Oxidation of Styrene Oxide by Diperoxomolybdenum(VI)

ÉVA ZÁHONYI-BUDÓ and LÁSZLÓ I. SIMÁNDI*

Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary

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Diperoxomolybdenum(VI) complexes of the formula $MoO(O_2)_2L$, where L is hexamethylphosphoramide (HMPT), dimethylformamide, etc., have been reported to act as stoichiometric reagents for olefin epoxidation [1, 2]. These complexes as well as their monoperoxo analogs also effect selective oxygen atom transfer to various other organic substrates [3–7]. Epoxides too react with peroxomolybdenum complexes; that is why a high excess of olefin must be used to achieve selective epoxidation [1, 2]. Even under such conditions, oxidative cleavage products were consecutively formed, when olefins were epoxidized by the very reactive monoperoxo complex $MoO(O_2)L_2Cl_2$ [8]. The details of epoxide oxidation in these systems have not yet been reported. We have found that epoxidation of propylene by $MoO(O_2)_2HMPT$ shows an autocatalytic behaviour [9], indicating an important role of the epoxide in this reaction. In order to obtain more information, we investigated the reaction of styrene oxide with $MoO(O_2)_2HMPT$ (**I**). The results are discussed in this paper.

The reaction, carried out under dry nitrogen at 30 °C in dichloroethane as solvent, was followed by gas chromatography and arsenometric titration of the peroxo-oxygen, using the procedure of Siggia [10]. The time course of the reaction of styrene oxide (STO) with complex **I** is illustrated in Fig. 1. Gas-chromatographic product analysis shows 1 mole of benzaldehyde formed per 2 mole STO and 1 mole of **I** consumed. No other product could be detected by GC. The second molecule of STO could be traced by hydrolysis of the product solution with MeOH/HCl, affording Ph–CHOH–CH_2OMe, which can also be made by the hydrolysis of styrene oxide. This indicates that the second STO that disappeared in the reaction did not undergo oxidation, but had entered the coordination sphere of Mo probably via ring opening (*cf.* **II**). As complex **I** has 4 oxidation equivalents (formally 2 atoms of active O), the stoichiometric equation of STO oxidation should be:

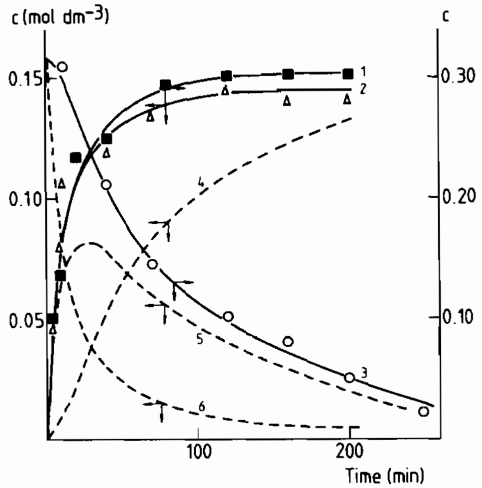
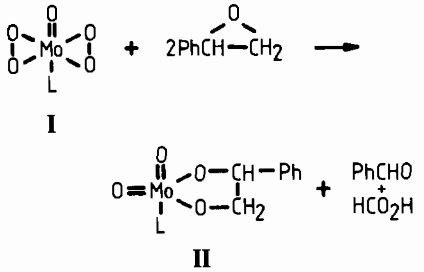


Fig. 1. Time course of the oxidation of styrene oxide (STO) by $MoO(O_2)_2HMPT$ (I) (t = 30 °C; solvent: dichloroethane; $[STO]_0 = 0.330$ mol dm^{-3}; $[I]_0 = 0.158$ mol dm^{-3}). 1, $[STO]_0 - [STO]$; 2, $[PhCHO]_{exp}$; 3, [O] (O-atom dm^{-3}); 4, $[PhCHO]_{free}$; 5, [complex III]; 6, [complex I]. Curves 4, 5 and 6 are calculated from experimental data using eqns. (4)–(6).



I

II

(1)

The formic acid co-product required by eqn. (1) has been detected by HPLC in the aqueous solution obtained by steam distillation of evaporated and acidified (50% H_3PO_4) samples; yield 70%.

Reaction (1) is followed by secondary transformations, as indicated by the evolution of *ca.* 15% CO_2 and the appareance of ν(Mo–O–Mo) at *ca.* 800 cm^{-1} in the product spectrum [1]. They involve further oxidation of formic acid, probably by **II**, accompanied by dimerization of the reduced complexes, which is the reason why the major product **II** could not be isolated in pure form. However, the solid product precipitated with ether revealed ^1H NMR signals at 3.6 and 4.7 ppm, assignable to methylene and methine protons, respectively.

According to Fig. 1, the consumption of STO is initially much faster than the decrease in active oxygen atom content, *i.e.* STO oxidation to benzaldehyde. This time-lag clearly shows the accumulation of an intermediate. In the IR spectrum of the reacting

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*Author to whom correspondence should be addressed.

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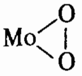
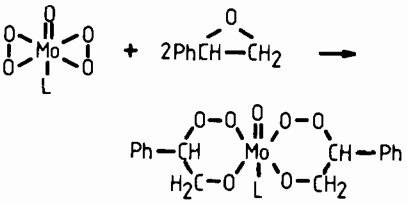
solution, the strong ν(O–O) band at 870 cm^{-1}, characteristic of **I**, disappeared within 60 min under the conditions given in Fig. 1. Remarkably, no new peroxo band could be observed despite the significant amount of peroxo oxygen found in the same sample by titration. We propose that the new peroxo complex, which (i) contains titratable (active) peroxo oxygen, but (ii) lacks the



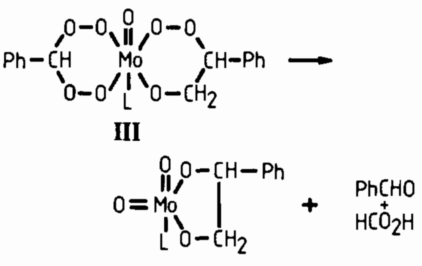
moiety and exhibits no intensive ν(O–O) band, and (iii) contains STO or its unoxidized (open-ring) derivative, has the structure **III** and is formed according to eqn. (2).


(2)

III

Peroxo–platinum complexes of a similar type, having 5-membered rings, have been reported to show very weak ν(O–O) bands [11]. Attempts to isolate molybdenum complexes of type **III** failed, but our results may provide indirect evidence for their existence, already supposed by Frimer to explain the oxidative cleavage of dihydropyran [5].

Decomposition of **III** to the final products requires apparently the breaking of both O–O bonds and one of the C–C bonds:


III

II

(3)

The mechanism of this decomposition is not known. The possibility of formation of free formaldehyde and its consecutive oxidation to formic acid can be excluded, as aldehydes, including formaldehyde, cannot be oxidized by the starting complex, and the same oxidation by **III** seems unlikely. Formic acid might be formed in the coordination sphere of molybdenum, after benzaldehyde elimination.

Decomposition (3) is relatively slow under the reaction conditions employed, but it occurs promptly at the high temperature of the injector, when the samples are analyzed by gas chromatography. Therefore

$$[\mathrm{PhCHO}]_{\mathrm{exp}} = [\mathrm{PhCHO}]_{\mathrm{free}} + [\mathbf{III}] \tag{4}$$

Using eqn. (4) and the mass balances

$$\frac{[\mathrm{O}]}{2} = [\mathbf{I}] + [\mathbf{III}] \tag{5}$$

$$[\mathrm{PhCHO}]_{\mathrm{free}} = [\mathbf{I}]_0 - \frac{[\mathrm{O}]}{2} \tag{6}$$

where [O] is the titratable (active) peroxo oxygen concentration, the individual concentrations of the two kinds of peroxo complexes can be evaluated; their time-dependence is shown in Fig. 1 by curves 5 and 6.

The strong interaction found between peroxomolybdenum(VI) and epoxides, which leads to oxidative cleavage of the latter, may have additional importance in the epoxidation of olefins. The role of epoxides in the reaction of olefins with peroxomolybdenum complexes is currently being investigated in this laboratory and will be dealt with in a forthcoming paper.

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