PRJ, Vol. 8 (January 1996): P. 75–78, 2 FIGS, 3 TABLES.

Production of Glycerine by Tungstate Catalyzed Oxidation of Allyl Alcohol by Hydrogen Peroxide: a Kinetic and Mechanistic Study

Iftikhar Ahmad* and Masood Degam*

دراسة تركيب وحركية أليل الكحول مع فوق أكسيد الهيدروجين في وجود التنجستات كعامل حفاز لنتاج الجلسرين

أفتخار أحمد و مسعود دغيم

تمت دراسة حركية وميكانيكية الحصول على الجلسرين من أليل الكحول بواسطة فوق أكسيد الهيدروجين في وجود تنجستات الصوديوم كعامل مساعد. كان التفاعل من الدرجة الأولى بالنسبة إلى أليل الكحول والعامل المساعد ومن درجة الصفر بالنسبة إلى فوق أكسيد الهيدروجين.

أما بالنسبة لحركية تكوين الجلسرين فهي عملية أكسدة أليل الكحول إلى جليسيدول ومن ثم إلى جلسرين وهي تعتمد على تأثير الملح وأحلاله لحركية تكوين الجليسيدول وهي عملية ترتكز على الضاحية القطبية (الكتروفيلك). وقد تم حساب طاقة التنشيط وكانت 68.9 (كيلوجول/مول$^{1-}$).

Abstract *The kinetics and mechanism of formation of glycerine from allyl alcohol by hydrogen peroxide in the presence of sodium tungstate as catalyst have been studied. The reaction is first order with respect to allyl alcohol and catalyst and zero order with respect to hydrogen peroxide. The mechanism of formation of glycerine is considered to be through epoxidation of allyl alcohol to glycidol and then hydrolysis of glycidol to glycerine. Based on substituent and salt effects the mechanism of formation of glycidol is believed to be concerted with considerable polar (electrophilic) character. The energy of activation has been calculated to be* 68.9 kJ mol^{-1}.

INTRODUCTION

Glycerine is a chemical which enjoys wide use in industry because of both its chemical and physical properties. Its major use as a chemical is in the manufacture of alkyds resins. Glycerine is also used in drugs, cosmetics, tobacco, food and beverages, explosives, manufacture of cellophanes and polyethers. Glycerine is produced as a by-product in soap industry. It is also produced (Lowenheim and Moran, 1975) synthetically as petrochemical from propylene via either allyl chloride or acrolein as intermediates. Another possible synthetic route of manufacturing of glycerine is from the oxidation of allyl alcohol by hydrogen peroxide using tungstic acid or its salt as catalyst. This paper describes the kinetics and mechanism of the formation of glycerine from allyl alcohol by hydrogen peroxide using sodium tungstate as catalyst.

EXPERIMENTAL

All the chemicals used were of B.D.H. (Analar) grade. Hydrogen peroxide was standardized (Kolthoff *et al.*, 1969) by permanganate method and allyl alcohol was standardized using bromate-bromide procedure (Lucas and Pressman, 1938). The ionic strength of the reaction mixture was maintained by the addition of sodium perchlorate. The pH of the reaction mixture was adjusted by addition of perchloric acid solution. In the kinetic runs, the concen-

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*Petroleum Research Centre P.O. Box 6431, Tripoli, G.S.P.L.A.J.

tration of hydrogen peroxide was measured colorimetrically (Reichert *et al.*, 1939, Ahmad and Degam, 1991).

The kinetics of the reaction was followed by monitoring the concentration of hydrogen peroxide. Every run was at least 90% complete. After the reactants had reached thermostat temperature, the reaction was started by addition of hydrogen peroxide. The kinetics were followed by examining 5 ml aliquots of the reaction mixture for hydrogen peroxide content. The aliquots were added to a test tube which already contains 10 ml distilled water and 5 ml titanium sulphate solution to stop the reaction. Optical density of this solution was measured at 420 nm and the concentrtion of hydrogen peroxide was read from a calibration graph.

The concentration of glycerine was measured quantitatively by using gas chromatographic technique. Chrompack Packard Gas Chromatograph (model 439) equipped with flame ionization detector (FID) was used. The column was 10 m long and packed with the material used for analysis of acohols. Nitrogen was used as carrier gas. The yield of glycerine at pH 3.0 was found to be 95%. The presence of glycidol as an intermediate was also detected by pyridinium chloride-pyridine method (Jungnickel *et al.*, 1953).

RESULTS AND DISCUSSION

The progress of the reaction was followed by examining the concentration of hydrogen peroxide at different time intervals. The isolation method was applied for determining the kinetics of the reaction. In all experiments the concentration of allyl alcohol was at least fifteen times higher than the concentration of hydrogen peroxide. The disappearance of hydrogen peroxide in kinetic run obeys a simple zero order reaction. The plots of concentration of hydrogen peroxide versus time were good straight lines and their slope yields k_{obsd}. The pseudo-zero order rate constants (k_{obsd}) were found to be independent of the concentration of hydrogen peroxide. The results are reported in Table 1. The average k_{obsd} was found to be $3.45 \times 10^{-7} \pm 0.012 \times 10^{-7}$ mol dm^{-3} sec^{-1}.

Table 1. Pseudo-zero order rate for tungstate catalyzed formation of glycerine from allyl alcohol by hydrogen peroxide

$[H_2O_2] \times 10^3$ (M)	$k_{obsd} \times 10^7$ (mol dm^{-3} sec^{-1})
2.50	3.45
3.00	3.47
3.50	3.44
4.00	3.46
4.50	3.45
5.00	3.44

$[Na_2WO_4] = 5.00 \times 10^{-4}$ M; [Allyl alcohol] = 0.10 M; Temp., 40°C; pH = 3.0; $\mu = 50.00 \times 10^{-4}$ M.

The order of reaction with respect to sodium tungstate (catalyst) was determined by varying its concentration and keeping all other variables constant. The plot of k_{obsd} against the concentration of sodium tungstate was a straight line (Fig. 1) which passes through the origin. This shows first order dependence of rate on catalyst (sodium tungstate) concentration and it also confirms that there is no reaction in the absence of sodium tungstate. Similarly, the dependence of rate on allyl alcohol concentration was determined by varying its concentration while keeping all other variables constant. The observed pseudo-zero-order rate constants (k_{obsd}), when divided by allyl alcohol concentration, gave a constant value (Table 2). This shows that the order of reaction with respect to allyl alcohol is first order.

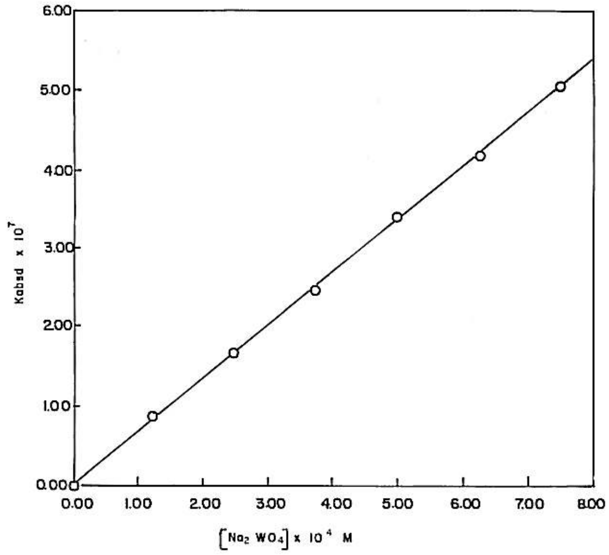


Fig. 1. First order dependence of rate on catalyst concentration $[H_2O_2] = 4.00 \times 10^{-3}$ M [Allyl alcohol] = 0.10 M pH, 3.0; Temp., 40°C.

Table 2. First order dependence of rate on allyl alcohol concentration for the formation of glycerine by hydrogen peroxide using sodium tungstate as catalyst

[Allyl alcohol]	$k_{obsd} \times 10^7$ (mol dm^{-3} sec^{-1})	$\frac{k_{obsd}}{[Allyl\ alcohol]} \times 10^7$
0.10	3.45	34.5
0.15	5.19	34.6
0.20	6.88	34.4
0.25	8.63	34.5
0.30	10.40	34.7
0.35	12.10	34.6

$[H_2O_2] = 4.00 \times 10^{-3}$; $[Na_2WO_4] = 5.00 \times 10^{-4}$ M; Temp., 40°C; pH = 3.0; $\mu = 50.00 \times 10^{-4}$ M.

In aqueous solutions tungstate gave tungstate anions by the following equation

$$WO_4^{2-} + H_2O \rightleftharpoons HWO_4^- + {}^-OH. \tag{1}$$

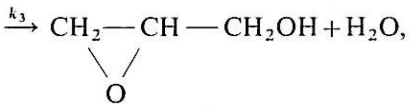
Preliminary studies have shown that the formation of glycerine from allyl alcohol is through the intermediate glycidol (epoxy allyl alcohol). Secondly at our experimental conditions, hydrogen peroxide does not bring about the formation of glycerine from allyl alcohol without the catalyst and the catalyst alone (without hydrogen peroxide) as well fails to bring about the formation of glycerine. These observations suggest that hydrogen peroxide oxidizes tungstic acid anion into peroxytungstic acid anion which then brings about the epoxidation of allyl alcohol to glycidol. The glycidol hydrolyses at low pH values and gives glycerine as the final product.

$$HWO_4^- + H_2O_2 \rightarrow HWO_5^- + H_2O. \tag{2}$$

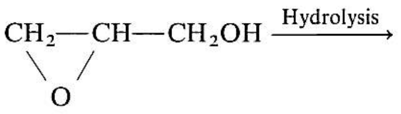
It has been reported earlier (Beg and Ahmad, 1975) that the HWO_5^- is the active species for epoxidation reactions in such system. The most probable mechanism is as follows

$$CH_2{=}CH{-}CH_2OH + HWO_5^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \text{(intermediate complex)}, \tag{3}$$

(intermediate complex)



$$\xrightarrow{k_3} \underset{\diagdown\, O\, \diagup}{CH_2{-}CH}{-}CH_2OH + H_2O, \tag{4}$$



$$\underset{\diagdown\, O\, \diagup}{CH_2{-}CH}{-}CH_2OH \xrightarrow{\text{Hydrolysis}}$$

$$HOCH_2{-}CH(OH){-}CH_2OH \quad \text{(Glycerine)}, \tag{5}$$

$$\text{Rate of reaction} = k_3\,[\text{intermediate complex}]. \tag{6}$$

Applying steady-state approximation of the concentration of intermediate complex, we get

$$k_1\,[CH_2{=}CH{-}CH_2OH][HWO_5^-] - k_2\,[\text{intermediate complex}] - k_3\,[\text{intermediate complex}] = 0, \tag{7}$$

$$[\text{intermediate complex}] = \frac{k_1[CH_2{=}CH{-}CH_2OH][HWO_5^-]}{k_2+k_3}. \tag{8}$$

Substituting the concentration of intermediate complex from equation (8) into equation (6), we get

$$\text{Rate of reaction} = k[CH_2{=}CH{-}CH_2OH]\,[HWO_5^-], \tag{9}$$

where

$$k = \frac{k_1 k_3}{k_2+k_3}.$$

Since the formation of peroxytungstic acid anion from tungstic acid anion is assumed to be instantaneous and complete, equation (9) can be written as

$$\text{Rate of reaction} = k'[CH_2{=}CH{-}CH_2OH]\,[Na_2WO_4]. \tag{10}$$

This explains the order of reaction with respect to allyl alcohol, catalyst and hydrogen peroxide. Hence

$$\text{Rate of reaction} = k_{obsd}, \tag{11}$$

where

$$k_{obsd} = k'[CH_2{=}CH{-}CH_2OH]\,[Na_2WO_4]. \tag{12}$$

Increasing in ionic strength did not affect the reaction rate. This was confirmed by changing the ionic strength of the medium by addition of sodium perchlorate solution from 50.00×10^{-4} M to 300.00×10^{-4} M and determining the rate of reaction (k_{obsd}). In all the cases k_{obsd} was found to be the same within reproducibility limit of the experiments. The reaction rate of crotyl alcohol was performed under the same conditions as for allyl alcohol given in Table 1. In place of 0.10 M allyl alcohol, crotyl alcohol of the same concentration was used to observe the substituent effect of methyl group on reaction rate. The average value of k_{obsd} was found to be 3.84×10^{-7} mol $dm^{-3}\,sec^{-1}$. The faster oxidation rate of crotyl alcohol compared to that of allyl alcohol under identical conditions shows that the presence of methyl group at the double bond is rate enhancing. This points to an electrophilic addition which is generally observed in the corresponding reaction of olefins with organic peracids and in other three-centered additions (Swern, 1957). The salt effects and the methyl substituent effect described above give an insight into the nature of the transition state of the oxygen transfer from peroxytungstic acid anion to the double bonds of the olefinic substrate as described elsewhere (Ahmad and Degam, 1991). The mechanism of the reaction is given in Fig. 2.

The reaction was studied at six different temperatures ranging from 35°C to 60°C, and the results are given in Table 3. The plots of log k_{obsd} against recip-

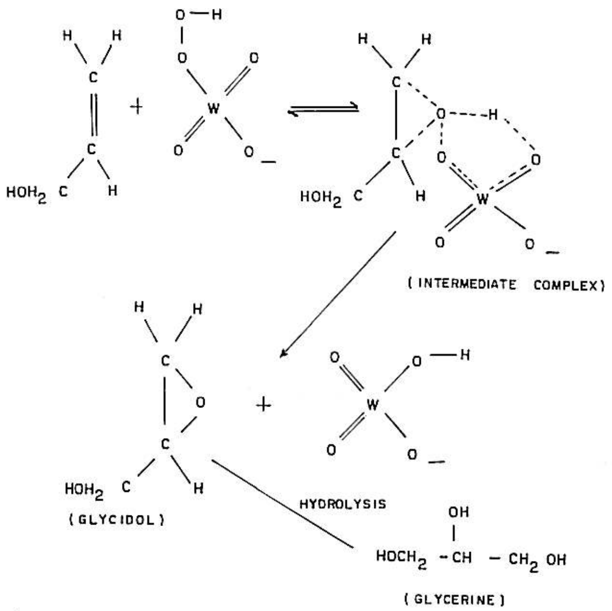


Fig. 2. Mechanism of the reaction.

Table 3. Dependence of rate on temperature

Temperature	$\frac{1}{T}\times 10^3$	$k_{obsd}\times 10^7$	$7+\log k_{obsd}$
308	3.25	2.18	0.3385
313	3.19	3.45	0.5378
318	3.14	4.87	0.6875
323	3.10	7.01	0.8513
328	3.05	11.22	1.0499
333	3.00	15.85	1.2000

$[H_2O_2]=4.00\times 10^{-3}$ M; $[Na_2WO_4]=5.00\times 10^{-4}$ M;
[Allyl alcohol] = 0.10 MpH = 3.0; $\mu=50.00\times 10^{-4}$ M.

rocal of temperature gave a straight line. The energy of activation was calculated from the slope of the plot to be 68.9 kJ mol^{-1}.

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