Catalytic Epoxidation of Cyclohexene with *t*-Butyl Hydroperoxide in the Presence of Various Molybdenum Complexes

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(Received March 1, 1983)

Synopsis. A ligand can play an important role in the activity of the molybdenum-catalyzed epoxidation. Molybdenum complex was changed to the reactive intermediate through the reaction of catalyst with *t*-BuOOH. Oxalate, edta, and phenoxyl groups were selected as ligands. The phenoxyl group was most effective for the epoxidation. This effect was interpreted by the HSAB concept.

Epoxidations of olefins with hydroperoxide in the presence of molybdenum(VI) or (V) complexes have been reported by Trifilo *et al.*,[1] Sheldon,[2] and Gould *et al.*[3] Also, Henry presented a review about molybdenum compounds for epoxidation with hydroperoxide.[4]

Ziolkowski presented the oxalatomolybdenum(V) complex as a catalyst for epoxidation.[5] Mitchell[6] and Komura *et al.*[7] reported the properties and reactivity of oxalatomolybdenum(V) complexes. Ziolkowski *et al.* used oxalic, malonic, succinic, glutaric, adipic, oxoacid, water, pyridine, and anionites containing $-N(CH_3)_2$ and $-\overset{+}{N}(CH_3)_3\overset{-}{Cl}$ groups as the ligands of the complex mentioned above.[8,9] In this paper, we report the relation between the reactivity and the ligand in case of epoxidation with molybdenum complexes.

1 was obtained in the usual way.[8] An exchange reaction of the ligand of oxalatomolybdenum(V) complex was carried out by the method reported by Komura and co-workers.[7] Epoxidation of cyclohexene with *t*-BuOOH was carried out in the presence of materials **1**—**8**. The reaction proceeded according to the reported scheme by Ziolkowski and Sobczak.[8,9] The results are shown in Table 1. Hydrazinium ion is more reactive than barium ion, proton, or pyridinium ion in the cationic ligands used in our experiments. Also, the complex with pyridine as the inner ligand shows higher reactivity. An induction period was observed in this case, since the formation of active intermediate was promoted by the reaction of *t*-BuOOH with oxalato complexes. The UV-spectrum of *t*-BuOOH and complex in benzene is shown in Fig. 1(a), where the absorption band is shown at 370 nm after 60 min. The time dependency of the spectrum of *t*-BuOOH–$H_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]$ system is shown in Fig. 1(b). The maximum band was observed after 40 min. The formation of the reactive intermediate was inferred from Fig. 1(b).

Table 1. Epoxidation of cyclohexene with *t*-BuOOH by oxalato-complexes

Oxalato complex	Method[a)]	Reaction time/min	Cyclohexene conversion/%	Epoxide Selectivity/%	Epoxide Yield/%
1	A	360	56.5	90.6	51.6
2	B	360	98.4	61.8	60.8
3	A	150	83.4	95.8	79.9
	B	150	81.3	79.9	81.2
4	A	150	78.2	69.8	54.6
	B	150	78.3	73.1	57.2
5	A	150	78.1	79.7	62.2
	B	150	70.7	83.2	58.3
6	A	360	64.3	98.0	63.0
	B	150	65.2	88.5	57.7
7	A	360	86.4	99.8	87.7
8	A	360	80.0	80.8	65.1

Reaction conditions: cat 0.1 mmol, cyclohexene 50 mmol, *t*-BuOOH 50 mmol, benzene 50 cm³, temp 60 °C. a) See Ref. 12.

Trifiro and co-workers reported the formation of the intermediate in the epoxidation of olefin with *t*-BuOOH and molybdenum complex.[1] They reported that when the bond between metal and ligand was stable, the activity of epoxidation was low. On the other hand, a weak bond complex was effective for the decomposition of hydroperoxide and the selectivity for epoxide became lower. Since Figs. 1(a) and (b) show that epoxides are obtained after the formation of an intermediate from *t*-BuOOH and molybdenum complex, it is interesting to apply method B[12] for molybdenum complex with ethylendiamintetraacetic acid (H_4edta), which is reported to be a stable compound by Trifiro.[1] The result obtained by method B is better than that obtained method A[12] in Table 2. After *t*-BuOOH and Mo^V–edta complex were allowed to react 4 h, cyclohexene was added to the reaction mixture. In the case of Mo^V–edta complex, pre-reaction of Mo^V–edta complex with *t*-BuOOH improved the reactivity. The high yield of cyclohexene epoxide was obtained at 73 °C. The rate of the epoxidation with Mo^{VI}–edta complex at 73 °C was slower than

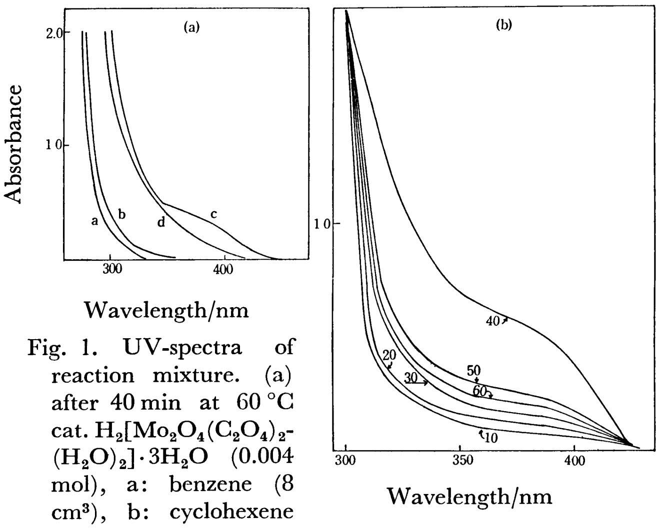

Fig. 1. UV-spectra of reaction mixture. (a) after 40 min at 60 °C cat. $H_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$ (0.004 mol), a: benzene (8 cm³), b: cyclohexene (0.82 mmol/cm³), c: *t*-BuOOH (0.82 mmol/cm³) in benzene, d: *t*-BuOOH (0.82 mmol/cm³), cyclohexene (0.82 mmol/cm³) in benzene. (b) After 10, 20, 30, 40, 50, 60 min at 60 °C, cat.; $H_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$ (0.004 mol) benzene (8 cm³), *t*-BuOOH (0.2 cm³).

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TABLE 2. EPOXIDATION BY Mo^{V}- AND Mo^{VI}-EDTA COMPLEX

Catalyst	Method[a]	Reaction conditions		Cyclohexene conversion/%	Epoxide	
		Time/min	Temp/°C		Selectivity/%	Yield/%
Mo(V)-edta	A	420	74	55.0	88.6	48.7
	B	240	73	74.7	101	83.6
Mo(VI)-edta	A	420	75	39.8	106	43.9

Reaction conditions: cat 0.1 mmol, cyclohexene 50 mmol, *t*-BuOOH 50 mmol, benzene 50 cm^3. a) See Ref. 12.

TABLE 3. EPOXIDATION OF CYCLOHEXENE BY $Mo_2O_4(OH)_2(pHO)_2$ AND $MoO_2(sala)_2$

Catalyst	Temp/°C	Decomp of *t*-BuOOH/%	Yield of epoxide/%	Selectivity/ %
Mo-ph	8	18.3	15.7	86
	35	68.3	66.7	98
	44	81.3	76.9	94
$Mo(sala)_2$	10.5	31.0	33.6	100
	20	45.1	45.4	100
	31.5	66.3	55.5	84

Reaction conditions: cyclohexene 3.95 $mmol/cm^3$, *t*-BuOOH 1.05 $mmol/cm^3$, Mo-ph, 0.603 $mmol/cm^3$, Mo-$(sala)_2$ 0.541 $mmol/cm^3$, time 60 min, solv., benzene 25 cm^3.

that of Mo^{VI}–edta complex, but the effect of pre-reaction of Mo^{VI}–edta complex with *t*-BuOOH was not observed. The epoxidation with Mo^{VI}–edta complex with *t*-BuOOH was not observed. The epoxidation with Mo^{V}–edta complex was inhibited in a polar solvent (*e.g.* CH_3CN). This may indicate the association of polar species to the active sites of the catalyst.

Ziolkowski proposed that the *t*-BuO–Mo bond participated in epoxidation, and that the coordination of the transition metal complexes for hydroxyl(–OH) or alkoxyl(–OR) oxygen occurred on active site.[13] Also, Sheldon reported that Mo^{VI}–1,2-diol system showed higher reactivity for epoxidation.[14] In order to examine this effect of the RO–Mo bond, di-μ-oxobis[hydroxo(oxo) (phenoxo) molybdenum (VI)] [$Mo_2O_4(OH)_2(phO)_2$] and dioxobis[salicylaldehydatomolybdenum(VI)][$MoO_2(sala)_2$] were applied for the epoxidation of cyclohexene. The results are summarized in Table 2. In each case, selectivity and yield are higher than in other cases. The activation energy was calculated from the initial rates and at various reaction temperature (Table 3). [$Mo_2O_4(OH)_2(phO)_2$] and [$MoO_2(sala)_2$] were the most reactive catalysts, compared with the other catalysts cited in Table 3. The alkoxyl group is a hard base and the phenyl group is a soft base. Our information suggests that the phenoxyl group is a soft base and that MoO^{3+} is a hard acid.[10] So, it would be understandable that the interaction of Mo–Oph with *t*-BuOOH is most effective for the occurrence of an electrophilic hydroxyl group.

Experimental

Synthesis of Oxalate Complexes. $Ba[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$ (**1**), $H_2[Mo_2O_4(C_2O_4)(OH)_2(H_2O)_2]\cdot H_2O$ (**2**), $H_2[Mo_2O_4(C_2O_4)_2(py)_2]$ (**3**), $(pyH)_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$ (**4**), $(pyH)_2[Mo_2O_4(C_2O_4)_2(py)_2]$ (**5**), $Ba[Mo_2O_4(C_2O_4)_2(py)_2]\cdot 8H_2O$ (**6**), $HH_2NNH_3[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 2H_2O$ (**7**), $H_2[Mo_2O_4(C_2O_4)_2(H_2O)_2]\cdot 3H_2O$. These compounds were synthesized by the methods of Mitchell,[6] Komura,[7] and Ziolkowski.[8]

Di-μ-oxobis[oxohydroxydiphenoxymolybdate(VI)] [$Mo_2O_4(OH)_2phO_2$], Dioxobis[salicylaldehydatomolybdenum(VI)] [$MoO_2(sala)_2$]: these compounds were synthesized in the usual way.

TABLE 4. ACTIVATION ENERGY OF THE EPOXIDATION WITH VARIOUS Mo COMPOUND

Catalyst	Substrate	Solvent	E_a/kJ mol^{-1}
Mo-Powder	Cyclohexene	Cyclohexane	100.5[c]
Mo-y[a]	Cyclohexene	Cyclohexane	44.0[d]
MoO_3	Cyclohexene	Dioxane	112.6[e]
$MoO_2(DCC)_2$[b]	Cyclohexene	Benzene	79.5[f]
$MoO_2(acac)_2$	1-Octene	Benzene	50.2[g]
$Mo(CO)_6$	1-Octene	Benzene	79.5[h]
$MoO_2(oxine)_2$	Cyclohexene	Benzene	66.7[i]
Mo^{V}-edta	Cyclohexene	Benzene	104.7—49.0
Mo^{VI}-edta	Cyclohexene	Benzene	319.8—239.4
$Mo_2O_4(OH)_2(phO)_2$	Cyclohexene	Benzene	49.0
$MoO_2(sala)_2$	Cyclohexene	Benzene	72.4

a) Mo-y=Molybdenum peroxide obtained by the oxidation of molybdenum powder or molybdenum trioxide with hydrogen peroxide. b) DCC=Dimethyldithiocarbamate. c) Y. Kurusu *et al.*, *Nippon Kagaku Kaishi*, **1978**, 1262. d) S. Sawamura's graduation thesis(Sophia Univ.), (1977). e) F. Mashio *et al.*, *Yuki Gosei Kagaku Kyokai Shi*, **26**, 363 (1968). f) T. Ikawa *et al.*, *Sekiyu Gakkai Shi*, **18**, 492 (1975). g) N. Indictor and W. F. Brill, *J. Org. Chem.*, **30**, 2074 (1965). h) T. N. Baker *et al.*, *J. Org. Chem.*, **38**, 1145 (1973). i) F. Trifiro *et al.*, "Proceedings of 1st Int. Conf. on Chemistry and Uses of Mo 1973," (1974), p. 169.

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12) *Method A*: The reactor was charged with a solvent, cyclohexene and catalyst. The mixture was kept at a reaction temperature for a given time with stirring, and then *t*-BuOOH was added. *Method B*: A mixture of a solvent, catalyst and *t*-BuOOH was stirred in the reactor at the reaction temperature for a given time, and the reaction was initiated by adding cyclohexene.

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