PRJ, Vol. 3 (January 1991); P. 53–56, 4 FIGS, 2 TABLES.

THE COMPARATIVE CATALYTIC ACTIVITIES OF TUNGSTATE AND MOLYBDATE IONS IN THE EPOXIDATION OF MALEIC ANHYDRIDE BY HYDROGEN PEROXIDE

Iftikar Ahmad*, Massod Degam* and Abdel Razak Labib*

دراسة لمقارنة حركية تفاعل انتاج مشتق الأبوكسي من مركب الماليك اللامائي بواسطة فوق أكسيد الهيدروجين في وجود تنجستات الصوديوم ومليبدات الصوديوم كعامل مساعد

د. افتخار أحمد ، مسعود دغيم ، عبد الرزاق لبيب

هذا البحث يتعلق بدراسة مقارنة لحركية تفاعل انتاج مشتق الابوكسي من مركب الماليك اللامائي بواسطة فوق أكسيد الهيدروجين في وجود تنجستات الصوديوم أو موليبدات الصوديوم كعامل مساعد.

درجة التفاعل صفر بالنسبة لتركيز فوق أكسيد الهيدروجين أما بالنسبة للعامل المساعد (سواء تنجستات أو موليبدات الصوديوم) فهو من الدرجة الأولى. التفاعل في وجود التنجستات أسرع منه في حالة استخدام الموليبدات كعامل مساعد.

لقد تم اقتراح معادلة مركبة تربط ما بين سرعة التفاعل وتراكيز مركب الماليك اللامائي والعامل المساعد وفوق أكسيد الهيدروجين. كما تم إقتراح ميكانيكية لكيفية حدوث التفاعل.

ABSTRACT

The comparative kinetics of epoxidation of maleic anhydride by hydrogen peroxide in the presence of sodium tungstate or sodium molybdate as catalyst have been studied. The reaction is zero order with respect to hydrogen peroxide concentration and the reaction is first order with respect to maleic anhydride and catalyst (sodium tungstate or sodium molybdate). Tungstate catalysed epoxidation of maleic anhydride is faster than that of molybdate catalysis. A complex rate equation, describing the dependence of rate on maleic anhydride, catalyst and hydrogen peroxide has been proposed. A reaction mechanism has also been proposed.

INTRODUCTION

Epoxides have shown a growing industrial importance, particularly in the polymer field. The simple epoxides are obtained by aerial oxidation of unsaturated hydrocarbons such as ethylene or propylene over silver catalyst [1–3]. More complex unsaturated substrates are usually converted into their epoxides through the intermediacy of organic peracids [4–6] but the compounds having strong electron withdrawing substituents adjacent to the double bonds are not readily epoxidized by them [7]. More recently hydroperoxides [8–12] are being used for the epoxidation of such alkenes, but these are limited only to nonaqueous medium. In aqueous medium inorganic peracids are often used as specially effective epoxidizing reagents [7]. These inorganic oxidants are usually generated in situ [13] from hydrogen peroxide and a soluble compound of much less common metals as Os, Ti, Zr, Rh, U, Ru, Ta, Cr, Se, W, Mo, V etc. Mugdan and Young [14] made a qualitative comparison of osmic, tungstic, molybdic, selenious, tantalic and titanic acids as catalysts for the direct addition of hydrogen peroxide to ethylenic compounds. The kinetics of the reaction of pertungstic acid with allyl alcohols [15–17] have been reported.

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

This paper presents the results of kinetics of the epoxidation of maleic anhydride by hydrogen peroxide in the presence of sodium tungstate and sodium molybdate as catalysts. Maleic anhydride is a petrochemical which can be produced by the oxidation of butane, benzene and butenes [18]. The epoxydicarboxylic acids should be of potential commercial interest because of their easy conversion into tin epoxysuccinates which are important plasticizer-stabilizers for polyvinyl chlorides [19] as well as for cross linkable epoxy containing film-forming polyamides [20].

EXPERIMENTAL

Standardization of the maleic anhydride and hydrogen peroxide solutions were carried out using a bromate-bromide mixture [21] for the former and permanganate [22] for the latter. In kinetic runs, the concentration of hydrogen peroxide was measured colorimetrically [23]. After the reactants had reached thermostat temperature, the reaction was started by addition of the catalyst. 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 the hydrogen peroxide was read from a calibration graph. The catalyst concentration was too small to affect the colorimetric estimation of hydrogen peroxide. Every run was followed until the reaction was at least 90% complete.

The epoxysuccinic acid formed in this reaction was measured quantitatively by the pyridinium chloride-pyridine method [24]. Instead of methanolic sodium hydroxide, an aqueous solution was used for titration. Maleic anhydride, at pH 6.0, gave cis-epoxysuccinic acid. No tartaric acid was detected in the reaction mixture above pH 5.0. However, below pH 5.0, the test of tartaric acid [25] was positive and its form was identified by a chromatographic method [26]. The results suggest that maleic anhydride gives a dl form of tartaric acid.

RESULTS AND DISCUSSION

The progress of the reaction was observed by measuring the disappearance of hydrogen peroxide in the presence of high concentration of maleic anhydride. Trial and error plots of the rate data for runs indicate that the reaction is zero order in hydrogen peroxide. The plots of concentration of hydrogen peroxide versus time were 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 summarized in Table 1.

Table 1. Pseudo-Zero-Order Rates for the Epoxidation of Maleic Anhydride in the Presence of Catalyst

$[H_2O_2] \times 10^3$ (M)	kobsd $\times 10^7$ (mol lit^{-1} sec^{-1})	
	Sodium tungstate	Sodium molybdate
2.50	5.25	3.50
3.00	5.28	3.49
3.50	5.23	3.52
4.00	5.26	3.51
4.50	5.25	3.49
5.00	5.25	3.50

[Catalyst] $= 1.00 \times 10^{-3}$M; [Maleic anhydride] $= 0.20$M
Temp., 50°C; pH, 6.0

The order of reaction with respect to catalyst (sodium tungstate or sodium molybdate) was determined by varying its concentration and keeping other variables constant. The plot of k_{obsd} against the concentration of catalyst was straight line (Fig. 1)

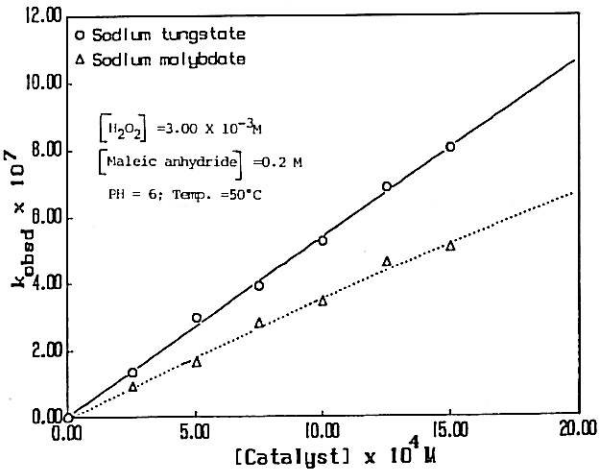


FIG. 1. First order dependence of rate on catalyst concentration.

which passes through the origin for all two catalysts. This confirms first order dependence of rate on catalyst concentration and it also shows that there is no reaction in the absence of catalyst. Similarly, the dependence of rate on maleic anhydride concentration was determined by varying its concentration while keeping all other variables constant. k_{obsd} is directly proportional to the con centration of maleic anhydride in case of all the two catalysts used. This is an indicative of first order dependence of rate on maleic anhydride concentration. The results are presented in Table 2.

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

[Maleic anhydride] $\times 10^2$ (M)	kobsd $\times 10^7$ (mol lit^{-1} sec^{-1})	
	Sodium tungstate	Sodium molybdate
20.00	5.25	3.49
30.00	8.20	5.02
40.00	10.51	6.84
50.00	13.54	8.41
60.00	15.87	10.23

[Catalyst] $= 10.00 \times 10^{-4}$M; [H_2O_2] $= 3.00 \times 10^{-3}$M Temp., 50°C; pH, 6.0

In aqueous solutions of tungstate and molybdate gave acid anions by the following equation:

$$MO_4^{2-} + H_2O \rightleftharpoons HMO_4^- + OH^- \quad (1)$$

Where, M is W or Mo.

Preliminary studies have shown that under our experimental conditions, hydrogen peroxide does not bring about epoxidation of maleic anhydride without the catalyst and the catalyst alone (without hydrogen peroxide) as well fails to bring about the epoxidation. These observations suggest that hydrogen peroxide oxidises acid anions into peroxyacid anions which then bring about the epoxidation.

$$HMO_4^- + H_2O_2 \rightarrow HMO_5^- + H_2O \quad (2)$$

It has been reported earlier [27] that the concentration of acid anions are pH dependent. HWO_4^- is maximum around pH 4.7 and $HM_oO_4^-$ is maximum around pH 3.6. The epoxidation rates catalysed by tungstate or molybdate are maximum at the pH at which (HWO_4^-) or ($HMoO_4^-$) are maximum (Figs. 2 and 3).

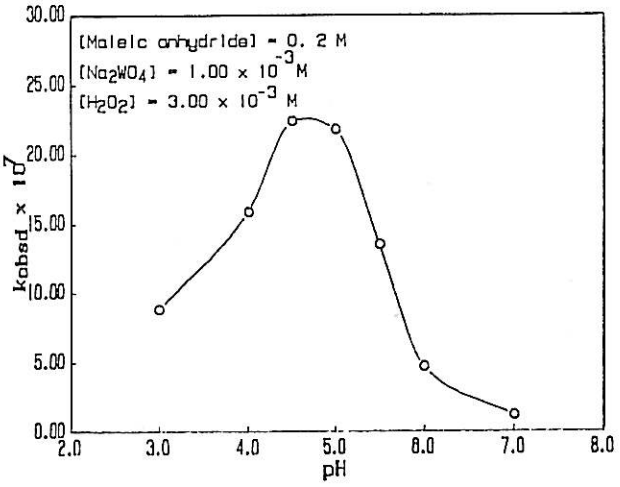


FIG. 2. Tungstate catalyzed epoxidation rate dependence on pH of the medium.

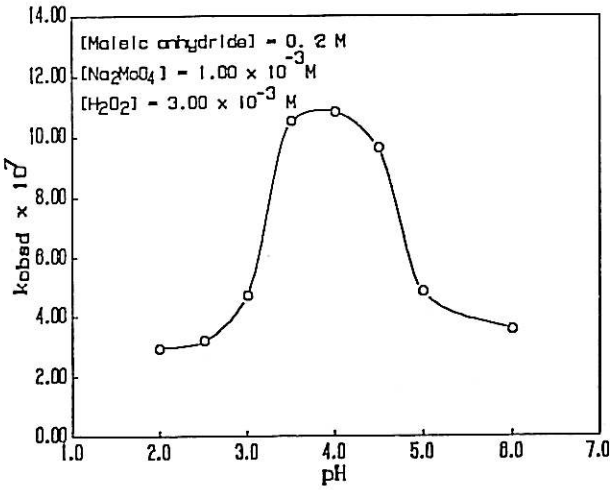


FIG. 3. Molybdate catalyzed epoxidation rate dependence on pH of the medium.

This clearly suggests that the peroxyacid anions are the expoxidizing agents. The most probable mechanism is as follows:

$$MA + HMO_5^- \underset{k2}{\overset{k1}{\rightleftharpoons}} \text{(intermediate complex)} \quad (3)$$

$$\text{(intermediate complex)} \xrightarrow{k3} MAO + HMO_4^- \quad (4)$$

$$\text{Rate of reaction} = k3\ \text{(intermediate complex)} \quad (5)$$

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

$$k1[MA][HMO_5^-] - k2\ \text{(intermediate complex)} - k3\ \text{(intermediate complex)} = 0 \quad (6)$$

$$\text{or (intermediate complex)} = \frac{k1[MA][HMO_5^-]}{k2 + k3} \quad (7)$$

where MA represents maleic anhydride.

Substituting the concentration of intermediate complex in eqn. 5, we get,

$$\text{Rate of reaction} = k[MA][HMO_5^-] \quad (8)$$

Where,

$$k = \frac{klk3}{k2+k3}$$

since the formation of peroxyacid anions from acid anions is assumed to be instantaneous and complete, eqn. (8) can be written as:

$$\text{Rate of reaction} = k'[MA][Na_2WO_4 \text{ or } Na_2MoO_4] \quad (9)$$

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

$$\text{Rate of reaction} = k_{obsd} \quad (10)$$

Where,

$$k_{obsd} = k'[MA][Na_2WO_4 \text{ or } Na_2MoO_4] \quad (11)$$

Figure 1 shows that among the two catalyst system investigated, the tungstate is the superior catalyst for the epoxidation of maleic anhydride. This may be a reflection of the fact that the formation of the reactive peroxyacid anion of tungstate in situ is comparatively larger, since within the same group of Periodic Table, the stability of peroxyacid anion increases with increasing atomic weight [28]. The proposed transition state of the reaction is shown in Fig. 4.

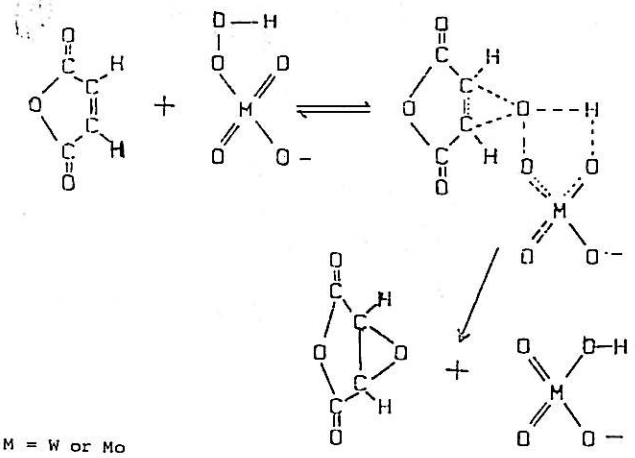


FIG. 4. Mechanism of epoxidation reaction.

ACKNOWLEDGEMENT

The authors are thankful to the management of Petroleum Research Centre for providing facilities to conduct this work.

REFERENCES

[1] Lefort T.E., U.S. Patent Reissues, 20370, 18 May 1937; 22241, 29 December 1942.
[2] Seree I.-Deroch *Bull. Soc. Chi., Fr.*, 1979 (1966).
[3] Weinstein, S. and Henderson, R.D., 1950, Heterocyclic Compounds, Vol. I, edited by R.C. Elderfield, Wiley, New York, pp. 1.
[4] Popescu A. and Croc N., 1967, *Studii Cercetari Chim.*, 15,909.
[5] Takagi T. and Kobayshi M., 1967, Kogyo Kagaku Zasshi, 70,1446.
[6] Takagi T, 1967., *J. Polymer Sci.*, B5, 1031.
[7] Payne G.B., 1959, Fifth Petroleum Congress Proceedings, New York N.Y., Section IV, Paper 16, pp. 185.
[8] Jochsberger T. Miller D., Herman F. and Indicator, 1971, *J. Org. Che.*, 36,4078 (1971).
[9] Howe G.R. and Hiatt R.R., 1971, *J. Org. Chem.*, 36,2493.
[10] Sheng M.N. and Zajacek J.G., 1968, *Adv. Chem. Ser.*, 76,481.
[11] Su C., Reed J.W. and Gould, R.S., 1973, *Inorg. Chem.*, 12,337.
[12] Gould E.S., Hiatt R.R. and Irwin K.C., 1968, *J. Amer. Chem. Soc.*, 90,4573.
[13] Allan G.G., 1964, U.S. Patent, 3156709; 10 Nov.
[14] Mugdan M. and Young D.P., 1949, *J. Chem. Soc.*, 2988.
[15] Raciszewski Z., 1960, *J. Amer. Chem. Soc.*, 82,1267.
[16] Stevens H.C. and Kaman A.J., 1965, *J. Amer. Chem. Soc.*, 87,734.
[17] Sapunov V.M. and Lebedev N.N. 1966, *Zh. Org. Khim.*, 2,272.
[18] Hatch L.F. and Matar S., 1981. From Hydrocarbons to Petrochemicals, Gulf. Pub. Co., pp. 144.
[19] Bavley A. and Knuth C.J., 1961, U.S. Patent, 2972595, Feb. 21.
[20] Campbell, T.W. and McDonald R.N., 1963, *J. Polymer Sci.*, Part A. 1,2525.
[21] Lucas H.J. and Pressman D., 1938, *Ind. Eng. Chem., Anal. Ed.*, 10,140.
[22] Kolthoff I.M., Sandell E.B., Meehan E.J. and Stanley B., 1969, in "Qualitative Chemical Analysis", 4th Ed., pp. 834, Macmillan Co. Collier Macmillan Ltd., London.
[23] Reichert J.S., McNeight S.A. and Rudel H.W., 1939, *Ind. Eng. Chem., Anal Ed.*, 11,194.
[24] Jungnickel J.L., Peters E.D., Polgar A., Weiss F.T., Proskauer E.S. and Weissberger A., 1953, *Organic Analysis*, Wiley (Interscience), New York, Vol. I, pp. 136.
[25] Perkin M.F., 1924, "Qualitative Chemical Analysis", Longmans, Green and Co., New York, N.Y., pp. 219.
[26] Buchan J.C., Dekkar C.A. and Long A.G., 1950, *J. Chem. Soc.*, 3162.
[27] Beg M.A. and Ahmad I, 1975, *J. Catal.*, 39,260.
[28] Melikoff P. and Jelhchaninoff E., 1909, *Chem. Ber.*, 42,2291.