[Chem. Pharm. Bull.
32(2) 418—423 (1984)]

Epoxidation of Alkenes with Hydrogen Peroxide in the Presence of Molybdenum Oxide–Tributyltin Chloride on Charcoal Catalysts

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(Received June 13, 1983)

By using molybdenum oxide fixed on active charcoal in the form of molybdenum blue, various alkenes of cyclopentene, cyclohexene, methylcyclohexene, styrene, methylstyrene, octene, and decene were selectively epoxidized with aqueous hydrogen peroxide (30%) in isopropyl alcohol. The yields increased in the presence of organotin compounds. Among them, tri-*n*-butyltin chloride gave good yields; cyclopentene and cyclohexene were epoxidized in yields of 71 and 60%, respectively. The catalyst could be separated by filtration and used repeatedly. By adjusting the pH value of the charcoal support with acid or base, both the epoxide yield and the selectivity could be varied widely, and good results were obtained between pH 6 and 7.

Keywords——epoxidation; hydrogen peroxide; tri-*n*-butyltin chloride; cyclopentene oxide; cyclohexene oxide; cyclopentene; cyclohexene

In recent years, the catalytic epoxidation of simple olefins with organic peroxides, *tert*-butyl hydroperoxide (TBHP) and cumene hydroperoxide, has been investigated with the aim of producing key compounds for the syntheses of medicines and pesticides. As catalysts for such reactions, various molybdenum compounds such as molybdenum dioxyacetylacetonate ($MoO_2(acac)_2$) and molybdenum naphthenate have been claimed in patents.[1] As for the peroxy compounds, the use of aqueous hydrogen peroxide (30% H_2O_2) is preferable on the grounds of ease of handling and low cost. However, no epoxy compound had been obtained, except when highly concentrated H_2O_2 or anhydrous H_2O_2 solution was used,[2] though we epoxidized several alkenes using 30% H_2O_2 in the presence of $MoO_2(acac)_2$ and alkyltin compounds in isopropyl alcohol.[3]

In the chemical industry, heterogenized catalyst systems are widely used since the separation of the product from the catalyst is easy. Ivanov *et al.* fixed $Mo(CO)_6$ on cation-exchange resin (IRC-50) and epoxidized propylene repeatedly on the same catalyst with TBHP,[4] while Dai *et al.* prepared molybdenum–zeolite catalyst and epoxidized cyclohexene with TBHP.[5] We fixed molybdenum oxide (molybdenum blue) on charcoal and selectively epoxidized cyclohexene with 30% H_2O_2.[6] The yield of cyclohexene oxide was increased by the addition of organotin compounds.[6] This report deals with properties of the heterogenized molybdenum catalyst and with various factors promoting the epoxidation of simple olefins in the presence of organotin compounds.

Experimental

Materials——Aqueous hydrogen peroxide (30% H_2O_2) was obtained from Hayashi Pure Chemical Industries Ltd. Cyclohexene and other olefins were distilled prior to use. Trimethyltin chloride ($(CH_3)_3SnCl$) and tri-*n*-butyltin chloride (Bu_3SnCl) were obtained from Aldrich Chemicals Ltd., bis(tri-*n*-butyltin) oxide ($(Bu_3Sn)_2O$) from Kyodo Yakuhin Co., Tokyo, dibutyltin oxide (Bu_2SnO) and tricyclohexyltin hydroxide ($(C_6H_{11})_3SnOH$) from Wako Pure

Chemical Industries Ltd., and triphenyltin chloride (($(C_6H_5)_3SnCl$) from Tokyo Kasei Kogyo Co., Ltd. In preliminary experiments,[6] palm charcoal was found to be a good support for molybdenum blue. Therefore, active charcoal from palm (DC-5200, Dia Catalysts & Chemicals Ltd.) (passed through a 65 mesh sieve) was used in these experiments.

Pretreatment of Charcoal——Powdered charcoal (0.4 g) was dispersed in 10 ml of distilled water. The pH of the dispersed solution was maintained at pH 6.0 or 7.0 by the addition of 0.1 N HCl or 0.1 N NaOH during 2 h. After the charcoal had been separated by filtration and washed with distilled water, it was washed once with ethanol and dried at room temperature for 15 h.

Preparation of Molybdenum Oxide–Charcoal Catalyst——As the molybdenum oxide species, a blue dye, "molybdenum blue," was used. The dye was prepared from an excess amount of molybdenum powder and aqueous H_2O_2 according to the method reported previously.[6] Molybdenum blue (5 mg) was dissolved in one or two drops of water and diluted with isopropyl alcohol (5 ml), then the charcoal powder (0.4 g) was added to the solution. After adsorption was complete (30 min), an isopropyl alcohol solution of an organotin compound was added dropwise with stirring and the whole was left to stand for half an hour.

The Epoxidation Procedure——The epoxidation was started by the addition of cyclohexene (4 g) and 30% H_2O_2 (1 ml) to a flask (50 ml) equipped with a condenser and a magnetic stirrer in a thermostated oil bath at 50 ± 1 °C. After the reaction, the catalyst was separated by centrifugation, and toluene was added as an internal standard. The reaction products were analyzed by gas-liquid chromatography (Hitachi Ltd., type 063) using 20% PEG 20M (3 mm i.d. × 2 m in length) as a column packing material in the temperature range from 40 to 150 °C (3 °/min) with He as a carrier gas (30 ml/min).

Results and Discussion

The Oxidation of Cyclohexene with Aqueous H_2O_2 in the Presence of CrO_3, MoO_3, and WO_3 on Charcoal

Cyclohexene was oxidized with H_2O_2 (30%) in the presence of a VI B-oxide, *i.e.*, Cr_2O_3, CrO_3, MoO_3 or WO_3, mounted on charcoal. It was found that the MoO_3–charcoal gave cyclohexene oxide selectively. The results are shown in Table I.

A similar selectivity was expected for both the chromium and the tungsten catalysts, since these elements belong to the same group in the periodic table. However, *trans*-1,2-cyclohexanediol and 1,2-cyclohexanediol mono-isopropylether were formed in the presence of WO_3–charcoal catalyst. The monoether was also obtained in good yield by heating cyclohexene oxide with WO_3 in isopropyl alcohol. Therefore, the WO_3–charcoal catalyst seems to afford the monoether by way of cyclohexene oxide. In contrast, CrO_3–charcoal did not gave the monoether or the diol, and 2-cyclohexen-1-one was produced from cyclohexene with H_2O_2 as a major product. However, we had previously observed that propylene oxide is an intermediate compound in the oxidation of propylene to acetone, acetic acid, and carbon

TABLE I. The Epoxidation of Cyclohexene with Aqueous H_2O_2 (30%) in the Presence of Oxide of Cr, Mo, or W on Charcoal

Catalyst	Conv. (%)	Yield (%)[a]			
		CH oxide[b]	1-one[c]	Ether[d]	Diol[e]
Cr_2O_3–C	0	0	0	0	0
CrO_3–C	36.1	3.3	25.9	0.5	0 ol[f] 4.1% one[g] 2.3%
MoO_3–C	11.9	10.9	0	0.8	0.2
WO_3–C	53.8	6.3	9.2	14.2	17.5 ol 6.6%

Cyclohexene 3.25 M, H_2O_2 5.88×10^{-2} M, 1.25% metal oxide–charcoal 0.4 g, Bu_3SnCl 1.40×10^{-2} M. Solvent isopropyl alcohol, temp. 50 °C, time 15 h.

a) Based on H_2O_2. *b*) Cyclohexene oxide.

c) 2-Cyclohexen-1-one. *d*) 1,2-Cyclohexanediol mono-isopropylether.

e) *trans*-1,2-Cyclohexanediol. *f*) Cyclohexanol. *g*) Cyclohexanone.

Table II. The Epoxidation of Various Olefins with Aqueous H_2O_2 (30%) in the Presence of 1.25%-MoO_3–Charcoal

Olefin	pH[a)]	Temp. (°C)	Yield (%)	
			Epoxide	By-product
Cyclopentene	6.0	23	71.9	0
Cyclohexene	6.0	50	60.2	4.3 (Ether)
1-Methyl-1-cyclohexene	6.0	50	53.8	0
1-Octene	7.0	50	20.8	0
Styrene	7.0	50	9.5	11.4 (Benzaldehyde)
α-Methylstyrene	7.0	50	5.9	18.4 (Acetophenone)
1-Decene	7.0	50	10.1	0

Olefins 1.76 M, H_2O_2 1.76 M, 1.25% MoO_3–charcoal 0.2 g, Bu_3SnCl 1.31×10^{-2} M. Solvent isopropyl alcohol, time 15 h.

a) The pH of the support was adjusted with 0.1 N HCl or 0.1 N NaOH.

dioxide with aqueous chromic acid on the basis of both kinetics and a tracer experiment with propylene-1-^{14}C.[7)] Recently, Miyaura *et al.* separated various epoxides from alkenes after oxidation with chromyl nitrate at −78 °C.[8)]

In our catalyst system, MoO_3–charcoal was the most suitable catalyst for the epoxidation of simple olefins. However, the addition of Bu_3SnCl as a cocatalyst to MoO_3–charcoal remarkably increased the yields of epoxide from simple olefins, *e.g.*, from 8.0% in the case of cyclopentene in the absence of Bu_3SnCl to 71.9% in the presence of the chloride, and from none to 10.1% for 1-decene (Table II). These results led us to investigate the role of organotin compounds in this epoxidation.

Effect of Organotin Compounds on the Epoxidation of Olefins

In the epoxidation of cyclohexene with MoO_3–charcoal, various organotin compounds such as Bu_3SnCl, $(Bu_3Sn)_2O$, Bu_2SnO, $(C_6H_5)_3SnCl$, $(C_6H_{11})_3SnOH$, $(CH_3)_3SnCl$, and $(CH_3)_3SnOH$ increased the yield of cyclohexene oxide in that order under the reaction conditions of Table III. However, $(CH_3)_3SnCl$, which had previously given a higher yield,[6)] was less effective in this series of experiments. On the other hand, Bu_3SnCl gave good results; for cyclohexene a 60.2% yield was obtained. To elucidate the effects of the alkyl groups of these organotin compounds, the epoxidation rate with 1.25% MoO_3–charcoal in the presence of $(CH_3)_3SnCl$ was compared with that in the presence of Bu_3SnCl on the same kind of support and under the same conditions. The initial reaction rate increased significantly with increasing concentration of Bu_3SnCl and reached saturation at a molar ratio of Bu_3SnCl to MoO_3 of 6 : 1 (Fig. 1). In contrast, the rate gradually increased with increasing amount of $(CH_3)_3SnCl$ (Fig. 2).

In general, such lipophilic and bulky groups as butyl (giving 60.2% yield) and phenyl (50.2%) in organotin chlorides were more effective than methyl (24.3%) under the same reaction conditions. Thermodynamic data on the transition state in the presence and the absence of Bu_3SnCl also support the effectiveness of Bu_3SnCl. The apparent energy of activation estimated from an Arrhenius plot (Fig. 3) was 8.6 kcal/mol for MoO_3–charcoal and 13.5 kcal/mol for MoO_3–Bu_3SnCl–charcoal; thus, the MoO_3–charcoal system seems to be more advantageous for this epoxidation. However, the epoxidation rate in the presence of Bu_3SnCl was faster than that with MoO_3–charcoal and the entropy of activation increased from −58 eu for the MoO_3–charcoal system to −38 eu for the MoO_3–Bu_3SnCl–charcoal system; the lower reaction rate on the former catalyst is caused by this term, which was consid-

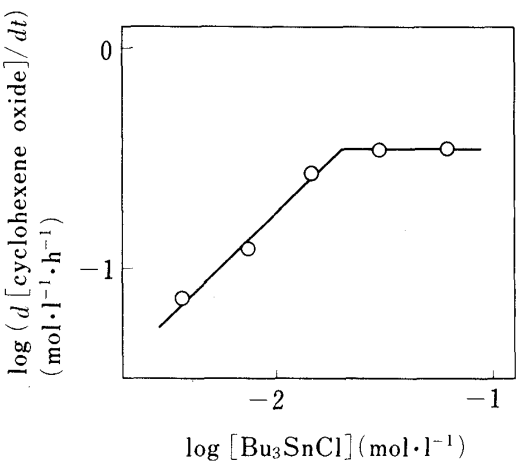

Fig. 1. Effect of Bu_3SnCl on the Initial Rate of Epoxidation of Cyclohexene with Aqueous H_2O_2 in the Presence of MoO_3–Charcoal at 50 °C

Cyclohexene 4.43 M, H_2O_2 8.02×10^{-1} M, 1.25% MoO_3–charcoal 0.4 g. Solvent isopropyl alcohol, pH of support 8.5.

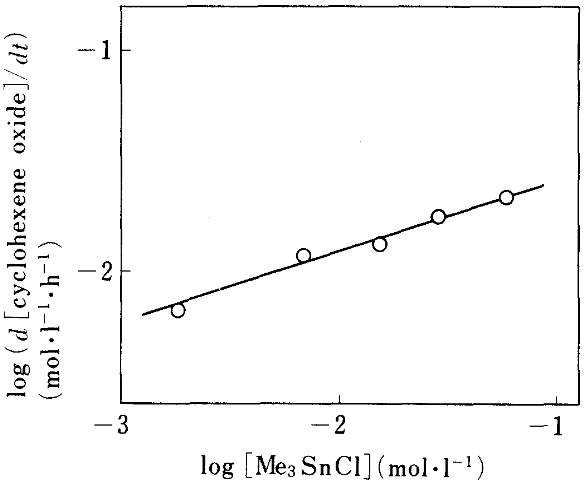

Fig. 2. Effect of $(CH_3)_3SnCl$ on the Initial Rate of Epoxidation of Cyclohexene with Aqueous H_2O_2 in the Presence of MoO_3–Charcoal at 50 °C

Cyclohexene 4.43 M, H_2O_2 8.02×10^{-1} M, 1.25% MoO_3–charcoal 0.4 g. Solvent isopropyl alcohol, pH of support 8.5.

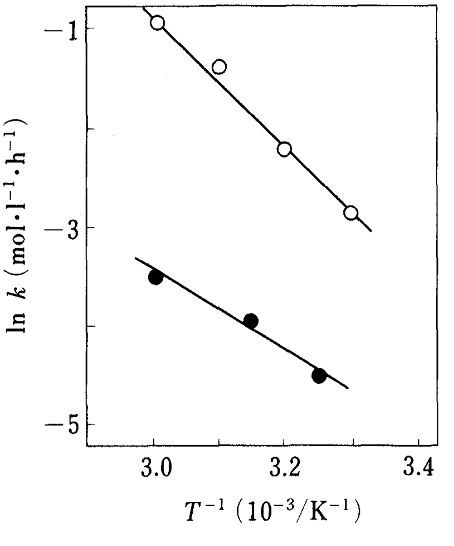

Fig. 3. Arrhenius Plot of the Epoxidation of Cyclohexene with Aqueous H_2O_2 in the Presence of MoO_3–Charcoal (●) and MoO_3–Bu_3SnCl–Charcoal (○)

Cyclohexene 4.43 M, H_2O_2 8.02×10^{-1} M, 1.25% MoO_3–charcoal 0.4 g, Bu_3SnCl 1.48×10^{-2} M. Solvent isopropyl alcohol, pH of support 8.5.

ered to reflect a restriction of water molecules.[9] Furthermore, the rate in the case of MoO_3–charcoal was first-order with respect to both cyclohexene and H_2O_2, while that in the case of MoO_3–Bu_3SnCl–charcoal was zero-order with respect to both cyclohexene and H_2O_2. These results suggest that the activity of the MoO_3–charcoal catalyst is weakened by the coordination of water molecules present in the H_2O_2 agent on the molybdenum species.

Fixation of Molybdenum Oxide on Charcoal in the Presence of Bu_3SnCl

The effect of charcoal as a support is distinct; the charcoal-supported molybdic acid gave cyclohexene oxide selectively, whereas oxidation of cyclohexene with 30% H_2O_2 in the presence of molybdic acid without charcoal afforded cyclohexanediol mono-isopropylether and cyclohexanediol. In the epoxidation of olefins on heterogeneous molybdenum catalysts, the role of insolubilized molybdenum species has been unclear since the epoxide dissolves molybdenum oxide by forming a diol–molybdenum complex.[10] In a previous communication,[6] we reported that molybdenum oxide can be well fixed on charcoal. In the present work, the fixation of the molybdenum oxide catalyst was examined in the presence of

TABLE III. Effect of pH of Charcoal as a Support in the Epoxidation of Cyclohexene on MoO_3–Charcoal Catalyst

pH	Conv. (%)	Yield (%)[a]		
		CH oxide	Ether	Diol
2.0	58.9	42.2	10.4	6.3
4.0	61.5	53.6	7.9	0
6.0	65.9	61.6	4.3	0
7.0	54.8	54.8	0	0
8.0	50.8	50.8	0	0
10.0	46.6	46.6	0	0

Cyclohexene 4.43 M, H_2O_2 8.02×10^{-1} M, 1.25% MoO_3–charcoal 0.4 g, Bu_3SnCl 1.48×10^{-2} M. Solvent isopropyl alcohol, temp. 50 °C, time 15 h.
a) Based on H_2O_2.

Bu_3SnCl. The epoxidation of cyclohexene with 1.25% MoO_3–charcoal (0.4 g) by the addition of Bu_3SnCl (1.39×10^{-2} M) reached 53% yield after 15 h at 50 °C (the reaction conditions were the same as in Table I). After reaction for 1 h, the solution was separated from the charcoal catalyst. At this time the epoxidation yield was 34%. The solution was continuously heated at 50 °C for a further 15 h. If active species were dissolved in the liquid phase, the amount of epoxide in the filtrate was expected to increase. However, the conversion remained the same (34%) as that obtained after 1 h. When cyclohexene, H_2O_2, and isopropyl alcohol were newly added to the recovered catalyst and heated at 50 °C for 15 h, the yield again reached 52%. Two more cycles of epoxidation were carried out on the same catalyst, and yields of 50 and 49% were obtained. These results indicate that the epoxidation occurred on the heterogenized surface of the catalyst.

Effect of pH of the Support on Epoxidation

Both acidic and basic properties of the charcoal surface affected the yield of epoxides drastically. Usually, 0.4 g of charcoal dispersed in 10 ml of water showed a pH value between 8.5 and 8.7. Therefore, the pH of the charcoal surface was adjusted with HCl or NaOH, and epoxidation of cyclohexene using the charcoal as a support was performed (Table III). The maximum yields were obtained at pH values of 6.0 and 7.0. Though the selectivity for epoxide was high, the yield decreased on the basic side. On the other hand, a lower selectivity and a higher conversion were obtained on the acidic side. The ratio of molybdenum oxide to charcoal also affected the rate of the epoxidation; saturation was observed at 5 mg of molybdenum blue to 1 g of charcoal. From the adsorption isotherm of molybdenum blue on charcoal in isopropyl alcohol at 50 °C, it is clear that charcoal adsorbs molybdenum blue to the extent of more than 100 mg per 1 g of charcoal. Therefore, only a small part of the charcoal surface which is able to neutralize the acidity of molybdic acid, *e.g.*, a basic site, is considered to be effective for the epoxidation.

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