PRJ, Vol. 4. (January 1992); P. 52–55, 3 FIGS, 6 TABLES.

KINETICS OF ORTHOVANADATE CATALYSED EPOXIDATION OF MALEIC ANHYDRIDE BY HYDROGEN PEROXIDE

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حركية تفاعل الماليك إنهيدرايد مع فوق أكسيد الهيدروجين في وجود الأورثوفانيدات كعامل حفاز

إفتخار أحمد ومسعود دغيم

تم دراسة حركية وميكانيكية تحويل الماليك أنهيدرايد إلى أيبوكسيد الهيدروجين في وجود أورثوفانيدات الصوديوم كعامل حفاز.
كان التفاعل من الدرجة الأولى بالنسبة إلى الماليك إنهيدرايد والعامل المساعد وكان من الدرجة الصفر بالنسبة إلى فوق أكسيد الهيدروجين.
كما تم حساب طاقة التنشيط فكانت 68.93 ك جول/مول.

ABSTRACT

The kinetics and mechanism of epoxidation of maleic anhydride by hydrogen peroxide in the presence of sodium orthovanadate as catalyst have been studied. The reaction was found to be first order with respect to maleic anhydride and catalyst and zero order with respect to hydrogen peroxide. Based on substituent, solvent and salt effects the mechanism of epoxidation step is believed to be concerted with considerable polar (electrophilic) character. The energy of activation has been calculated to be 69.93 KJ mol^{-1}.

INTRODUCTION

Maleic anhydride is a compound which can be produced by the oxidation of butane, butenes or benzene [1]. The value of maleic anhydride can be increased by converting it to its epoxide. The epoxy of maleic anhydride should be of potential commercial interest because of its easy conversion into tin epoxysuccinates which are important plasticizer-stabilizers of polyvinil chlorides [2] as well as for cross linkable epoxy containing film forming polyamides [3]. Although organic peracids [4] are generally used for the epoxidation of alkenes, compounds having strong electron-withdrawing substituents adjacent to the double bonds are not readily epoxidised by them [5]. Recently hydroperoxides [6–10] are being used for the epoxidation of such alkenes, but these are limited to only nonaqueous medium. In these cases hydroperoxide metal [V(V), Mo(VI) and W(VI)] complexes [8–10] bring about epoxidation through metal-hydroperoxide-olefin complexes, whereas aqueous hydrogen peroxide in the presence of tungstate or molybdate epoxidises through peroxyacid [11–13]. More recently we have studied [14, 15] the catalytic activities of tungstate and molybdate ions on the epoxidation of maleic anhydride by hydrogen peroxide. This paper presents kinetic study of the epoxidation of maleic anhydride by hydrogen peroxide in the presence of sodium orthovanadate as catalyst.

EXPERIMENTAL

All the chemicals used were the analar (B.D.H.) grade. Maleic anhydride was standardised using bromate-bromide procedure [16] and hydrogen peroxide was standardised by permanganate method [17]. The ionic strength of the reaction mixture was maintained by the addition of sodium perchlorate. The pH of the reaction mixture was adjusted by perchloric acid on the lower side and that on the upper side by triethanolamine.

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The kinetics of the reaction was followed by monitoring the concentration of hydrogen peroxyde which is measured colorimetrically described elsewhere [18]. Every run was followed until reaction 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 5 ml titanium sulphate solution to stop the reaction. Optical density was measured at 420 nm and the concentration of hydrogen peroxide was read from a calibration graph. The catalyst concentration was too small to affect the colorimetric estimation of hydrogen peroxide.

The epoxysuccinic acid formed in this reaction was measured quantitatively by the pyridinium chloride-pyridine method [19]. Instead of methanolic sodium hydroxide, an aqueous solution was used for titration. No tartaric acid was detected in the reaction mixture above pH 6.0. However, below pH 6.0, the test of tartaric acid [20] was positive.

RESULTS AND DISCUSSION

The progress of the reaction was followed by examining the concentration of hydrogen peroxide at different time intervals. Trial and error plots of the rate data for runs with excess maleic anhydride concentration indicate that the reaction is zero order in hydrogen peroxide. The plots of concentration of hydrogen peroxide versus time were good straight lines and their slope yields K_{obsd}. The calculated k_{obsd} were found to be independent of the concentration of hydrogen peroxide. The results are reported in Table 1. The standard deviation of K_{obsd} is 0.01.

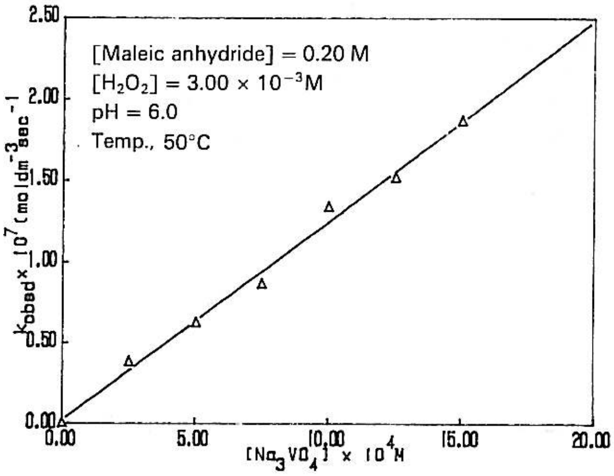

FIG. 1. First order dependence of rate on sodium orthovanadate concentration.

The order of reaction with respect to sodium orthovanadate (Na_3VO_4) was determined by varying its concentration and keeping other variables constant. The plot of k_{obsd} against the concentration of sodium orthovanadate was a straight line (Fig. 1). This confirms first order dependence of rate on sodium orthovanadate concentration. The plot of k_{obsd} versus concentration of sodium orthovanadate passes through the origin which shows that there is no reaction in the absence of sodium orthovanadate. Similarly, the dependence of rate on maleic anhydride concentration was determined by varying its concentration and keeping all other variables constant. k_{obsd} thus found were directly proportional to the concentration of maleic anhydride (Table 2). This shows first order dependence of rate on maleic anhydride concentration.

Table 1. Pseudo-Zero-Order Rate for Vanadate Catalysed Epoxidation of Maleic Anhydride by Hydrogen Peroxide

$[H_2O_2] \times 10^3$ (M)	$K_{obsd} \times 10^7$ (mol dm^{-3} sec^{-1})
2.00	6.19
2.50	6.20
3.00	6.22
3.50	6.19
4.00	6.21
4.50	6.20
5.00	6.18

[MA] = 0.20 M; $[Na_3VO_4] = 5.00 \times 10^{-4}$ M; pH, 6.0; Temp., 50°C

Preliminary studies have shown that under our experimental conditions, hydrogen peroxide does not ring about epoxidation of maleic anhydride without sodium orthovanadate alone (without hydrogen peroxide) fails to bring about the epoxidation. This clearly suggests the involvment of some more oxygenated form of vanadium in the process as oxygen carrier. Jander and Jahr [21] have shown that in the acidic medium, orthovanadate changes into vanadium pentoxide, which according to Flood and co-workers [22] dissolves in aqueous hydrogen peroxide giving peroxyvanadic acid. It is thus presumed here that in the system under investigation, peroxyvanadic acid is the epoxidising species and in a

Table 2. First Order Dependence of Rate on Maleic Anhydride Concentration

$[MA] \times 10^2$ (M)	$k_{obsd} \times 10^7$ (mol dm^{-3} sec^{-1})	$\frac{k_{obsd}}{[MA]} \times 10^5$
20.00	6.22	0.311
30.00	9.33	0.311
40.00	12.40	0.310
50.00	15.61	0.312
60.00	18.62	0.310

$[H_2O_2] = 3.00 \times 10^{-3}$ M; $[Na_3VO_4] = 5.00 \times 10^{-4}$ M; pH, 6.0; Temp., 50°C.

rate controlling step it reacts with the unsaturated acids giving epoxysuccinic acid and regenerating vanadic acid. Vanadic acid is then reconverted into peroxyvanadic acid by hydrogen peroxide. The following seems to be the most probable mechanism:

$$H_3VO_5 \xrightleftharpoons{K_1} H_2VO_5^- + H^+ \qquad (1)$$

$$\text{where, } k_1 = \frac{[H_2VO_5^-][H^+]}{[H_3VO_5]} \qquad (2)$$

$$MA + H_3VO_5 \xrightleftharpoons[K_{-2}]{K_2} \text{(intermediate complex)} \qquad (3)$$

$$\text{(intermediate complex)} \xrightarrow{k_3} MAE + H_3VO_4 \qquad (4)$$

MA and MAE are maleic anhydride and maleic anhydride epoxide, respectively.

Assuming steady-state approximation for the complex formation.

$$\text{epoxidation rate} = k'[MA][H_3VO_5] \qquad (5)$$

$$\text{where, } k' = \frac{k_2 k_3}{k_{-2} + k_3}$$

The catalyst (Na_3VO_4), at any stage in the process, is distributed in three forms according to eqn. (6),

$$[Na_3VO_4] = [H_3VO_5] + [H_2VO_5^-] + [\text{intermediate complex}] \qquad (6)$$

The concentration of intermediate complex in eqn. (6) is negligible in comparison to other terms of eqn. (6). Hence,

$$[Na_3VO_4] = [H_3VO_5) + [H_2VO_5^-] \qquad (7)$$

Substituting for $[H_3VO_5]$ from eqn. (2) and (7) in eqn. (5), we get,

$$\text{epoxidation rate} = \frac{k'[H^+][Na_3VO_4][MA]}{K_1 + [H^+]} \qquad (8)$$

$$\text{or epoxidation rate} = k_{obsd} \qquad (9)$$

Here,

$$k_{obsd} = \frac{k'[H^+][Na_3VO_4][MA]}{k_1 + [H^+]} \qquad (10)$$

Eqn. (8) explains the observed order of reaction with respect to maleic anhydride, sodium orthovanadate and hydrogen peroxide. The results of variation of epoxidation rate with pH are shown in Table 3. The straight line plot (Fig. 2) between inverse of k_{obsd} and inverse of $[H^+]$ is in agreement with eqn. (10).

Table 3. Dependence of Rate on pH of the Medium

pH	$\frac{1}{[H^+]}$ (dm^3 mol^{-1})	$k_{obsd} \times 10^7$ (mol dm^{-3} sec^{-1})	$\frac{1}{k_{obsd}} \times 10^{-7}$
5.0	1.00×10^5	8.37	0.12
5.5	3.16×10^5	7.14	0.14
6.0	1.00×10^6	6.22	0.16
6.5	3.16×10^6	4.26	0.23
7.0	1.00×10^7	2.40	0.42

$[H_2O_2] = 3.00 \times 10^{-3}$ M; $[Na_3VO_4] = 5.00 \times 10^{-4}$ M; [MA] = 0.20 M; Temp., 50°C.

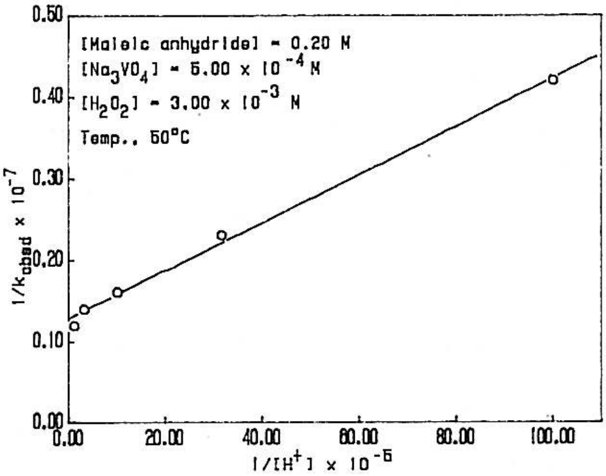

FIG. 2. Plot of inverse of k_{obs} against inverse of hydrogen ion concentration.

Increase in ionic strength did not affect the epoxidation rate (Table 4). The epoxidation rate of citraconic anhydride was performed under the same conditions as for maleic anhydride given in Table 1. In place of 0.20 M maleic anhydride citraconic acid of the same concentration was used to observe the substituent effect. The average value of k_{obsd} was found to be 7.35×10^{-7} mol dm^{-3} sec^{-1}. The faster epoxidation rate of citraconic anhydride as compared to that of maleic anhydride under identical

Table 4. Dependence of Vanadate-Catalysed Epoxidation Rate of Maleic Anhydride on Ion Strength of the Medium

Ionic Strength $\mu \times 10^4$ M	$k_{obsd} \times 10^7$ (mol dm^{-3} sec^{-1})
40.00	6.22
50.00	6.18
60.00	6.23
70.00	6.20
80.00	6.22
90.00	6.21
100.00	6.23

$[H_2O_2] = 3.00 \times 10^{-3}$ M;
$[Na_3VO_4] = 5.00 \times 10^{-4}$ M;
[MA] = 0.20 M; pH, 6.0; Temp., 50°C.

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-centre-type additions [23, 24]. The epoxidation rate decreases (Table 5) as the percentage of water in alcohol-water mixture decreased (dielectric constant lowered) but no linear relation between epoxidation rate and dielectric constant was obtained. Solvent and salt effects described above give an insight into the nature of the transition state of the oxygen transfer from the peracids to the double bonds of the olefinic substrate as described elsewhere [25].

Table 5. Dependence of Vanadate-Catalysed Epoxidation Rate of Maleic Anhydride in Ethanol-Water Mixture on the Composition of the Solvent

% of ethanol	Dielectric Constant	$k_{obsd} \times 10^7$ (mol dm^{-3} sec^{-1})
0	78.5	6.22
15.4	69.5	5.89
31.5	60.0	5.31
50.0		4.65

$[MA]=0.20$ M; $[Na_3VO_4]=5.00\times10^{-4}$ M; $[H_2O_2]=3.00\times10^{-3}$ M; Temp., 50°C; pH = 6.0.

Table 6. Effect of Temperature on Epoxidation Rate

Temperature (*K*)	$\frac{1}{T}\times10^3$	$k_{obsd}\times10^7$ (mol dm^{-3} sec^{-1})	$7+\log k_{obsd}$
333	3.00	25.88	1.4130
328	3.05	17.78	1.2499
323	3.10	13.40	1.1271
318	3.14	7.08	0.8500
313	3.19	4.76	0.6776
308	3.25	3.33	0.5224

$[MA]=0.20$ M; $[Na_3VO_4]=10.00\times10^{-4}$ M; $[H_2O_2]=3.00\times10^{-3}$ M; pH = 6.0.

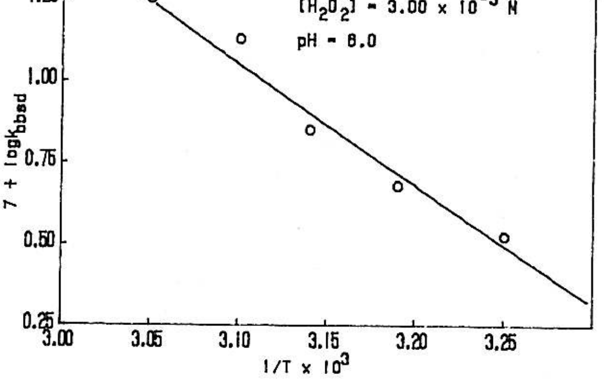

FIG. 3. Plot of log k_{obs} vs. reciprocal of absolute temperature.

The reaction was studied at six different temperatures ranging from 35°C to 60°C, and the results are given in Table 6. The plots of log k_{obsd} against reciprocal of temperature gave a straight line. The energy of activation was calculated from the slope of this plot to e 68.93 kJ mol^{-1}.

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