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Epoxidation of Olefins with Hydrogen Peroxide on the Molybdenum Oxide–Bu_3SnCl–Charcoal Catalyst. Effect of Using Chemically Pretreated Charcoal

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The epoxidation of C_5 to C_8 olefins with hydrogen peroxide (30%) was studied on molybdenum oxide–Bu_3SnCl–charcoal in isopropyl alcohol at 50 °C. The yields were remarkably increased by using chemically pretreated charcoals as supports. As modifiers of charcoal, butylating or trimethylsilylating agents gave good results. Cycloolefins of C_5 to C_8 and an inner olefin, 2-octene, selectively gave epoxides in 90 to 70% yields compared with yields of 60 to 40% on the catalyst prepared from raw charcoal. The increase in yield was attributed to the prevention of the decomposition of hydrogen peroxide.

Keywords——epoxidation; hydrogen peroxide; molybdenum catalyst; cyclohexene oxide; cyclooctene oxide; cyclohexene; cyclooctene

Epoxides are useful in organic chemistry for the synthesis of various intermediates, and are of pharmacological interest because of their mutagenic action toward living cells. Since molybdenum compounds were patented as epoxidation catalysts for olefins by Halcon Co.[1] in the 1970's, many efforts have been made to develop heterogeneous catalysts from molybdenum species by fixing them on various supports.[2] We have reported that charcoal is a good support for molybdenum oxide as a catalyst for the selective epoxidation of C_5 to C_8 olefins with aqueous hydrogen peroxide (30% H_2O_2), though considerable decomposition of H_2O_2 took place, reducing the yield of cyclohexene oxide (51%) from cyclohexene.[3] However, treatment of the charcoal with an aqueous solution of mineral acids or bases to give pH 6 to 7 suppressed the loss of H_2O_2 to some extent, resulting in a 60% yield from cyclohexene.[4] Further investigation revealed that various alkylating and alkylsilylating agents known to be modifiers of alcohols or carboxylic acids were useful for pretreating the charcoal; a 79% yield was obtained from cyclohexene.

This report deals with the effect of chemically treated charcoals as supports in the epoxidation of C_5 to C_8 olefins such as cyclopentene, cyclohexene, cycloheptene, cyclooctene, 1- and 2-octenes, *etc.*, with 30% H_2O_2 on heterogenized molybdenum oxide catalysts. Bu_3SnCl was selected as the most suitable co-catalyst for molybdenum oxide in the epoxidation of olefins with 30% H_2O_2.

Experimental

Reagents and Analysis of Products——Cyclohexene, 30% H_2O_2 (Hayashi Pure Chemicals Co.), *N,O*-bis(trimethylsilyl)acetamide (BSA), *N,N*-dimethylformamidedibutylacetal (DMFBA), 1,1,1,3,3,3-hexamethyldisilazane (Wako Pure Chemicals Co.), and other olefins (Tokyo Chemical Industry Co.) were purchased. Tetraalkylgermanes were prepared from germanium tetrachloride by means of the Grignard reaction. Trialkylgermanium halogenides were obtained from tetraalkylgermanes by monohalogenation according to the literature.[5] Organotin compounds were obtained from Kyodo Yakuhin Co., Tokyo. Charcoal from palm (DC-5200) was obtained from Dia Catalyst & Chemicals Ltd. and material that passed through a 65 mesh sieve was used.

Products were analyzed by gas-liquid chromatography (GLC) using an FID detector, OV-17 (3 mm i.d. × 2 m in length) as a column packing material, and helium as a carrier gas. The temperature was programmed from 50 to 150 °C at the rate of 3 °C/min. The retention times were 1.4 min for cyclohexene, 6.0 min for cyclohexene oxide, 17.1 min for *trans*-2-hydroxycyclohexyl isopropyl ether, and 17.8 min for *trans*-1,2-cyclohexanediol at a flow rate of 12.5 ml/min of the carrier gas.

Pretreatment of Charcoal——Charcoal was stirred with BSA or DMFBA (50 mg/g-charcoal) in 20 ml of hexane at 50 °C for 2 h. After the reaction, the charcoal was filtered off. The filtrate was washed with hexane and dried.

Preparation of Catalyst——Molybdenum oxide–charcoal catalyst was prepared by allowing molybdenum blue (5 mg) and charcoal (0.4 g) in isopropyl alcohol (2 ml) to stand overnight at room temperature, then the catalyst was filtered off, washed with ethanol, and dried before used.

Epoxidation Procedure——The molybdenum oxide–charcoal catalyst (0.4 g) was dispersed in isopropyl alcohol (2 ml) and Bu_3SnCl (50 mg) was added. The mixture was allowed to stand at room temperature for 30 min, then isopropyl alcohol (4 ml), cyclohexene (1.5 g), and 30% H_2O_2 (2 ml) were added. The reaction was started at 50 ± 1 °C in an oil bath under magnetic stirring.

Results and Discussion

Effect of Chemical Pretreatment of Charcoal on the Epoxidation of Olefins

The oxidation of C_5 to C_8 olefins with H_2O_2 was carried out in isopropyl alcohol in the presence of the molybdenum catalyst at 50 °C. As the molybdenum species, we used molybdenum blue, a kind of blue dye prepared from molybdenum metal and H_2O_2.[3,6] The results are shown in Table I. First of all, the catalytic activity of molybdenum oxide itself was examined with cyclohexene and 30% H_2O_2 in a homogeneous system.[7] The products obtained were a mixture of *trans*-1,2-cyclohexanediol as the chief product, together with cyclohexene oxide, and *trans*-2-hydroxycyclohexyl isopropyl ether. When molybdenum oxide was supported on palm charcoal and used as a heterogenized catalyst, the selectivity for cyclohexene oxide increased from 8 to 75%, though the conversion decreased from 43 to 21%.

TABLE I. Effect of Chemical Treatment of the Charcoal Support in the Epoxidation of Cyclohexene with Hydrogen Peroxide (30%) Using Molybdenum Oxide–Charcoal Catalyst

Catalyst (Modifier)	Conv. (%)	Yield (%)		
		Epoxide[a]	Ether[b]	Diol[c]
Molybdenum blue	43.3	3.6	9.7	30.0
Charcoal	0	0	0	0
MO[d]–charcoal	20.8	15.6	1.5	3.7
MO–Bu_3SnCl–charcoal	50.8	50.8	0	0
Bu_3SnCl–charcoal (DMFBA[e])	0	0	0	0
MO–Bu_3SnCl–charcoal (DMFBA)	70.9	70.9	0	0
MO–Bu_3SnCl–charcoal (BSA[f])	70.5	70.5	0	0
MO–Bu_3SnCl–charcoal (HMDS[g])	65.1	60.4	2.1	2.6

Cyclohexene 1.8 M, H_2O_2 1.8 M, 1.25% MO–charcoal 0.4 g, Bu_3SnCl 1.57×10^{-2} M, solvent isopropyl alcohol, temp. 50 °C, time 15 h. *a*) Cyclohexene oxide. *b*) *trans*-2-Hydroxycyclohexyl isopropyl ether. *c*) *trans*-1,2-Cyclohexanediol. *d*) Molybdenum oxide. *e*) *N,N*-Dimethylformamidedibutylacetal. *f*) *N,O*-Bis(trimethylsilyl)acetamide. *g*) 1,1,1,3,3,3-Hexamethyldisilazane.

The addition of organotin compounds such as Bu_3SnCl increased both the conversion and the selectivity; the latter reached almost 100%. On the other hand, the conversion remained at 50% since about a half of the H_2O_2 was decomposed competitively on charcoal during the oxidation. It is well known that the decomposition of H_2O_2 is induced on the surface of charcoal. However, chemically treated charcoal is often less effective in the decomposition of H_2O_2; the treatment of charcoal with inorganic acids or bases to give pH 6 to 7 can increase the yield of cyclohexene oxide from 51 to 62% in the epoxidation of cyclohexene.[4] Further investigation revealed that the pretreatment of charcoal with alkylating or alkylsilylating agents increased the cyclohexene oxide yield up to 71%. DMFBA, BSA, and 1,1,1,3,3,3-hexamethyldisilazane were effective agents. These results suggest that the bulky and hydrophobic substituents (butyl and trimethylsilyl groups) anchored on the surface of charcoal *via* oxygenated carbon atoms protected H_2O_2 from decomposition.

The treatment did not affect the adsorption of molybdenum blue in isopropyl alcohol; the disappearance of the dye in solution was visually apparent. The role of DMFBA was confirmed by comparing the rate of decomposition of H_2O_2 on various charcoals in isopropyl alcohol; Fig. 1 shows the results. Charcoals were dispersed in isopropyl alcohol and shaken at 50 °C for 8 h. Hydrogen peroxide was analyzed by iodometry after the liberation of iodine by the addition of potassium iodide followed by titration with 0.1 N sodium thiosulfate. As expected raw charcoal decomposed H_2O_2 vigorously. On the other hand, the alkylated or alkylsilylated charcoals decomposed H_2O_2 more slowly.

Figure 2 shows the effect of the chemical pretreatment of charcoal with DMFBA on the epoxidation of cyclohexene. The yield of cyclohexene oxide increased up to 71% with increase in the amount of DMFBA, and was saturated at 8×10^{-5} mol of DMFBA per one gram of charcoal. In our experiments, DMFBA at 24.6×10^{-3} mol/g-charcoal was used. However, as shown in Fig. 1, about 30% of H_2O_2 was still decomposed after 15 h at 50 °C. Therefore, a 30% molar excess of H_2O_2 over olefins was needed for effective epoxidation. Several olefins were oxidized by using the catalyst at a molar ratio of olefins to H_2O_2 of 1 : 1.3 or 1 : 1. The results are shown in Table II. Epoxides were formed exclusively in good yields from a series of olefins. The yields from cyclic olefins of C_5 to C_8 fell between 96 and 70%. The yield from an inner olefin, 2-octene, was about twice that from 1-octene. The yield of

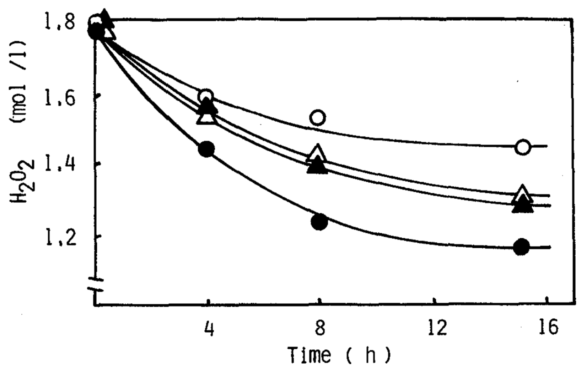

Fig. 1. The Decomposition of H_2O_2 in the Presence of BSA- or DMFBA-Treated Charcoal and Untreated Charcoal in Isopropyl Alcohol at 50 °C

(○), blank (△), BSA-treated charcoal; (▲), DMFBA-treated charcoal; (●), untreated charcoal.

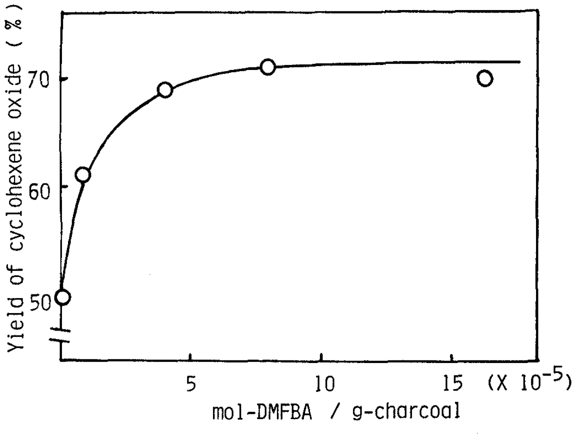

Fig. 2. Effect of the Ratio of DMFBA to Charcoal Support in the Epoxidation of Cyclohexene on Molybdenum Oxide–Bu_3SnCl–Charcoal Catalyst

Cyclohexene 1.8 M, H_2O_2 1.8 M, 1.25% MO[a]–charcoal 0.4 g, Bu_3SnCl 1.57×10^{-2} M, solvent isopropyl alcohol, temp. 50 °C, time 15 h.
a) Molybdenum oxide.

Table II. Epoxidation of Various Olefins with Hydrogen Peroxide (30%) Using Molybdenum Oxide–Bu_3SnCl–Charcoal (DMFBA) Catalyst

Olefin	H_2O_2/olefin (mol)/(mol)	Temp. (°C)	Yield of epoxide (%)
Cyclopentene	1.0	23	77.5
	1.3	23	87.0
Cyclohexene	1.0	50	70.9
	1.3	50	79.3
1-Methyl-1-cyclohexene	1.0	50	65.0
Cycloheptene	1.3	50	87.2
Cyclooctene	1.3	50	96.0
1-Octene	1.0	50	32.5
	1.3	50	40.0
2-Octene	1.0	50	76.2
	1.3	50	88.7
1-Decene	1.0	50	36.4
	1.3	50	41.1
Styrene	1.3	50	18.4
α-Methylstyrene	1.3	50	10.4

Olefin 1.8 M, H_2O_2 1.8 or 2.34 M, 1.25% MO[a]–charcoal (DMFBA) 0.4 g, Bu_3SnCl 1.57×10^{-2} M, solvent isopropyl alcohol, time 15 h. Yields are based on the olefins. *a*) Molybdenum oxide.

Table III. The Epoxidation of Cyclohexene and Cyclooctene with Hydrogen Peroxide by Using Recovered Catalysts

Olefin	Catalyst (Modifier)	Number of reactions	Yield of epoxide (%)
Cyclohexene	MO[a]–Bu_3SnCl–charcoal (DMFBA[b])	1	73
		2	67
		3	60
Cyclooctene	MO–Bu_3SnCl–charcoal (BSA[c])	1	95
		2	96
		3	90

Olefin 1.8 M, H_2O_2 2.34 M, 1.25% MO–charcoal 0.4 g, Bu_3SnCl 1.57×10^{-2} M, solvent isopropyl alcohol, temp. 50 °C, time 15 h. *a*) Molybdenum oxide. *b*) *N*,*N*-Dimethylformamidedibutylacetal. *c*) *N*,*O*-Bis(trimethylsilyl)acetamide.

decene oxide from 1-decene was 40%. Previously, this compound had been obtained in a poor yield of 10%.[4)]

Reuse of catalysts in the epoxidation of cyclohexene and cyclooctene using molybdenum oxide–Bu_3SnCl–charcoal was examined (Table III). The oxidation was repeatedly carried out (three cycles) on the recovered catalyst. The yields of cyclohexene oxide from cyclohexene decreased from 73 to 60%. Cyclooctene also gave high yields of product (96 to 90%) with little decrease in yield. We showed previously that molybdenum oxide–Bu_3SnCl–charcoal catalyst could be used repeatedly.[6)] The molybdenum oxide catalyst on the pretreated charcoal could be recovered simply by filtration and reused effectively.

Effect of Organogermanium, Organotin and Organolead Compounds as Co-catalysts

Molybdenum blue was adsorbed on charcoal (DMFBA) followed by an organogermanium, organotin or organolead compound, and the oxidation of cyclohexene was carried out in isopropyl alcohol at 50 °C for 15 h (Table IV). In the series of triphenylbromo

Table IV. Effect of Co-catalysts with Molybdenum Oxide in the Epoxidation of Cyclohexene

Co-catalyst	Conv. (%)	Yield (%)		
		Epoxide[a]	Ether[b]	Diol[c]
Bu_3GeCl	23.5	9.6	2.9	11.0
Ph_3GeBr	24.1	5.7	5.8	12.6
Bu_3SnCl	70.5	70.5	0	0
Ph_3SnBr	25.6	18.3	2.2	5.1
Ph_3PbBr	44.9	5.9	18.0	21.0

Cyclohexene 1.8 M, H_2O_2 1.8 M, 1.25% MO[d]–charcoal 0.4 g, co-catalyst 1.57×10^{-2} M, solvent isopropyl alcohol, temp. 50 °C, time 15 h. *a*) Cyclohexene oxide. *b*) *trans*-2-Hydrocyclohexyl isopropyl ether. *c*) *trans*-1,2-Cyclohexanediol. *d*) Molybdenum oxide.

derivatives of group 4B elements, the activity increased in the order of Ge < Sn < Pb. This may be the same as the order of the degree of coordination to molybdenum oxide. In fact, a mixture of molybdenum oxide with Bu_3SnCl or Ph_3PbBr gave a white precipitate in isopropyl alcohol. On the other hand, no change was observed on the addition of Bu_3GeCl or Ph_3GeBr to a solution of molybdenum oxide.

In the presence of various organogermanium compounds such as Bu_3GeCl, Bu_3GeBr, $(Bu_3Ge)_2O$, and Ph_4Ge, conversions of 24 to 23% and poor selectivities of 62 to 24% were obtained, compared with a conversion of 16% and a selectivity of 75% on molybdenum oxide-untreated charcoal at a 1 : 1 molar ratio of H_2O_2 to cyclohexene. $(Ph_3Ge)_2O$, Ph_3GeCl, Bu_4Ge, Bu_3GeBr, Et_4Ge, and $(Et_3Ge)_2O$ also gave lower conversions of 18 to 14%. On the other hand, organotin compounds such as Bu_3SnCl (a 71% yield) and $(Bu_3Sn)_2O$ (a 63% yield) were suitable as a co-catalyst for the epoxidation. However, conversions were different with alkyl and halogen substituents of the tin compounds, and depended on the presence or absence of acetates in alkyltin hydroxides: the conversions obtained with several organotin compounds were 22.2% for Ph_4Sn, 25.6% for Ph_3SnBr, 40.5% for Ph_3SnCl, 31.2% for Bu_4Sn, 49.9% for Bu_3SnBr, 43.2% for Bu_2SnO, 41.9% for $BuSn(OAc)_3$, 31.3% for $Ph_3Sn(OAc)$, 46.5% for $Bu_2Sn(OAc)_2$, 22.4% for $(BuSn)_2O$, 28.3% for Me_3SnCl, 28.0% for Me_3SnOH, and 20.7% for $Sn(OAc)_2$.

In conclusion, organotin compounds of Bu_3SnCl and $(Bu_3Sn)_2O$ was suitable as co-catalysts for molybdenum oxide in the selective epoxidation of olefins with H_2O_2. The catalyst system did not hydrolyze the epoxides to diols. Though an organolead compound, Ph_3PbBr, afforded better yields than the organogermanium and organotin compounds, its poisonous character is disadvantageous. It is considered that the complex of molybdenum oxide–organotin compound is tightly adsorbed on charcoal and effectively catalyzes the epoxidation. The suppression of side-reactions on charcoal was achieved by using butylating or the trimethylsilylating agents as modefiers, as has been done previously in the asymmetric hydrogenation of α-acetamidocinnamic acid with chiral rhodium complex on charcoal modified with acetates or trimethylamine.[8]

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