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KINETICS AND MECHANISM OF CLEANER PRODUCTION OF EPICHLOROHYDRIN

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A R T I C L E I N F O

A B S T R A C T

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. Currently, epichlorohydrin is produced by chlorohydrination of allyl chloride, derived by chlorination of propylene but the yield is limited to 60-65%. The process also releases chlorine causing air pollution problems in the area.

This paper presents another alternative method of production of epichlorohydrin from allyl chloride using hydrogen peroxide as an oxidant and sodium tungstate or sodium molybdate as catalysts. This process will be environmentally safer and a cleaner process. The kinetics and mechanism of this process have been studied. The reaction is first order with respect to allyl chloride and catalyst (sodium tungstate or sodium molybdate) but zero order with respect to hydrogen peroxide. The energy of activation has been determined. A reaction mechanism has also been proposed.

1.   Introduction

Epichlorohydrin is a petrochemical which is used in the manufacture of epoxy resins. Epoxy resins have countless applications. 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 glycerine. 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. Curently, epichlorohydrin is produced [1] by chlorohydrination of allyl chloride, derived by chlorination of propylene which is not environmentally safe process since chlorine is released during this process. An alternative method cleaner production of epichlorohydrin from allyl chloride is described in this paper. In this process hydrogen peroxide is used as an oxidant and sodium tungstate and sodium molybdate have been used as catalysts.

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 epoxidizing agent in the presence of sodium tungstate and sodium molybdate as catalysts.

2.   Experimental Section

All the chemicals used were of Analar (B.D.H.) grade. The concentration of hydrogen peroxide in kinetic runs was measured colorimetrically as described elsewhere [6]. 0.1M sodium hydroxide solution prepared in isopropanol was used to maintain the required pH of the medium. Measured quantities of allyl chloride, catalyst (sodium tungstate or sodium molybdate), sodium hydroxide solution (to maintain the required pH) and solvent (50:50 v/v mixture of water and isopropanol) were taken in a stoppered round bottom flask and placed 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 ionization detector. The column used was 10 m long packed with WCOT fused silica and cp-sil-5CB. Nitrogen was used as a carrier gas.

3.   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 concentrations against time were straight lines indicating zero order dependence of rate on hydrogen peroxide concentration. Pseudo-zero-order rate constants (k_{obsd}) were calculated from the slope of these lines and tabulated in Table-1.

Table – 1: Pseudo-zero-order rate for the epoxidation of allyl chloride by hydrogen peroxide in the presence of catalyst.

[H$_2$O$_2$] x 10^3 (M)	k_{obsd} x 10^6 (in mol dm^{-3} sec^{-1})	
	Na$_2$WO$_4$ Catalyst	Na$_2$MoO$_4$ Catalyst
4.00	12.38	8.14
4.50	12.39	8.02
5.00	12.36	8.15
5.50	12.35	8.23
6.00	12.39	8.18
Average k_{obsd} (mol dm^{-3} sec^{-1})	12.37 $\pm$ 0.018	8.14 $\pm$ 0.078

[Allyl chloride] = 20.00 x 10^{-2} M ; [Na$_2$WO$_4$ or Na$_2$MoO$_4$] = 5.00 x 10^{-4}M ; pH = 6.0 ; Temp., 50 °C ; Solvent, 50% v/v

The order of reaction with respect to catalyst (sodium tungstate or 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 catalyst was a straight line (Fig. 1) 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 catalyst.

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$_2$O$_2$] versus time. k_{obsd} is directly proportional to the concentration of allyl chloride (Fig.2). This shows first order dependence of rate on substrate concentration.

Preliminary studies have shown that under our experimental conditions, hydrogen peroxide does not change allyl chloride into epichlorohydrin without the presence of catalyst and also the catalyst alone without hydrogen peroxide fails to bring allyl chloride into epichlorohydrin. This suggests the involvement of some oxygenated form of catalyst (tungsten or molybdenum) in the process as oxygen carrier and the source of oxygen is hydrogen peroxide. In aqueous solution molybdate ions hydrolyze into the acid anions as in eqns. (1) and (2).

$$MO_4^{2-} + H^+ \rightleftharpoons HMO_4^- \qquad \ldots\ldots\ldots\ldots (1)$$

$$HMO_4^- + H^+ \rightleftharpoons H_2MO_4 \qquad \ldots\ldots\ldots\ldots (2)$$
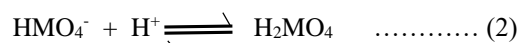
Where, M is W or Mo.

It may be called that tungstic acid and molybdic acid are converted to peroxytungstic acid and peroxymolybdic acid, respectively when treated with aqueous hydrogen peroxide which suggests that hydrogen peroxide rapidly and completely oxidize acid anions to peroxyacid anions as shown below:
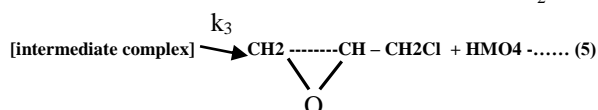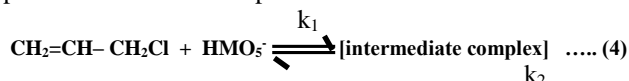
$$HMO_4^- + H_2O_2 \longrightarrow HMO_5^- + H_2O \quad \ldots\ldots (3)$$
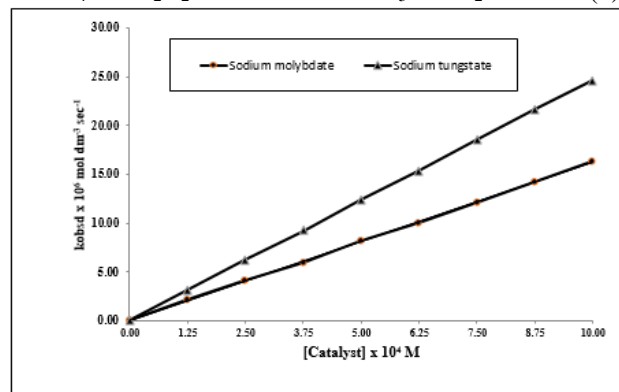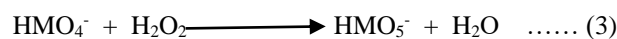
[H$_2$O$_2$] = 5.00x10^{-3}M ; [Allyl chloride] = 0.20 M ; pH, 5.0; Temp., 50 °C ; Solvent, 50% v/

Fig. 1: First order dependence of rate on catalyst concentration
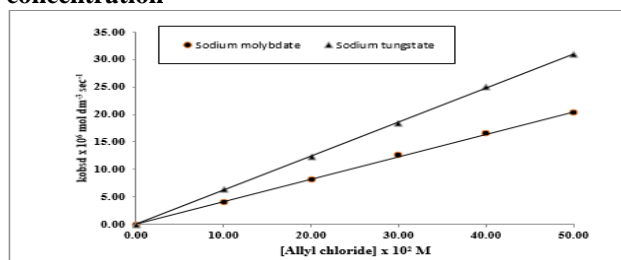
H_2O_2] = 5.00 x10^{-3}M ; [Catalyst] = 5.00x10^{-4}M; pH, 5.0
Temp., 50 °C; Solvent 50% v/v

Fig.2: First order dependence of rate on allyl chloride concentration

It is presumed here that in the system under investigation peracid anion (HWO_5^- or $HMoO_5^-$) is the epoxidizing species and in rate-controlling step it reacts with allyl chloride giving epichlorohydrin and regenerating acid anion (HWO_4^- or $HMoO_4^-$). Acid anion is then reconverted into peracid anion by hydrogen peroxide. The most probable mechanism is presented below:

$$CH_2=CH–CH_2Cl + HMO_5^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{[intermediate complex]} \quad \text{..... (4)}$$

$$\text{[intermediate complex]} \overset{k_3}{\rightarrow} CH_2\text{--------}CH – CH_2Cl + HMO_4^- \text{...... (5)}$$
$$O$$

The rate of reaction was calculated considering intermediate concentration into steady-state.

Rate of reaction= k' [CH$_2$ = CH – CH$_2$Cl] [Na$_2$MO$_4$] [H$_2$O$_2$]^0 ... (11)

Or, Rate of reaction = k$_{obsd}$ [H$_2$O$_2$]^0 .... (12)

Where, k$_{obsd}$ = k'[CH$_2$ = CH-CH$_2$Cl] [Na$_2$MO$_4$] .... (13)

The equation (11) explains the observed order of reaction with respect to allyl chloride, catalyst and hydrogen peroxide.

The reaction of epoxidation of allyl chloride in presence of sodium molybdatre catalyst was studied at six different temperatures ranging from 35 to 60 °C, and the rate constants were calculated and presented in Table-2. The plots of log k_{obsd} against reciprocal of temperature (1/T) gave straight line (Fig. 3). The energy of activation was calculated from the slopes of the plot to be 51.06 kJ mol^{-1}.

Table 2: Effect of temperature on the formation of epichlorohydrin

Temp. (K)	1/T x 10^3	k$_{obsd}$ x10^6 (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
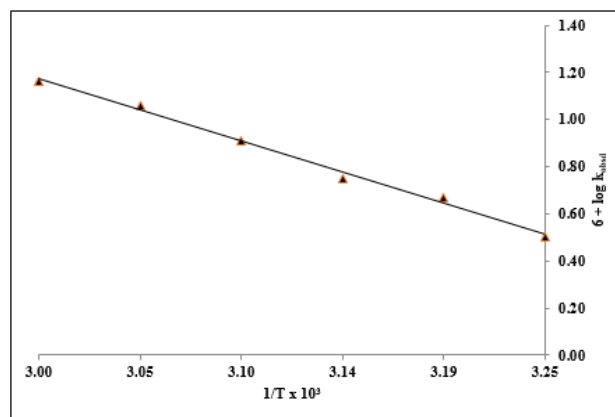
[H_2O_2] = 5.00x10^{-3}M ; [Na_2MoO_4] = 5.00x10^{-4}M ; pH, 5.0 ;
Solvent 50% v/v isopropanol

Fig.3: Dependence of rate on temperature

4. References

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