Epoxidation of α, β-unsaturated acids catalyzed by tungstate(VI) or molybdate (VI) in H$_2$O: influence of pH on epoxidation rate and a quantum chemical explanation

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Abstract

The epoxidation rate of α, β-unsaturated acids catalyzed by Na$_2$WO$_4$ or Na$_2$MoO$_4$ in H$_2$O has a close relationship with pH of the solution. The epoxidation rate is the highest at pH 5.0–6.0. A quantum chemical ab initio method (MP2/6–31G** level) was used to calculate the molecules and anions of some α, β-unsaturated acids. The results indicate that the orbital energy of MO which bonding π orbital of double bond in monoanion lies in is a determinant factor for the rate. If pH is low (pH < 3), α, β-unsaturated acid exits mainly in a molecule state and the bonding π orbital of double bond usually lies in HOMO. The energy of HOMO is very low, in the range of −10 to −12 eV, so it is difficult to be epoxidized. If pH is in the range of 4.0–6.5, the organic acids mainly exit in monoanion state, and the orbital energy of the MO which bonding π orbital in the monoanion lies in is in the range of −4.5 to −6.5 eV. Increase of the energy is about 5 eV that is large enough to increase reactivity of double bond to initiate the epoxidation. If pH > 7, though molecules can exist as a dianion for dicarboxylic acid or dibasic acid, the epoxidation is almost impossible. Therefore, the epoxidation of α, β-unsaturated acid is to be carried out in their monoanionic states. The results support the direct oxygen transfer mechanism suggested by Sharpless.
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Keywords: α, β-Unsaturated acid; Epoxidation rate; pH; Ab initio

1. Introduction

For the epoxidation of α, β-unsaturated acids catalyzed by Na$_2$WO$_4$ or Na$_2$MoO$_4$ in H$_2$O, pH of the reaction solution is an important factor influencing the epoxidation rate. Though some researchers paid great attention to the question, over a long period, it is still not clear why the pH would lead to such significant influence on epoxidation rate. The study hopes to give an unequivocal answer.

Long time ago, a number of researchers found that the epoxidation rate was pH-dependent [1–3]. Table 1 shows the dependence of pH on the epoxidation rate for the epoxidations of crotonic acid and citraconic acid by using Na$_2$WO$_4$ as a catalyst in H$_2$O according to Ahmad and Beg [2(b)]. The data indicate that the highest epoxidation rate appeared in the pH range of 5.0–6.0.

The above result is in agreement with our kinetic study [4] on epoxidation of *cis*-1-propenylphosphonic acid (CPPA) catalyzed by Na$_2$WO$_4$ and Na$_2$MoO$_4$ in H$_2$O. The rate constants of the epoxidation of CCPA at 40 °C under different pH are shown in Table 2. Table 2 indicates that the pH 5.0–6.0 are the most suitable also for the epoxidation of CPPA.

The influence of pH on the epoxidation rate has first been attributed to behavior of the catalysts [4]. Reactive peroxo group in the epoxidation is metal-dioxygen ring in peroxo complex **2**. The H$^+$ concentration can influence the equilibrium constant K between **1** and **2** (Scheme 2), and thus would change the concentration of reactive peroxocomplex **2**. The concentration of **2** is high when pH is in the range of 5.0–6.0. Lower pH or higher pH both would decrease the concentration of **2** and then the epoxidation rate was reduced.

However, pH not only influences the reactivity of catalysts but also has a profound effect on the reactivity of α, β-unsaturated acids. The following equilibrium (Scheme 2)

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Table 1
Rate constants for epoxidation of crotonic and citraconic acid in different pH at 40 °C

pH	k_{obs} ($\times 10^5$) (mol l^{-1} min^{-1})	
	Crotonic acid	Citraconic acid
3.0	2.29	1.48
4.0	4.99	2.98
5.0	10.21	5.38
6.0	8.28	4.97
7.0	4.01	3.25

[Crotonic acid] = [citraconic acid] = 5.33×10^{-2} M; [Na$_2$WO$_4$] = 1.00×10^{-4} M; $\mu = 3.00 \times 10^{-4}$ M [H$_2$O$_2$] = 3.00×10^{-3} M.

Table 2
Rate constants for epoxidation of CPPA in different pH at 40 °C

pH	k ($\times 10^4$) (mol l^{-1} 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}; [Na$_2$WO$_4$] = 7.05×10^{-4} mol l^{-1}; [Na$_2$MoO$_4$] = 1.92×10^{-3} mol l^{-1}; [H$_2$O$_2$] = 10.50×10^{-2} mol l^{-1}.

would be established in H$_2$O for α, β-unsaturated acids (such as CPPA, fumaric acid, and crotonic acid).

When pH increases, equilibrium moves toward left, and vice versa, thus the content of those molecules and ions in solution would be changed. Quantum chemical calculation indicates that energy and electron population of some MOs would have a great difference between anion and molecule of a α, β-unsaturated acid that changed epoxidation reactivity of the acids. Therefore, the dependence of epoxidation rate on pH should be also attributed to the behavior of α, β-unsaturated acids.
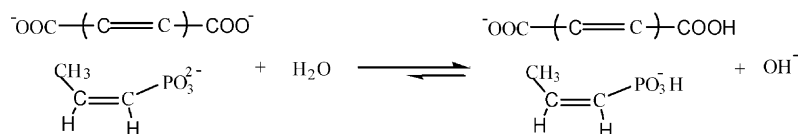
2. Results and discussion

A quantum chemical ab initio method (MP2/6–31G** level) was used to calculate the molecules or anions of various α, β-unsaturated acids. The calculation results indicated that the two Pz orbital (AO) on carbon atoms of double bond generally is the main composition of a MO and still display a localized bonding π orbital in the MO. Therefore, energy of the MO can reflect or represent the reactivity of

π-electrons on double bond in molecules or anions. The results are shown in Table 3 and Fig. 1.

In Table 3, integer n shows a α, β-unsaturated acid in molecule state and n^{1-} shows monoanion of the acid. N shows the number of a molecular orbital starting from HOMO and according to energy order, N of HOMO is assigned to zero. If orbital energy of a MO is higher than that of HOMO, N is a negative integer, for example, the N of LUMO is -1. If the energy of a MO is lower than that of HOMO, N is a positive integer, for example, N of occupied MO next to HOMO is 1. E_{HOMO} shows the energy of the highest occupied molecular orbital. $N_{Mo\pi}$ shows the number of the MO which bonding π orbital of double bond lies in and $E_{MO\pi}$ is the orbital energy of the MO. In the study, we are paying a good deal of attention to be $N_{MO\pi}$ and $E_{MO\pi}$.

If the acid exits in the molecular state (such as **1**, **2**, **3** in Scheme 2), then the bonding π orbital of double bond lies in HOMO. Thus, $N_{MO\pi} = -1$, $E_{MO\pi} = E_{HOMO}$. The orbital energy of HOMO is very low, -10 to -12 eV usually (see Table 3). Therefore, the two electrons in HOMO are very stable and have no ability to complete oxygen transfer from peroxo complex. However, when the molecules are in the monoanionic state (such as **1^{1-}**, **2^{1-}** and **3^{1-}** in Scheme 1), the $E_{MO\pi}$ is much higher than the $E_{MO\pi}$ in molecular state, usually -4.5 to -6.5 eV (Table 3). By comparison, increase of $E_{MO\pi}$ is about 5 eV that is large enough to increase the reactivity of double bond in monoanion to initiate epoxidation. However, in this case, the MO is not HOMO, $N_{MO\pi}$ of the MO is three usually ($N_{MO\pi}$ of CPPA' monoanion alone is still zero). Three MOs with higher energy in the monoanions are mainly located in –COO$^-$ or –PO$_3^-$H. Their energy is between -4.0 and -5.5 eV. For molecules **1**, **2**, **3**, and monoanions **1^{1-}**, **2^{1-}**, and **3^{1-}**, graphs and $E_{MO\pi}$ of the MOs which bonding π orbital of double bond lies in are shown in Fig. 1.
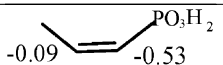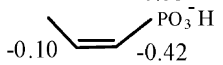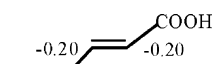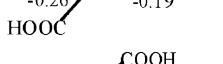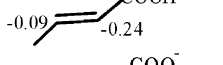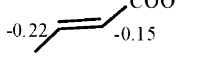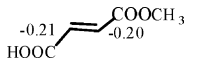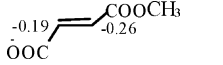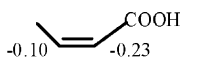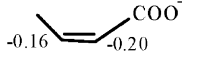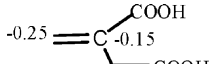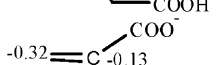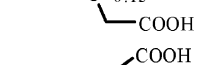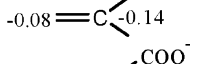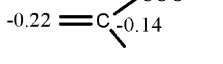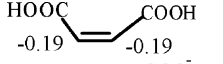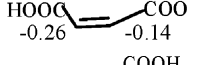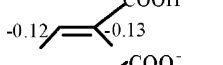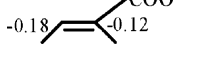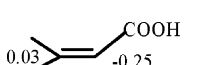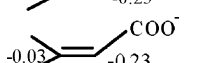
Some acids can exit in dianionic forms (such as **1** and **2** in Scheme 2). The dianions have very strong alkalinity because the following equilibrium would appear in H$_2$O.

$E_{MO\pi}$ of dianions normally is -1.0 to -2.0 eV, much higher than that of monoanions. The MO is not HOMO either; $N_{MO\pi}$ of the MO is usually six. The six MOs with higher energy than the MO mainly appear in two –COO$^-$ or one –PO$_3^{2-}$ groups of the dianion. Their energies are often higher than -1 eV, even positive. It shows that the dianionic states are very unstable and very few in the aqueous solution unless pH changes into very high through adding a large amount of NaOH.

More importantly, when pH is high (>7.0), H$_2$O$_2$ would be decomposed by the catalyst to release O$_2$, and the higher pH is, the faster release of O$_2$ would become

Table 3
Quantum chemical ab initio (MP2/6–31G** level) calculation results for the molecules and monoanions of some α, β-unsaturated acids

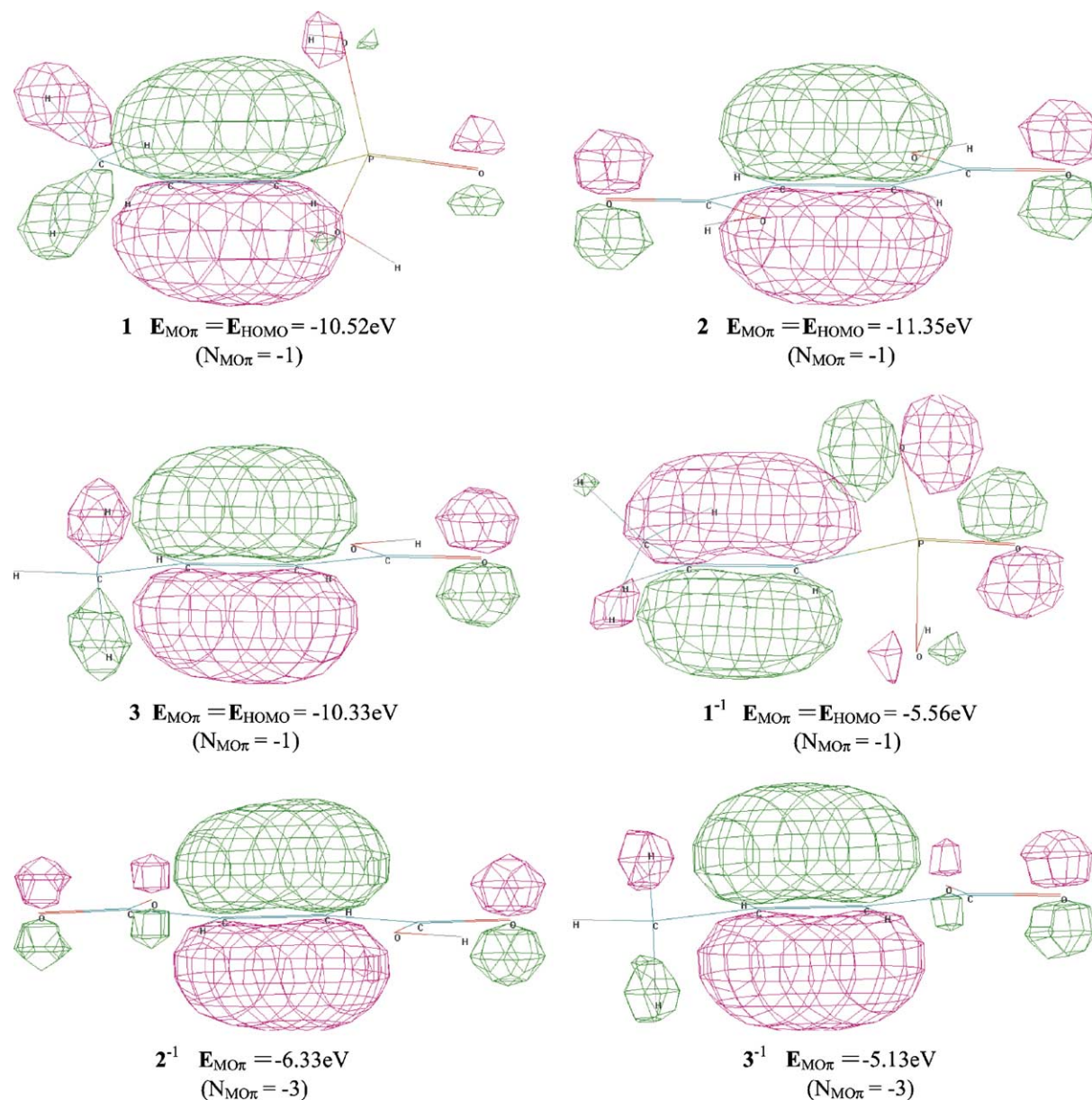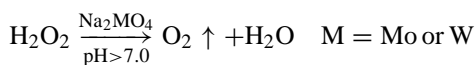| n	α, β-Unsaturated acid	E_{HOMO} (eV)	Bonding π orbital located MO		Difference of partial charges on double bond	Relative rate
			$N_{MO\pi}$	$E_{MO\pi}$ (eV)		
1	(structure: CH=CH–PO_3H_2; −0.09, −0.53)	−10.52	0	−10.52	0.44	
1^{-1}	(structure: CH=CH–PO_3^-H; −0.10, −0.42)	−5.56	0	−5.56	0.32	
2	(structure: HOOC–CH=CH–COOH; −0.20, −0.20)	−11.35	0	−11.35	0.00	<0.05
2^{-1}	(structure: HOOC–CH=CH–COO^-; −0.26, −0.19)	−5.25	3	−6.33	0.07	
3	(structure: CH=CH–COOH; −0.09, −0.24)	−10.33	0	−10.33	0.15	1.00
3^{-1}	(structure: CH=CH–COO^-; −0.22, −0.15)	−4.59	3	−5.13	0.07	
4	(structure: HOOC–CH=CH–$COOCH_3$; −0.21, −0.20)	−11.20	0	−11.20	0.01	<0.05
4^{-1}	(structure: ^-OOC–CH=CH–$COOCH_3$; −0.19, −0.26)	−5.19	3	−6.22	0.07	
5	(structure: CH=CH–CH=CH–COOH; −0.10, −0.23)	−10.30	0	−10.30	0.13	1.65
5^{-1}	(structure: CH=CH–CH=CH–COO^-; −0.16, −0.20)	−4.63	3	−5.14	0.04	
6	(structure: CH_2=C(COOH)–COOH; −0.25, −0.15)	−10.54	0	−10.54	0.10	2.13
6^{-1}	(structure: CH_2=C(COO^-)–COOH; −0.32, −0.13)	−5.00	3	−5.53	0.19	
7	(structure: CH_2=C(COOH); −0.08, −0.14)	−10.63	0	−10.63	0.06	2.45
7^{-1}	(structure: CH_2=C(COO^-); −0.22, −0.14)	−4.17	3	−5.73	0.08	
8	(structure: HOOC–CH=CH–COOH (cis); −0.19, −0.19)	−11.27	0	−11.27	0.00	2.48
8^{-1}	(structure: HOOC–CH=CH–COO^- (cis); −0.26, −0.14)	−4.62	3	−6.35	0.12	
9	(structure: CH_3CH=C(COOH); −0.12, −0.13)	−9.88	0	−9.88	0.01	4.10
9^{-1}	(structure: CH_3CH=C(COO^-); −0.18, −0.12)	−4.62	0(~40%) / 2(~60%)	−4.62 / −4.94	0.06	
10	(structure: ($CH_3)_2$C=CH–COOH; 0.03, −0.25)	−10.22	0	−10.22	0.28	19.3
10^{-1}	(structure: ($CH_3)_2$C=CH–COO^-; −0.03, −0.23)	−4.14	2	−4.88	0.20	
11	(structure: cyclohexene-1,2-dicarboxylic acid, COOH/COOH; −0.08, −0.07)	−10.17	0	−10.17	0.01	≫20
11^{-1}	(structure: cyclohexene-1,2-dicarboxylic acid, COO^-/COOH; −0.03, −0.14)	−5.12	1(~30%) / 3 (~70%)	−5.15 / −6.04	0.11	

Fig. 1. Graphs (orbital contour value: 0.06) and energy (Table 3) of MOs which bonding π orbital of double bond lies in for **1**, **2**, **3**, $\mathbf{1}^{-1}$, $\mathbf{2}^{-1}$, and $\mathbf{3}^{-1}$.

$$H_2O_2 \xrightarrow[\text{pH}>7.0]{\text{Na}_2\text{MO}_4} O_2 \uparrow + H_2O \quad M = \text{Mo or W}$$

Therefore, the epoxidation by using Na_2WO_4 or Na_2MoO_4 as a catalyst and H_2O_2 as an oxidant should not operated under pH > 7. The kinetic studies of epoxidation
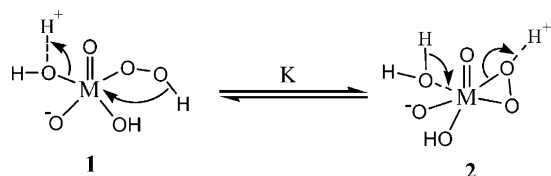
Scheme 1. Changing H^+ concentration would lead to change of the concentration of **2**. M = Mo or W.

of α, β-unsaturated acids in reference [1–4] were conducted always under pH 3–7. It is unnecessary to consider the influence of the dianions on epoxidation, and thus, the data of quantum chemical calculation of dianions have not been listed.

Kirshenbaum and Sharpless [3] investigated relative epoxidation rates of various α, β-unsaturated acids. They set pH of reaction mixture at 5.5, supposed that the epoxidation rate of crotonic acid **3** was 1.0, and then determined the relative epoxidation rates of α, β-unsaturated acids **2–11** (Table 3). At pH 5.5, **2–11** would mainly be in monoanionic states. For those α, β-unsaturated acids similar in molecular structure, $E_{MO\pi}$ is closely related to the relative rate. Table 3 shows the $E_{MO\pi}$ is higher, the relative rate higher. For example, the $E_{MO\pi}$ of $\mathbf{9}^{-1}$ and $\mathbf{10}^{-1}$ is -4.81 (average value)
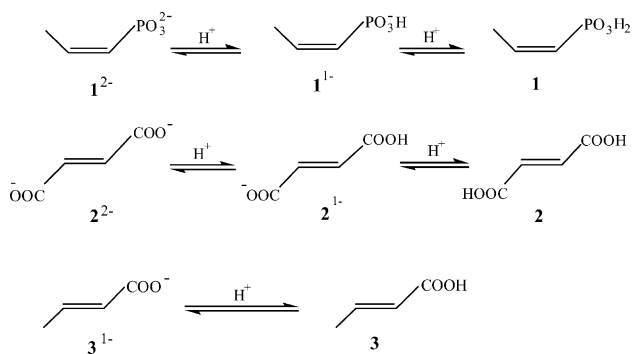
Scheme 2. Ionic equilibriums of α, β-unsaturated acids in H_2O.

and −4.88 eV, respectively, and their relative rate is 4.10 and 19.3, respectively. Because the both MO' energies are higher than −5.13 eV of 3^{-1}, the epoxidation rate of 9^{-1} and 10^{-1} faster than 3^{-1}. For acids 2^{-1} and 4^{-1}, the $E_{MO\pi}$ is −6.33 and −6.22 eV, respectively, and their relative rates are both <0.05. The first cause is that their $E_{MO\pi}$ is much lower than −5.13 eV of 3^{-1}. For acids 6^{-1} and 7^{-1}, the orbital energy is −5.53 and −5.73 eV, respectively. Their relative rate is 2.13 and 2.45. It seems that the epoxidation proceeds easily if $E_{MO\pi}$ of monoanion is >−6.0 eV.

Although $E_{MO\pi}$ is a determinant factor affecting the epoxidation rate, the molecular steric structure, substituted groups, molecular size, and especially cis-trans-isomersism of olefins, also have important influence on the epoxidation rate. It seems that the cis-form always reacts faster than the trans-form. For the cis-trans-isomers of molecules **3** and **5**, $E_{MO\pi}$ of their monoanion is almost the same (−5.13 and −5.14 eV), but the epoxidation rate of **5** is faster 65% than that of **3**. For **8** and **2** cis-trans-isomers, $E_{MO\pi}$ of monoanion 8^{-1} is −6.35 eV, slightly lower than 2^{-1} (−6.33 eV). However, the relative rate of **8** is 2.45, much faster than 2 (≪0.05) because **8** is a cis-isomer. For molecules **9** and **10**, $E_{MO\pi}$ of 10^{-1} is −4.88 eV and lower than −4.81 eV of 9^{-1}, but the relative rate (19.3) of **10** is much faster than that (4.10) of **9** because **10** is a cis-isomer and **9** is a trans-isomer. Among **2**–**11**, the relative rate of 11 is the

fastest (≫20), an important cause is that **11** is a cis-olefin. However, the reason why the reactivity of the cis-form is always faster than the trans-form remains unknown.

High $E_{MO\pi}$ of monoanion is a determinant factor for the epoxidation rate of α, β-unsaturated acids, which may be confirmed by epoxidation of other olefins under the same conditions. For example, molecule **14** is α, β-unsaturated methyl vinyl sulfone (Fig. 2). It is freely soluble in water, but the epoxidation has not occurred by using Na_2WO_4 or Na_2MoO_4 as a catalyst and H_2O_2 as an oxidant at 100 °C for 2 h. This can be accounted for by the fact that the molecule has only a molecular state and no monoanionic state. $E_{MO\pi} = E_{HOMO}$ of the molecular state is very low, −11.48 eV, according to calculation by the ab initio method (MP2/6–31G**). Therefore, it is impossible to cause a successful nucleophilic attack of π-electron of the olefin toward the π* orbital of the peroxo bond.

Over the last 30 years, two different descriptions have been suggested about the mechanism of olefin epoxidation by using Mimoun type diperoxo complexes, such as $MoO(O_2)_2(OPR_3)$. One is the Mimoun' mechanism [5]. He suggested that the epoxidation follows a stepwise pathway (Scheme 3, top). Key steps of the mechanism are π coordination of double bond to metal center and subsequent cycloinsertion yielding a metalladioxolane. Actually, the mechanism is perfectly consistent with the π–π rearrangement (cis-insertion), which occurs in most transition-metal catalyzed transformation of olefins [6]. The other was suggested by Sharpless et al. [7]. He insisted that the oxygen atom is directly transferred from metal peroxide to the olefin through a transition state TS $\underline{4}$ (Scheme 3, bottom).

The previous researchers have already considered the orientation of the olefin molecules in the insertion reaction catalyzed by transition metals. 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 a mode was called "Markownikoff mode" of insertion [8]. If the epoxidation occurs according to the mechanism suggested by Mimoun, the polarity of double bonds would result in a big influence on the epoxidation
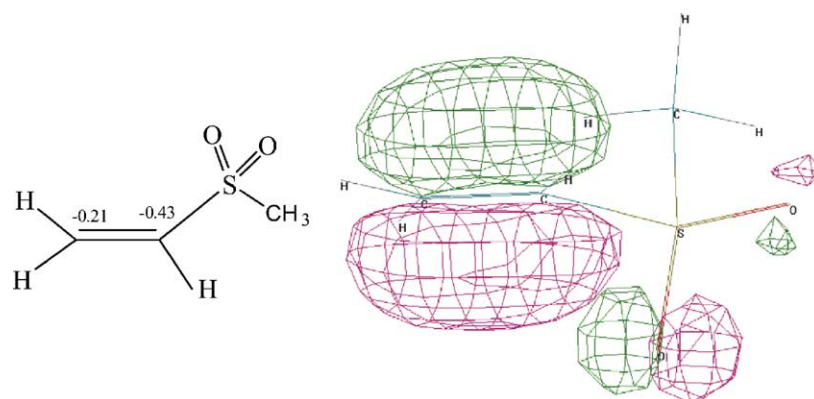
Fig. 2. α, β-Unsaturated sulfone methane. $E_{MO\pi} = E_{HOMO} = -11.48$ eV (orbital contour value: 0.06).
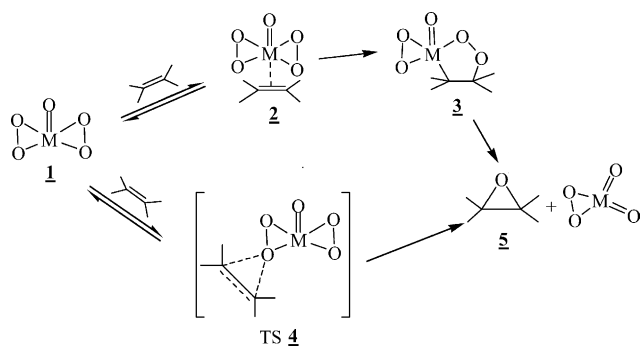
Scheme 3. Two pathways of the epoxidation of olefins suggested by Mimoun (top) and by Sharpless (bottom).

rate. The double bonds with higher polarity form easily the new metal–carbon bond and thus have faster epoxidation rate than that with lower polarity. The partial charge difference between two carbon atoms of double bond is a direct measurement of the polarity. However, Table 3 indicates the polarity of double bond does not relate to the relative rate. For example, polarity of double bond in monoanion 5^{-1}, 7^{-1}, 8^{-1}, 9^{-1}, and 11^{-1} is very low (charge difference is 0.04, 0.08, 0.12, 0.06, and 0.11, respectively), but their relative rate is high (relative rate is 1.65, 2.45, 2.48, 4.10, $\gg$20, respectively). Therefore, Mimoun's mechanism is difficult to understand the influence of pH on epoxidation rate.

Recently, the quantum chemical study on epoxidation mechanism achieved important progress [9]. The calculation results obtained under the help of density functional method (DFM) and charge decomposition analysis (CDA) strongly support the mechanism suggested by Sharpless. The results show that the epoxidation should be considered as nucleophilic attack of π-electron of double bond toward the π^* orbital of the peroxo bond. Therefore, if the epoxidation occurs according to the mechanism suggested by Sharpless, the higher $E_{MO\pi}$ of monoanion the faster the epoxidation rate because high $E_{MO\pi}$ is favorable for the nucleophilic attack of π-electron toward the π^* orbital of peroxo bond. The above good correlation between the calculation results obtained by ab initio method (MP2/6–31G** level) and the relative rate gained by experiments support the direct oxygen transfer mechanism suggested by Sharpless.

Moreover, we notice that though the direct oxygen transfer mechanism suggested by Sharpless has gripped the essence and key of the epoxidation process, it is still unable to explain some experimental results of epoxidation of α, β-unsaturated acids. For example, the mechanism is unable to explain why the epoxidation of CPPA catalyzed by Na_2WO_4 or Na_2MoO_4 is zero-order on CPPA [4]. Because the epoxidation is a bimolecular process according to the mechanism, the reaction should be first-order on CPPA.

The mechanism is also unable to answer why the epoxidation reactivity of *cis*-α, β-unsaturated acid is always faster than its trans-isomer. Therefore, for the epoxidation of α, β-unsaturated acids catalyzed by Na_2WO_4 or Na_2MoO_4 in H_2O, it is in need of a mechanism specific and consistent with the direct oxygen transfer mechanism. Further studies are in progress to probe into the specific mechanism.

3. Conclusion

This study indicates that the orbital energy of MO which bonding π orbital of double bond lies in is a determinant factor for the epoxidation rate of α, β-unsaturated acids. In the pH range of 4–6, the organic acids mainly exit in a monoanion states, and the orbital energy is in the range of -4.5 to 6.5 eV usually. Thus, the reactivity of double bond is greatly enhanced and epoxidation can be initiated. Therefore, the epoxidation of α, β- unsaturated acid is to be conducted in their monoanion state. The results support the direct oxygen transfer mechanism suggested by Sharpless because the monoanionic state has higher π-electron energy than the molecular state, being favorable to the nucleophilic attack of π-bonding electron toward the π^* orbital of peroxo bond.

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