Kinetic Studies on Olefin Epoxidation by Peroxo Molybdenum Complex $(MoO(O_2)_2HMPT)$

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Oxidation of olefin by peroxo molybdenum complex selectively yields epoxide at room temperature. The nature of the interaction of olefin with molybdenum and that of the peroxo molybdenum complex has been investigated in terms of coordination constant K of olefin and rate constant k_2 of decomposition of the peroxo molybdenum-olefin complex, attention being paid to the substituent effect of olefin. The coordination constant increases with the extent of alkyl substitution on double bonded carbon, a tendency opposite to that on Pd(II), or Rh(I). The coordination state of olefin on molybdenum seems to differ from that on Pd(II) or Rh(I), for which π-back donation of metal d-electron is accepted to play an important role. The coordination complex on molybdenum is accordingly assigned to a π-complex with some electron donated to molybdenum. A remarkable steric effect of alkyl substituent is observed, disclosing a difference from the oxidation of uncoordinated olefin. Since k_2 increases with K, revealing a similar substituent effect of olefin, the peroxo oxygen seems to be electrophilic, and the peroxo oxygen-molybdenum bond seems to be rather covalent than ionic, thus giving rise to epoxidation.

The selective epoxidation of olefin by new peroxo complexes of molybdenum(VI) such as $MoO(O_2)_2L$[1] was found by Mimoun *et al.*,[2] followed by the demonstration by Sharpless *et al.*[3] by means of ^{18}O tracer that the peroxo oxygen of complex I is exclusively transferred to the olefin, the oxo oxygen not being involved in the oxidation:

$+ 2$ olefin $\rightarrow$ 2 epoxide $+ MoO_3 + L$ (1)

L: Ligand. HMPT Hexamethylphosphotriamide

I

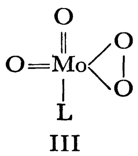
Some molybdenum salts act as an effective catalyst for the epoxidation of olefin with organic hydroperoxides.[4] The peroxo species of molybdenum such as I seems to be important as a key intermediate in the oxidation of olefins by organic peroxides. Thus the nature of interaction between molybdenum and olefin calls for further investigation. This has been done in terms of kinetic constants associated with Reaction (1).

According to Mimoun *et al.*,[2] the epoxidation of olefin by I consists of two steps; A reversible coordination of olefin to I to form a one to one adduct (complex II) and an irreversible decomposition of complex II to form epoxide.

$$\underset{\text{I}}{MoO(O_2)_2L} + \text{olefin} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \underset{\text{II}}{MoO(O_2)_2L(\text{olefin})} \qquad (2)$$

$$k_1/k_{-1} = K$$

$MoO(O_2)_2L(\text{olefin}) \xrightarrow{k_2}$



$+$ epoxide (3)

II III

We determined coordination constants K of olefin to a peroxo molybdenum complex $MoO(O_2)_2HMPT$, and rate constants k_2, for the decomposition of II to epoxides for 22 mono-olefins by kinetic measurements. From the results the nature of active oxygen of peroxo molybdenum complex and that of the interaction between olefin and molybdenum are discussed.

Experimental

Preparation of Peroxo Complex. $MoO(O_2)_2HMPT$ was prepared by the method of Mimoun *et al.*[1] 50 g (0.348 mol) of molybdenum trioxide was suspended in 250 ml of 30% hydrogen peroxide with stirring at 40 °C for 2 hr. 62.3 g of HMPT(0.348 mol) was added dropwise to the suspension and the mixture was stirred for 2 hr at 10 °C. A yellow crystalline precipitate was obtained $(MoO(O_2)_2HMPT\text{-}(H_2O))$. The precipitate was filtered off, washed three times with ethyl ether, and recrystallized from methanol solution at 40 °C; yield 76.2 g (80%). This was allowed to stand for 1 week in a cool and dark place *in vacuo* on phosphoric anhydride to remove water. Removal of water was confirmed by IR spectroscopy.

IR;

ν_{O-O} 865 cm^{-1}, 875 cm^{-1}; $\nu_{Mo<^{O}_{O}}$ *sym* 540 cm^{-1}, *asym* 595 cm^{-1}; $\nu_{Mo=O}$ 965 cm^{-1}; ν_{P-O} 1188 cm^{-1}; ν_{N-P-O} 755 cm^{-1}, 765 cm^{-1}.

Found: C, 20.34; H, 5.25; N, 11.80%. Calcd for $C_6H_{18}N_3O_4PMo$: C, 20.34; H, 5.25; N, 11.92%.

Procedure. All the runs for liquid olefin were carried out under ambient pressure with dry nitrogen in a 30 ml glass flask. The solvent used was dry ethylene dichloride. The reaction was started by addition of olefin to the ethylene dichloride solution of I. All kinetic measurements were made in the solution of a fixed concentration of I with excess olefin. When the initial concentration of olefin was changed, the corresponding amount of parafin was added to keep the total amount of hydrocarbon constant, thus avoiding a change in the solvent effect. The standard composition of the reaction mixture was as follows; $MoO(O_2)_2$ HMPT 0.05 mol/l, ethylene dichloride 9.6 mol/l, olefin 0.5—2.5 mol/l, and paraffin balance. The selectivity to epoxide being higher than 95% with respect to the active oxygen consumed, the reaction rates were measured by increase in the concentration of epoxide which was determined by gas chromatography. The runs for gaseous olefins were carried out with a conventional apparatus for gas absorption under constant pressure. The reaction rates were determined by the rates of absorption of gaseous olefins after the dissolution equilibrium had been attained. It was confirmed that epoxide formation can be followed by the absorption.

Analysis of Kinetic Result. The kinetic constants were determined according to the mechanism and rate equation given by Mimoun *et al.*[2] If the reaction of Eq. (2) is fast and the reaction of Eq. (3) is rate-determining, the rate of disappearance of the complex I is given by

$$V = -\frac{d[\mathrm{I}]}{dt} = \frac{k_2K[\text{olefin}][\mathrm{I}]}{1+K[\text{olefin}]} = k'[\mathrm{I}] \qquad (4)$$

under the present conditions of excess olefin, where k' is a constant under a fixed excess concentration of olefin, and represents the specific rate of epoxidation. The values of k' were obtained from the first-order plots with respect to I under different concentrations of olefin and plotted against the olefin concentration according to the equation

$$\frac{1}{k'} = \frac{1}{k_2} + \frac{1}{k_2K[\text{olefin}]} \qquad (5)$$

Straight lines were obtained for different olefins. k_2 and K were determined from the intercept and slope of the straight line.

For the sake of confirmation, temperature dependence of k_2 and K was examined with cyclohexene in the range 0—30 °C. The Arrhenius plots are shown in Fig. 1. Straight lines were obtained as expected. The activation energy and the heat of coordination are 17.2 kcal/mol and 5.7 kcal/mol respectively.

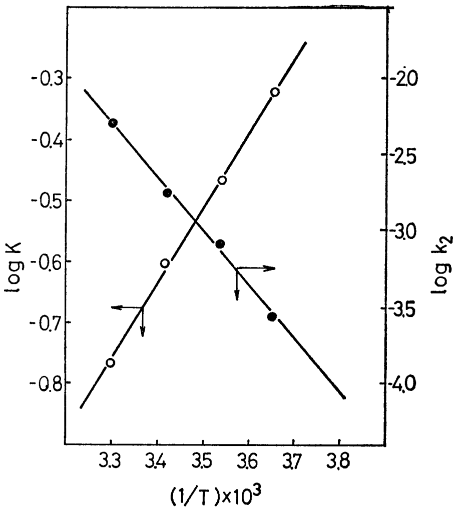


Fig. 1. The Arrhenius plots of k_2 and K with cyclohexene. Condition; olefin concentration: 1.0 mol/l, temperature: 0°C—30°C, solvent: ethylene dichloride.

Results and Discussion

The Effect of Olefin Structure on the Kinetic Constant. The epoxidation of olefins tested were selective and stereo-specific as reported by Mimoun *et al.* The kinetic constants were determined at 20 °C with 22 olefins. Values of k_2 and K are summarized in Table 1, together with the rate of epoxidation k' at 1.0 mol/l of olefin concentration.

The following general trends are indicated.

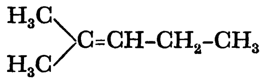
(1) The larger the reaction rate k', the larger both k_2 and K. There is a parallelism between k_2 and K.

(2) Steric effect is observed in both k_2 and K. The alkyl substitution on the double-bonded carbon

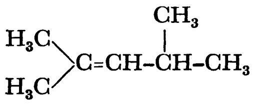
TABLE 1. KINETIC DATA OF VARIOUS OLEFINS AT 20 °C IN ETHYLENE DICHLORIDE

Type of substitution		Olefin	Rate constant $k_2\times10^3$ (s^{-1})	Coordination constant K (l/mol)	Specific rate at 1.0 mol/l-olefin $k\times10^5$ (s^{-1})
		C_4			
α	1-Butene		0.25	0.16	3.4
αβ	*cis*-2-Butene		0.87	0.27	21.5
αβ	*trans*-2-Butene		0.44	0.18_4	5.3
αα	Methyl propene		0.72	0.34	21.0
		C_5			
α	1-Pentene		0.20	0.14_4	2.5
α	3-Methyl 1-butene		0.17	0.15	2.2
αβ	*cis*-2-Pentene		1.11	0.23	16.0
αβ	*trans*-2-Pentene		0.43	0.17_4	4.9
αα	2-Methyl 1-butene		0.53	0.24	11.5
ααβ	2-Methyl 2-butene		1.65	0.39	42.8
αβ	Cyclopentene		0.81	0.23	16.4
		C_6			
α	1-Hexene		0.19	0.13	2.0
α	3,3-Dimethyl 1-butene		0.16	0.15	1.8
αα	2-Methyl 1-pentene		0.50	0.32	12.1
ααβ	2-Methyl 2-pentene		1.69	0.51	57.8
ααββ	2,3-Dimethyl 2-butene		1.96	0.80	86.2
αβ	Cyclohexene		0.89	0.25	17.8
		Others			
αβ	4-Methyl cyclohexene		0.86	0.25	17.7
ααβ	1-Methyl cyclohexene		1.22	0.33	30.4
ααβ	2,4-Dimethyl 2-pentene		1.00	0.16	10.2
ααβ	2,4,4-Trimethyl 2-pentene		0.50	0.10	4.8
ααββ	2,3-Dimethyl 2-pentene		2.08	0.77	94.7

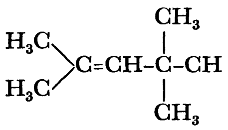
atoms by secondary or tertiary alkyl group instead of primary alkyl group reduces both k_2 and K. For example,



$k_2=1.69$
$K=0.51$



1.00
0.16



0.50
0.10

The values for *cis*-olefin are larger than those for the corresponding *trans*-olefin.

(3) In the absence of the steric effect, the values of k_2 and K increase with the number of alkyl substituents;

$$\alpha\alpha\beta\beta > \alpha\alpha\beta > \alpha\alpha,\ \alpha\beta > \alpha$$

where α and β denote the number and position respectively, of the alkyl substitution.

Interaction of Olefin with Peroxo Molybdenum Complex. The nature of metal ion-olefin complex has been extensively investigated in terms of coordination constant or stability constant.[5,6] According to Hartely,[7] metal ions can be classified into two groups by the electronic effect of olefin substituents on the stability of metal ion-olefin complex. The first group (type A), comprising Ag(I) and Cu(I), shows a decrease in stability, while the second group (type B), Ni(0), Pt(0), Pt(II), Rh(I), shows an increase in stability as the electron-withdrawing ability of the olefin substituents increases.

In order to clarify the interaction between olefin and peroxo molybdenum complex, the values of K we obtained are compared with the stability constants of acacRh(C_2H_4)-olefin determined by Cramer.[6] Both constants are plotted in Fig. 2. In order to eliminate the steric effect, comparison is made only for those olefins having primary alkyl substituents. The electronic effect of alkyl substituent is exactly the opposite in the two systems, *viz.*, K_{Mo} increases, while K_{Rh} decreases, with the extent of substitution at the double-bonded carbon. Since the alkyl substituent is electron donating, the above result indicates that Mo(VI) belongs to type A.

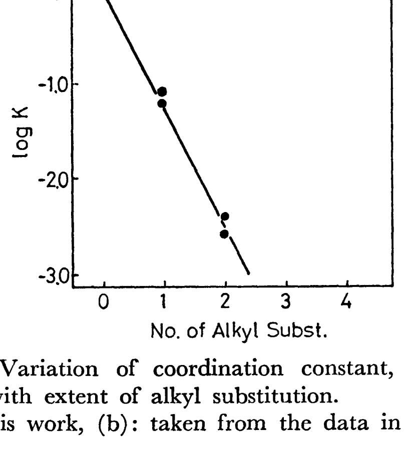


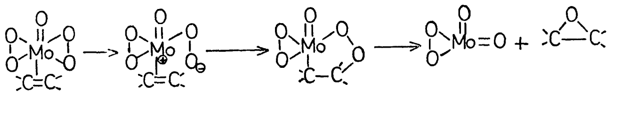
Fig. 2. Variation of coordination constant, K_{Rh} and K_{Mo}, with extent of alkyl substitution.
(a): this work, (b): taken from the data in Ref. 6.

The metal ion-olefin interaction has been interpreted in terms of the molecular orbital description of metal-olefin bond. In case of type A ion, the σ (olefin to metal) bond is important. An increase in the availability of the olefinic π-electrons increases the stability of the metal-olefin complex, while in the case of type B ion, the π(metal to olefin) bond is important and the effect of the olefinic π-electrons is opposite. This is demonstrated by the result shown in Fig. 2.

Since the formal charge of molybdenum is Mo(VI), the back-donation of olefin seems unlikely. This was suggested by Mimoun *et al.*, and confirmed by us. The steric effect and the larger coordination constant of *cis*-olefin than of corresponding *trans*-isomer are reported in π-complex.[5–7]

Effect of Alkyl Substitution on k_2. All the data of of k_2 are plotted against K in Fig. 3., where an open circle denotes secondary or tertiary alkyl-substituted olefin. k_2 appears to increase linearly with K. However there are some deviations. i) The k_2 of $\alpha\alpha$ type olefin is substantially less than that of the corresponding $\alpha\alpha\beta$ and even $\alpha\beta$, although K is of the same magnitude. It appears that $\alpha\beta$ disubstitution preferentially increases k_2. The relatively large k_2 of 2,4-dimethyl- and 2,4,4-trimethyl-2-pentene is in conformity with this tendency, while their low values of K may be due to the steric effect. ii) The k_2 of $\alpha\alpha\beta\beta$ type olefins (2,3-dimethyl-2-butene and 2,3-dimethyl-2-pentene) are not so large as expected from its K value. It is obvious that the alkyl substitution favorable for the coordination is not always favorable for the reaction of coordinated olefin, suggesting a steric effect in the reaction.

The general trend of k_2 increasing with K might be understood as a linear free energy relationship. It is also explainable in terms of reaction scheme as suggested by Mimoun *et al.*:



Since the charge transfer from olefin to molybdenum would be increased by the alkyl substitution, resulting in a more positively charged olefin molecule, the nucleophilic attack of peroxo oxygen on the coordinated olefin might be enhanced by the alkyl substitution at the double bonded carbon.

Nature of Peroxo Oxygen in the Molybdenum Complex. The nature of peroxo oxygen is examined by comparing k_2 with rates or rate constants of various addition reactions of oxygen to olefin. Rates or rate constants are plotted against the number of primary alkyl substituents on double bonded carbon of olefins (Fig. 4). The quoted values are the average of olefins of the same alkyl substituent number, the reactants being peracetic acid,[8] atomic oxygen[8] and singlet oxygen $O_2(^1\Delta_g)$.[9] The last one is accepted to be the active species of dye-sensitized photo-oxidation to form allylic peroxide. These three reactants are admittedly electrophilic and directly attack the unsaturated carbon atom.[10,11]

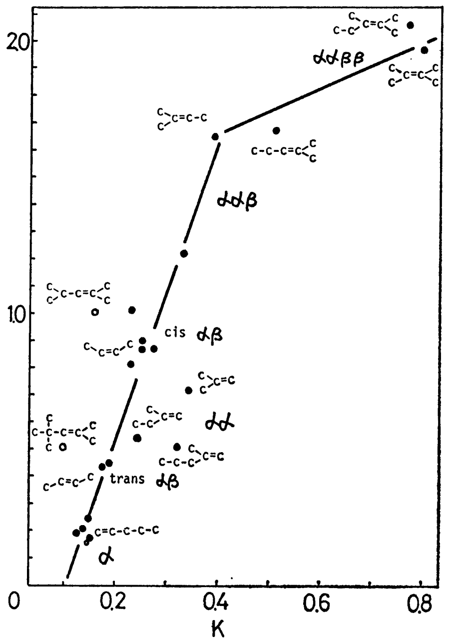


Fig. 3. Correlation between k_2 and K for olefins.

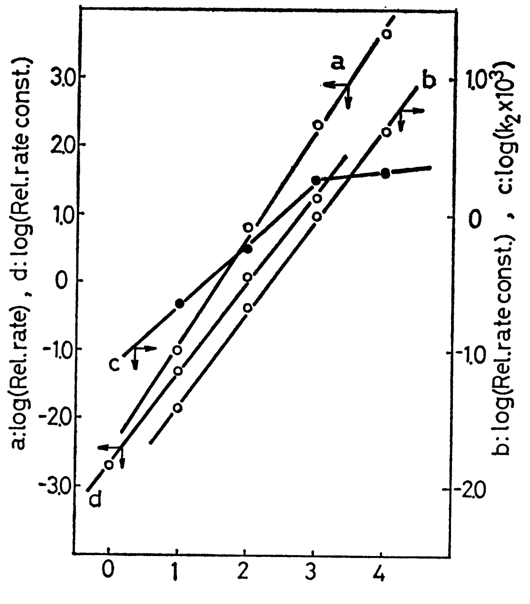


Fig. 4. Relative rate or rate constant of electrophilic oxygen as functions of number of alkyl substituents on double bonded carbon atom.

a: $O_2(^1\Delta g)$ Relative rate. Taken from the data in Ref. 10. b; O(3P) Relative rate constant. Taken from the data in in Ref. 8. c: k_2x10^3 of this work. d: Peracetic acid Relative rate constant. Taken from the data in Ref. 8.

Since k_2 increases with the extent of alkyl substitution as other rate or rate constants (Fig. 4), the peroxo oxygen in $MoO(O_2)_2$HMPT can be accepted as electrophilic.

The results are in line with the suggestion made by Mimoun *et al.* on the basis of k' instead of k_2 we have examined. This would be expected if k' runs parallel with k_2. However, since k' is a function of k_2, K and olefin concentration, there should be difference between k' and k_2. In fact, k_2 remarkably deviates from the linear relationship with K (Fig. 3), whereas k' is approximately linear with respect to K. A similar feature is obvious in Fig. 4. The k_2 of ααββ olefin is substantially less than expected from linearity, whereas the linearity is extended to include ααββ olefin for the other three, non-coordinated oxygen species. Another feature characteristic of k_2 would be the steric effect of olefin, which is not observed with the other three compounds. Such characteristic features observed with k_2 are assumed to be caused by the required coordination of olefin to molybdenum.

The selective epoxidation of olefin by $MoO(O_2)_2$-HMPT complex should be explained in terms of the electrophilic nature of peroxo oxygen. In fact, oxygen anion O^- and superoxide O_2^- having negative values of electron affinity do not give epoxide, whereas the atomic oxygen and $O_2(^1\Delta_g)$ have positive values and give epoxide. Oxygen complexes of group VIII metals are also known to be ineffective for epoxidation. Cook *et al.* estimated the effective charge of coordinated oxygen in $PtO_2(P\phi_3)_2$ as $O_2^{1.8-}$ by means of ESCA.[12] Since the electrophilicity of oxygen depends on its effective charge, the electrophilic nature of peroxo oxygen suggests that the peroxo oxygen has a much lower effective charge than its formal one O_2^{2-}. The higher selectivity of epoxidation by molybdenum complex, in constrast to group VIII metal complexes, may be understood on the basis of different effective charges of O_2 in the complexes.

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