JOURNAL OF CATALYSIS 39, 260–264 (1975)

Kinetics and Mechanism of the Epoxidation of Fumaric Acid with Aqueous Hydrogen Peroxide Catalyzed by Sodium Tungstate or Sodium Molybdate

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Received December 27, 1974

The kinetics of epoxidation of fumaric acid by hydrogen peroxide in the presence of sodium tungstate or molybdate have been studied. Tungstate catalyzed epoxidation of fumaric acid to *trans*-epoxysuccinic acid is faster than that for molybdate catalysis. The reaction is first order with respect to substrate and catalyst and zero order with respect to hydrogen peroxide. Based on substituent, solvent, and salt effects, our opinion is that the mechanism of the epoxidation step is related to polar (electrophilic) character.

INTRODUCTION

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 (*1–9*). Kinetic studies of the reaction of peroxytungstic acid with amines (*10*), allyl and substituted allyl alcohols (*11–13*) have been reported. Later Allan and Neogi (*14*) studied the epoxidation of maleic acid using tungstate, molybdate and vanadate ions as catalysts. This paper presents a quantitative and comparative study of the catalytic activity of tungstate and molybdate ions on the hydrogen peroxide epoxidation of fumaric acid to *trans*-epoxysuccinic acid. The results suggest that the peroxyanion formed in the system acts as oxygen carrier.

EXPERIMENTAL METHODS

Standardization of the fumaric, mesaconic acids and hydrogen peroxide solutions were carried out using a bromate–bromide mixture (*15*) for the former and permanganate (*16*) for the latter. The ionic strength of the reaction mixture was maintained by the addition of sodium perchlorate. In kinetic runs, the concentration of hydrogen peroxide was measured colorimetrically (*17*).

After the reactants had reached thermostat temperature, the reaction was started by addition of the catalyst. Triethanolamine was used to adjust the pH. The kinetics were followed by examining 5 ml aliquots of the reaction mixture for hydrogen peroxide content. The aliquots had been added to 5 ml of a titanium sulfate solution to stop the reaction. Optical density was measured at 420 nm, and the concentration of the hydrogen peroxide was read from the calibration graph. The catalyst concentration was too small to affect the colorimetric estimation of hydrogen peroxide. Every run was followed until reaction was at least 80% complete.

Decomposition of Hydrogen Peroxide by Tungstate or Molybdate

Aqueous solutions of hydrogen peroxide, catalyst and hydrochloric acid were mixed under experimental conditions and hydrogen peroxide was estimate after 2 hr. In the presence of tungstate the decomposition of hydrogen peroxide is negligible below pH 6 and significant above pH 6. With molybdate the decomposition is negligible only up to pH 4 and above that it increases rapidly.

Acid Dissociation Constants of Tungstic and Molybdic Acids

Aqueous solutions (0.025 *M*) of sodium salts were titrated with 0.62 *M* aqueous hydrochloric acid and the concomitant pH was read by using a pH meter. In either titration, only one inflection was obtained at one equivalence of acid added. pK_2 is the pH at the half equivalence point and this was read from the derivative plot (Table 8) (*21*). Before the first equivalence point, the abundance of HWO_4^- and $HMoO_4^-$ species were calculated from the formula

$$K_2 = [H^+][MO_4^{2-}]/[HMO_4^-],$$

where K_2 is the second dissociation constant and M is W or Mo.

At any point after the first equivalence, $[HMO_4^-]$ is $[HMO_4^-]$ at the first equivalence point minus $[H_2MO_4]$ formed up to that point.

Identification of Products

The presence of *trans*-epoxysuccinic acid in the reaction mixture was confirmed by the method of Jungnickel *et al.* (*18*), while *dl*-tartaric acid was detected (*19*) by a chromatographic method (*20*).

RESULTS AND DISCUSSION

The plots of hydrogen peroxide concentration against time (Table 1) were straight lines with identical slopes. Pseudo-zero order rate constant is reported as k_{obs}. The log log plot of the rate constants and fumaric acid concentration (Table 2) was a straight line with unit slope and this shows first order dependence of rate on the fumaric acid concentration. The unit slope of the log log plot of k_{obs} against the catalyst concentration (Table 3) is indicative of the first order dependence of rate on the catalyst concentration.

TABLE 1

PSEUDO-ZERO ORDER RATE CONSTANTS FOR THE EPOXIDATION OF FUMARIC ACID BY HYDROGEN PEROXIDE IN THE PRESENCE OF TUNGSTATE OR MOLYBDATE[a]

$[H_2O_2] \times 10^3$ (*M*)	$k_{obs} \times 10^5$ (mol liter^{-1} min^{-1}) Sodium tungstate	Sodium molybdate
2.00	1.76	1.08
2.25	1.77	1.07
2.50	1.77	1.08
2.75	1.78	1.09
3.00	1.76	1.07

[a] $[Na_2WO_4] = [Na_2MoO_4] = 1.0 \times 10^{-4}$ *M*; [fumaric acid] = 5.33×10^{-2} *M*; temp, 38°C; pH 4.0.

In aqueous solutions tungstate and molybdate ions hydrolyze into the acid anions,

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

M being Mo or W. The experimental evidence clearly indicates that hydrogen peroxide does not oxidize fumaric acid directly. It rather suggests that hydrogen perox-

TABLE 2

FIRST ORDER DEPENDENCE OF TUNGSTATE OR MOLYBDATE CATALYZED EPOXIDATION RATE OF FUMARIC ACID ON THE CONCENTRATION OF FUMARIC ACID[a]

[Fumaric acid] $\times 10^2$ (*M*)	$k_{obs} \times 10^6$ (mol liter^{-1} min^{-1}) Sodium tungstate	Sodium molybdate
2.66	8.89	5.45
3.33	—	6.81
4.00	13.45	8.09
4.66	15.58	9.53
5.33	17.85	10.90

[a] $[H_2O_2] = 2.0 \times 10^{-3}$ *M*, $[Na_2WO_4] = [Na_2MoO_4] = 10.0 \times 10^{-5}$ *M*; temp, 38°C; pH 4.0.

TABLE 3

First Order Dependence of Tungstate or Molybdate Catalyzed Epoxidation Rate of Fumaric Acid on Catalyst Concentration[a]

$[Na_2WO_4] \times 10^5$ (M)	$k_{obs} \times 10^6$ (mol liter^{-1} min^{-1})	$[Na_2MoO_4] \times 10^5$ (M)	$k_{obs} \times 10^6$ (mol liter^{-1} min^{-1})
5.0	9.28	5.0	—
10.0	17.80	10.0	10.71
15.0	26.85	15.0	16.23
20.0	37.33	20.0	21.56
25.0	45.20	25.0	27.02
30.0	—	30.0	32.50

[a] $[H_2O_2] = 2.5 \times 10^{-3}$ M; [fumaric acid] $= 5.33 \times 10^{-2}$ M; pH 4.0; temp, 38°C; $\mu = 9.0 \times 10^{-4}$ M.

ide rapidly and completely oxidizes acid anions into peroxyacid anions, HMO_5^-, shown in Eq. (2):

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

It may be recalled that tungstic and molybdic acids are converted to peroxyacids (*22,23*) when treated with aqueous hydrogen peroxide. The mode of pH dependency suggests that peroxyacid anions are the epoxidizing agents. The probable oxidation mechanism is as follows:

$$H_2F + HMO_5^- \xrightleftharpoons[k_{-1}]{k_1} \text{[intermediate complex]}, \quad (3)$$

$$\text{[intermediate complex]} \xrightarrow{k_2} H_2E + HMO_4^-, \quad (4)$$

where H_2F and H_2E represent fumaric acid and *trans*-epoxysuccinic acid, respectively. Assuming a steady state concentration for the complex, it follows that the

$$\text{epoxidation rate} = k' \, [H_2F][HMO_5^-], \quad (5)$$

where

$$k' = k_1k_2/(k_{-1} + k_2).$$

Since in each set the pH and the concentration of catalyst added were both constant, rate Eq. (5) can be rewritten as:

$$\text{epoxidation rate} = k' \, [H_2F][Na_2MO_4]. \quad (6)$$

This explains the order of the reaction with respect to the substrate, catalyst and the oxidant.

The pH dependency of the process as illustrated in Table 4 cannot be explained by Eq. (1) alone which suggests a decrease in the concentration of MO_4^{2-} and an increase in the concentration of HMO_4^- with decrease in pH. In acid medium, the oxyanions undergo protonation as:

$$MO_4^{2-} + H^+ \rightleftharpoons HMO_4^-, \quad (7)$$

$$HMO_4^- + H^+ \rightleftharpoons H_2MO_4. \quad (8)$$

It is obvious from these equilibria that $[HMO_4^-]$ will depend upon the acidity of the medium and will be optimum at a particular pH and that this optimum will be different with different peroxy anions. In case of tungstate, $[HWO_4^-]$ is maximum

TABLE 4

Dependence of Tungstate or Molybdate Catalyzed Epoxidation Rate of Fumaric Acid on the pH of the Medium[a]

Epoxidation pH	Sodium tungstate $k_{obs} \times 10^5$ (mol liter^{-1} min^{-1})	Sodium molybdate $k_{obs} \times 10^6$ (mol liter^{-1} min^{-1})
3.0	0.85	6.42
4.0	3.73	9.56
5.0	7.85	—
6.2	3.22	—
7.0	2.73	—

[a] [Fumaric acid] $= 4.84 \times 10^{-2}$ M; $[Na_2WO_4] = 1.82 \times 10^{-4}$ M; $[Na_2MoO_4] = 1.0 \times 10^{-4}$ M; $[H_2O_2] = 2.27 \times 10^{-3}$ M; temp, 38°C.

TABLE 5

DEPENDENCE OF TUNGSTATE OR MOLYBDATE CATALYZED EPOXIDATION RATE OF FUMARIC ACID IN ETHANOL–WATER MIXTURE ON THE COMPOSITION OF THE SOLVENT[a]

Solvent (%)	Dielectric constant	$k_{obs} \times 10^6$ (mol liter^{-1} min^{-1}) Sodium tungstate	Sodium molybdate
0 Ethanol	78.5	8.89	5.43
15.4	69.5	7.43	4.95
31.5	60.0	5.12	—
50	—	2.96	1.82
50 t-Butyl alcohol	—	2.98	1.81

[a] $[H_2O_2] = 2.0 \times 10^{-3}\,M$; $[Na_2WO_4] = [Na_2MoO_4] = 1.0 \times 10^{-4}\,M$; [fumaric acid] = 2.66 M; temp, 38°C; pH 4.0. The dielectric constant values have been taken from Frost, A. A., and Pearson, R. G., "Kinetics and Mechanism," 2nd ed., p. 146. Wiley, New York, 1961.

TABLE 7

DEPENDENCE OF TUNGSTATE OR MOLYBDATE CATALYZED EPOXIDATION RATE OF FUMARIC ACID ON THE IONIC STRENGTH OF THE MEDIUM[a]

Ionic strength ($\mu \times 10^4\,M$)	$k_{obs} \times 10^6$ (mol liter^{-1} min^{-1}) Sodium tungstate	Sodium molybdate
3.0	17.60	10.80
4.5	17.42	10.73
6.0	17.81	10.81
7.5	17.55	10.89
9.0	17.69	10.77
12.0	17.83	10.84

[a] [Fumaric acid] = $5.33 \times 10^{-2}\,M$; $[Na_2WO_4] = [NaMoO_4] = 1.0 \times 10^{-4}\,M$; temp, 38°C; pH 4.0.

at pH 4.7. The catalytic activity of Na_2WO_4 is also maximum around the same pH (Table 4) and it falls off rapidly thereafter due to a rapid decrease in $[HWO_4^-]$. The catalytic activity of sodium molybdate has also been studied in solutions of pH 3–4, but unlike tungstate catalysis, molybdate catalysis does not show an optimum, but increases with pH from 3 onwards. This is because the rate has been measured in terms of disappearance of hydrogen peroxide which also disappears by decomposition. Hence the expected decrease in catalytic activity of Na_2MoO_4 at higher pH could not be detected due to increased decomposition of hydrogen peroxide.

A comparison of the epoxidation rate of mesaconic and fumaric acids show that the presence of methyl group at the double bond is strongly rate-enhancing (Table 6). This points to an electrophilic addition and is generally observed in the corresponding reaction of olefins with organic peracids and in other three-center-type additions (*24,25*). A brief study of solvent and salt effect (Tables 5 and 7) gives an insight to the nature of the transition state of the oxygen transfer from the peracid to the double bond of the substrate. The absence

TABLE 6

DEPENDENCE OF TUNGSTATE CATALYZED EPOXIDATION RATE OF MESACONIC ACID ON THE CONCENTRATION OF HYDROGEN PEROXIDE[a]

$[H_2O_2] \times 10^3$ (M)	$k_{obs} \times 10^5$ (mol liter^{-1} min^{-1})
2.0	4.29
2.5	4.26
3.0	4.28
3.5	4.29

[a] $[Na_2WO_4] = 1.0 \times 10^{-4}\,M$; [mesaconic acid] = $5.33 \times 10^{-2}\,M$; temp, 38°C; pH 4.0.

TABLE 8

DEPENDENCE OF $[HMO_4^-]$ ON pH OF THE MEDIUM[a]

pH	$[HWO_4^-] \times 10^3\,M$	pH	$[HMoO_4^-] \times 10^3\,M$
3.0	17.99	3.0	22.92
4.0	21.78	3.6	24.65
4.7	24.89	4.0	18.45
5.0	22.20	5.0	5.49
6.0	11.06	6.0	0.66
7.0	1.83	7.0	0.07

[a] pK_2 for tungstic acid, 6.9; pK_2 for molybdic acid, 5.45; $[Na_2WO_4] = [Na_2MoO_4] = 25.0 \times 10^{-3}\,M$.

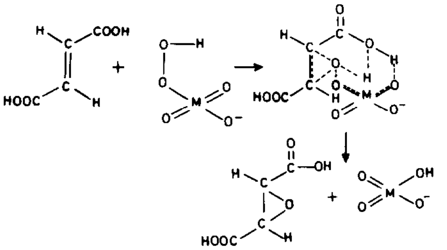

FIGURE 1.

of a salt effect and moderate reduction in rate with decrease in the dielectric constant of the reaction medium discredit and polar, stepwise, addition mechanisms involving charge-separated intermediates visualized from an attack by an OH^+ fragment (*26*). The results are thus in accord with the concept of an intramolecular, concerted reaction progressing at a rate subject to the nucleophilic activity of the double bond and the equilibrium concentration of fumaric pertungstate and fumaric permolybdate esters present. The transition state shown in Fig. 1 is analogous to that visualized earlier for other unsaturated compounds (*12*).

The larger value of the tungstate catalyzed epoxidation rate constant in comparison to the molybdate catalyzed one is a reflection of the greater stability of the peroxyanion of tungstate since within the same group of periodic table, the stability of peroxyanion increases with increasing atomic weight (*27*) and this is in conformity with our reported pK_2 values.

ACKNOWLEDGMENTS

The authors are grateful to Professor Wasiur Rehman for providing research facilities. One of the authors (I. A.) is also thankful to C.S.I.R (New Delhi) for financial assistance.

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