



Kinetics and mechanism on the epoxidation of *cis*-1-propenylphosphonic acid in H₂O catalyzed by tungstate(VI) or molybdate(VI)

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Abstract

Epoxidation of *cis*-1-propenylphosphonic acid (CPPA) was carried out by using Na₂WO₄ or Na₂MoO₄ as catalyst, 30% hydrogen peroxide as an oxidant in H₂O. Kinetic study showed that the epoxidation was zero-order both in H₂O₂ and in CPPA with perfect linearity. The reaction was first-order only in catalysts. IR spectra showed that the active peroxy group in the epoxidation was a metal–dioxygen ring. The characteristic absorption peaks were 856 and 866 cm⁻¹ for Mo– and W–dioxygen rings, respectively. A mechanism of the epoxidation was suggested and discussed. The pH value of reaction solution and the negative charge on the carbon atoms of double bonds play an important role because they could influence the concentration of active complexes and the rate of insertion reaction. The research indicated that not only in non-protic solvents but also in H₂O, the active peroxy groups were the metal–dioxygen rings for the epoxidation of olefins catalyzed by W(VI) or Mo(VI) complexes. © 2003 Elsevier B.V. All rights reserved.

Keywords: Na₂WO₄; Na₂MoO₄; Epoxidation; Mechanism; *cis*-1-Propenylphosphonic acid (CPPA)

1. Introduction

Many α,β -unsaturated acids, such as maleic acid, fumaric acid, citraconic acid and *cis*-1-propenylphosphonic acid (CPPA) can easily dissolve in water because they have strong hydrophilic groups, such as carboxyl, phosphonic group in the molecules. For this reason, their epoxidation can carry out in water [1]. (–)(1*R*,2*S*)-1,2-epoxypropyl phosphonates (Fosfomycin) is a broad-spectrum antibiotic [2], which can be obtained by the epoxidation of *cis*-1-propenylphosphonic acid (CPPA) and the res-

olution of the racemic products. We have carried on many epoxidation experiments of CPPA in H₂O without any catalyst present but no epoxide was obtained. However, when Na₂WO₄ or Na₂MoO₄ was used as catalysts, the epoxidation could be completed easily. The mechanism study of the epoxidation of olefins was mainly aimed at non-protic solvents before [3,4]. Therefore, the mechanism of CCPA epoxidation in H₂O is an interesting problem.

Mimoun has summarized as two paths concerning the mechanism of W(VI) or Mo(VI) complexes catalyzed epoxidation of olefins in non-protic solvents [5]. The mechanisms were shown in Scheme 1(a) and (b).

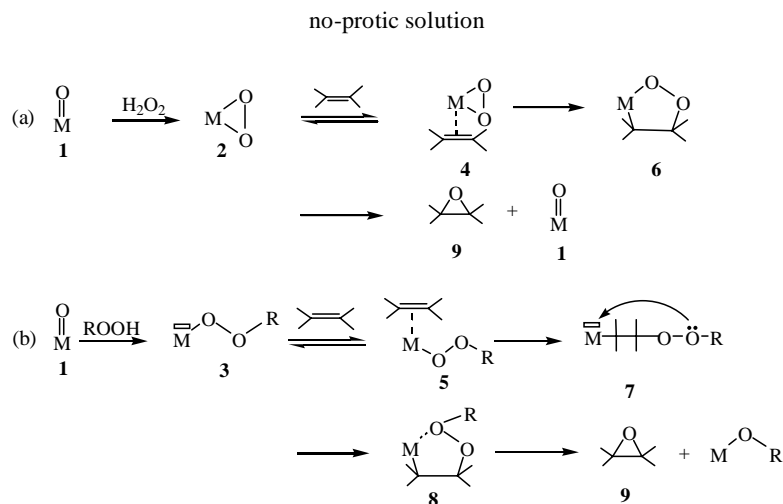
In path (a), the active peroxy group was a metal–dioxygen ring **2**. The peroxy complex behave as a 1,3-dipolar reagent M⁺–O–O⁻ [5]. The key active

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Scheme 1. Mechanism of W(VI) or Mo(VI) catalyzed epoxidation of olefins in non-protic solution.

intermediate was the metal–olefin–dioxacycle complex **4**. The olefin in **4** inserted into the metal–oxygen bond and formed a closed five-membered dioxametallacycle adduct **6**.

In path (b), the complexation of metal center with ROOH and olefin formed an acyclic metal–olefin–peroxo complex **5**. The insertion of the olefins into the M–O bond via intra-molecular nucleophilic attack of the –OOH or –OOR group at the coordinated olefin would lead to the formation of an acyclic adduct and leave a vacant coordination site on the metal **7**. A quasi-opened, five-membered dioxethylmetal adduct **8** was formed from electron donation of peroxo oxygen. Mimoun [5], and Chong and Sharpless [6] considered that M–OOR was the active peroxo group in the path while Mimoun also pointed out that the active intermediates in the path have not yet been fully characterized.

Our objective of the research is to make clear the epoxidation mechanism of CPPA in H₂O catalyzed by tungstate(VI) or molybdate(VI).

2. Results and discussion

CPPA is a strong acid, it must be neutralized to pH 5.0–6.0 by an organic or inorganic base (such as NaOH) before epoxidation. Among organic bases,

racemic α -phenylethylamine was used often, while it was also used as resolution reagent producing Fosfomycin [7]. The epoxidation is shown in Scheme 2.

The kinetic study showed that the epoxidation was zero-order both in H₂O₂ and in CPPA with perfect linearity (Figs. 1 and 2). It was first-order only in catalysts (Fig. 3). The rate constants are shown in Table 1.

As shown in Table 1, the reaction rate was independent of the concentration of the two reactants and was only dependent on the concentration of the catalyst. It was indicated the process involved a rapid irreversible metal–olefin–peroxo complex formation from the catalysts, CPPA and H₂O₂ in H₂O. The concentration of the complex was precisely equal to that of catalyst. M–OOH should be first formed in the reaction of tungstate(VI) or molybdate(VI) with H₂O₂. Therefore, if M–OOH were really the active peroxo group, the epoxidation of CPPA would be carried out through path (b) in Scheme 1 to form metal–olefin–peroxo complex **5** rapidly.

However, IR spectra showed that the metal–dioxo ring complexes (**2** in Scheme 1) were formed in H₂O and displayed strong activity of epoxidation.

The solution of Na₂MoO₄ (2.05 mol l⁻¹) and Na₂WO₄ (2.05 mol l⁻¹) were neutralized to pH 5.5 by adding equal molar hydrochloric acid (**a**₁, **b**₁ in Fig. 4). When equal moles 30% of H₂O₂ was added, the solution immediately turned into yellow that was

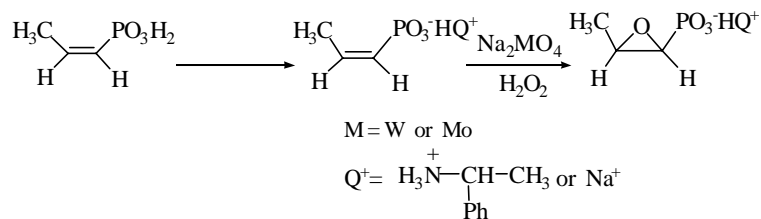
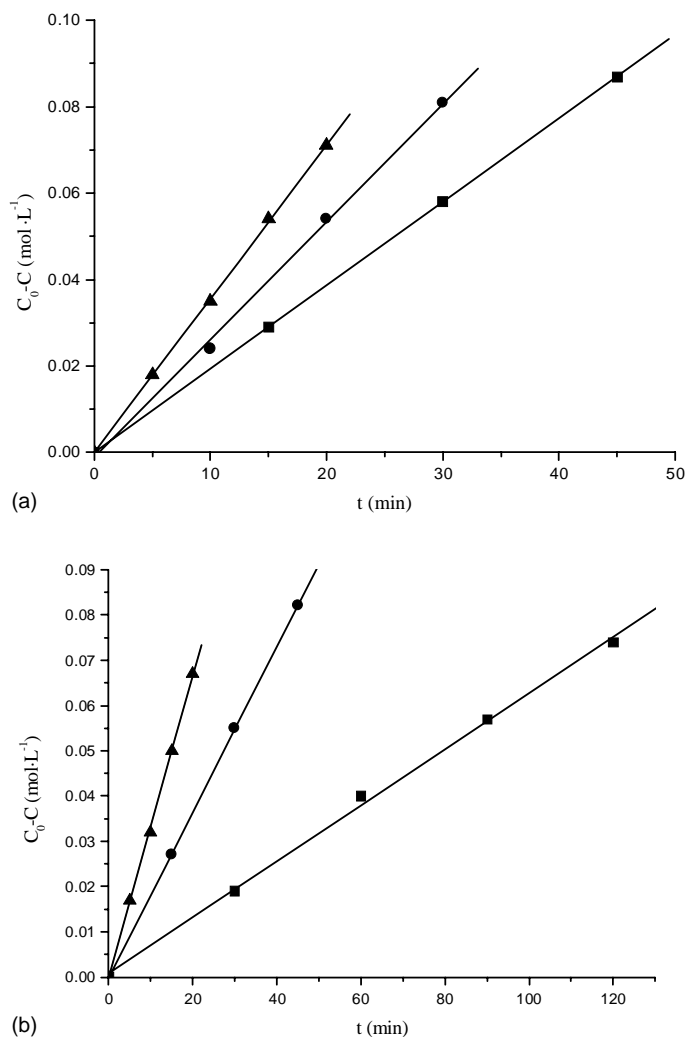
Scheme 2. Epoxidation of CPPA catalyzed by Na_2WO_4 or Na_2MoO_4 in H_2O .

Fig. 1. Zero-order plot in hydrogen peroxide for the epoxidation catalyzed by Na_2WO_4 and Na_2MoO_4 in H_2O at different temperatures: (a) Na_2WO_4 ; (b) Na_2MoO_4 . Molar concentrations (mol.l⁻¹): CPPA, 1.36; H_2O_2 , 0.087; Na_2WO_4 , 0.61×10^{-3} ; Na_2MoO_4 , 1.62×10^{-3} . Reaction temperatures ($\pm 0.1^\circ\text{C}$): (a) (■) 30, (●) 35, (▲) 40; (b) (■) 30, (●) 40, (▲) 50.

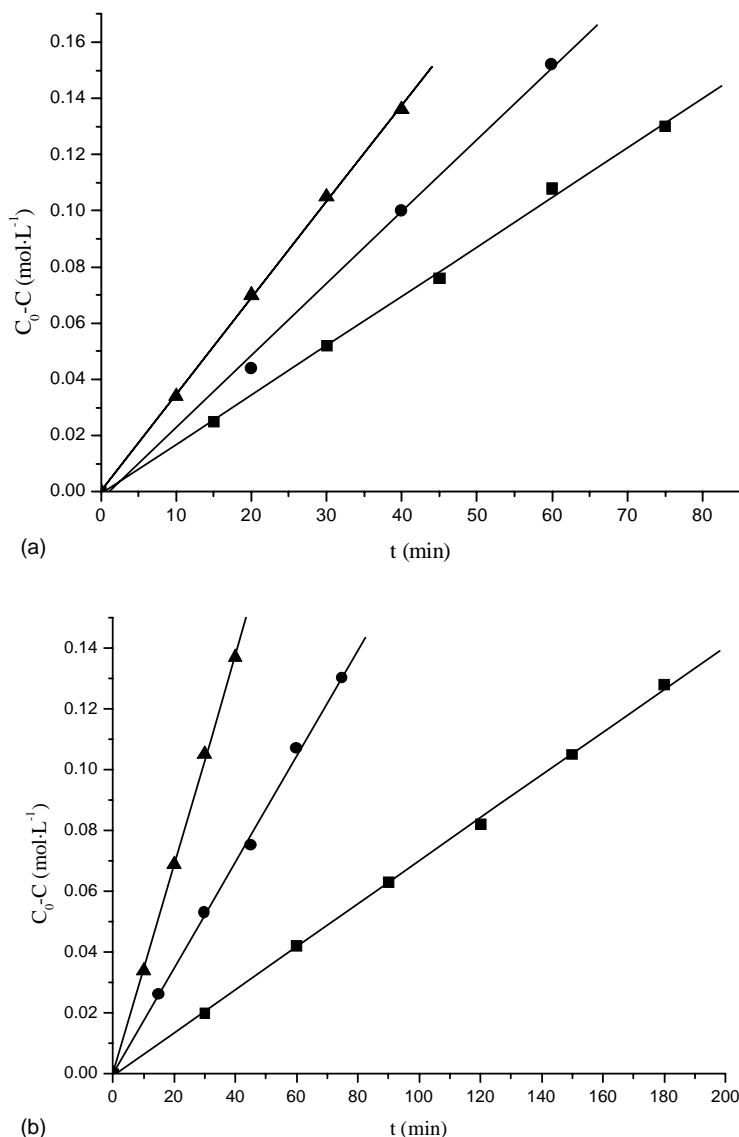


Fig. 2. Zero-order plot in CPPA for the epoxidation catalyzed by Na_2WO_4 and Na_2MoO_4 in H_2O at different temperatures: (a) Na_2WO_4 ; (b) Na_2MoO_4 . Molar concentrations (mol.l⁻¹): CPPA, 0.174; hydrogen peroxide, 1.131; sodium tungstate, 0.78×10^{-3} ; sodium molybdate, 2.06×10^{-3} . Reaction temperatures (± 0.1 °C): (a) (■) 30, (●) 35, (▲) 40; (b) (■) 30, (●) 40, (▲) 50.

the characteristic color of metal (Mo or W)-dioxygen ring. The characteristic absorption peaks were 856 and 866 cm^{-1} for Mo- and W-dioxygen rings, respectively (**a**₂, **b**₂ in Fig. 4). The temperature of the above solution was dropped to 10 °C and then equal moles of CPPA solution (neutralized to pH 5.0 by equal moles of NaOH) was added. The epoxidation

occurred immediately and the temperature of the mixture goes up soon. ¹H NMR showed that the reaction was completed in 10 min. The absorption peaks at 856 and 866 cm^{-1} in IR spectra disappeared (**a**₃, **b**₃ in Fig. 4).

The IR spectra indicated that in the epoxidation of CPPA the active peroxy group was the metal-dioxygen

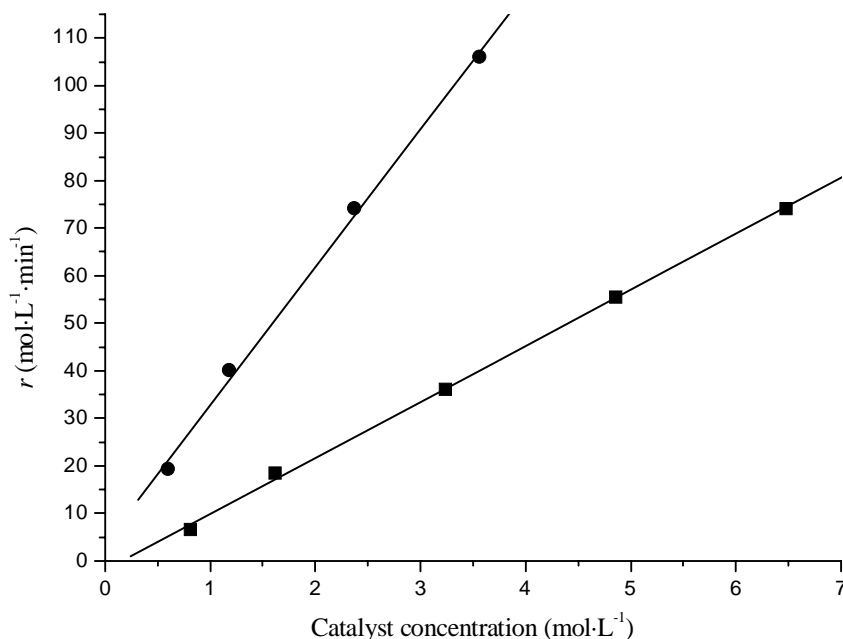


Fig. 3. First-order plot in catalyst for the epoxidation at 40 °C catalyzed by: (a) (■) Na₂WO₄; (b) (●) Na₂MoO₄. Molar concentrations (mol l⁻¹): CPPA, 1.36; Na₂WO₄, (6.10–3.57) × 10⁻⁴; Na₂MoO₄, (0.81–6.48) × 10⁻³; H₂O₂, 8.65 × 10⁻².

ring **2**, not M–OOR **3** and the active intermediate was **4**, not **5** (see Scheme 1). Therefore, we suggested a mechanism for the epoxidation of CPPA catalyzed by Na₂WO₄ or Na₂MoO₄ in H₂O as shown in Scheme 3.

The mechanism was actually the combination of Scheme 1(a) and (b) because **12** in Scheme 3 (**5** in Scheme 1) was formed first though it was not a active peroxy complex and then it could be transformed into the active peroxy complex **13** (**4** in Scheme 1).

(1) The solution was alkaline (pH 7.5–8.0) when Na₂WO₄ or Na₂MoO₄ was dissolved in H₂O. Equal moles of hydrochloric acid was added to neutralize the solution to pH 5.5, so tungstate and molybdate mainly existed in the form of MO₄H⁻ at pH 5.0–6.0 (**10** in Scheme 3). CPPA could be neutralized to pH 5.0 by adding equal moles of α-phenylethylamine or NaOH to the solution. Therefore, CPPA mainly existed in the

Table 1
Rate constants for the epoxidation of CPPA catalyzed by Na₂WO₄ or Na₂MoO₄

Temperature (°C)	$k \times 10^4$ (mol (l min) ⁻¹) ^a		$k \times 10^4$ (mol (l min) ⁻¹) ^b		$k' \times 10^4$ (min ⁻¹) ^c	
	Na ₂ WO ₄	Na ₂ MoO ₄	Na ₂ WO ₄	Na ₂ MoO ₄	Na ₂ WO ₄	Na ₂ MoO ₄
30	19.50 ± 0.10	6.20 ± 0.08	18.80 ± 0.09	7.20 ± 0.11	29.20 ± 1.04	
35	27.20 ± 0.45		25.60 ± 0.34			
40	35.60 ± 0.33	18.50 ± 0.09	34.40 ± 0.25	17.00 ± 0.21		11.78 ± 0.22
50		33.40 ± 0.50		34.70 ± 0.54		

^a Zero-order rate constants in H₂O₂ (mol l⁻¹): [CPPA] = 1.36; [Na₂WO₄] = 6.10 × 10⁻⁴; [Na₂MoO₄] = 1.62 × 10⁻³; [H₂O₂] = 8.65 × 10⁻².

^b Zero-order rate constants in CPPA (mol l⁻¹): [CPPA] = 0.17; [Na₂WO₄] = 7.77 × 10⁻⁴; [Na₂MoO₄] = 2.06 × 10⁻³; [H₂O₂] = 1.13.

^c First-order rate constants in catalyst (mol l⁻¹): [CPPA] = 1.36; [Na₂WO₄] = (6.10–3.57) × 10⁻⁴; [Na₂MoO₄] = (0.81–6.48) × 10⁻³; [H₂O₂] = 8.65 × 10⁻².

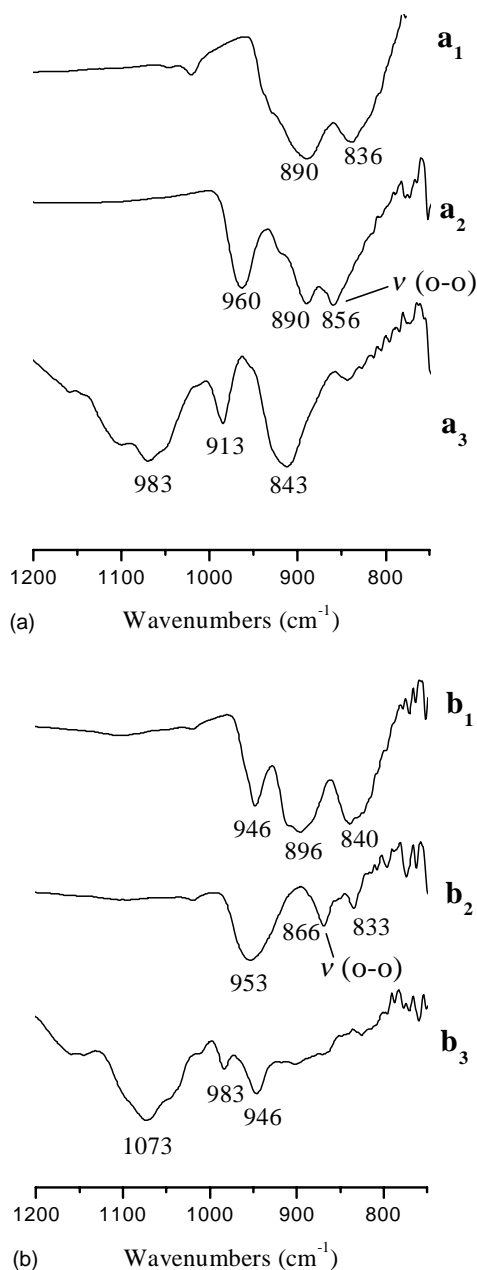


Fig. 4. IR spectra of Na_2WO_4 and Na_2MoO_4 in H_2O (measured with Spectrum GX, FT-IR system, made by PE company. Horizontal ATR affix of ZnSe crystal was used, 32 times scanning with resolution of 4 cm^{-1}). (**a**₁) Na_2MoO_4 (2.05 mol l^{-1} , pH 5.5); (**a**₂) equal moles of H_2O_2 was added; (**a**₃) equal moles of CPPA (pH 5.0) was added at 10°C and the reaction was completed. (**b**₁) Na_2WO_4 (2.05 mol l^{-1} , pH 5.5); (**b**₂) equal moles of H_2O_2 was added; (**b**₃) equal moles of CPPA (pH 5.0) was added at 10°C and the reaction was completed.

mono-negative ionic form ($\text{CH}_3\text{CH}=\text{CHPO}_3^-$, **12–15** in Scheme 3) at pH 5.0–6.0.

- (2) The epoxidation was zero-order both in H_2O_2 and in CPPA. This indicates that the formation of **10** and **11** were rapid. The equilibrium was present between non-active peroxy complex **12** and active peroxy complex **13**. It was obviously that the reaction was first-order in catalyst.

$$K = [\mathbf{13}]/[\mathbf{12}]$$

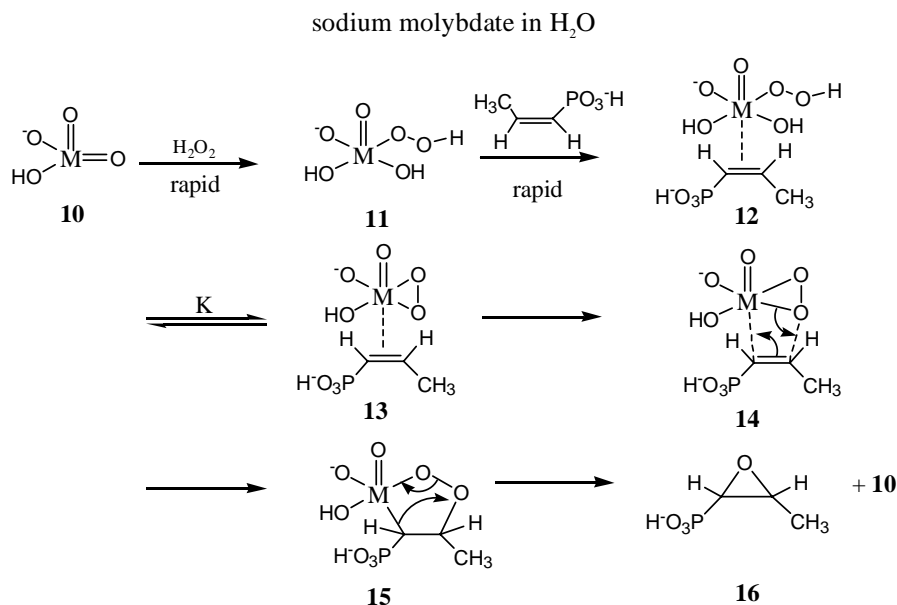
$$r = k[\mathbf{13}] = kK[\mathbf{12}]$$

$$= k'[\text{catalyst}]$$

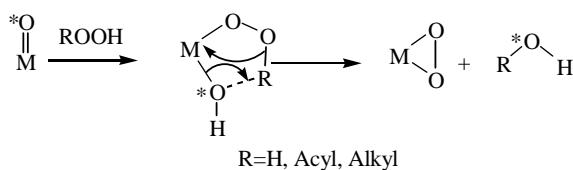
The concentration of catalyst was usually very low, thus the concentration of **13** was much lower. Although **13** was very active, the epoxidation was slow below room temperature because of the very low concentration of **13**. The concentration of **13** would be increased when the reaction temperature was raised. It means that K was increased. Therefore, the epoxidation was usually carried out at $50\text{--}60^\circ\text{C}$. The epoxidation of CPPA in H_2O has excellent retention of configuration (*cis*-CPPA can produce 100% *cis*-epoxide). According to the mechanism shown in Schemes 1(a) and 3, the retention of configuration could be realized because the active group was metal–dioxygen ring. The olefin inserted into M–O bond through a 1,3-dipolar cycloaddition and the process should be concerted. If **12** or **5** are active intermediates, $-\text{O}-\text{O}-\text{R}$ would fall off from the metal center as a whole and then connected to a carbon of the double bond. It was difficult to guarantee the concertedness of the process and 100% retention of configuration, especially at high reaction temperature.

- (3) Sharpless et al. [8] proved that the oxygen atom in epoxide could only come from M–O–O–R according to the experiments of ^{18}O labeled epoxidation of olefins. However, it could not yet be made sure that the M–OOR is an active peroxy complex. We speculated the M–OOR would be transformed into the active metal–dioxygen ring complex through the process shown in Scheme 4.

Our experiments showed when Na_2WO_4 or Na_2MoO_4 was used as catalyst (catalyst:CPPA = 1:50), H_2O_2 or AcOOH as oxidant, the epoxidation of CPPA could be completed in 0.5 h at

Scheme 3. Mechanism of epoxidation of CPPA catalyzed by sodium tungstate or sodium molybdate in H₂O.

50 °C. However, if *t*-Bu-OOH was used as oxidant, the epoxidation did not occur within 24 h under 100 °C. Scheme 4 indicated that the R–O bond must be disconnected to form the active metal–dioxygen ring peroxo complex. If R was H- or acyl-, the disconnection was easy, and so the active metal–dioxygen ring complex formed easily. However, the disconnection of *t*-Bu–O bond was difficult which led the active metal–dioxygen ring peroxo complex difficult to form. Therefore, Chong and Sharpless's ¹⁸O labeled epoxidation of olefins catalyzed by Mo(CO)₆ with *t*-Bu-OOH cost 24 h at 115 °C [6]. While in the molybdenum(VI) catalyzed epoxidation of propylene with *t*-Bu-OOH (Halcon process) [9], the epoxidation was carried out at 130 °C for 2 h! It indicated

Scheme 4. ¹⁸O labeled process of the epoxidation.

t-butyl hydroperoxide as an oxidant is unfavorable to form the active metal–dioxygen ring peroxo complex, and so reaction temperature must be raised greatly. It means also that M–OOH was not an active peroxo group in the epoxidation.

- (4) The previous workers have already considered the orientation of the olefin molecule in the transition metals catalyzed insertion reaction. They concluded that for a polar double bond, the carbon atom bearing larger negative charge would attach to the metal center to form a new metal–carbon bond. Such mode was defined as “Markownikoff mode” of insertion [10]. We have also found that when a carbon atom of the double bond has high negative charge, the epoxidation could often be carried out using Na₂WO₄ and Na₂MoO₄ as catalysts. CPPA is an olefin having high negative charge on a carbon of the double bond. The calculation by semi-empirical quantum chemical method PM3 showed that a carbon has high negative charge (Table 2, 17). Thus, the carbon can combine easily with metal center that has positive charge and then the insertion reaction can easily occur (transition state 14 in Scheme 3). In Table 2, a carbon on double bonds of 18–20

Table 2

Influence of the negative charges on the carbons of double bonds to the catalytic activity of Na₂WO₄

	Olefin ^a	Solvent	pH	Temperature (°C)	Reaction time (h)	Yield (%)
17		H ₂ O	5.5	50	0.5	100 ^b
18		H ₂ O	4–5.5	63–65	1.5	95 ^c
19		H ₂ O	4–5.5	63–65	3	86 ^c
20		H ₂ O	4–5.5	63–65	1	80 ^c

^a PM3 method in Hyperchem. 6.0 Demo software package was used for calculating the charges on the carbon atoms of the double bonds.

^b The yield of **17** was determined by ¹H NMR; Na₂WO₄:CPPA = 1:50.

^c The yields of **18–20** were reported by Payne and Williams [1]; Na₂WO₄:**18** = 1:50; Na₂WO₄:**19** = 1:10; Na₂WO₄:**20** = 1:10.

also has high negative charges, and so all of them could be epoxidized by using Na₂WO₄ as catalyst [1]. However, their epoxidation rate was much slower than that of CPPA. The reason originated probably from their lower negative charges on the carbon of double bonds than CPPA. Therefore, a carbon with double bond has high negative charge is favorable to the tungstate or molybdate catalyzed epoxidation.

- (5) The pH of the solution was an important factor influencing the reaction rate. The rate constants of the epoxidation of CPPA catalyzed by Na₂WO₄ or Na₂MoO₄ at 40 °C under different pH values were shown in Table 3. The suitable pH range

Table 3

Rate constants for epoxidation of CPPA at different pH value at 40 °C

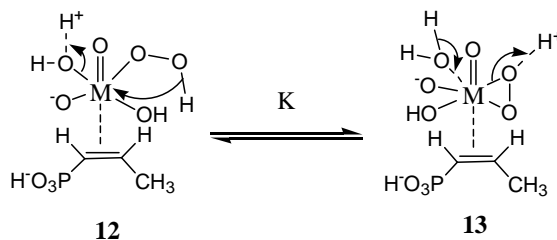
pH	$k \times 10^4$ (mol (l min) ⁻¹)	
	Na ₂ WO ₄	Na ₂ MoO ₄
3.0	32.20 ± 0.38	9.47 ± 0.05
4.0	52.00 ± 1.15	11.20 ± 0.17
5.5	60.10 ± 0.63	16.10 ± 0.5
6.5	55.40 ± 0.68	14.80 ± 0.31
7.0	29.70 ± 0.53	12.30 ± 0.35

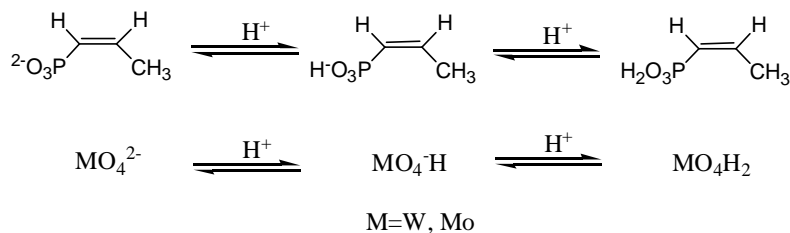
[CPPA] = 1.58 mol l⁻¹; [Na₂WO₄] = 7.05 × 10⁻⁴ mol l⁻¹;
[Na₂MoO₄] = 1.92 × 10⁻³ mol l⁻¹; [H₂O₂] = 10.50 × 10⁻² mol l⁻¹.

of Na₂WO₄ was 4.0–6.5. As for Na₂MoO₄, the suitable pH range was 5.0–6.5. The pH value of 5.5 was proved to be most suitable for the reaction. The epoxidation rates were decreased soon if the pH was in excess above the ranges.

The H⁺ concentration has mainly influenced the equilibrium constant *K* between **12** and **13** (Scheme 5). The concentration of **13** should be largest at pH 5.0–6.0 and then the epoxidation rate was most rapid. Lower or higher pH values would decrease the concentration and the reaction rate was decreased.

In addition, CPPA, Na₂WO₄ and Na₂MoO₄ in H₂O have the following equilibriums (Scheme 6). It was indicated that the active complex **13** has many and varied ionic structures with different activity under different pH value. For example,

Scheme 5. The influence of H⁺ concentration.

Scheme 6. The ionic equilibrium of CPPA, Na₂WO₄ and Na₂MoO₄ in H₂O.

when pH >6.0, more CPPA ions having two negative charge (CH₃CH=CHPO₃²⁻) would be formed and decreased the negative charge quantity on the carbon atom with the double bond. The calculation using PM3 method showed that the negative charge was turned into -0.39 on the carbon from -0.52 (17 in Table 2). It was unfavorable to the insertion of double bond in the epoxidation.

- (6) Phosphoric and phosphonic acids are known to form complexes with tungstic and molybdic anions in their peroxy- and non-peroxy forms. Recent investigation [11] indicated that some complexes are very efficient catalysts for the epoxidation of alkenes, by far more efficient than the uncomplexed Mo or W anions. Having a large number of P–O–W or P–O–Mo bonds is an important structural feature of the complexes. Therefore, if the complexes were formed, ³¹P chemical shifts must be changed greatly [11a]. However, ³¹P NMR spectra indicated that phosphonate (–PO₃⁻H) of CPPA did not have complexes with tungstate or molybdate because no other new ³¹P chemical shift peak appeared except ³¹P peak of epoxide in the course of the epoxidation. Furthermore, the formation of P–O–W or P–O–Mo bonds in our reaction system is difficult because this situation requires dehydrate in H₂O (it needs to eliminate one molecule of H₂O to form a P–O–W or P–O–Mo).

Kinetic study also has been done in order to determine the phosphonate in CPPA molecule through forming complex with catalysts to influence the reaction. We added NaH₂PO₃ (equal molar weight of catalyst) to the reaction system. If the influence existed, the reaction rate should change. However, no change has been observed. It was indicated that phosphonate

group did not participate in the epoxidation. Therefore, Na₂WO₄ or Na₂MoO₄ play independently catalysis role in the epoxidation of CPPA in H₂O.

3. Conclusion

It was the first time we specialized in the kinetics and mechanism of the epoxidation of CPPA in H₂O catalyzed by Na₂WO₄ or Na₂MoO₄. The research indicated that not only in non-protic solvents but also in H₂O, the active peroxy groups were the metal-dioxygen rings formed by complexing of W(VI) or Mo(VI) compounds with H₂O₂. Some results on kinetics and mechanism may have general significance for the epoxidation of some olefins such as α,β-unsaturated acids by using W(VI) or Mo(VI) compounds as catalysts in H₂O.

4. Experiments

Unless otherwise specified, all reagents were purchased from commercial suppliers and were used without purification. CPPA was 83% in content including impurities of propylphosphonic acid (CH₃CH₂CH₂PO₃H₂, about 7%), phosphonic acid (H₃PO₄, about 6%) and ethanol (about 2–3%). We did not purify the crude CPPA because the impurities have no obvious influence on the reaction. The temperature was controlled by thermostat with variation of ±0.1 °C. ¹H NMR spectra were recorded on a Bruker AC 300 MHz NMR spectrometer using D₂O as solvent and were referenced to Me₄Si. IR spectra were measured with Spectrum GX, FT-IR system, made by PE Company. Horizontal ATR affix of ZnSe crystal was used, 32 times scanned with resolution of 4 cm⁻¹. The reproducibility of our experiments was

very good and the data in the present work were the average values of 2–3 runs.

4.1. Kinetics in hydrogen peroxide

CPPA (5 g, 0.04 mol) was dissolved in H₂O (15 ml) at room temperature. (±)α-Phenylethylamine (5 g, 0.04 mol) was added to neutralize the solution to pH 5.5. To the solution was added sodium tungstate (0.005 g, 1.52×10^{-5} mol, dissolved in 1 ml H₂O) or sodium molybdate (0.01 g, 4.13×10^{-5} mol, dissolved in 1 ml H₂O). The reaction flask loaded with the mixture was then moved to thermostat. After stirring for half an hour, the mixture was kept at a certain temperature. Hydrogen peroxide (0.25 ml, 30% in aqueous, 2.43×10^{-3} mol) was then added to the solution. The reactions were carried out at several invariable temperatures during which aliquots were taken out at intervals for the iodometric titration analysis to determine the concentration of hydrogen peroxide. The analytical method was also used in experiments below.

4.2. Kinetics in CPPA

CPPA (0.5 g, 4.09×10^{-3} mol) was dissolved in H₂O (15 ml) at room temperature. (±)α-Phenylethylamine (0.5 g, 4.06×10^{-3} mol) was added to neutralize the solution to pH 5.5 followed by addition of sodium tungstate (0.005 g, 1.52×10^{-5} mol, dissolved in 1 ml H₂O) or sodium molybdate (0.01 g, 4.13×10^{-5} mol, dissolved in 1 ml H₂O). The reaction flask loaded with the mixture was then moved to thermostat. After stirring for half an hour, the mixture was kept at a certain temperature. Hydrogen peroxide (2.5 ml, 30% in aqueous, 2.43×10^{-2} mol) was then added to the solution. The following steps were the same as above.

4.3. Kinetics in catalysts

CPPA (5 g, 0.04 mol) was dissolved in H₂O (15 ml) at room temperature. (±)α-Phenylethylamine (5 g, 0.04 mol) was added to neutralize the solution to pH 5.5 followed by addition of sodium tungstate (0.005–0.03 g, $(1.52–9.09) \times 10^{-5}$ mol l⁻¹, dissolved in 1 ml water) or sodium molybdate (0.005–0.04 g, $(2.07–16.5) \times 10^{-5}$ mol, dissolved in 1 ml H₂O). The reaction flask loaded with the mixture was then moved to thermostat. After stirring for half an hour, the

mixture was kept at a certain temperature. Hydrogen peroxide (0.25 ml, 30% in aqueous, 2.43×10^{-3} mol) was then added to the solution. The following steps were the same as above.

4.4. Kinetic studies at different pH value

CPPA (5 g, 0.04 mol) was dissolved in H₂O (20 ml) at room temperature. Sodium hydroxide ((g): 1.00; 1.20; 1.50; 1.60; 2.50; 2.90) was added to neutralize the solution to pH 2.5, 3.0, 4.0, 5.5, 6.5 and 7.0, respectively, followed by addition of sodium tungstate (0.005 g, 1.52×10^{-5} mol, dissolved in 1 ml H₂O) or sodium molybdate (0.01 g, 4.13×10^{-5} mol, dissolved in 1 ml H₂O). The reaction flask loaded with the mixture was then moved to thermostat. After stirring for half an hour, the mixture was kept at a certain temperature. Hydrogen peroxide (0.5 ml, 30% in aqueous, 2.43×10^{-3} mol) was then added to the solution. The following steps were the same as above.

4.5. IR spectra

The solution of Na₂MoO₄ (2.00 g, 8.26×10^{-3} mol, solved in 4 ml H₂O) and Na₂WO₄ (2.73 g, 8.26×10^{-3} mol, solved in 4 ml H₂O) were neutralized to pH 5.5 by adding equal moles of hydrochloric acid. After that, H₂O₂ (0.85 ml, 30% in aqueous, 8.26×10^{-3} mol) was added. The temperature of the above solution was dropped to 10 °C and then CPPA solution (1.01 g, 8.26×10^{-3} mol, neutralized to pH 5.5 by equal moles of NaOH) was added.

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