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Tungstic Acid-Tributyltin Chloride on a Charcoal Catalyst in the Epoxidation of Alkenes with Hydrogen Peroxide

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Several alkenes, such as cyclopentene, cyclohexene, 1-octene, 2-octene, 1-decene, styrene, and 1-methyl-1-cyclohexene, were epoxidized with aqueous (30%) hydrogen peroxide. n-Bu$_3$SuCl was a good co-catalyst of H_2WO_4 for the selective epoxidation. The conversion was improved by modifying charcoal as the carrier with such alkylating or alkylsilylating agents as *N,N*-dimethylformamide dibutyl acetal (DMFBA) or *N,O*-bis(trimethylsilyl)acetamide. Cyclopentene oxide, cyclohexene oxide, and 2-octene oxide were obtained from the corresponding olefins in the good yields of 74, 64, and 76% respectively by using DMFBA-modified charcoal as the support. The epoxidation was first-order with respect to both cyclohexene and H_2O_2. The apparent activation energy of the epoxidation of cyclohexene was 11.2 kcal/mol.

In the last decade much interest has been directed to the epoxidation of olefins for the synthesis of valuable key intermediates in the chemical industry. Also, attention has been paid to several kinds of hormones and mutagens involving an oxirane moiety in their structure. For the selective epoxidation of simple olefins, molybdenum complexes[1] are well known to catalyze under mild reaction conditions. Various complexes of Ti[2], Cr[3], and Pt[4] have also been used as catalysts for the epoxidation of allyl alcohols, alkenes, and terminal olefins respectively. However, among VIA-group metal oxides, tungstic acid (H_2WO_4) has not yet been found to catalyze the epoxidation of alkenes with *t*-butyl hydroperoxide. The use of H_2O_2 as an oxidizing agent has given diol exclusively.[5] Recently, however, it has been claimed that the addition of Me_3SnOH to tungstic acid catalyzes the epoxidation of cyclohexene with concentrated (70—90%) H_2O_2 to give cyclohexene oxide,[6] though the yields are not sufficiently high. Under the presence of phase-transfer agents, olefins have also been epoxidized with diluted aqueous H_2O_2 in the presence of Na_2WO_4–Na_3PO_4–H_3PO_4 at pH=9.[7] However, the use of a heterogenized tungstic acid catalyst in the epoxidation of olefins has not been proposed. Previously, authors have found that molybdenum oxide fixed on charcoal epoxidized olefins selectively with 30% H_2O_2 in the presence of n-Bu$_3$SnCl.[8] The yields were improved by using chemically modified charcoals as support.[9] When this catalyst system was applied to H_2WO_4, several alkenes, especially inner olefins, were epoxidized in good yields. In this report, the properties of tungsten catalysts will be studied in comparison with those of molybdenum catalysts.

Experimental

Materials. The cyclohexene, 30% aqueous hydrogen peroxide (Hayashi Pure Chemicals), *N,O*-bis(trimethylsilyl)acetamide, *N,N*-dimethylformamide dibutyl acetal, tungstic acid (Wako Pure Chemicals), organotin compounds (Kyodo Yakuhin), and charcoal (palm DC-5200) (Dia Catalysts & Chemicals) were purchased. The cyclohexene and other olefins were distilled before use.

Preparation of Catalyst. The H_2WO_4–charcoal catalyst was prepared by fixing H_2WO_4 on charcoal (65 mesh) by stirring it overnight with a H_2WO_4 solution dissolved with a small amount of 30% H_2O_2 in 2-propanol. The catalyst was then filtered off, washed with 2-propanol, and dried.

Pretreatment of Catalyst. *Acid or Base Treatment of Charcoal.* Charcoal powder (1 g) was dispersed in 25 mL of distilled water. The pH value of the charcoal-dispersed solution was adjusted at 2 to 12 by the addition of 0.1 M† HCl or 0.1 M NaOH. The solution, once heated, was left to stand at room temperature and the pH of the solution was readjusted. *Butylation or Trimethylsilylation of Charcoal.* Charcoal powder (1 g) was treated with *N,O*-bis(trimethylsilyl)acetamide or *N,N*-dimethylformamide dibutyl acetal in 20 mL of hexane by stirring at 50 °C. After 2 h, the charcoal was filtered off, washed with hexane, and dried.

Epoxidation Procedure. The tungstic acid–charcoal catalyst (0.4 g) was dispersed in 2-propanol (2 mL), and n-Bu$_3$SnCl (50 mg) was added. After the catalyst had stood at room temperature for 30 min, 2-propanol (4 mL), cyclohexene (1.5 g), and 30% hydrogen peroxide (1 to 2 mL) were added. The reaction was started at 50 °C±1° in an oil bath under magnetic stirring.

Analyses of Products. The reaction products were analyzed by means of gas-liquid chromatography (Shimadzu GC-8A), using OV-17 (3 mm i.d.×2 m in length) as the column-packing material and helium as the carrier gas (12.5 mL/min). The column temperature was programmed from 30° to 150 °C at a rate of 3°/min. The retention times were 1.4 min for cyclohexene, 6.0 min for cyclohexene oxide, 17.1 min for *trans*-1,2-cyclohexanediol monoisopropyl ether, and 17.6 min for *trans*-1,2-cyclohexanediol.

Results and Discussion

Epoxidation of Alkenes in the Presence of Tungsten Catalysts.

The oxidation of cyclohexene with aqueous (30%)

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† 1 M=1 mol dm^{-3}.

Table 1. Oxidation of cyclohexene with 30% H_2O_2 in the presence of several tungstic catalysts

Catalyst	Conversion	Yield/%		
	%	Epoxide[a]	Ether[b]	Diol[c]
H_2WO_4 (10 mg)	87.5	1.6	10.7	75.2
H_2WO_4-charcoal	34.8	5.5	6.6	22.7
H_2WO_4-*n*-Bu_3SnCl-charcoal	41.1	41.1	0	0
n-Bu_3SnCl-charcoal	0	0	0	0
Charcoal	0	0	0	0

Cyclohexene (1.6 M), H_2O_2 (1.6 M), 1.8% H_2WO_4-charcoal (0.4 g), *n*-Bu_3SnCl (1.58×10^{-2} M), and 2-propanol as the solvent were used. The reaction was carried out at 50 °C for 15 h. a) Cyclohexene oxide. b) *trans*-1,2-Cyclohexanediol monoisoporpyl ether. c) *trans*-1,2-Cyclohexanediol.

Table 2. Epoxidation of various olefins with 30% H_2O_2 on the H_2WO_4-*n*-Bu_3SnCl-charcoal catalyst

Olefin	Molar ratio of olefin to H_2O_2	Epoxide yield/%	By-product/%
Cyclopentene	1	74.4[a]	0
	2	81.0[b]	0
Cyclohexene	1	63.7[a]	0
	2	60.5[b]	0
1-Methyl-1-cyclohexene	2	53.7[b]	0
1-Octene	2	17.5[b]	0
2-Octene	1	76.3[a]	0
	2	56.0[b]	0
Styrene	2	30.3[b]	11.1[c]
1-Decene	2	16.5[b]	0

Olefin (1.6 M), H_2O_2 (0.8 or 1.6 M), 1.8%-H_2WO_4-charcoal (0.4 g), *n*-Bu_3SnCl (1.58×10^{-2} M), and 2-propanol as the solvent were used. Reaction was carried out at 50 °C for 15 h. a) Charcoal was pretreated with DMFBA. b) Charcoal was pretreated with BSA. c) Benzaldehyde.

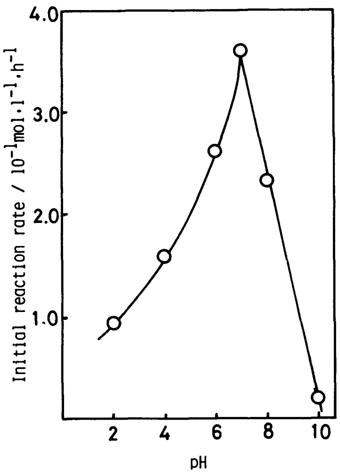

Fig. 1. Effect of pH of charcoal as support in the epoxidation of cyclohexene with 30% H_2O_2 on H_2WO_4-Bu_3SnCl-charcoal catalyst.
Cyclohexene 4.43 M, H_2O_2 8.02×10^{-1} M, 1.8%-H_2WO_4-charcoal 0.4 g, Bu_3SnCl 1.59×10^{-2} M, and solvent 2-propanol were used. Reaction was carried out at 50 °C.

H_2O_2 in the presence of H_2WO_4 catalysts was carried out in 2-propanol at 50 °C. The results are shown in Table 1. H_2WO_4 gave 1,2-cyclohexanediol, a hydrolysate of cyclohexene oxide, as the major product. Similar results were obtained in H_2WO_4-charcoal catalysts. However, the addition of *n*-Bu_3SnCl, as the best choice of the co-catalysts, prevented the hydrolysis and thus gave cyclohexene oxide selectively in a low yield (41%). The yield was not improved by changing the reaction conditions such as the solvent, the temperature, or the reaction time, since charcoal itself decomposed H_2O_2 considerably. By shaking the 2-propanol solution of H_2O_2 in the presence of a catalytic amount of charcoal (0.4g/5 mL) at 50 °C for 15 h, about three-tenths of the H_2O_2 was decomposed. We have observed that a chemically-modified charcoal supressed the decomposition of H_2O_2 to improve the yields of epoxides.[9] Therefore, charcoal was treated with DMFBA or BSA and several alkenes were epoxidized in the presence of H_2WO_4-*n*-Bu_3SnCl-charcoal catalysts. As is shown in Table 2, cyclic olefins of C_5–C_6 and inner olefins of 2-octene gave epoxides in 70—80% yields (based on H_2O_2), with a 1:2 ratio of olefins to H_2O_2. However, rather weak activity was observed in such terminal olefins as 1-octene and 1-decene. The order of yields closely resembled that obtained with the molybdenum oxide-*n*-Bu_3SnCl-charcoal (DMFBA) catalyst.[9]

Effect of the Pretreatment of Charcoal. In the oxidation of alkenes with aqueous H_2O_2, the pretreatment of charcoal drastically affected the conversion and the selectivity. Figure 1 shows the change in the conversions and selectivities when the epoxidation of cyclohexene was carried out in the presence of H_2WO_4 catalysts, using as supports charcoals which had been treated with solutions of various pH values. The oxidation rate for cyclohexene decreased according to the increase in the treated pH, though the selectivity was high. On the other hand, both the conversion and the selectivity became poor on the acidic side. The best result was obtained by treating charcoal with a solution of pH 7. However, when equivalent amount of cyclohexene and H_2O_2 were used, the yield was as low as 40% by the decomposition of H_2O_2 on charcoal.

The suppression of the decomposition of H_2O_2 was examined by treating charcoal with various agents. The presence of such substituents as amino, carboxyl, and hydroxyl groups on the surface of charcoal is well known. We supposed that the decomposition of H_2O_2 was accelerated by those hydrophilic substituents on charcoal which concentrate H_2O_2 on the surface of charcoal. Therefore, the functional groups were blocked by alkylating or alkylsilylating agents, such as DMFBA, BSA, or diazomethane. Among those compounds, DMFBA is a good surface-modifier. The decomposition of H_2O_2 was suppressed by treating the charcoal with DMFBA; the decomposition rate of 50% in raw charcoal was decreased to 30% under heating for 15 h at 50 °C in a 2-propanol solution.

Effect of the Concentrations of Cyclohexene, H_2O_2 and H_2O on the Epoxidation. In the epoxidation of cyclohexene on H_2WO_4-*n*-Bu_3SnCl-charcoal catalysts, the concentrations of the olefins affected the rates. The initial rates of the oxidation of cyclohexene were first-order with respect to cyclohexene. Usually we used 4.43 M of cyclohexene in 2-propanol to keep a solution homogeneous by mixing in aqueous H_2O_2, cyclohexene, and 2-propanol. The reaction order with respect to the concentration of H_2O_2 was also unity. In the molybdenum oxide-*n*-Bu_3SnCl-charcoal catalyst, the initial rates of the oxidation of cyclohexene were zero-order for both cyclohexene and H_2O_2.[8] These results suggest that the affinity of cyclohexene or H_2O_2 to H_2WO_4 is weaker than that of the Mo catalyst. Though the presence of H_2O decreased the reaction rate in proportion to the amount added to the system, the selectivity to epoxide was excellent. Therefore, it was considered that a moderately hydrophobic surface was formed by the treatment of charcoal.

On the Arrhenius plot of the epoxidation of cyclohexene with H_2O_2 in the presence of the tungstic acid catalyst, an apparent activation energy of 11.2 kcal/mol (1 cal=4.184 J) was obtained. This value is smaller than those of molybdenum oxide-*n*-Bu_3SnCl-charcoal (13.5 kcal/mol),[8] or bis(dimethyldithiocarbamato)molybdenum(VI) oxide (19.0 kcal/mol).[10] Among the oxides of the VIA elements of the periodic table, Mo and W showed similar properties of giving epoxides selectively in the presence of alkyltin compounds. On the other hand, no epoxide was obtained with chromium(VI) oxide, not even in the presence of *n*-Bu_3SnCl, except for the use of $O_2Cr(NO_3)_2$ under mild reaction conditions (−78 °C).[3]

Effect of Organotin Compounds in the Selective Epoxidation. The effect of the co-catalyst of organotin compounds for H_2WO_4 was studied in the epoxidation of cyclohexene with aqueous (30%) H_2O_2. Different conversions and selectivities were obtained according to the kinds of substituents and alkyl groups of organotin chlorides, oxides, or acetates. Among these co-catalysts, *n*-Bu_3SnCl gave the highest yield (Table 3); the butyl group was more effective than the methyl or phenyl group. Furthermore, di or tributyltin compounds gave higher yields than monobutyltin compounds. These results

TABLE 3. EFFECTS OF VARIOUS ORGANOTIN COMPOUNDS USED AS CO-CATALYSTS ON THE EPOXIDATION OF CYCLOHEXENE WITH 30% H_2O_2 ON H_2WO_4-CHARCOAL

Organotin compound	Conversion	Yield/%		
	%	Epoxide[a)]	Ether[b)]	Diol[c)]
Me_3SnCl	30.3	30.3	0	0
n-Bu_3SnCl	68.0	68.0	0	0
Ph_3SnCl	55.8	51.5	4.3	0
Me_3SnOH	30.4	30.4	0	0
(*n*-$BuSnO)_2O$	42.8	35.6	7.2	0
n-Bu_2SnO	59.2	59.2	0	0
(*n*-$Bu_3Sn)_2O$	59.2	59.2	0	0
n-$Bu_2Sn(OCOCH_3)_2$	61.3	58.6	0	2.7
n-$BuSn(OCOCH_3)_3$	53.2	51.6	0	1.6
$Ph_3SnOCOCH_3$	58.0	52.5	5.5	0
(Cyclohexyl)$_3$SnOH	48.6	48.6	0	0
n-Bu_4Sn	64.6	38.5	26.0	0.1
Ph_4Sn	35.2	24.9	10.3	0

Cyclohexene (4.43 M), H_2O_2 (8.02×10^{-1} M), 1.8% H_2WO_4-charcoal (0.4 g), organotin compound (50 mg), and 2-propanol as the solvent were used. The reaction was carried out at 50 °C for 15 h. a) Cyclohexene oxide. b) *trans*-1,2-Cyclohexanediol monoisopropyl ether. c) *trans*-1,2-Cyclohexanediol.

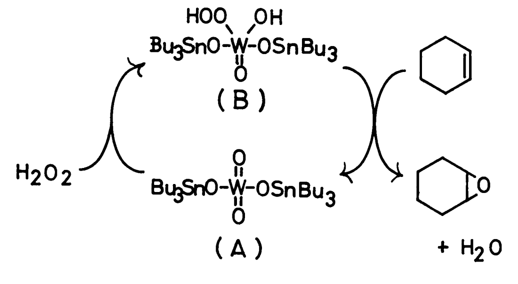

Chart 1.

suggest that the hydrophobic effect increases the yield of cyclohexene oxide. However, such tetraalkyltin as n-Bu_4Sn or Ph_4Sn gave lower selectivities for cyclohexene oxide. Therefore, the formation of tightly-bonded complexes between H_2WO_4 and such trialkyltin compounds of chloro, hydroxyl, oxy, or acetoxyl groups are considered to be an element for the selective epoxidation.

$$(HO)_2WO_2 + 2n\text{-}Bu_3SnCl \longrightarrow (n\text{-}Bu_3SnO)_2WO_2 + 2HCl$$

When cyclohexene and H_2O_2 were reacted in the presence of H_2WO_4 and n-Bu_3SnCl in 2-propanol at 50 °C for 15 h, white precipitates involving tungsten were obtained. These precipitates separated from the system and then catalyzed the selective epoxidation again. From these results, we considered the precipitates to be pre-active species with the (A) structure in Chart 1. The elemental analyses (C and H) of the precipitates were reasonable for $(n\text{-}Bu_3SnO)_2WO_2$. The treatment of Complex (A) with H_2O_2 gave an oxidized products. The IR spectra of this peroxy complex showed a remarkable decrease in the broad band at 800—900 cm^{-1}, probably because of the W=O bond observable in the IR spectra of H_2WO_4. Also, the absorption bands of Mo=O have been observed at 800—1000 cm^{-1}[11] in $(NH_4)_2[MoO_3F_2]$.

On the other hand, the band of the hydroxyl groups at 3400 cm^{-1} increased remarkably. Therefore, in our tungsten catalyst, a μ-peroxo-type[12] complex was suggested as an active species for the oxidation, as is shown in Chart 1 (B).

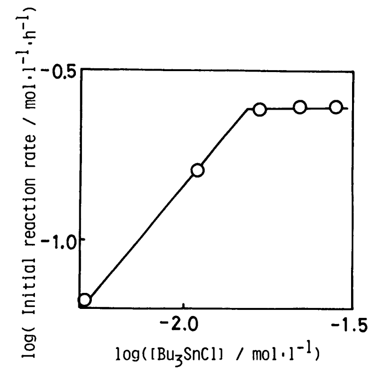

Fig. 2. Effect of the concentration of Bu_3SnCl as co-catalyst in the epoxidation of cyclohexene with 30% H_2O_2 on H_2WO_4–charcoal catalyst.
Cyclohexene 4.43 M, H_2O_2 8.02×10^{-1} M, 1.8%-H_2WO_4–charcoal 0.4 g, and solvent 2-propanol were used. Reaction was carried out at 50 °C.

Then, the effect of the amount of n-Bu_3SnCl relative to that of H_2WO_4 in the epoxidation of cyclohexene was examined for the initial rate of the epoxidation. As is shown in Fig. 2, both the selectivity and the yield increased linearly with an increase in the amount of n-Bu_3SnCl and reached the saturation point at a molar ratio of 1 : 4 of H_2WO_4 to n-Bu_3SnCl. This fact supports a complex formation between H_2WO_4 and n-Bu_3SnCl until the molar ratio of 1 : 4. Therefore, the organotin compounds bound on the acid groups of H_2WO_4 effectively prevent the hydrolysis of epoxides.

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