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Epoxidation of Olefins with Aqueous Hydrogen Peroxide in the Presence of Molybdenum Acetylacetonate-Bis(tri-*n*-butyltin)oxide

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The epoxidation of olefins with 28% aqueous hydrogen peroxide was investigated. A catalyst system composed of $MoO_2(acac)_2$ and $(n\text{-}Bu_3Sn)_2O$ selectively gave 72—12% yields of epoxides from olefins such as cyclohexene, styrene and 1-octene in an isopropyl alcohol solvent at 50°C for 24 h. The epoxidation rates were first order with respect to cyclohexene and zero order with respect to H_2O_2. An apparent activation energy of 10 $kcal \cdot mol^{-1}$ and an entropy of activation of -53 eu. were obtained. $MoO_2(n\text{-}Bu_3SnO)_2$ is proposed to be the active species for the epoxidation.

Keywords——epoxidation; cyclohexene oxide; styrene oxide; 1,2-epoxyoctane; hydrogen peroxide; molybdenum acetylacetonate–bis(tri-*n*-butyltin)oxide catalyst

Epoxides are useful materials in the pharmaceutical industry for the synthesis of alcohols, diols, alkanolamines, and polyethers. Recently, various kinds of epoxides have been found among drug metabolites and insect hormones. For this reason, the synthesis of these compounds is of interest to chemists and biochemists. Various olefins have been epoxidized directly with organic peroxides such as *tert*-butyl hydroperoxide (TBHP)[1] and cumene hydroperoxide (CHP)[2] by making use of molybdenum-based catalysts. Though hydrogen peroxide is a readily available oxygen source, the presence of water affects the epoxidation activity severely.[3] One of the authors has found that in the epoxidation of olefins a molybdenum acetylacetonate–organotin catalyst system gives epoxides selectively when used with concentrated H_2O_2 (70%).[4] However, the use of aqueous hydrogen peroxide (30—35%) would be preferable as regards ease of handling and cost. This report deals with the reaction conditions suitable for the epoxidation of olefins by using 28% aqueous hydrogen peroxide in the presence of $MoO_2(acac)_2$ and alkyltin oxides and hydroxides. The mechanism was also investigated kinetically, and binary complexes of the molybdenum oxide-organotin compounds are proposed to be the active species.

Experimental

Kinetics——$MoO_2(acac)_2$ and $(n\text{-}Bu_3Sn)_2O$ in isopropyl alcohol solvent and cyclohexene (distilled before use) were added to a 50 ml round-bottomed flask fitted with a Dimroth condenser. The epoxidation was started by the addition of 28% aqueous hydrogen peroxide. The reaction vessel was kept at 50 ± 0.01°C in a water bath. At intervals, a portion of the reactants was pipetted out and toluene was added as an internal standard. The products were analyzed on a gas-chromatograph (Hitachi Ltd., type 063) using a 20% PEG 20 M column (3 mm i.d. × 1 m in length; 2 m in length for iso- and *n*-butyl alcohol solvents) with He (30 ml/min) as the carrier gas. The column temperature was programmed from 40 to 150°C (3°C/min).

Analysis of the Precipitates prepared from $MoO_2(acac)_2$ and $(n\text{-}Bu_3Sn)_2O$ in Isopropyl Alcohol——The molybdenum content in the precipitate obtained from $MoO_2(acac)_2$ and $(n\text{-}Bu_3Sn)_2O$ was estimated from the absorption at 470 nm by the thiocyanate method.[5] Tin content was determined after calcination to SnO_2 by using ethylenediaminetetraacetic acid (EDTA) and a 0.01 N thorium nitrate in the presence of an XO indicator.[6]

Organotin Compounds——Trimethyltin hydroxide was prepared from trimethyltin chloride by hydrolysis with NaOH followed by sublimation according to the method of Kraus and Bullard.[7] Other organotin compounds such as Me_3SnCl, $n\text{-}Bu_3SnCl$, $(n\text{-}Bu_3Sn)_2O$, $n\text{-}Bu_2SnO$, and $(n\text{-}BuSnO)_2O$ were obtained from Kyodo Yakuhin Co., Tokyo.

Results and Discussion

The yields in the epoxidation of cyclohexene with 28% aqueous hydrogen peroxide in the presence of various metal acetylacetonates and bis-tributyltin oxide in isopropyl alcohol at 50°C for 24 h were estimated; without bis-tributyltin oxide, no cylohexene oxide was obtained. Among acetylacetonates of Mo, Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, Zr, Rh, Ce, and Ag, molybdenum acetylacetonate gave cyclohexene oxide (60%) in preliminary experiments. Nickel acetylacetonate also gave cyclohexene oxide in 2% yield, but other metal acetylacetonates did not afford the epoxide. In Table I, the results of the epoxidation of cyclohexene in the presence of $MoO_2(acac)_2$ and various alkyltin compounds are shown. Molybdenum acetylacetonate itself was inactive for the epoxidation of cyclohexene with 28% aqueous hydrogen peroxide, but the addition of various alkyltin compounds to $MoO_2(acac)_2$ led to good epoxidation yields. Among these alkyltin compounds, $(n\text{-}Bu_3Sn)_2O$ was the best cocatalyst and cyclohexene oxide was obtained in 70% yield at 50°C for 24 h. Since $(n\text{-}Bu_3Sn)_2O$ was inactive for the epoxidation of cyclohexene, it was considered that $MoO_2(acac)_2$ and $(n\text{-}Bu_3Sn)_2O$ formed a complex. Several olefins were epoxidized by using the catalyst system of $MoO_2(acac)_2$ (1.09×10^{-3} M) and $(n\text{-}Bu_3Sn)_2O$ (1.17×10^{-2} M), as shown in Fig. 1. The initial reaction rates were in the order of cyclohexene>styrene>1-octene, allyl chloride. The relative rates with respect to cyclohexene were 1 : 0.7 : 0.3 : 0. The order is in accord with the epoxidation rates by TBHP in the presence of $Mo(CO)_6$.[8] However, in our system, H_2O_2 epoxidized styrene more easily than TBHP; with the $Mo(CO)_6$ catalyst, the relative rate for styrene is 0.10[8] with respect to cyclohexene.

TABLE I. Epoxidation of Cyclohexene with Hydrogen Peroxide in the Presence of Various Organotin Compounds and $MoO_2(acac)_2$ at 50°C for 24 h

Organotin compound	Yield (%)[d]		
	CH oxide[a]	Monoether[b]	Diol[c]
None	0	24.0	19.3
Me_3SnCl	39.0	1.7	0
$n\text{-}Bu_3SnCl$	45.5	10.6	6.5
Me_3SnOH	8.6	0	0
$(n\text{-}Bu_3Sn)_2O$	72.7	0	0
$n\text{-}Bu_2SnO$	61.5	14.1	6.0
$(n\text{-}BuSnO)_2O$	36.3	1.1	0

Organotin compound 0.2 g, $MoO_2(acac)_2$ 10 mg, cyclohexene 4 ml, isopropyl alcohol 6 ml and 28% H_2O_2 1 ml.

a) Cyclohexene oxide. *b*) Cyclohexanediol mono-isopropyl ether. *c*) 1, 2-Cyclohexanediol. *d*) Based on H_2O_2.

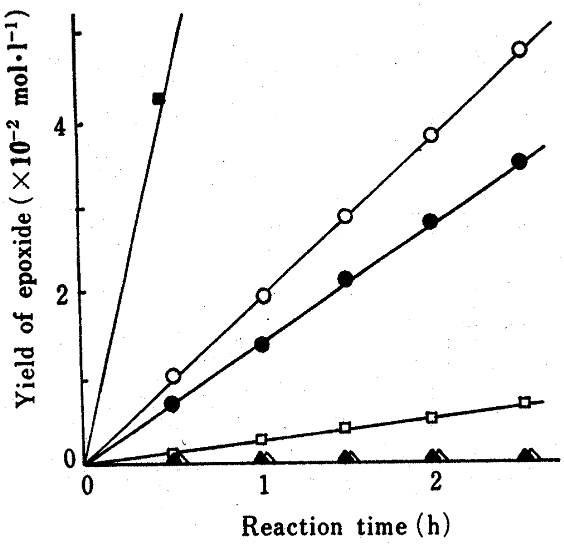


Fig. 1. Epoxidation of Olefins with Aqueous Hydrogen Peroxide in the Presence of $MoO_2(acac)_2$ and $(n\text{-}Bu_3Sn)_2O$

Olefins are cyclohexene (○), styrene (●), 1-octene (□), 1-decene (△) and allyl chloride (▲). Cyclohexene was oxidized in the presence of $MoO_2(acac)_2$ and TBHP (■).

Olefins 3.05 M, $MoO_2(acac)_2$ 1.09×10^{-3} M, $(n\text{-}Bu_3Sn)_2O$ 1.17×10^{-3} M, 28% H_2O_2 3.15×10^{-1} M and isopropyl alcohol 10 ml. The reaction was carried out at 50±0.01°C.

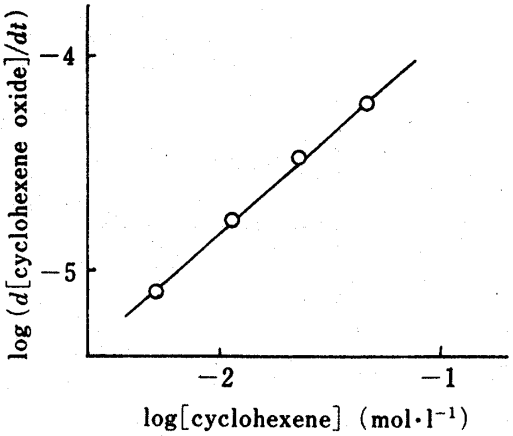


Fig. 2. Plot of the Concentration of Cyclohexene *vs.* the Initial Rate of Epoxidation at 50°C

$MoO_2(acac)_2$ 1.09×10^{-3} M, $(n\text{-}Bu_3Sn)O$ 1.17×10^{-3} M, 28% H_2O_2 3.15×10^{-1} M and isopropyl alcohol 10 ml.

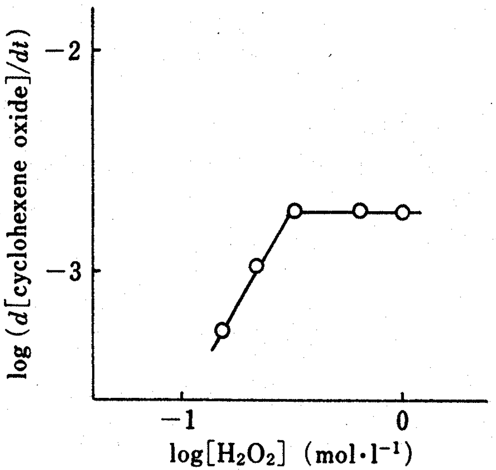


Fig. 3. Effect of the Concentration of Hydrogen Peroxide on the Epoxidation Rate of Cyclohexene

Cyclohexene 3.05 M, $MoO_2(acac)_2$ 1.09×10^{-3} M, $(n\text{-}Bu_3Sn)_2O$ 1.17×10^{-3} M, isopropyl alcohol 10 ml and 28% H_2O_2.

The reaction was carried out at 50°C.

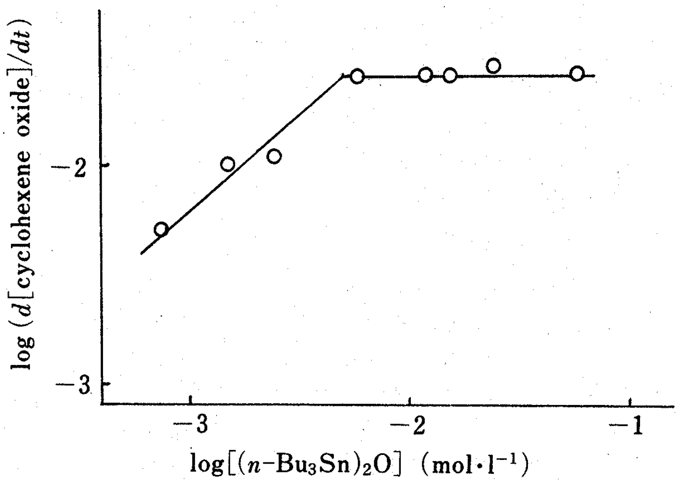


Fig. 4. Effect of the Concentration of $(n\text{-}Bu_3Sn)_2O$ on the Epoxidation Rate of Cyclohexene

Cyclohexene 3.05 M, $MoO_2(acac)_2$ 1.09×10^{-3} M, 28% H_2O_2 3.15×10^{-1} M, isopropyl alcohol 10 ml and $(n\text{-}Bu_3Sn)_2O$.

The reaction was carried out at 50°C.

Effect of the Concentrations of Cyclohexene, H_2O_2, $MoO_2(acac)_2$, and $(n\text{-}Bu_3Sn)_2O$ on the Epoxidation Rates

The effect of the concentration of each component on the epoxidation rate was investigated by adopting the isolation method[9] during an initial period of 2 h. Figure 2 shows the epoxidation rates at various concentrations of cyclohexene. The log-log plot between the concentration of cyclohexene and the reaction rate gave a linear relationship with a slope of unity, which in the range $[H_2O_2] < 3.15 \times 10^{-1}$ M

$$\frac{d\,[\text{cyclohexene oxide}]}{dt} = k_{\text{I}}\,[\text{cyclohexene}]\,[H_2O_2] \qquad (1)$$

and in the range $[H_2O_2] > 3.15 \times 10^{-1}$ M

$$\frac{d\,[\text{cyclohexene oxide}]}{dt} = k_{\text{II}}\,[\text{cyclohexene}] \qquad (2)$$

TABLE II. Effect of Solvents on the Epoxidation of Cyclohexene with Aqueous Hydrogen Peroxide

Isomer	k_{CH_3OH}[a)] $\times 10^{-2}$	$k_{C_2H_5OH}$ $\times 10^{-2}$	$k_{C_3H_7OH}$ $\times 10^{-2}$	$k_{C_4H_9OH}$ $\times 10^{-2}$	$k_{C_5H_{11}OH}$ $\times 10^{-2}$
n-	0.27	0.76	1.43	1.50	1.86
iso-	—	—	2.17	3.47	1.37
sec-	—	—	—	1.94	2.03
tert-	—	—	—	1.78	1.50

Cyclohexene 3.05M, $MoO_2(acac)_2$ 1.09×10^{-3}M, $(n\text{-}Bu_3Sn)_2O$ 1.17×10^{-2}M, 28% H_2O_2 3.15×10^{-1}M, and solvent 6 ml. The reaction was carried out at 50±0.01°C.

a) k : $\text{mol}\cdot\text{l}^{-1}\cdot\text{h}^{-1}$.

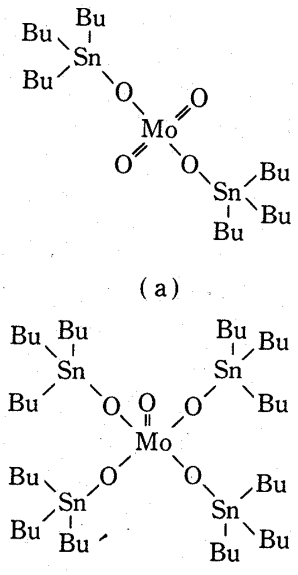
indicated that the reaction was first order. A saturation was observed at H_2O_2 concentrations above 3.15×10^{-1} M, as can be seen in Fig. 3. These results can be explained in terms of the retardation of the epoxidation by water present in H_2O_2 solutions added to the reaction system. As regards the effect of the concentration of $(n\text{-}Bu_3Sn)_2O$, the curve was divided into two ranges; a first order range below 5.08×10^{-3} M $(n\text{-}Bu_3Sn)_2O$, and a zero order range above this value, as shown in Fig. 4. From these results, the rate equation for the initial period of epoxidation of cyclohexene with aqueous H_2O_2 is as follows:
where k_{I} and k_{II} involve the concentration of molybdenum species (this is a constant, since the concentration of the catalyst is essentially the same before and after the reaction). In Fig. 4, the crossing point of the two lines is equivalent to 1.16×10^{-2} M $(n\text{-}Bu_3Sn)_2O$. This value corresponds to 1.9 molecules of $(n\text{-}Bu_3Sn)_2O$ to one molecule of $MoO_2(acac)_2$.

Effect of Solvents

In the epoxidation of cyclohexene with organic peroxide, various lipophilic solvents such as CH_2Cl_2,[10)] and benzene[11)] have been used. In the aqueous H_2O_2–cyclohexene system, alcohols were suitable solvents for the epoxidation. The results are shown in Table II. An increase in carbon number increased the epoxidation rate. However, when isoamyl alcohol was used as a solvent, H_2O_2 solution separated out of the reaction system. Therefore, C_3 and C_4 alcohols, particularly such branched alcohols as isopropyl alcohol and isobutyl alcohol, afforded good results. A reaction system composed of $MoO_2(acac)_2$ 2.77×10^{-3} M, $(n\text{-}Bu_3Sn)_2O$ 2.97×10^{-2} M, cyclohexene 7.79 M and H_2O_2 8.02×10^{-1} M in isopropyl alcohol as a solvent gave an excellent results; the yield of cyclohexene oxide reached 72.7% at 50°C for 24 h. An 18.8% yield of styrene oxide and a 12.2% yield of 1,2-epoxyoctane were obtained from styrene and 1-octene, respectively.

Active Species for the Epoxidation

On mixing of $MoO_2(acac)_2$ and $(n\text{-}Bu_3Sn)_2O$ in isopropyl alcohol solvent, turbidity appeared immediately. A few minutes later, a white solid precipitated at the bottom of the reaction vessel. The precipitate dissolved readily in an aqueous H_2O_2. An infrared (IR) analysis of the precipitate showed that the strong acetylacetone absorption band at 1580 cm^{-1} had disappeared, and CH deformation bands were observed at 1395, 1420 and 1460 cm^{-1},respec-



(a)

(b)

Chart 1

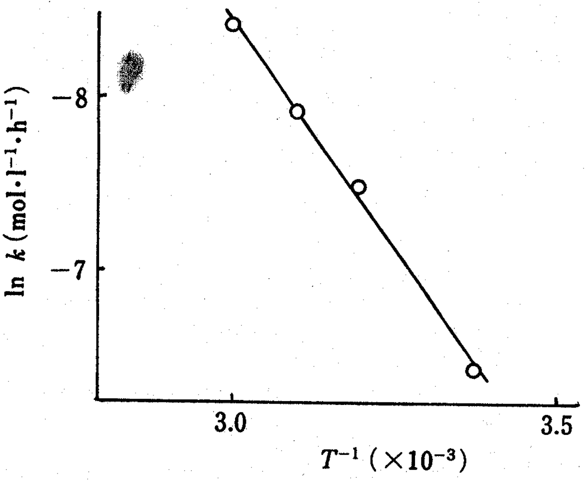


Fig. 5. Arrhenius Plot for the Epoxidation of Cyclohexene with Aqueous Hydrogen Peroxide

Cyclohexene 3.05 M, $MoO_2(acac)_2$ 1.09×10^{-3} M, $(n\text{-}Bu_3\text{-}Sn)_2O$ 1.17×10^{-2} M, 28% H_2O_2 3.15×10^{-1} M and isopropyl alcohol 10 ml.

TABLE III. Complexes prepared from $MoO_2(acac)_2$ and $(n\text{-}Bu_3Sn)_2O$

Compd. No.	Analysis (%) Calcd (Found) C	H
$MoO_2(n\text{-}Bu_3SnO)_2$	38.95	7.35
1	(38.74	7.22)
2	(38.89	7.01)

1 was precipitated from $MoO_2(acac)_2$ and $(n\text{-}Bu_3Sn)_2O$ 1 : 1 mixture in isopropyl alcohol and **2** was obtained from a 1 : 5 mixture.

tively. Further, the absorption bands at 1372 and 1525 cm^{-1}, considered to be due to a Sn–O–Sn bond, had disappeared and a new broad peak was observed at 823 cm^{-1}: these results are consistent with the report that a Sn–O–Sn bond reacts easily with various acids to form two molecules of additional compounds[12] (Chart 1 (a) and (b)).

The elemental analysis was in accord with the composition of $MoO_2(n\text{-}Bu_3SnO)_2$, as shown in Table III. Furthermore, a chelate analysis for Mo and Sn in the precipitate gave the atomic ratio of Sn/Mo=1.9. An attempt to separate the complex of Sn/Mo=4 failed; gel precipitates that formed mostly passed through a filter paper. However, the presence of two types of complexes, (a) and (b) in Chart 1, was suggested from Fig. 4, since the rate increased continuously beyond a 2: 1 ratio of $(n\text{-}Bu_3Sn)_2O$ to $MoO_2(acac)_2$. The complex (a), obtained from $(n\text{-}Bu_3Sn)_2O$ and $MoO_2(acac)_2$ in isopropyl alcohol, was separated and used as a catalyst. The observed k value, 3.71×10^{-4} mol·s^{-1}, in the presence of (a) 1.16×10^{-2} M, gave almost the same reaction rate as that obtained with $(n\text{-}Bu_3Sn)_2O$ and $MoO_2(acac)_2$ under the same reaction conditions in Fig. 4.

The apparent activation energy was estimated from an Arrhenius plot in the temperature range from 30 to 60°C. An activation energy of 10.2 kcal mol^{-1} was obtained (Fig. 5). This value is rather small compared with that of 26.9 kcal mol^{-1} in the system of MoO_3–TBHP,[13] 19.0 kcal mol^{-1} for Mo_2O_5–dimethyldithiocarbamate,[14] and 15.9 kcal mol^{-1} for MoO_5–hexamethylphosphotriamide,[15] but the epoxidation rate of cyclohexene with TBHP–$MoO_2(acac)_2$ was four times faster than that with H_2O_2–MoO_2(n-$Bu_3SnO)_2$ under the same reaction conditions, as can be seen in Fig. 1. This discrepancy is accounted for by the highly negative value (−53 eu.) of entropy of activation in our system.

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