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THE EPOXIDATION OF OLEFINS WITH HYDROGEN PEROXIDE ON MOLYBDENUM BLUE-CHARCOAL CATALYSTS

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The epoxidation of olefins was examined with aqueous hydrogen peroxide in the presence of molybdic acid-charcoal catalysts. On a molybdenum blue-charcoal catalyst, cyclohexene was oxidized to cyclohexene oxide in a good yield. Alkyltin compounds such as trimethyltin and tri-n-butyltin chloride cocatalyzed the epoxidation to give cyclohexene oxide in a 67% yield at 50°C for a 12 h reaction. The catalysts were recovered and reused.

Recently, the epoxidation of olefins has been developed by using organic peroxides and molybdenum complexes in homogeneous system.1) The use of aqueous hydrogen peroxide is also advantageous for the epoxidation reaction, although in general the activity and the selectivity are poor.2) Previously, one of authors has claimed in patents that highly concentrated solutions of hydrogen peroxide is an effective agent for the epoxidation of olefins under the coexistence of molybdenum oxide acetylacetonate and various organic tin compounds such as trimethyltin hydroxide in homogeneous system.3) But, few heterogeneous system of molybdenum catalysts are known hitherto, since, as often pointed out, a dissolution of an active molybdenum species from the surface occurred by forming a molybdenum-diol complex.4) Authors found that molybdic acid-charcoal catalysts in particular prepared by the adsorption of molybdenum blue(MoB), a type of a complex of mixed acids of Mo(V) and Mo(VI), on charcoal catalyze the epoxidation of olefins in good yields with 30% aqueous hydrogen peroxide. Further, the heterogenizing of MoB in the epoxidation was examined. Table I shows the results of the epoxidation of cyclohexene under various catalysts. The MoB-charcoal catalysts gave cyclohexene oxide(CH oxide) and a small amount of 1,2-cyclohexanediol(Diol) and cyclohexanediol isopropylmonoether(Monoether)

Table I. Epoxidation of cyclohexene with hydrogen peroxide on various molybdic acid-charcoal catalysts

Exp. No.	Catalyst (g)	Temp. (°C)	Time (h)	Yield CH oxide (%)	Yield Monoether (%)	Yield Diol (%)
1	MoB (10 mg)	25	24	1.1	17.3	0
2	MoB (5 mg)	50	15	0.9	15.5	5.8
3	Ammonium molybdate (5 mg)	50	15	4.1	13.9	3.3
4	Molybdic acid (5 mg)	50	15	1.4	13.0	4.5 a)
5	1.25wt% Ammonium molybdate-charcoal(palm) (0.4 g)	50	15	10.3	0.6	0.2
6	1.25wt% Molybdic acid-charcoal (palm) (0.4 g)	50	15	10.9	0.8	0.2
7	Charcoal(palm) (0.2 g)	50	15	0	0	0
8	2.5wt% MoB-charcoal(palm) (0.4 g)	50	15	22.2	2.4	1.3
9	1.25wt% MoB-charcoal(palm) (0.4 g)	50	15	17.1	0	0
10	1.25wt% MoB-charcoal(palm) (0.4 g)	50	1	4.6	0	0
11	(Filtrate of Exp. 10)	50	23	6.0	0.2	0.2 b)
12	Recovered catalyst of Exp. 11	50	24	17.2	4.8	1.2
13	Recovered catalyst of Exp. 12	50	24	19.3	3.2	5.7
14	Recovered catalyst of Exp. 13	50	24	17.1	2.8	4.6

Cyclohexene 39.5 mmol, 28% H_2O_2 8.2 mmol and isopropyl alcohol 10 ml were used. Yields were based on H_2O_2. a) Molybdic acids was dissolved with 28% H_2O_2 and was adsorbed on charcoal. b) After filtration, Exp.10 was continued for 23 h further.

from cyclohexene. On the other hand, MoB, ammonium molybdate and molybdic acid used as a carrier-free state, gave cyclohexanediol isopropylmonoether as a main product. From the stand point of both the activity and the selectivity, the most suitable amount of MoB to charcoal was 1-3wt%. Although the adsorption of MoB on charcoal was suggested by the disappearance of its blueness in isopropyl alcohol, the heterogenizing of the molybdenum catalysts was confirmed as followes: no significant increase in the cyclohexene oxide yield was observed between 1 h to 23 h when the solid catalyst was once removed from the reaction system as was seen in Exp.10 and 11. On the other hand, the recovered catalyst had an enough activity to yield cyclohexene oxide even if the reaction was repeated above 3 times.

In this reaction system, the decomposition of hydrogen peroxide was remarkable. After a 24 h reaction, about 90% of hydrogen peroxide had been consumed.

Table II. Effect of organotin compounds in the epoxidation of cyclohexene with hydrogen peroxide on molybdenum blue-charcoal

Exp. No.	Cocatalyst (g)	Temp. (°C)	Time (h)	Yield CH oxide (%)	Yield Monoether (%)	Yield Diol (%)
1	None	50	8	15.1	0.9	0.4
2	Trimethyltin chloride (0.05 g)	50	8	63.9	0	0
3	Trimethyltin hydroxide (0.05 g)	50	8	17.2	0	0.5
4	Tri-n-butyltin chloride (0.05 ml)	50	8	47.2	1.7	0.6
5	Bis(tri-n-butyltin) oxide (0.05 ml)	50	8	42.5	0.7	2.0
6	Di-n-butyltin oxide (0.05 g)	50	8	34.8	1.3	0

Cyclohexene 39.5 mmol, 28% H_2O_2 8.2 mmol, 1.25wt% MoB-charcoal(palm) 0.4 g and isopropyl alcohol 6 ml were used.

Table III. Epoxidation of various olefins with hydrogen peroxide on molybdenum blue-charcoal in the presence of trimethyltin chloride(0.05 g)

Exp. No.	Olefin	Temp. (°C)	Time (h)	Epoxide yield (%)
1	Cyclohexene	50	12	67.2
2	Styrene	50	12	23.6 a)
3	Styrene	50	24	12.2 b)
4	1-Octene	50	12	17.1
5	Allylchloride	50	12	0

Olefin 39.5 mmol, 28% H_2O_2 8.2 mmol, 1.25wt% MoB-charcoal(palm) 0.4 g, and isopropyl alcohol 6 ml were used. a) Benzaldehyde of 33.6% was obtained. b) Under the argon atmosphere, benzaldehyde of 2.9% was obtained.

Interestingly, by the addition of alkyltin compounds to the MoB catalysts, the yields of cyclohexene oxide were increased. These results are shown in Table II. Particularly, the addition of trimethyltin chloride gave a good yield(64%). Various olefins were also epoxidized with aqueous hydrogen peroxide in the presence of MoB-charcoal and trimethyltin chloride(Table III). The yields of epoxides were on the order of cyclohexene > styrene ≈ 1-octene > allylchloride as reported in the epoxidation with such organic peroxide as *tert*-butyl hydroperoxide and peracetic acid in the presence of $Mo(CO)_6$.[4)] Among these olefins, styrene was sensitive to oxygen, and gave benzaldehyde as a by-product. The side reaction was suppressed by adopting an inactive atmosphere of argon.

MoB has been prepared by various methods, e.g., the double decomposition between molybdenum chloride and ammonium molybdate,[5)] the electrolytic reduction of ammonium molybdate,[6)] and so on.[7)] Herein, the MoB was prepared with a simple method which was found by Kurusu[8)] and modified in our laboratory. A molybdenum metal powder of 0.5 g was dispersed in 20 ml of water. To this suspension, 1 ml of aqueous hydrogen peroxide(30%) was added dropwise with stirring. The oxidation took place mildly. Gradually, the solution changed its color from yellow to blue by standing overnight at room temperature. After the reaction, the unreacted molybdenum powder was centrifuged and the supernatant was evaporated to dryness under reduced pressure. A fine powder of MoB was obtained(yield 0.25 g). In the preparation of the catalyst, 5 mg of MoB was dissolved with a small amount(0.02 ml) of water and diluted with isopropyl alcohol homogeneously. Then, the MoB was adsorbed on 0.4 g of a charcoal powder(Dia Catalyst & Chemicals Ltd.) which was passed through a 65 mesh sieve. The reaction products were analyzed by a programmed gas-liquid chromatograph(Hitachi Ltd., type 063) using 20% PEG 20M(3 mm i.d., x 1 m in length) as a column packing material between the temperature range from 40° to 150°C(3°C/min) and He(30 ml/min) as a carrier gas.

References

1) N. Indictor and W. F. Brill, J. Org. Chem., 30, 2074 (1965).
2) R. A. Sheldon and J. K. Kochi, "Metal-Catalyzed Oxidation of Organic Compounds", Academic Press Inc., New York (1981), Part 1, Chap. 3, pp. 51.
3) Y. Watanabe, T. Nishizawa, and J. Kobayashi, U. S. Patent 3806467 (1974).
4) R. A. Sheldon, "Aspects of Homogeneous Catalysis", vol. 4, ed. by R. Ugo, D. Reidel Pub. Co., Dordrecht (1981), pp. 3-64.
5) Berzerius and Pogg, Ann., 6, 387 (1826).
6) W. D. Treadwell and Y. Schaeppi, Helv. Chim. Acta., 29, 771 (1946).
7) F. B. Schilmer, Jr. L. F. Audrieth, S. T. Gross, D. S. McClellan, and L. J. Seppi, J. Am. Chem. Soc., 64, 2543 (1942).
8) Y. Kurusu, Bull. Chem. Soc., Jpn., 54, 293 (1981).

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