalytic reactions, catalytic activities are seen to vary with the stability of high oxidation state species; the more stable the high-oxidation-state-manganese(IV) heteropolyanion (ZnW₁₁Mn^{IV}), the lower the epoxide yield. This is consistent with a mechanism implicating a high-oxidation-state-manganese intermediate [4].

It is possible that different oxidation pathways are involved in the oxidation and the catalytic reactions. The high-oxidation-state species could be stable in solution or on the surface of PhIO. Whether or not catalytic reactions occur on the surface of PhIO remains to be investigated.

Oxidation of both *cis*- and *trans*-stilbenes by oxygen is sluggish, although the *cis* isomer is the more easily oxidized [16,22,23]. Oxidation of *cis*-stilbene catalyzed by the manganese-sub-

stituted polyanions afforded *cis*- and *trans*-stilbene epoxides in a short time.

It has been reported [16] that oxidation of *cis*-stilbene with PhIO catalyzed by [P₂W₁₇O₆₁MBr]ⁿ⁻¹¹ (Mⁿ⁺ = Cu²⁺, Mn³⁺, Fe³⁺, and Co²⁺) gave a mixture of *trans*- and *cis*-stilbene epoxides and a small amount of *trans*-stilbene that was not involved in the *cis*-stilbene oxidation reaction. The *trans*-stilbene epoxide derived from the oxidation of *cis*-stilbene; no direct isomerization was observed. Although isomerization occurs with other transition metal-containing catalysts, such as metal porphyrin complexes [24], transition-metal salts [19], or PW₁₁Co [4], no isomerization product was found in the present study with the mono- or dimanganese-substituted Keggin anions. However, when P₂W₁₈Mn₄ was used as a catalyst, we observed both epoxidation and isomerization.

In view of the isomerization and the formation of *trans*-stilbene epoxide, the oxidation reaction must involve a pathway which allows rotation about the carbon-carbon bond. Many reaction schemes, which involve high-oxidation-state intermediates, have been described specifically for iron- or manganese-containing species [20,25–36]. The most reasonable intermediate permitting rotation is a radical or a cation [4,19].

Thermal oxidation of *cis*-stilbene with high-oxidation-state-manganese polyanions afforded different *cis/trans* ratios of the epoxides. The fraction of the thermodynamically-stable product, *trans*-stilbene epoxide, is much higher than that obtained in the catalytic reactions.

5. Final remarks

Oxidation of cyclohexene by PhIO under argon using mono-, di- and tetra-manganese heteropolyanions as catalysts selectively afforded the epoxide. When the reaction was carried out in the presence of air, a large amount of allylic

¹ The species responsible for the broad peak were found to be removed as a result of a necessary filtration through silica gel prior to GC/MS, and were therefore unidentifiable by this method.

alcohol and ketone was produced. The yield of epoxide is higher for the reaction under argon than in the presence of air, and, for the Keggin-based $XW_{11}Mn$ catalysts the yield decreased as the overall anion charge increased. The stability of high-oxidation-state manganese-substituted heteropolyanions appears to be a key factor controlling the amount of the epoxidation product. The more stable the high-oxidation-state manganese-substituted polyanions, i.e. $ZnW_{11}Mn^{IV}$, the less epoxide was formed. This trend has also been observed with other mono-substituted heteropolyanions [4–7].

In contrast to the oxidation of cyclohexene, the oxidation of *cis*-stilbene afforded more epoxide products in the presence of air than under argon. The ratio of *cis*-stilbene epoxide to *trans*-stilbene epoxide decreases as the negative charge of monomanganese-substituted Keggin increases. Oxidation of *cis*-stilbene catalyzed by $P_2W_{18}Mn_4$ has good selectivity toward *cis*-stilbene epoxide. High oxidation state $P_2W_{18}Mn_4$ catalyzes the isomerization of *cis*-stilbene to *trans*-stilbene.

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