PRJ, Vol. 5 (January 1993); P. 62–66, 6 FIGS, 3 TABLES.

KINETICS OF FORMATION OF EPICHLOROHYDRIN FROM ALLYL CHLORIDE BY HYDROGEN PEROXIDE USING SODIUM MOLYBDATE AS CATALYST

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حركية الحصول على الأبيكلورهيدرين من الأليل كلوريد مع ما فوق أوكسيد الهيدروجين باستعمال موليبدات الصوديوم كعامل حفاز

إفتخار أحمد و عبدالرزاق اللبيب

لقد تمت دراسة حركية وسبل الحصول على الأبيكلورهيدرين من الأليل كلوريد مع ما فوق أوكسيد الهيدروجين بوجود موليبدات الصوديوم كعامل حفاز، وكانت معادلة التفاعل من الدرجة الأولى بالنسبة للأليل كلوريد وكذلك بالنسبة لموليبدات الصوديوم ، وكانت من الدرجة صفر بالنسبة لما فوق أوكسيد الهيدروجين.

كما تمت دراسة تأثير تركيز أيون الهيدروجين على سرعة التفاعل. وتم تحديد طاقة التنشيط واقتراح طريقة التفاعل.

ABSTRACT

The kinetics and mechanism of formation of epichlorohydrin from allyl chloride by hydrogen peroxide in the presence of sodium molybdate as catalyst have been studied. The reaction is first order with respect to oth allyl chloride and sodium molybdate but zero order with respect to hydrogen peroxide. The effect of pH on the reaction rate is also studied. The energy of activation has been determined. A reaction mechanism has also been proposed.

INTRODUCTION

Epichlorohydrin is an important petrochemical which is a base material in the manufacture of epoxy resins. Epoxy resins have become firmly well established in countless applications and techniques. They are used as adhesives, coating and flooring materials. They have applications in paint and varnish industries. The other major use for epichlorohydrin is in the manufacture of synthetic glycerin. Minor applications include its use in epichlorohydrin based rubber, wet strength resins for paper industry, ion exchange resins, surface active agents, inks, dyes, asphalt improvers, corrosion inhibitors, antistats, textile additives and bioproducts. Currently, epichlorohydrin is produced [1] by the chlorohydrination of allyl chloride, derived by chlorination of propylene but the yield is limited to 60–65%.

Many papers and patents have been devoted to the epoxidation of olefins with hydrogen peroxide in the presence of some oxy-compounds of metals such as W, Mo, V, Os, Ti, Zr, Th, Nb, Ta, Cr, Ru and Se [2–5]. The present paper deals with the manufacture of epichlorohydrin from allyl chloride by using hydrogen peroxide as an epoxidising agent in the presence of sodium molybdate as catalyst.

EXPERIMENTAL SECTION

All the chemicals used were of analytical (B.D.H.) grade. The concentration of hydrogen peroxide in kinetic runs was measured colorimetrically as described elsewhere [6]. 0.1 M sodium hydroxide solution prepared in isopropanol was used to maintain the required pH of the medium. Measured quantities of allyl chloride, sodium molybdate, sodium hydroxide solution (to maintain required pH) and solvent (50:50 v/v mixture of water and isopropanol) were taken in a stoppered round bottom flask and placed

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in thermostated water bath at 50±0.1°C unless mentioned otherwise. After the reactants had reached thermostated temperature, the reaction was started by addition of temperature equilibrated hydrogen peroxide. The kinetics were followed by examining 5 ml aliquots of the reaction mixture for hydrogen peroxide content. The aliquots were added to 5 ml of titanium sulphate solution to stop the reaction. Optical density was measured at 420 nm, and the concentration of hydrogen peroxide was read from the calibration graph.

The presence of epichlorohydrin as a reaction product was confirmed by using Chrompack Packard Gas Chromatograph (model 439) equipped with flame ionisation detector. The column used was 10 m long packed with WCOT fused silica and cp-sil-5CB. Nitrogen was used as a carrier gas.

RESULTS AND DISCUSSION

The progress of the reaction was observed by measuring the disappearance of hydrogen peroxide in the presence of high concentration of allyl chloride. Isolation method is applied for determining the order of reaction. The plot of hydrogen peroxide concentration against time were straight lines (Fig. 1) indicating zero order dependence of rate on hydrogen peroxide concentration. Pseudo-zero-order rate constants were calculated from the slope of these lines and tabulated in Table 1 as k_{obsd}.

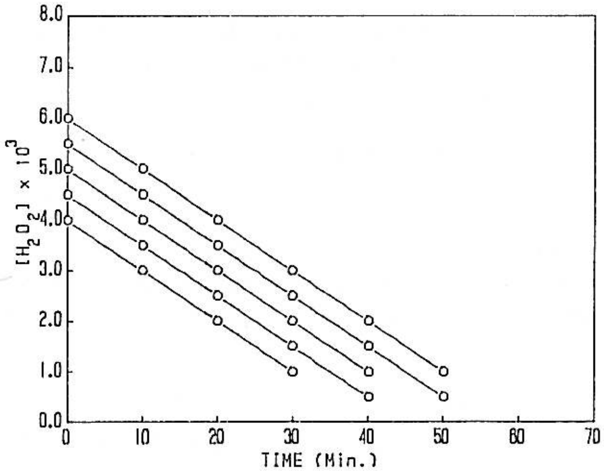


FIG. 1. Pseudo-zero order dependence of rate on hydrogen peroxide concentration.

The order of reaction with respect to catalyst (sodium molybdate) concentration was determined by varying the catalyst concentration and keeping all other variables, such as temperature, pH, concentrations of hydrogen peroxide and allyl chloride constants. k_{obsd} was calculated from the slope of the plots of hydrogen peroxide concentration versus time. The plot of k_{obsd} against the concentration of sodium molybdate was a straight line (Fig. 2) which passes through the origin. This shows first order dependence of rate on catalyst concentration and it also confirms that there is no reaction in the absence of sodium molybdate.

Table 1. Pseudo-Zero-Order Rate for the Oxidation of Allyl Chloride by Hydrogen Peroxide in the Presence of Sodium Molybdate

$[H_2O_2] \times 10^3$ (M)	$k_{obsd} \times 10^6$ (mole dm^{-3} sec^{-1})
4.00	8.14
4.50	8.02
5.00	8.15
5.50	8.23
6.00	8.18

[Allyl chloride] = 20.00×10^{-2} M; $[Na_2MoO_4] = 5.00 \times 10^{-4}$ M; pH, 5.0; Temp. 50°C, solvent, 50% v/v isopropanol.

Similarly the order of reaction with respect to allyl chloride was also determined by varying allyl chloride concentration and keeping all other variables constant. k_{obsd} were calculated from the slope of plots of $[H_2O_2]$ versus tme. k_{obsd} is directly proportional to the concentration of substrate [allyl chloride]. This is indicative of first order dependence of rate on substrate concentration. The results are presented in Table 2.

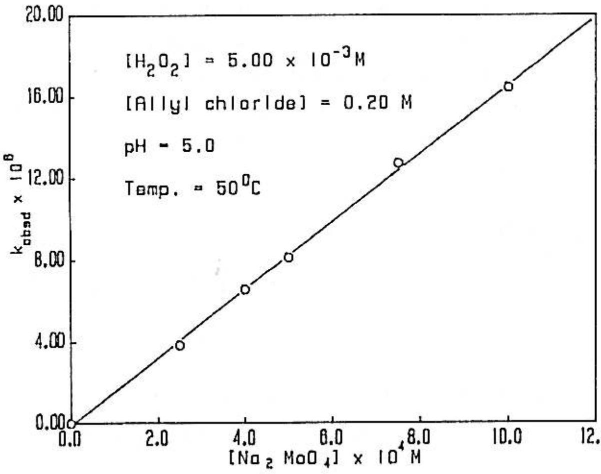


FIG. 2. First order dependence of rate on catalyst concentration.

Preliminary studies have shown that under our experimental conditions, hydrogen peroxide does not change allyl chloride into epichlorohydrin without the presence of catalyst (sodium molybdate) and also the catalyst alone without hydrogen peroxide fails to bring allyl chloride into epichlorohydrin. This suggests the involvement of some oxygenated form of molybdenum in the process as

Table 2. First Order Dependence of Molybdate Catalysed Oxidation Rate of Allyl Chloride on the Concentration of Allyl Chloride

[Allyl chloride] × 10^2 (M)	$k_{obsd} \times 10^5$ (mole dm^{-3} sec^{-1})	$\frac{k_{obsd}}{[\text{Allyl chloride}]} \times 10^3$
10.00	0.81	0.270
20.00	1.21	0.269
30.00	1.63	0.272
40.00	2.03	0.271
50.00	2.41	0.268

$[H_2O_2]=5.00\times10^{-3}$ M; $[Na_2MoO_4]=5.00\times10^{-4}$ M; pH, 5.0, Temp., 50°C; Solvent 50% v/v isopropanol.

oxygen carrier. In aqueous solution molybdate ions hydrolyse into the acid anions as in eqn. (1) and (2):

$$Mo_4^{2-}+H^+ \rightleftharpoons HMo_4^- \tag{1}$$

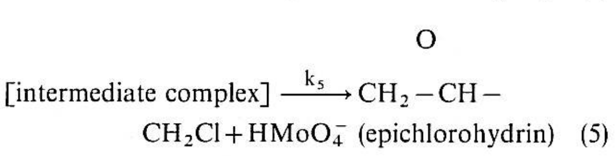
$$HMo_4^- +H^+ \rightleftharpoons H_2MoO_4 \tag{2}$$

It may be recalled that molybdic acid is converted to peroxymolybdic acid [7, 8] when treated with aqueous hydrogen peroxide which suggests that hydrogen peroxide rapidly and completely oxidise acid anions to peroxyacid anions as in eqn. (3):

$$HMoO_4^- +H_2O_2 \rightarrow HMoO_5^- +H_2O \tag{3}$$

It is presumed here that in the system under investigation peroxymolybdate anion ($HMoO_5^-$) is the epoxidising species and in rate-controlling step it reacts with allyl chloride giving epichlorohydrin and regenerating molybdate anion ($HMoO_4^-$). Molybdate anion is then reconverted into peroxymolybdate anion by hydrogen peroxide. The following indicates the most probable mechanism:

$$CH_2=CH-CH_2Cl+HMoO_5^- \underset{k_4}{\overset{k_3}{\rightleftharpoons}} [\text{intermediate complex}] \tag{4}$$



$$[\text{intermediate complex}] \xrightarrow{k_5} \overset{O}{CH_2-CH}-CH_2Cl+HMoO_4^- \text{ (epichlorohydrin)} \tag{5}$$

Assuming steady-state for the concentration of intermediate complex, the rate of reaction is given by eqn. (6):

$$\text{Rate of reaction}=k_5\,[\text{intermediate complex}] \tag{6}$$

Applying steady state approximation for intermediate complex,

$$k_3\,[CH_2=CH-CH_2Cl]\,[HMoO_5^-]-k_4\,[\text{intermediate complex}]-k_5\,[\text{intermediate complex}]=0 \tag{7}$$

Thus,

$$[\text{intermediate complex}]=\frac{k_3\,[CH_2=CH-CH_2Cl]\,[HMoO_5^-]}{k_4+k_5} \tag{8}$$

Substituting eqn. (8) into eqn. (6) gives:

$$\text{Rate of reaction}=\frac{k_3k_5\,[CH_2=CH-CH_2Cl]\,[HMoO_5^-]}{k_4+k_5} \tag{9}$$

Or

$$\text{Rate of reaction}=k\,[CH_2=CH-CH_2Cl]\,[HMoO_5^-] \tag{10}$$

where, $k=\frac{k_3k_5}{k_4+k_5}$

For each experimental set, the pH and catalyst concentration were constant. Then eqn. (10) in terms of catalyst concentration is:

$$\text{Rate of reaction}=k'\,[CH_2=CH-CH_2Cl]\,[Na_2MoO_4] \tag{11}$$

As discussed in the previous section, the progress of the reaction was observed by measuring the disappearance of hydrogen peroxide, which is represented by the following:

$$\text{Rate of reaction}=k'\,[CH_2=CH-CH_2Cl]\,[Na_2MoO_4] \tag{12}$$

or,

$$\text{Rate of reaction}=k_{obsd} \tag{13}$$

where,

$$k_{obsd}=k'\,[CH_2=CH-CH_2Cl]\,[Na_2MoO_4] \tag{14}$$

Eqn. (12) explains the observed order of reaction with respect to allyl chloride, catalyst (Na_2MoO_4) and hydrogen peroxide.

It has been reported [9] earlier that the formation of $HMoO_4^-$ is maximum around pH 3.6. The rates of reaction catalysed by molybdate increase with increasing pH and are maximum at the pH at which $HMoO_4^-$ formation is maximum and thereafter the rates decrease with further increase in pH (Fig. 3). This clearly suggests that peroxymolybdic acid anion is the epoxidizing agent. At this stage it looks instructive to argue why negative charged peroxymolybdate anion and not the unionised peroxymolybdate acid attacks the double bond of the allyl chloride.

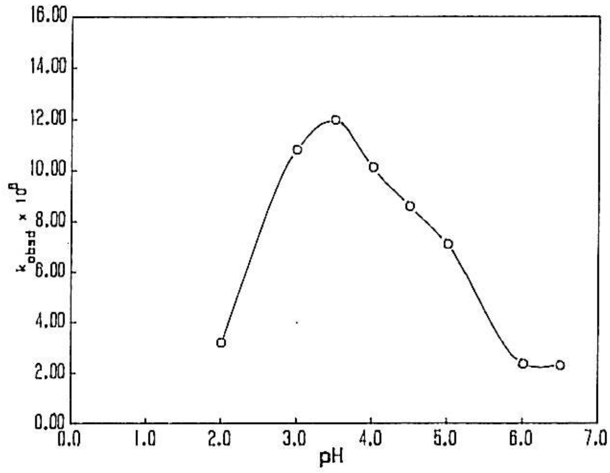


FIG. 3. Dependence of rate on pH of the medium.

In view of the intramolecular hydrogen bond in the epoxidation of olefins by organic peracids [10, 11] and the fact that molybdate has the maximum catalytic activity at a pH where concentrations of the peroxymolybdic acid anion species ($HMoO_5^-$) is maximum. It is proposed that peroxymolybdic acid anion (I) in Fig. 4 is in equilibrium with hydrogen bonded cyclic structure (II) which due to partial positive charge on the peroxy oxygen acts like an electrophile. The proposed transition state of the reaction is shown in Fig. 5.

The reaction was studied at six different temperatures ranging from 35 to 60°C, and the results are given in Table 3. The plots of log k_{obsd} against reciprocal of temperature (1/T) gave a straight line (Fig. 6).

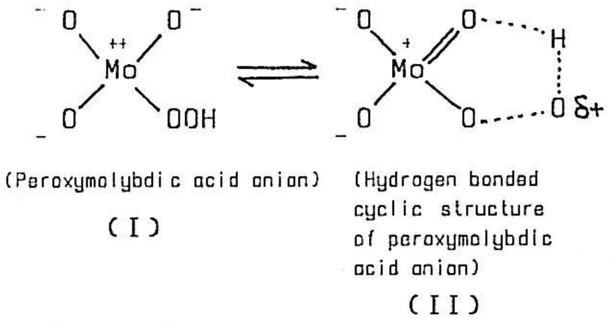


FIG. 4. Cyclic structure of peroxymolybdic acid.

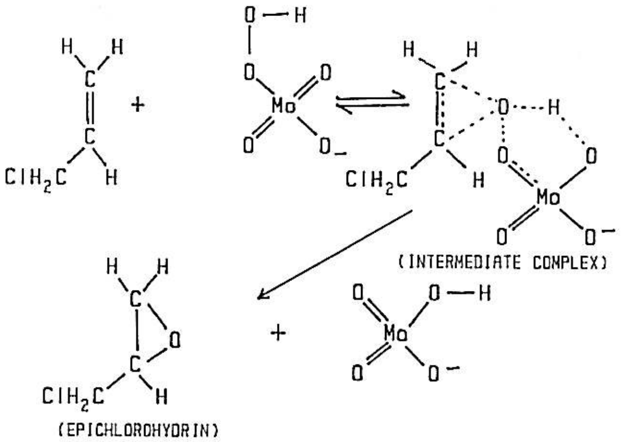


FIG. 5. Mechanism of the reaction.

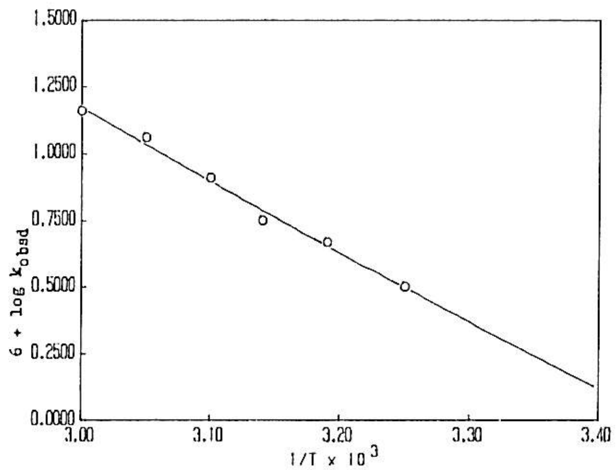


FIG. 6. Dependence of rate on variation of temperature.

Table 3. Effect of Temperature on the Formation of Epichlorohydrin Rate

Temperature (K)	$\frac{1}{T} \times 10^3$	$k_{obsd} \times 10^6$ (mol dm^{-3} sec^{-1})	$6 + \log k_{obsd}$
308	3.25	3.16	0.4997
313	3.19	4.68	0.6702
318	3.14	5.62	0.7497
323	3.10	8.14	0.9106
328	3.05	11.48	1.0599
333	3.00	14.45	1.1599

$[H_2O_2] = 5.00 \times 10^{-3}$ M; $[Na_2MoO_4] = 5.00 \times 10^{-4}$ M; pH, 5.0 [Allyl Chloride] = 0.20 M; Solvent, 50% v/v isopropanol.

The energy of activation was calculated from the slope of this plot to be 51.06 kJ ml^{-1}.

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