Transactions C: Chemistry and Chemical Engineering
Vol. 17, No. 2, pp. 131–138
© Sharif University of Technology, December 2010

SCIENTIA
IRANICA

Epoxidation of Olefins Catalyzed by Some *cis*-Dioxomolybdenum(VI)-Tridentate Schiff Base Complexes with *tert*-Butyl Hydroperoxide

M. Bagherzadeh[1,*] **and S. Ghazali Esfahani**[1]

Abstract. *Some cis-dioxomolybdenum (VI) complexes with tridentate Schiff base ligands derived from salicylaldehyde and aminophenols, aminoalcohol or o-aminobenzenethiol were examined as catalysts for epoxidation of different aliphatic and aromatic olefins, with tert-butyl hydroperoxide as oxidant. All complexes exhibited high activity and selectivity for epoxidation of aliphatic substrates during a short time period (95% conversion of cyclooctene after 30 min). The epoxide yield increased with the nucleophilic character of olefin. The catalysts activation strongly depends on the reaction temperature and nature of the solvent. Epoxidation of olefins by these catalysts is inhibited by ligands or coordinating solvents such as alcohols.*

Keywords: *Epoxidation; Olefin; cis-dioxomolybdenum complexes; Tridentate Schiff base ligands; tert-butyl hydroperoxide.*

INTRODUCTION

Epoxides are important organic intermediates, since they undergo ring-opening reactions with a variety of reagents to give mono- or bi-functional organic products. They can be formed from corresponding olefins by oxidation with various oxygen sources in the presence of a catalyst [1,2]. High-valent d^0 transition metal complexes, such as Mo(VI) ,V(V) and Ti(IV), are versatile catalysts for the epoxidation of alkenes [3-5]. Various Molybdenum complexes with different ligands are considered to be very effective catalysts for olefin epoxidation in the homogeneous [6-8] and heterogeneous phases [8,9-11]. In the homogeneous phase, molybdenum catalysts are commercially applied to the production of propylene oxide using alkyl hydroperoxides as oxidants (Arco and Halcon processes) [12,13]. Type $MoO(O_2)_2LL'$ and MoO_2X_2LL' (X= Cl, Br, CH_3 and L, L$'$= Lewis base ligand) complexes have been experimentally characterized and tested as catalysts for epoxidation reactions, usually employing *tert*-butyl hydroperoxide (TBHP) as the mono-oxygen source [14-23].

Recently, some reports on the catalytic properties of Mo(VI) Schiff base complexes in the epoxidation of olefins have been reported [24-29]. Schiff bases derived from salicylaldehyde and aminoalcohols, bearing both alcoholic and phenolic hydroxyl groups and also one neutral nitrogen donor (CH=N group), can be used as multidentate ligands in molybdenum chemistry [30,31]. Tridentate Schiff bases, such as sap (2-(salicylideneamino)phenolate) and ssp (2-(salicylideneamino)benzenethiolate), have been prominently featured in oxo-transfer chemistry and demonstrated to act as oxidation catalysts [32-35].

We report here the application of some *cis*-dioxomolybdenum-tridentate Schiff base complexes (Scheme 1) as efficient homogeneous catalysts in the epoxidation of olefins with TBHP as a terminal oxidizing agent.

EXPERIMENTAL

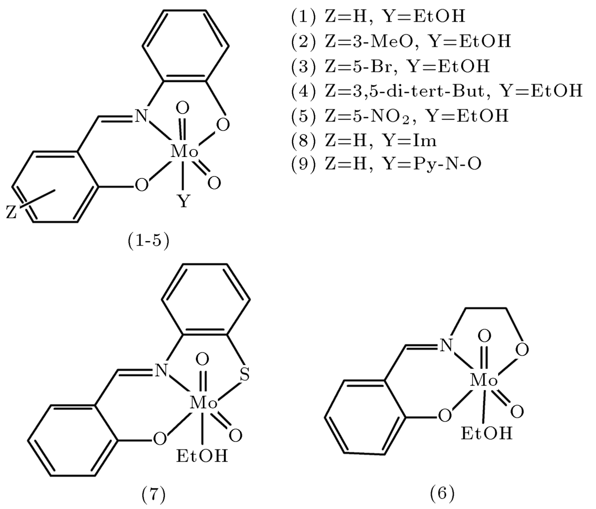
Reagents

Salicylaldehyde, 3-methoxy-2-hydroxybenzaldehyde, 5-boromo-2-hydroxybenzaldehyde and 5-nitro-2-

---

1. *Department of Chemistry, Sharif University of Technology, Tehran, P.O. Box 11155-3516, Iran.*
*. *Corresponding author. E-mail: bagherzadehm@sharif.edu*

Received 29 January 2010; received in revised form 1 June 2010; accepted 28 June 2010



(1) Z=H, Y=EtOH
(2) Z=3-MeO, Y=EtOH
(3) Z=5-Br, Y=EtOH
(4) Z=3,5-di-tert-But, Y=EtOH
(5) Z=5-NO$_2$, Y=EtOH
(8) Z=H, Y=Im
(9) Z=H, Y=Py-N-O

(1-5)

(7)

(6)

Scheme 1. The structure of complexes numbered 1-9.

hydroxybenzaldehyde are available commercially and used without further purification. 3,5-di-*tert*-butyl salicylaldehyde was prepared according to literature procedures [36]. The tridentate Schiff base ligands were obtained via a Schiff base condensation reaction between the appropriate aldehyde and amine. The reactions were run in ethanol. *tert*-butyl hydroperoxide (TBHP) was purchased from Fluka (80% in di-*tert*-butylperoxide/H_2O 3:2). The solvents were used without drying.

$MoO_2(acac)_2$ was obtained by the reported procedure [37]. Complexes are prepared by reacting respective ligands with $MoO_2(acac)_2$ according to the method of Rajan and Chakravorty [38] (Scheme 1). In these complexes, the reaction solvent, i.e. ethanol, coordinates to Mo(VI) and occupies the sixth coordination site (**1-7**). MoO_2(sap)(Im) and MoO_2(sap)(py-N-O) were prepared by treating MoO_2(sap)(EtOH) with an excess of imidazole (Im) or pyridine-N-oxide (Py-N-O) in ethanol medium (8,9) [38].

Epoxidation Reaction

Epoxidation of olefin by dioxomolybdenum (VI) Schiff base complexes with TBHP was carried out according to the following general procedure: A mixture of catalyst (0.001 mmol), olefin (0.8 mmol), 1,2-dichloroethane (0.5 mL) as solvent, and chlorobenzene (0.8 mmol) as an internal standard was placed in a two-necked round-bottomed flask equipped with a condenser and a magnetic stirrer. The mixture was stirred at 80°C under air and then 0.8 mmol *t*-butyl hydroperoxide (TBHP) was added. The molar ratio of the catalyst to substrate and TBHP was 1:800:800, which was chosen for the ratio of catalyst: substrate: oxidant after the optimization process.

The activity of complex 1, as a typical catalyst, was also investigated in the absence of solvent. An excess of substrate was placed in the reaction mixture instead of solvent, so 1.6 mmol of olefin, 0.002 mmol of catalyst and 0.16 mmol of cholorobenzene as an internal standard were placed in the reaction vessel. After stirring of the mixture at 80°C, 1.6 mmol TBHP was added to the reaction mixture. The complete reaction was monitored at certain time intervals to determine the concentrations of olefin and epoxide using a gas chromatograph equipped with a capillary column (19019 J-413 HP-5, 5% Phenyl Methyl Siloxane, Capillary 60.0 m × 250 μm × 1.00 μm) and a flame ionization detector.

The stability of complex 1 was also investigated by taking UV-Vis spectra of the reaction mixture during the epoxidation of cyclooctene in 1,2-dicholoroethane as solvent.

RESULT AND DISCUSSION

Temperature Effect

The effect of temperature was evaluated by MoO_2(sap)EtOH (1) and cyclooctene as a model substrate (Figure 1). It can be seen that the epoxycyclooctane yield strongly depends on the reaction temperature. It seems that the catalyst activity starts at about 40°C and increases significantly with an increase in temperature. The yield increased up to 96% at 80°C.

Solvent Effect

We have studied the catalytic epoxidation of cyclooctene with MoO_2(sap)EtOH in different solvents (Table 1). Epoxide conversion is found to be strongly dependent on the solvent. Apparently, coordinating solvents, such as *n*-butanol, *tert*-butanol and DMF, inhibit the reaction (Table 1, entries 3-5), because of their

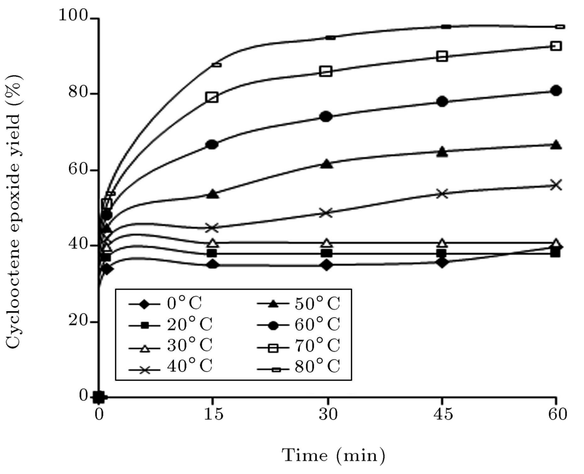


Figure 1. The effect of temperature on the yield of cyclooctene epoxide catalyzed MoO_2(sap)EtOH.

Table 1. The effect of various solvents on the epoxidation of cyclooctene with TBHP using *cis*-MoO$_2$(sap)EtOH [a].

Entry	Solvent	Conversion (%) [b]	TOF (h^{-1}) [d]
1	*n*-noane	82	656
2	toluene	83	664
3	Dimethylformamide(DMF)	53	416
4	*n*-butanol	35	280
5	*tert*-butanol	53	424
6	chlorobenzene	97	776
7	1,2-dichlorobenzene (DCE)	99	792
8	1,2-dichlorobenzene (DCE)	78 [c]	624
9	*n*-hexane	40 [c]	320
10	methanol	30 [c]	240

a: Conditions: The molar ratio for *cis*-MoO$_2$(sap)EtOH: substrate: TBHP are 1:800:800. The reactions were run for 60 min at 80°C.

b: GC yields based on the starting olefin.

c: The reactions were run at 50°C.

d: Turnover frequency (TOF)= (mol of olefin / mol of catalyst) × conversion per hour.

competition with TBHP to occupy the coordination sites of the molybdenum catalyst. It seems that a less steric effect of *n*-butanol causes a better coordination ability to occupy the coordination sites of the molybdenum center than *tert*-butanol. So, using *n*-butanol as solvent reduced the epoxidation yield more than *tert*-butanol. It is known that chlorinated solvents facilitate epoxidation of olefins (Table 1, entries 6 and 7) [39]. The best solvent was found to be 1,2-dicholoroethane (DCE). Another advantage of this solvent is its boiling point, which was able to increase the temperature of the reaction up to 80°C. The reaction proceeds at a lower rate in nonpolar solvents, such as toluene and *n*-nonane.

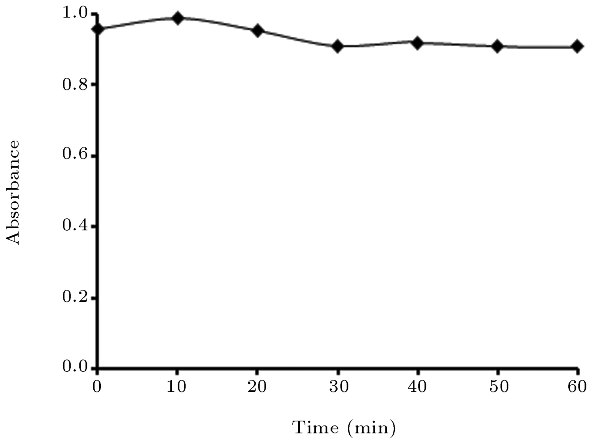


Figure 2. The changes of the absorption in 225 nm of [MoO$_2$(sap)(EtOH)] in oxidation of cyclooctene after addition of TBHP.

Stability of Catalysts

Figure 2 shows that the variation of intensity of the absorbance of MoO$_2$(sap)EtOH (1) at $\lambda_{\max}$ (225 nm) during the epoxidation reaction is nearly constant. It seems that the catalyst remained intact after the end of the reaction. In fact, this dioxomolybdenum-Schiff base catalyst shows good stability in the reaction of olefins by TBHP.

Activity of Different Complexes with Different Substituents

The catalytic activities of *cis*-dioxomolybdenum(VI) complexes **1-7** were determined by the yield of epoxidation of cyclooctene and 1-octene (Figure 3). The selectivity of epoxidation was found to be close to 100%, either for epoxycyclooctane or 1,2-epoxyoctane. As shown in Figure 3, the substituents of the Schiff base ligands have no major effect on the yield and

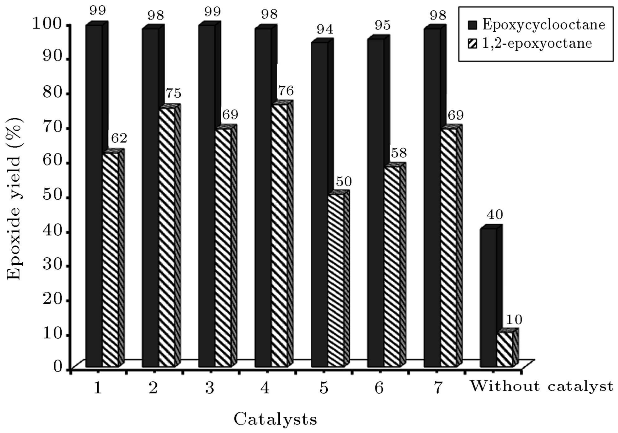


Figure 3. The yield of epoxidation of 1-octene and cyclooctene catalyzed by *cis*-dioxomolybdenum(VI)-Schiff base complexes after 60 min at 80°C.

selectivity of the epoxidation of cyclooctene in comparison with 1-octene. In fact, the high activity of cyclooctene in the epoxidation reaction catalyzed by all complexes **1-7** made a difficult comparison between the catalytic activities of complexes. The different activities of complexes are better noticed during the epoxidation of 1-octene. However, it seems that the electron releasing substituents on the Schiff base ligands, such as the *tert*-butyl group, increases the yield of 1-octene epoxidation. However, in accordance with the known electrophilic nature of the oxidizing species (the coordinated TBHP as oxidant to the Mo complex) in the catalytic epoxidation with Mo(VI) complexes [26,29], it is expected that introducing the electron-withdrawing group to the salicylidene ring increases the effectiveness of the catalyst. However, we observed that the presence of the nitro group on the salicylidene ring of the complex reduced the catalytic activity for 1-octene epoxidation. A similar effect of an electron withdrawing nitro group was reported for some *cis*-dioxomolybdenum(VI) complexes with tetradentate Schiff base ligands [24].

Time-dependent reaction courses of the 1-octene catalytic epoxidation with different complexes during 150 min are shown in Figure 4. In fact, all the catalysts show similar time-dependent curves. Initially, reactions proceed quickly indicating that an active catalytic species is formed rapidly after the addition of TBHP. During the course of the reaction, however, the velocity slows down considerably, since an increasing amount of *tert*-butanol (*t*-BuOH) molecules are competing for the same coordination sites as the TBHP. A similar effect was observed when using *t*-BuOH as a solvent for the catalytic reaction (Table 1, entry 5). It seems that adding *t*-BuOH to the catalytic reaction mixture slows down the catalytic activity but does not inhibit the reaction completely.

We considered the effect of the presence of some strong coordinating ligand in the medium of the reaction, such as imidazole and pyridine-N-oxide. As shown in Table 2, complex 8, MoO_2(sap)(Im), which is the sixth coordination site of Mo(VI) occupied with imidazole as a strong monodentate ligand, shows lower catalytic activity than MoO_2(sap)(EtOH) (Table 2, entries 1 and 2). It was also found that the catalytic activity of MoO_2(sap)EtOH drastically decreased with addition of 10 equiv of basic ligand, such as imidazole, 1-methylimidazole and triethylamine, to the medium of reaction (Table 2, entries 5, 6 and 8). This may be due to ability of these ligands to coordinate to the central metal, which restricts the number of free coordination sites that would be required for coordination of TBHP. Interestingly, it was observed that the presence of pyridine-N-oxide did not inhibit the catalytic reaction (Table 2, entries 3 and 7). It can be related to the oxidation ability of py-N-O [40].

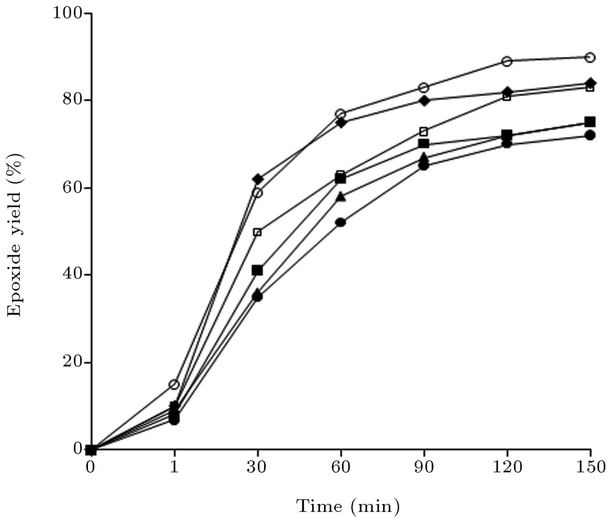


Figure 4. Time-dependent reaction courses of the 1-octene catalytic epoxidation at 80°C up to 150 min. key: catalyst 1, ■; catalyst 2, ♦; catalyst 4, ○; catalyst 5, ●; catalyst 6, ▲; catalyst 7, □.

Table 2. The effect of basic ligands[a] on the epoxidation of cyclooctene with TBHP.

Entry	Catalyst/Base	Conversion(%)[b]
1	MoO_2(sap)EtOH	95
2	MoO_2(sap)Im	89
3	MoO_2(sap)Py-N-O	97
4	MoO_2(sap)Im /9 eq Im	50
5	MoO_2(sap)EtOH / 10 eq Im	51
6	MoO_2(sap)EtOH / 10 eq 1-Me-Im	51
7	MoO_2(sap)EtOH / 10 eq Py-N-O	98
8	MoO_2(sap)EtOH / 10 eq Et_3N	64

a: Conditions: The molar ratio for catalyst: cyclooctene: oxidant are 1:800:800.
The reactions were run for 30 min at 80°C.
b: GC yields based on the starting olefin.

Table 3. Epoxidation of different olefins with MoO_2(sap)EtOH as catalyst[a].

Entry	Substrate	Conversion (%)		Selectivity (%)[b]
		30 min	60 min	
1	Cyclooctene	95	99	100
2	Cyclohexene	79	92	100
3	1-Methylcyclohexene	99	99	100
4	1-Heptene	77	86	100
5	1-Octene	45	63	100
6	2-Octene	80	91	100
7	Styrene	42	46	65
8	α-Methylstyrene	37	44	63
9	4-Methylstyrene	24	26	58
10	4-Methoxystyrene	11	20	60
11	Indene	29	29	70
12	2-cyclohexene-1-one	-	15	74
13	2-cyclohexene-1-ol	-	84	95
14	α-terpineol	-	43	58

a: Conditions: The molar ratio for using catalyst: substrate: oxidant are 1:800:800. The reactions were run at 80°C.

b: selectivity to epoxide at 60 min.

Epoxidation of Different Olefins

The catalytic activity of MoO_2(sap)EtOH in the epoxidation of various cyclic and linear alkenes was tested and the results are summarized in Table 3. In general, the olefin conversions and epoxide selectivities are higher for aliphatic substrates than those for aromatic olefins. The best epoxide yield and selectivity is obtained for cyclooctene. The epoxide yield increases with the nucleophilic character of olefin. Generally, the Lewis acidity of dioxomolybdenum(VI) complexes is an important factor that determines the catalytic performance of the catalyst in olefin epoxidation [19,41]. The major role of the Mo(VI) centre is to withdraw electrons from the peroxidic oxygen making it more susceptible to attack by nucleophiles, such as olefins. Thus, the epoxide yields tend to decrease as the olefin becomes less substituted by electron donating groups, such as methyl. So, higher epoxide yields were obtained with the 1-methylcyclohexene and 2-octene, with respect to cyclohexene and 1-octene, respectively. It is expected that the higher electronic density of an internal olefinic double bond (compared with a terminal C=C bond) should favor nucleophilic attack on an electrophilic oxidizing species. It should be noted that adding 2,6-di-*tert*-butyl-*p*-cresol as a radical scavenger (with an equivalent amount, with respect to cyclooctene as the substrate) to a mixture of the reaction had no significant effect on the reaction rate. Thus, it confirmed that the mechanism did not involve radical pathways.

It is observed that epoxide yield increases with the decreasing chain length of the olefin [28,42,43]. Thus, 1-octene shows lower reactivity, probably due to presence of more steric hindrance arisen from a larger hexyl group with respect to a smaller pentyl group present in 1-heptene. These results indicate that, besides the intrinsic reactivity of the double bond, olefin size and accessibility to the active sites of the catalyst can be recognized as the limiting factors of the catalytic reaction.

The catalytic activity of MoO_2(sap)EtOH is investigated in the epoxidation of some olefins with functional groups (Table 3, entries 12-14). It seems the substitution of an electron-withdrawing group, such as carbonyl, conjugated with the double bond (Table 3, entry 12), decrease the yield of epoxidation. This would be expected based on the electrophilic mechanism proposed for this reaction [25,29,44]. In comparison with 1-methylcyclohexen, α-terpinolperoxide yield is very low (Table 3, entry 14). Noting that the molar ratio of the substrate to catalyst is high (1000:1), it seems that the presence of the OH group causes α-terpinol competition with TBHP for coordination to the molybdenum center, such as that observed for alcoholic solvents (Table 1, entries 4,5).

Table 4. Epoxidation of olefins with MoO_2(sap)EtOH as catalyst using no solvents [a].

Entry	Substrate	Conversion (%) [b]
1	Cyclooctene	95
2	1-octene	43
3	Indene	28(19 [c])

a: Conditions: The molar ratio for using catalyst: substrate: oxidant are 1:800:800. The reactions were run at 80°C.

b: After 60 min.

c: % Indeneoxide.

Solventless Epoxidation of Olefins

Mo(sap)EtOH (1) was used as a typical catalyst for the catalytic epoxidation of olefins in the absence of solvent. The catalyst became soluble in the reaction medium after adding the oxidant, so it acts as a homogeneous catalyst. Table 4 shows the results of the solventless catalytic epoxidation of some olefins. It is observed that epoxidation conversions in solventless systems are similar to that of epoxidation reactions in the 1,2-dicholoroethane as the best solvent of the reaction.

CONCLUSIONS

Several complexes of dioxomolybdenum(VI)-tridentate Schiff base have been tested for their catalytic epoxidation activity for some olefins. These complexes are easily synthesized and showed very good catalytic activity, stability and selectivity for epoxidation of cyclooctene and 1-octene. However, it appeared that the efficiency of the catalytic system is strongly dependent on the temperature and nature of the solvent, thus the best yields were achieved at 80°C and 1,2-dichloroethane. Epoxidation of several aliphatic and aromatic olefins with MoO_2(sap)EtOH showed that this catalytic system is more efficient for aliphatic substrates and the epoxide yields increased with the nucleophilicity of olefins.

ACKNOWLEDGMENTS

Financial support of this work by the Research Council of Sharif University of Technology is greatly appreciated.

REFERENCES

1. Jørgensen, K.A. “Transition-metal-catalyzed epoxidations”, *Chem. Rev.*, **89**, pp. 431-358 (1989).
2. Xia, Q.H., Ge, H.Q., Ye, C.P., Liu, Z.M. and Su, K.X. “Advances in homogeneous and heterogeneous catalytic asymmetric epoxidation”, *Chem. Rev.*, **105**(5), pp. 1603-1662 (2005).
3. Talsi, E.P., Shalyaev, K.V. and Zamaraev, K.I. “^{17}O, ^{95}Mo and ^{1}H NMR study of the mechanism of epoxidation of alkenes with hydrogen peroxide in the presence of molybdenum complexes”, *J. Mol. Catal. A: Chem.*, **83**, pp. 347-366 (1993).
4. Bregeault, J.M. “Transition-metal complexes for liquid-phase catalytic oxidation: Some aspects of industrial reactions and of emerging technologies”, *J. Chem. Soc, Dalton Trans.*, pp. 3289-3302 (2003).
5. Dickman, M.H. and Pope, M.T. “Peroxo and superoxo complexes of chromium, molybdenum, and tungsten”, *Chem. Rev.*, **94**, pp. 569- 583 (1994).
6. Kotov, S.V., Kolev, T.M. and Georgieva, M.G. “Preparation and use of novel molybdenum-containing organic complexes as catalysts in the epoxidation of cyclohexene”, *J. Mol. Catal. A: Chem.*, **195**, pp. 83-94 (2003).
7. Gharah, N., Chakraborty, S., Mukherjee, A.K. and Bhattacharyya, R. “Highly efficient epoxidation method of olefins with hydrogen peroxide as terminal oxidant, bicarbonate as a co-catalyst and oxodiperoxo molybdenum(VI) complex as catalyst”, *Chem. Commun.*, **22**, pp. 2630-2632 (2004).
8. Bregeault, J.M., Vennat, M., Salles, L., Piquemal, J.Y., Mahha, Y., Briot, E., Bakala, P.C., Atlamsani, A. and Thouvenot, R. “From polyoxometalates to polyoxoperoxometalates and back again; Potential applications”, *J. Mol. Chem. A: Chem.*, **250**, pp. 177-189 (2006).
9. Bruno, S.M., Fernandes, J.A., Martins, L.S., Goncalves, I.S., Pillinger, M., Ribeiro-Claro, P., Rocha, J. and Valente, A.A. “Dioxomolybdenum(VI) modified mesoporous materials for the catalytic epoxidation of olefins”, *Catal. Today*, **114**, pp. 263-271 (2006).
10. Mbeleck, R., Ambroziak, K., Saha, B. and Sherrington, D.C. “Stability and recycling of polymer-supported Mo(VI) alkene epoxidation catalysts”, *React. Funct. Polym.*, **67**, pp. 1448-1457 (2007).
11. Masteri-Farahani, M., Farzaneh, F. and Ghandi, M. “Molybdenum incorporated silicalite as catalyst for epoxidation of olefins”, *J. Mol. Catal. A: Chem.*, **192**, pp. 103-111 (2003).
12. Kollar, J. (Halcon). US Patents., 3,350,422 and 3,351,635 (1967).
13. Sheng, M.N. and Zajaczek, G.J (ARCO). UK Patent., 1,136,923 (1968).
14. Thiel, W.R., Angstl, M. and Priermeier, T. “Substituierte N,N-chelat-liganden-anwendungen in der molybdan-katalysierten Olefin-epoxidation”, *Chem. Ber.*, **127**, pp. 2373-2379 (1994).
15. Thiel, W.R., Angstl, M. and Hansen, N. “Metal catalyzed oxidations. Part 2. Molybdenum catalyzed olefin epoxidation in nonpolar solvents”, *J. Mol. Catal. A: Chem.*, **103**, pp. 5-10 (1995).

16. Thiel, W.R. and Priermeier, T. "The first olefin-substituted peroxomolybdenum complex: Insight into a new mechanism for the molybdenum-catalyzed epoxidation of olefins", *Angew. Chem. Int. Ed. Engl.*, **34**, pp. 1737-1738 (1995).
17. Kuhn, F.E., Herdtweck, E., Haider, J.J., Herrmann, W.A., Goncalves, I.S., Lopes, A.D. and Romao, C.C. "Bis-acetonitrile(dibromo)dioxomolybdenum(VI) and derivatives: Synthesis, reactivity, structures and catalytic applications", *J. Organomet. Chem.*, **583**, pp. 3-10 (1999).
18. Kuhn, F.E., Lopes, A.D., Santos, A.M., Herdtweck, E., Haider, J.J., Romao, C.C. and Santos, A.G. "Lewis base adducts of bishalogeno-dioxomolybdenum(VI): Syntheses, structures, and catalytic applications", *J. Mol. Catal. A: Chem.*, **151**, pp. 147-160 (2000).
19. Kuhn, F.E., Santos, A.M., Lopes, A.D., Goncalves, I.S., Herdtweck, E. and Romao, C.C. "(Dimethyl)dioxomolybdenum(VI) complexes: Syntheses and catalytic applications", *J. Mol. Catal. A: Chem.*, **164**, pp. 25-38 (2000).
20. Kuhn, F.E., Groarke, M., Bencze, E., Herdtweck, E., Prazeres, A., Santos, A.M., Calhorda, M.J., Romao, C.C., Goncalves, I.S., Lopes, A.D. and Pillinger, M. "Octahedral bipyridine and bipyrimidine dioxomolybdenum(VI) complexes: Characterization, application in catalytic epoxidation, and density functional mechanistic study", *Chem. Eur. J.*, **8**, pp. 2370-2383 (2002).
21. Kuhn, F.E., Santos, A.M., Goncalves, I.S., Romao, C.C. and Lopes, A.D. "Organorhenium(VII) and organomolybdenum(VI) oxides: synthesis and application in oxidation catalysis", *Appl. Organomet. Chem.*, **15**, pp. 43-50 (2001).
22. Groarke, M., Goncalves, I.S., Herrmann, W.A. and Kuhn, F.E. "New insights into the reaction of *t*-butylhydroperoxide with dichloro- and dimethyl(dioxo)molybdenum(VI)", *J. Organomet. Chem.*, **649**, pp. 108-112 (2002).
23. Monteiro, B., Balula, S.S., Gago, S., Grosso, C., Figueiredo, S., Lopes, A.D., Valente, A.A., Pillinger, M., Lourenco, J.P. and Goncalves, I.S. "Comparison of liquid-phase olefin epoxidation catalyzed by dichlorobis-(dimethylformamide)dioxomolybdenum(VI) in homogeneous phase and grafted onto MCM-41", *J. Mol. Catal. A: Chem.*, **297**, pp. 110-117 (2009).
24. Ambroziak, K., Pelech, R., Milchert, E., Dzembowska, T. and Rozwadowski, Z. "New dioxomolybdenum(VI) complexes of tetradentate Schiff base as catalysts for epoxidation of olefins", *J. Mol. Catal. A: Chem.*, **211**, pp. 9-16 (2004).
25. Bagherzadeh, M, Latifi, R., Tahsini, L., Amani, V., Ellern, A. and Woob, L.K. "Synthesis, characterization and crystal structure of a dioxomolybdenum(VI) complex with a N,O type bidentate Schiff base ligand as a catalyst for homogeneous oxidation of olefins", *Polyhedron*, **28**, pp. 2517-2521 (2009).
26. Sui, Y., Zeng, X., Fang, X., Fu, X., Xiao, Y., Chen, L., Li, M. and Cheng, S. "Syntheses, structure, redox and catalytic epoxidation properties of dioxomolybdenum(VI) complexes with Schiff base ligands derived from tris(hydroxymethyl)amino methane", *J. Mol. Catal. A: Chem.*, **270**, pp. 61-67 (2007).
27. Bruno, S.M., Balula, S.S., Valente, A.A., Almeida Paz, F.A., Pillinger, M., Sousa, C., Klinowski, J., Freire, C., Ribeiro-Claro, P. and Goncalves, I.S. "Synthesis and catalytic properties in olefin epoxidation of dioxomolybdenum(VI) complexes bearing a bidentate or tetradentate salen-type ligand", *J. Mol. Catal. A: Chem.*, **270**, pp. 185-194 (2007).
28. Masteri-Farahani, M., Farzaneh, F. and Ghandi, M. "Synthesis of tetradentate N_4 Schiff base dioxomolybdenum(VI) complex within MCM-41 as selective catalyst for epoxidation of olefins", *Catal. Commun.*, **8**, pp. 6-10 (2007).
29. Sobczak, J.M. and ZiolKowski, J.J. "Molybdenum complex-catalyzed epoxidation of unsaturated fatty acids by organic hydroperoxides", *Appl. Catal. A.*, **248**, pp. 261-268 (2003).
30. Liimatainen, J., Lehtonen, A. and Sillanpaa, R. "cis-dioxomolybdenum(VI) complexes with tridentate and tetradentate Schiff base ligands. Preparation, structures and inhibition of aerial oxidation of aldehydes", *Polyhedron*, **19**, pp. 1133–1138 (2000).
31. Rao, C.P., Sreedhara, A., Rao, P.V., Verghese, M.B., Rissanen, K., Kolehmainen, E., Lokanath, N.K., Sridhar, M.A. and Prasad, J.S. "Syntheses, structure, reactivity and species recognition studies of oxo-vanadium(V) and -molybdenum(VI) complexes", *J. Chem. Soc, Dalton Trans.*, pp. 2383–2393 (1998).
32. Craig, J.A., Harlan, E.W., Synder, B.S., Whitener, M.A. and Holm, R.H. "Oxomolybdenum(IV,V,VI) complexes: Structures, reactivities, and criteria of detection of binuclear (μ-oxo)molybdenum(V) products in oxygen atom transfer systems", *Inorg. Chem.*, **28**, pp. 2082-2091 (1989).
33. Boyd, I.W. and Spence, J.T. "Molybdenum(IV)-oxo complexes with oxygen, nitrogen and sulfur ligands. Syntheses and electrochemical studies", *Inorg. Chem.*, **21**, pp. 1602-1606 (1982).
34. Topich, J. and Lyon, J.T. "Synthesis and electrochemistry of *cis*-dioxomolybdenum(VI) complexes with tridentate Schiff base ligands containing O, N and S donor atoms", *Polyhedron*, **3**, pp. 55-60 (1984).
35. Topich, J. and Lyon, J.T. "Ligand control of *cis*-dioxomolybdenum(VI) redox chemistry: Kinetic and activation parameter data for oxygen atom transfer", *Inorg. Chem.*, **23**, pp. 3202-3206 (1984).
36. Casiraghi, G., Casnati, G., Sartori, G. and Terenghi, G. "Selective reactions between phenols and formaldehyde. A novel route to salicylaldehydes", *J. Chem. Soc; Perkin Trans.*, pp. 1862-1865 (1980).
37. Chen, G.J., Madonald, J.W. and Newton, W.E. "Synthesis of Mo(1V) and Mo(V) complexes using oxo

abstraction by phosphines mechanistic implications", *Inorg. Chem.*, **15**, pp. 2612-2615 (1976).

38. Rajan, O.A. and Chakravorty, A. "Molybdenum complexes. 1. Acceptor behavior and related properties of Mo(VI)O_2(tridentate) systems", *Inorg. Chem.*, **20**, pp. 660-664 (1981).

39. Reichardt, B.C. "Solvents and solvent effect in organic chemistry", VCH, Weinheim (1998).

40. Ito, R., Umezawa, N. and Higuchi, T. "Unique oxidation reaction of amides with pyridine-N-oxide catalyzed by ruthenium porphyrin: Direct oxidative conversion of N-Acyl-l-proline to N-Acyl-l-glutamate", *J. Am. Chem. Soc.*, **127**, pp. 834-835 (2005).

41. Sheldon, R.A. and Kochi, J.K. "Metal-catalyzed oxidations of organic compounds in the liquid phase: A mechanistic approach", *Adv. Catal.*, **25**, pp. 272-413 (1976).

42. Valente, A.A., Moreira, J., lopes, A.D., Pillinger, M., Nunes, C.D. and Goncalves, I.S. "Dichloro and dimethyl dioxomolybdenum(VI)-diazabutadiene complexes as catalysts for the epoxidation of olefins", *New. J. Chem.*, **28**, pp. 308-313 (2004).

43. Arnold, U., Serpa da Cruz, R., Mandelli, D. and Schuchardt, U. "Activity, selectivity and stability of metallosilicates containing molybdenum for the epoxidation of alkenes", *J. Mol. Catal. A.*, **165**, pp. 149-158 (2001).

44. Bagherzadeh. M., Tahsini, L., Latifi, R. and Woo, L.K. "*cis*-dioxo-molybdenum(VI)-oxazoline complex catalyzed epoxidation of olefins by *tert*-butyl hydroperoxide", *Inorg. Chim. Acta*, **362**, pp. 3698-3702 (2009).

BIOGRAPHIES

Mojtaba Bagherzadeh, Professor in the Chemistry Department of Sharif University of Technology, obtained a Ph.D. in Inorganic Chemistry from Shiraz University in 1998. His research interests include: Metal Complex Catalyzed Oxidations of Organic Compounds, Synthesis of Inorganic Complexes, Biomimetic Catalytic Systems and Experimental and Theoretical Mechanistic Studies of Catalytic Reactions.

Saeedeh Ghazali Esfahani received a B.S. degree in Pure Chemistry from Tehran University in 2005 and a M.S. degree in Inorganic Chemistry from Sharif University of Technology in 2007, where she has been working since 2008 on her Doctoral Degree project.