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ISOLATION OF REACTION INTERMEDIATE OF OLEFIN EPOXIDATION CATALYZED BY MOLYBDIC ANHYDRIDE-HEXAMETHYLPHOSPHORICTRIAMIDE CATALYST

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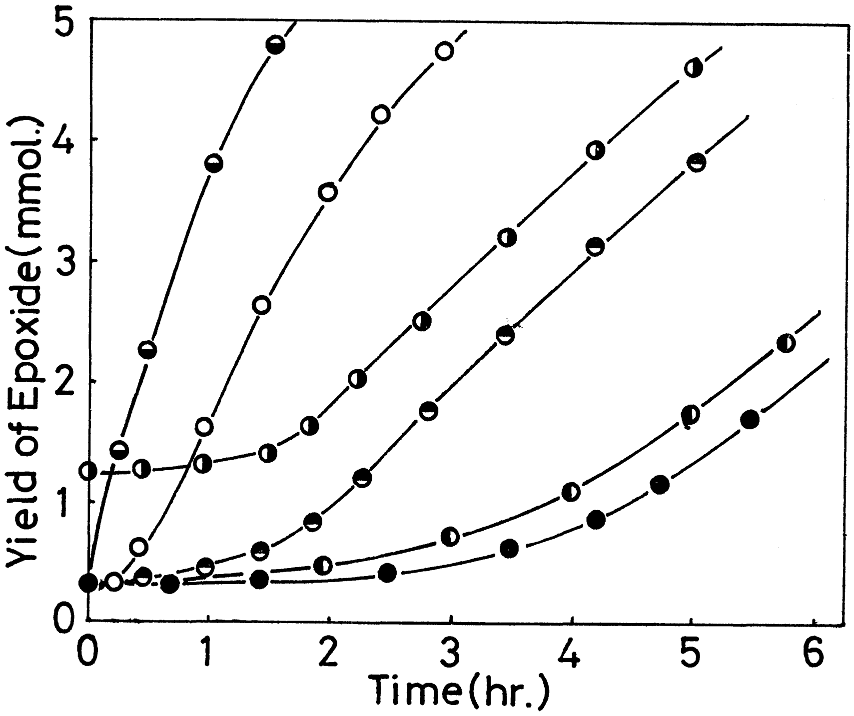
The molybdic anhydride-catalyzed epoxidation of olefin by t-butyl hydroperoxide was studied with particular reference to the induction period and the effect of additives. The epoxidation in the presence of hexamethylphosphorictriamide(HMPT) proceeds through an intermediate complex, $MoO(O_2)_2$-HMPT, which was isolated as an adduct with bipyridyl.

It has been known that peroxy compound are formed by reaction of transition metal compounds with hydrogen peroxide.[1)] The peroxo molybdenum complex($MoO(O_2)_2$-L; L:Ligand), first reported by Mimoun, de Roch and Sajus, was formed by the reaction of MoO_3 with 30% aqueous solution of H_2O_2.[2)] Although the peroxo molybdnum complex has been regarded as a possible reactive intermediate of the molybdenum-catalyzed epoxidation of olefin by hydroperoxide,[3)] there has been no report on the formation of peroxo complex in the reaction of MoO_3 with hydroperoxide instead of hydrogen peroxide. The stoichiometric epoxidation of olefin with $MoO(O_2)_2$-L[4)] as well as the molybdenum-catalyzed epoxidation of olefin by hydroperoxide has been studied in this laboratory and the peroxo molybdenum complex has been found in the reaction product of MoO_3 with t-butyl hydroperoxide and isolated as an adduct with bipyridyl.

Ethylene dichloride as the solvent(20 ml), MoO_3(1 mmol), additive(1 mmol, e.g., HMPT, 1,2-cyclohexanediol, epoxycyclohexane) and t-butyl hydroperoxide (50 mmol) were introduced in a 30 ml glass flask under ambient pressure of dry nitrogen. The reaction was started by addition of cyclohexene(50 mmol) to the above solution stirring at 40 °C. It was confirmed that the hydroperoxide was free from hydrogen peroxide.

Fig. 1. The reaction time courses with various additives.



Reaction Conditions;

t-BuOOH	50 mmol
Cyclohexene	50 mmol
Solv.(CH_2ClCH_2Cl)	20 ml
Cat.(MoO_3)	1 mmol
Cat.(Additive)	1 mmol
Temp.	40 °C

○: MoO_3 + HMPT

◑: MoO_3 + Epoxycyclohexane

◐: MoO_3 + DMF

◓: MoO_3 + 1,2-Cyclohexanediol

◒: $MoO_2(acac)_2$

●: MoO_3

Fig. 1. illustrates the time course of epoxycyclohexane formation with various additives. Induction periods are observed except the run with $MoO_2(acac)_2$. It is to be noted that the presence of HMPT reduces the induction period for MoO_3 from 3-4 hr to 20 min, accompanying about two fold increase in the stationary rate of epoxidation. The observed absence of induction period in the case of $MoO_2(acac)_2$-catalyzed reaction appears to suggest that the induction period is caused by the dissolution process of MoO_3, because $MoO_2(acac)_2$ is a soluble catalyst. In this respect the effects of 1,2-cyclohexanediol and epoxycyclohexane as additive were examined since molybdenum diol complex($MoO_2(diol)_2$) has been claimed to be the active species of the molybdenum-catalyzed epoxidation of olefin by Sheldon.[5)] However, as shown in Fig. 1., those additives are not so effective as HMPT. HMPT was chosen because it is effective in enhancing the stoichiometric epoxidation with $MoO(O_2)_2$-L. However, the more effective ligands, DMF and DMA, for the stoichiometric epoxidation[6)] were ineffective in reducing the induction period, indicating the unique behavior of HMPT.

In order to isolate the active species, a catalytic amount of bipyridyl (1 mmol) was added to the reaction mixture of epoxidation by MoO_3 with or without HMPT.

The reaction was found to stop immediately, giving a white precipitate, which was identified as a MoO_3-bipyridyl complex as shown in Fig. 2. In this way it was proved that MoO_3 is dissolved in the reaction mixture and retains its trioxide structure during the epoxidation. The induction period must be caused by the dissolution process.

The nature of dissolution process was elucidated by changing the combinations of components(MoO_3, HMPT, t-butyl hydroperoxide and cyclohexene) in the system. That is, each combination of mixture was kept stirring for 30 min at 40 °C before the complete set of components were mixed. The induction periods after such treatment are tabulated in Table 1

Table 1. Effect of Pretreatment.

Reagent for Pretreatment				Induction Period (min.)
MoO_3	HMPT	t-BuOOH	cyclohexene	
○	○	----	----	20
---	○	○	----	20
---	----	○	○	20
○	○	○	----	0

Reaction Conditions;

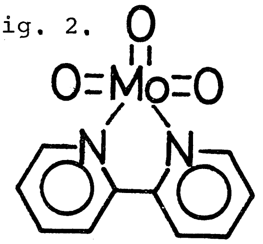
MoO_3	1 mmol
HMPT	1 mmol
t-BuOOH	1 mmol
cyclohexene	1 mmol
Soiv.(CH_2clCh_2cl)	20 ml
Pretreatment Temp.	40 °C
Pretreatment Time	30 min.

It is obvious that only when tree components of MoO_3, HMPT and t-butyl hydroperoxide are involved in the mixture, the induction period disappears, demonstrating that a soluble complex is formed by the reaction of these three components. This was also suggested by a yellow color of the solution.

In order to isolate the complex, bipyridyl was added to the ethylene dichloride solution of three components after stirring for 30 min. A yellow crystalline precipitate was obtained. It was identified as peroxo molybdenum complex as shown in Fig. 3.

From these results it is suggested that the epoxidation by MoO_3 in the presence of HMPT proceeds via the peroxo molybdenum intermediate which rapidly reacts with olefin as illustrated in Fig. 4.

Fig. 2.



I.R. (cm^{-1})

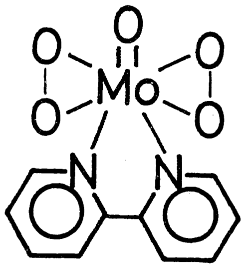
νMo=O 875-920

Bipy. 630,660
770

Elemental Analysis

	H	C	N %
Calcd.	2.6;	40.0;	9.3
Found	2.6;	39.8;	8.8

Fig. 3.



I.R. (cm^{-1})

Mo=O 940

νO-O 860,865

νMo<O|O sym.540
asym.580

Bipy. 650,665
770

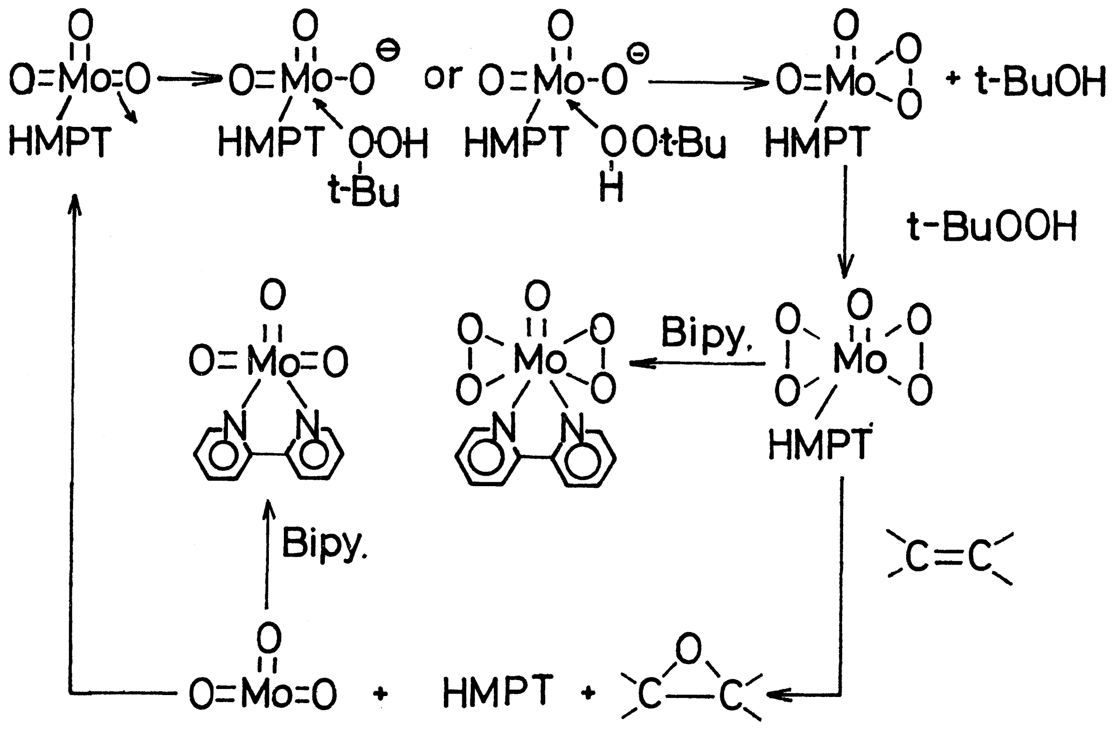
Elemental Analysis

	H	C	N %
Calcd.	2.4;	36.2;	8.4
Found	2.3;	36.2;	8.4

The fact that the stationary state of molybdenum during the epoxidation assumes the trioxide form seems to indicate that the formation of peroxo complex is the slow step.

In the absence of HMPT, however, the peroxo complex could not be detected; suggesting that the reaction intermediate is different from other systems.

Fig.4.



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