Polymer-Supported Tetrabromooxomolybdate(V): A New Type of Catalyst for Oxidation by *t*-Butyl Hydroperoxide

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POLYMER-SUPPORTED TETRABROMOOXOMOLYBDATE(V): A NEW TYPE OF CATALYST FOR OXIDATION BY *t*-BUTYL HYDROPEROXIDE

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ABSTRACT

Tetrabromooxomolybdate(V) was immobilized in alkylammonium cation-type polymers obtained by the reaction of poly(*p*-chloromethyl-styrene-*co*-divinylbenzene-*co*-styrene) (abbreviated CMS) with amines and derived from poly(*p*-vinylpyridine) and poly(*p*-vinylpyridine-*co*-divinylbenzene). These immobilized polymers were active catalysts for the oxidation of alcohols and epoxidation of olefins with *t*-butyl hydroperoxide (abbreviated *t*-BuOOH). Among these polymers, we could find a polymer catalyst showing specificity, which was obtained by immobilization of tetrabromooxomolybdate(V) in the polymer derived from the reaction of CMS with trimethylamine. This immobilized polymer does not catalyze epoxidation of olefins but catalyzes oxidation of alcohols with *t*-BuOOH. Ammonium tetrabromooxomolybdate(V) complex was stabilized by the immobilization in the polymers, and it was found that the reactivity of the active group is due to the microenvironment supplied by the polymer chain.

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INTRODUCTION

t-Butyl hydroperoxide (*t*-BuOOH) is a bulk organic reagent that is available and easily recyclable at the industrial level, largely because of its greater thermal stability and reduced sensitivity to contamination by metals compared to other peroxy acids. For these reasons, *t*-BuOOH is widely used as one of the best sources of oxygen atoms for oxidations in organic synthesis [1].

In the course of our studies to exploit a new, effective application of *t*-BuOOH in the presence of molybdenum complexes as catalysts [2], we found that the ammonium tetrabromooxomolybdate(V) complexes showed high catalyst activity for the oxidation of alcohols and epoxidation of olefins [3]. However, the separation and recovery of catalyst from the reaction medium and the reuse are significant problems. Instability of the homogeneous catalyst is also troublesome for organic synthesis; for example, tetrabromooxomolybdate(V) is usually hygroscopic. Immobilization of ammonium tetrabromooxomolybdate(V) complex was carried out to remove these defects. In this report we present a strategy for the oxidation of alcohols with the tetrabromooxomolybdate(V)-*t*-BuOOH system. As an insoluble support, poly(*p*-chloromethylstyrene-*co*-divinylbenzene (9 mol%)-*co*-styrene (29 or 0 mol%) (abbreviated CMS) was used. This was treated with various amines, followed by anionic exchange with tetrabromooxomolybdate(V) synthesized by the method of Allen and Newman [4]. Here we report the immobilization of tetrabromooxomolybdate(V) in the polymer supports and the reactivity of the immobilized polymer catalyst for oxidation with *t*-BuOOH.

EXPERIMENTAL

Materials

Commercially available poly(*p*-chloromethylstyrene-*co*-divinylbenzene (9 mol%)-*co*-styrene (29 or 0 mol%) (Mitsubishi Chemicals Co.) was used after Soxhlet extraction with tetrahydrofurane. These polymers were reacted with various amines. After the separation of the polymer products, they were washed with tetrahydrofurane and dried at room temperature under reduced pressure to constant weight. A polymer reacted with triethylenetetramine, a gift from Mitsubishi Chemicals Co. and a commercial product (CR-20). This was used after washing with tetrahydrofuran and drying to constant weight.

Poly-*p*-vinylpyridine and poly(*p*-vinylpyridine-*co*-divinylbenzene) (2 mol%)

were supplied from Koei Kagaku Co. Poly-*p*-vinylpyridine was reprecipitated with the methanol-ether system. Poly(*p*-vinylpyridine-*co*-divinylpyridine (2 mol%)) was washed with methanol. These polymers were finally dried at 60°C under reduced pressure for at least 24 h. *t*-BuOOH, supplied by Nippon Oil & Fats Co., was used after purification by vacuum distillation. All solvents were guaranteed grade and used as received. Alcohols and olefins were used as substrates after purification by distillation or chromatography.

Immobilization of Tetrabromooxomolybdate(V)

Tetrabromooxomolybdate(V) solution was prepared according to the procedure of Allen and Newman [4]. Immobilization was carried out by the addition of the polymer containing ammonium groups to the tetrabromooxomolybdate(V) solution. The polymer, after filtration, was adequately washed with ether and methanol and then dried at room temperature under reduced pressure for at least 24 h. These immobilized polymers were identified by elemental analysis (Mo by the EDTA method; Br by the Volhard method) and spectral measurements.

General Procedure for Epoxidation of Olefin

Olefin (0.05 mol) was dissolved in benzene (50 mL), and the mixture was stirred at 60°C. Then immobilized polymer (0.2 meq) and *t*-BuOOH (0.05 mol) were added to the solution. The stirring was continued at 60°C for 60 min. Epoxide was separated by GC and identified by NMR and IR.

General Procedure for Oxidation of Alcohol

A solution of immobilized polymer (0.15 meq), *t*-BuOOH (5 mmol), and alcohol (3 mmol) in benzene (3 mL) was stirred at 60°C. After filtering off the immobilized polymer, the solution was evaporated. The product was purified by distillation or chromatography and identified by NMR and IR.

RESULTS AND DISCUSSION

Immobilization of Tetrabromooxomolybdate(V) into the Organic Polymer

CMS, poly-*p*-vinylpyridine, and poly(*p*-vinylpyridine-*co*-divinylbenzene) (2 mol%) were used as starting materials to immobilize tetrabromooxomolyb-

date(V) (Br_4MoO^-). The polymer-containing ammonium-group was synthe-
sized by the reaction of CMS with various amines. Br_4MoO^- prepared by the
method of Allen and Newman [4] was immobilized in the polymers men-
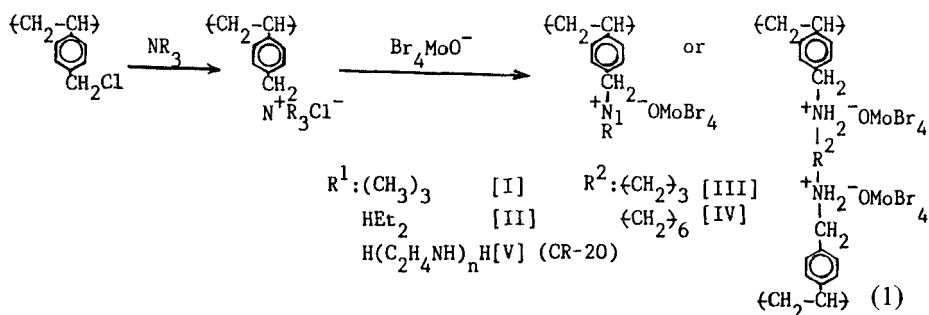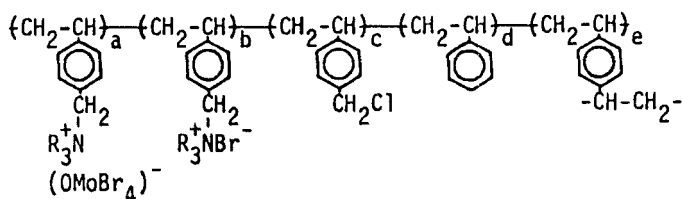tioned above as shown in Eq. (1)

$$ (1) $$

TABLE 1. Structure and Composition of the Various Polymers

| | Composition, mol% | | | | | Analysis | | | |
| | | | | | | Observed | | Calculated | |
Polymer	a	b	c	d	e	Mo	Br	Mo	Br
I	36	26	0	29	9	10.6	—	10.6	—
II	76	15	0	0	9	13.0	42.8	13.9	48.6
III	81	0	10	0	9	13.0	43.2	12.7	42.3
IV	22	5	64	0	9	9.9	32.9	10.2	36.4
V	—	—	—	—	—	8.8	38.9	—	—

Structures and compositions of the various polymers are shown in Table 1. Poly(p-vinylpyridine-co-divinylbenzene) (2 mol%) was treated with methyl iodide. Poly-p-vinylpyridine was reacted with 1,3-dibromopropane and 1,6-dibromohexane. Then, Br_4MoO^- was immobilized in poly(p-vinylpyridine-co-divinylbenzene) (2 mol%) or in the polymer containing alkylpyridinium ion by the anionic exchange reaction as shown in Eq. (2). Table 2 shows the content of Br_4MoO^- in the polymer.

$$(2)$$
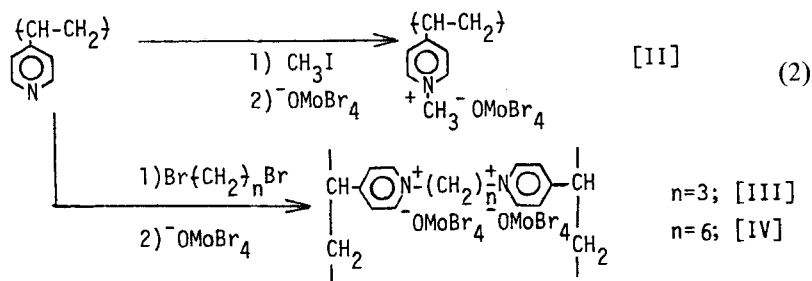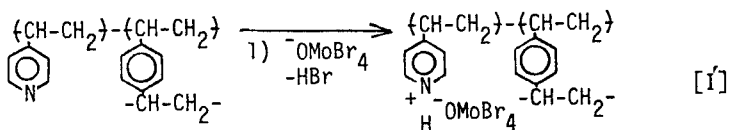
TABLE 2. Contents of Br_4MoO^- in the Polymers Containing Pyridinium Groups

Polymer	$MoBr_4O^-$, mol Mo/g
I'	1.74
II'	0.34
III'	0.93
IV'	1.06

Oxidation of Alcohol and Epoxidation of Olefin

When a equimolar mixture of cyclohexene and 2-octanol was treated with t-BuOOH in the presence of various immobilized polymer mentioned above, chemoselective oxidation was observed as shown in Table 3. Catalyst (I)

TABLE 3. Chemoselective Oxidation of Cyclohexene and 2-Octanol[a]

| | | Yield, % (GC) | |
| | | | |
Catalyst	Time, d		
I	10	0	72
II	4	43	4
III	3	69	2
IV	4	72	0
V	4	11	12
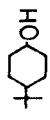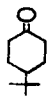
[a]Conditions: cyclohexene 3 mmol, 2-octanol 3 mmol, t-BuOOH 3.3 mmol, catalyst 0.15 mmol Mo, benzene 2 mL.

shows high catalytic selectivity for the oxidation of alcohol, and (II)-(IV) are used as good catalysts for the epoxidation of olefin. On the other hand, Catalyst (V) does not have very good activity but catalyzes both epoxidation and oxidation.

The oxidation of various alcohols and the epoxidation of olefins are summarized in Table 4. Secondary alcohols were easily oxidized to the corresponding ketones. The rate of oxidation is slower than that of epoxidation. The diffuse factor or high steric hindrance around the catalytic center has an effect on the epoxidation and the oxidation. This influence is shown for oxidation (Nos. 1 and 2) and epoxidation (Nos. 4 and 5) with Catalysts (II), (III), and (IV) of Table 4. Catalyst (I) shows selective oxidation of alcohols in the presence of olefins. The cyclic olefinic group of limonene was selectively epoxidized with Catalysts (II), (III), (IV), and (V) and t-BuOOH. The epoxidation proceeded by electrophilic species, for it is dependent of the nucleophilicity of double bond.

Olefinic alcohols could be also oxidized selectivity with t-BuOOH in the presence of the immobilized polymer (Table 5). Since the hydroxyl group of allylic alcohol was activated, it was easily oxidized and also easily epoxidized. On the other hand, the alcohol containing a carbon-carbon double bond at the γ-position was not oxidized, but its double bond was epoxidized. As the position of the hydroxyl group is so far from the position where molybdenum interacts with the carbon-carbon double bond, t-BuOOH activated by molybdenum complex [1, 2] cannot act on the hydroxyl group. In the presence of

TABLE 4. Oxidation of Alcohols and Olefins[a]

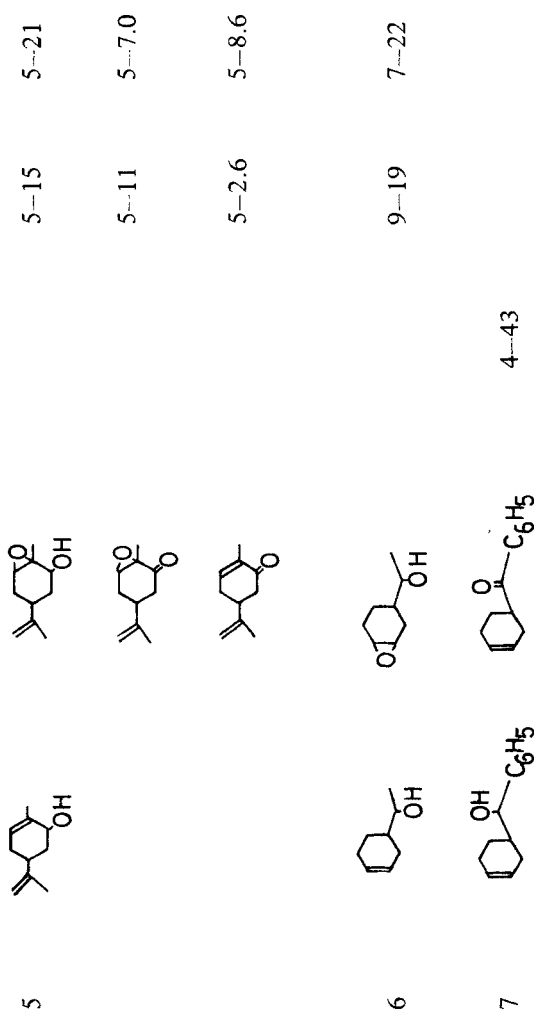| No.	Substrate	Product	I[c]	II	III	IV	V
			Reaction time, d–yield,[b] %				
1			8–72	7–51	7–50	7–55	7–77
2			6–66	6–(89)	7–(85)	7–(85)	3–(95)
3			10–0	4–(91)	4–(91)	3–(77)	9–(67)
4				2–(81)	2–(88)	2–(70)	5–(61)
5				3–(51)	8–(40)	8–(48)	8–(29)

[a]Substrate 3 mmol, t-BuOOH 3.3 mmol, Mo complex 0.15 mmol Mo, benzene 2 mL, 60°C.
[b]By isolation; if in parehtheses, by GC.
[c]Mo complex 0.05 mmol Mo.

TABLE 5. Oxidation of Olefinic Alcohols[a]

No.	Substrate	Products	Reaction time, d–yield,[b] %				
			I	II	III	IV	V
1	(cyclohexenol structure)	(epoxy-cyclohexanol structure)	1–0	5–35	5–68	5–67	5–11
		(cyclohexenone structure)	1–70	5–10	5–11	5–10	5–11
2	(structure)	(structure, OH)		3–28	2–52		
3	(structure)	(structure, OH)		10–30	5–38		
		(structure, O)		10–5.9	5–5.8		
4	(structure, OH)	(structure, OH)		3–38	4–11		
		(structure, O)		3–8.6	4–5.0		

5	[structure]	[structure]	5–15	5–21
		[structure]	5–11	5–7.0
		[structure]	5–2.6	5–8.6
6	[structure]	[structure]	9–19	
7	[structure]	[structure]	4–43	7–22

[a]Substrate 3 mmol, t-BuOOH 3.3 mmol, Mo complex 0.15 mmol Mo, benzene 2 mL, 60°C.
[b]By isolation.

TABLE 6. Oxidation of Alcohols with the Catalyst I-t-BuOOH System[a]

No.	Substrate	Product	Reaction time, d—yield,[b] %
1	$CH_3(CH_2)_7OH$	$CH_3(CH_2)_6CO\text{-}O(CH_2)_7CH_3$	10—(5)
2	$(CH_2)_{11}HC\text{-}OH$	$(CH_2)_{11}C=O$	8—63(74)
3			15—17(25)
4			3—77
5	$C_6H_5CH(OH)CH_3$	$C_6H_5COCH_3$	4—100
6			7—76

cyclohexene, the oxidation of 2-octanol with the t-BuOOH-benzyltrimethyl-ammonium tetrabromooxomolybdate(V) system was disturbed [5]. Lee and Noureldin reported the same reactivity in the presence of $Cu(MnO_4)_2 \cdot 8H_2O$ [6]. They proposed π-complex formation between permanganate and olefin. It may be that the interaction recognized in our case is the same as theirs.

Polymers (I), (II), and (III) are good catalysts for γ-hydroxyl olefins. Catalyst (I) is effective for oxidation, and (II) and (III) are active for epoxidation. This can be explained as follows: As the interaction between molybdenum and olefin in smaller in immobilized polymer than in the low molecular weight model compound benzyltrimethylammonium tetrabromooxomolybdate(V) [5], the activity of the immobilized polymer catalyst does not decline compared to the low molecular weight model compound. We investigated this steric effect by utilizing the low molecular weight model compound. Polymers (II), (III), (IV), and (V) are active catalysts for the epoxidation of olefins and oxidation of alcohols with t-BuOOH. On the other hand, (I) acts only as a catalyst of selective oxidation of alcohols. The results of the oxidation of various alcohols is shown in Table 6. Secondary alcohols were more easily oxidized than primary alcohol, from which ester was obtained in low yield. When the hydroxyl group was blocked by a bulky group, as for menthol, oxi-
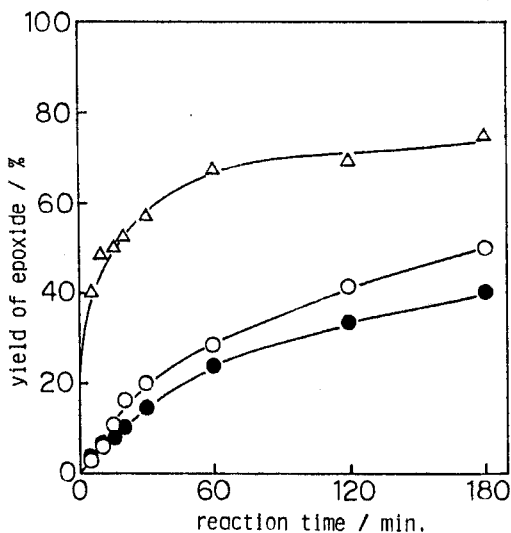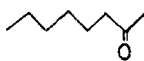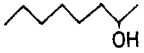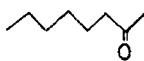
FIG. 1. Repeated epoxidation of cyclohexene with t-BuOOH in the presence of Catalyst I'. Temperature 60°C, benzene 50 mL, t-BuOOH 0.05 mol, cyclohexene 0.05 mol, I' 0.2 mmol Mo. Catalyst: (○) t-BuOOH (0.05 mol) and cyclohexene (0.05 mol) freshly added after 180 min reaction. (●) Polymer I' separated by filtration after epoxidation. (△) Fresh Polymer I'.

dation was difficult in this system. This behavior is also characteristic in the immobilized polymer in contrast to the model compound (low molecular catalyst-benzyltrimethylammonium tetrabromooxomolybdate(V)). The yield of menthone was 52% for benzyltrimethylammonium tetrabromooxomolybdate(V) at the same reaction conditions.

The above results demonstrate that ammonium ion as a counter cation of the tetrabromooxomolybdate(V) complex exerts an influence upon the chemoselectivity of t-BuOOH. That is to say, when the substituents on the nitrogen of the ammonium are alkyl groups, the oxidation of alcohols occurs quantitatively. On the other hand, if one or more of the substituents of the amine component are hydrogen atoms, epoxidation of olefins occurs preferentially.

In addition to this, we found that a steric effect was exerted on the reactivity owing to the immobilized polymer catalyst. Immobilized polymers derived from poly(vinylpyridine)s were used as catalysts for the oxidation of alcohols with t-BuOOH. Catalyst (I') is effective for the epoxidation of cyclohexene, but in reuse the polymer showed lower activity (Fig. 1). This change

TABLE 7. Oxidation with t-BuOOH in the Presence of Various Polymers Containing Pyridinium Groups

Substrate	Catalyst	Time, d	Product	Yield,[a] %
	III′	3		(50)[b]
	IV′	3		(51)[b]
	III′	7		55
	III′	4		(14)
	IV′	4		(14)
	III′	4		13
	IV′	4		13
	III′	5		(2.8)
	IV′	5		(3.0)
	III′	4		15, 3.2
	IV′	4		12, 3.4
	II′	8		
	III′	8		
	IV′	8		

[a]By isolation; if in parentheses, by GC.
[b]Methanol used as solvent.

of catalyst activity comes from the elimination of bromine from the tetrabeo-mooxomolybdate(V) ion. Although Catalysts (II′), (III′), and (IV′), containing the alkylpyridinium group, were effective for oxidation, 2-cyclododecanol was oxidized to the corresponding ketone with the formation of epoxide (Table 7). Epoxidation and oxidation were observed because of the mixture of alkylated and unalkylated pyridinium groups in the polymer.

CONCLUSIONS

The principal advantage of the immobilized polymer catalysts can be summarized as follows: We could find chemoselective catalysts for t-BuOOH oxidation by selection of the amine component in the functional group. Oxidation of the alcohol occurred selectively, and no epoxidation of olefin was observed with the Catalyst (I)-t-BuOOH system. Steric effects of the polymer were also found in this reaction system. The stability of the tetrabromo-oxomolybdate(V) complex is made possible by immobilization in the cationic polymers.

REFERENCES

[1] R. Hiatt, in *Organic Peroxides,* Vol. 2 (D. Swern, ed.), Wiley-Interscience, New York, 1971, Chap. 1; K. B. Sharpless and T. R. Verhoeven, *Aldrichimica Acta, 12,* 63 (1979); R. A. Sheldon, in *The Chemistry of Functional Groups, Peroxides* (S. Patai, ed.), Wiley, Chichester, England, 1983; R. A. Sheldon, *J. Mol. Catal., 20,* 1 (1983).

[2] Y. Kurusu, *Bull. Chem. Soc. Jpn., 54,* 293 (1981); M. Yamazaki, H. Endo, M. Tomoyama, and Y. Kurusu, *Ibid., 56,* 3523 (1983).

[3] Y. Masuyama, M. Takahashi, and Y. Kurusu, *Tetrahedron Lett., 25,* 4417 (1984); Y. Kurusu, Y. Masuyama, and M. Saita, *Bull. Chem. Soc. Jpn., 58,* 1065 (1985).

[4] J. F. Allen, H. M. Newman, *Inorg. Chem., 3,* 1612 (1964).

[5] Y. Kurusu and Y. Masuyama, *Polyhedron, 5,* 289 (1986); *Abstracts for the Climax Fifth International Conference on the Chemistry and Uses of Molybdenum,* 1985, p. 45.

[6] D. G. Lee and N. A. Noureldin, *J. Am. Chem. Soc., 105,* 3188 (1983).