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Macromolecular Organometallic Catalysis

I. Epoxidation. A Comparative Kinetic Study of Tungstate, Molybdate, and Vanadate Ions as Catalysts for the Epoxidation of Maleic Acid at pH 5

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As a prelude to an examination of the concept of macromolecular organometallic catalysis, a comparative kinetic study was made of the catalytic activity of tungstate, molybdate, and vanadate ions at pH 5 in order to select the preferred catalyst for the conversion of maleic acid to *cis*-epoxysuccinic acid using hydrogen peroxide. A facile method for the analysis of the degree of epoxidation achieved was theoretically deduced, confirmed experimentally, and used to establish the reaction kinetics under varying conditions of pH, catalyst concentration, and temperature. The tungsten-containing catalyst is superior to the others examined at pH 5 and the rate equation and activation energy for this system were determined.

INTRODUCTION

The importance of epoxides as industrial chemical intermediates is attested by the 1966 worldwide production capacity which was in excess of 5 billion lb/year (*2a, 3a,b*). The simplest epoxides are manufactured by the air oxidation of unsaturated hydrocarbons such as ethylene or propylene over silver catalysts (*3b, 4–9*). More complex unsaturated substrates are usually converted to their epoxides through the intermediacy of organic peracids in general (*2b, 3c, 9–12*) and peroxyacetic acid in particular (*13, 14*).

However, many unsaturated hydrocarbons are not amenable to peroxidation by either of these procedures and in these cases inorganic peracids are often especially effective (*15*). These inorganic oxidants are usually synthesized within the reaction mixture from hydrogen peroxide and a soluble compound of such less common metals as Os, Ti, Zr, Rh, U, Ru, Ta, Cr, Se, W, Mo, and V (*1*). Since the metals are not irreversibly consumed, these oxidations have been studied as examples of homogeneous catalytic systems. Thus, Mugdan and Young (*16*) 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. This was subsequently extended to include the hydroxylation of long-chain alkenes in various solvents using tungsten and molybdenum trioxide as catalysts (*17*). Later Payne and Williams (*18*) achieved the epoxidation of $\alpha\beta$-unsaturated acids and aldehydes in the presence of sodium tungstate or selenium dioxide while Indictor and Brill (*19*) demonstrated that the acetylacetonates of Cr, Mn, and Co are good catalysts for epoxidation. More recently attention has turned to less qualitative assessments of the oxidation performance of inorganic peroxyacids and kinetic studies of the reaction of peroxytungstic acid with amines (*20*) and allyl alcohols (*21–23*) have been reported.

This paper presents a quantitative and comparative study of the catalytic activity of tungstate, molybdate, and vanadate

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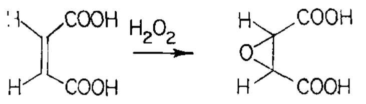
ions on the hydrogen peroxide epoxidation of maleic acid (I) to *cis*-epoxysuccinic acid (II) [Eq. (1)]



I II

The epoxydicarboxylic acid (II) should be of potential commercial interest because it is derived from benzene *via* low-cost maleic anhydride (*3d*) and because it can be converted into dialkyl tin epoxysuccinates which are plasticizer-stabilizers for polyvinyl chloride (*24*), as well as into cross-linkable epoxy-containing film-forming polyamides (*25*).

EXPERIMENTAL METHODS

Epoxidation Procedure

A spoutless beaker (800 ml) fitted with a rubber bung equipped with a stirrer, thermometer, and dropping funnel was charged with maleic anhydride (0.2 mole) and distilled water (200 ml). A 2 *N* sodium hydroxide solution was then added to bring the pH to 4.5. The whole solution was maintained at a temperature of 60° in a thermostatically controlled water bath. Sodium tungstate, molybdate, or vanadate was dissolved in amounts varying between 0.25 to 1% based on the moles of maleic anhydride. The pH of the solution was then adjusted to 5.0 by adding the necessary amount of the 2 *N* sodium hydroxide solution, the volume of which was noted. A 20% excess of hydrogen peroxide (30%, 30 g) was then added. The reaction starts with the evolution of heat and the temperature tends to increase, but is kept constant at 60 ± 0.5° by the intermittent removal of the reaction vessel from the heating bath. Moreover, as the maleic acid is converted to *cis*-epoxysuccinic acid the pH of the reaction mixture tends to drop, but is maintained at 5.0 ± 0.1 by the addition of 2 *N* sodium hydroxide solution, the volume of which is noted against time and serves as a measure of the conversion of maleic acid to *cis*-epoxysuccinic acid. Epoxidation at other pH values and temperatures was carried out similarly.

Determination of Conversion of Maleic Acid to cis-*Epoxysuccinic Acid*

During the reaction, as maleic acid is converted to *cis*-epoxysuccinic acid, there should be a large drop in pH due to the formation of a considerable stronger acid; the pK_2 value for *cis*-epoxysuccinic acid is 3.92 as against 6.50 for maleic acid (*26*, *27*). The drop of pH is dependent on the conversion of maleic acid and hence can be measured from the change in pH.

Instead of allowing the pH to change, it is more convenient to keep the pH constant because, as shown below, the effectiveness of epoxidation is highly dependent on this parameter. The pH is therefore kept constant by the addition of a standardized sodium hydroxide solution. The conversion is determined from the equivalents of sodium hydroxide needed to maintain the pH constant with time. Thus, let H_2M, H_2E and H_2P represent maleic, *cis*-epoxysuccinic and peroxytungstic acids, respectively, and moreover let the corresponding first and second degrees of dis-

$$\begin{array}{llll}
\mathrm{H_2M} & \rightleftharpoons \mathrm{H^+} & + \mathrm{HM^-} & (2) \\
C_m(1-d_{m_1})(1-f) & C_m(1-f)d_{m_1} & C_m(1-f)d_{m_1}(1-d_{m_2}), & \\
\mathrm{HM^-} & \rightleftharpoons \mathrm{H^+} & + \mathrm{M^{2-}} & (3) \\
C_m(1-f)d_{m_1}(1-d_{m_2}) & C_m(1-f\,d_{m_1}d_{m_2}, & & \\
\mathrm{H_2E} & \rightleftharpoons \mathrm{H^+} & + \mathrm{HE^-} & (4) \\
C_m(1-d_{c_1})f & C_m f d_{e_1} & C_m f d_{e_1}(1-d_{e_2}), & \\
\mathrm{HE^-} & \rightleftharpoons \mathrm{H^+} & + \mathrm{E^{2-}} & (5) \\
C_m(1-d_{e_2})f d_{e_1} & C_m f d_{e_1} d_{e_2}, & & \\
\mathrm{H_2P} & \rightleftharpoons \mathrm{H^+} & + \mathrm{HP^-} & (6) \\
C_c(1-d_{p_1}) & C_c d_{p_1} & C_c(1-d_{p_2})d_{p_1}, & \\
\mathrm{HP^-} & \rightleftharpoons \mathrm{H^+} & + \mathrm{P^{2-}} & (7) \\
C_c d_{p_1}(1-d_{p_2}) & C_c d_{p_1} d_{p_2}. & &
\end{array}$$

sociation be $d_{m_1}d_{m_2}$, $d_{e_1}d_{e_2}$, and $d_{p_1}d_{p_2}$. Then if C_m(moles/liter) is the initial concentration of maleic acid and f is the fractional conversion to *cis*-epoxysuccinic acid realized by a catalyst concentration of C_c(moles/liter) reactions (2)–(7) can be written in which the critical species and their concentrations are indicated.

Now the first dissociation constant K_{m1} for maleic acid is 1.42×10^{-2} at 25° (*27*) and therefore from Eq. (2)

$$K_{m_1} = [H^+][C_m(1 - f)d_{m_1}(1 - d_{m_2})]/[C_m(1 - d_{m_1})(1 - f)],$$

$$[H^+]d_{m_1}(1 - d_{m_2})/(1 - d_{m1}) = 1.42 \times 10^{-2}. \qquad (8)$$

Since the pH is maintained at 5 the hydrogen ion concentration is 10^{-5} and the second dissociation constant K_{m_2} is 8.57×10^{-7} at 25° (*27*) Eq. (8) is satisfied by $d_{m_1} = 0.999 \simeq 1$ and similarly $d_{e_1} = 1$. Moreover as C_c is very small compared to C_m the contribution of hydrogen ions from reactions (6) and (7) can be neglected. Furthermore if C_{NaOH} is the concentration of sodium hydroxide in the reaction mixture as a result of alkali addition to maintain the pH at 5 it follows that

$$C_{H^+d} - C_{NaOH} = [H^+] = 10^{-5},$$

since sodium hydroxide ionizes completely and C_{H^+d} is the total concentration of hydrogen ions produced due to dissociation. Hence $C_{H^+d} = C_{NaOH}$ and so from Eqs. (2)–(5)

$$C_{H^+d} = C_m[(1 - f)d_{m_1} + (1 - f)d_{m_1}d_{m_2} + fd_{e_1} + fd_{e_1}d_{e_2}],$$

$$\text{or} \quad C_{NaOH} = C_m[(1 - f) + (1 - f)d_{m_2} + f + fd_{e_2}], \qquad (9)$$

since d_{m1} and d_{e1} are unity. Simplification of Eq. (9) yields

$$C_{NaOH} = C_m[(1 - f)(1 + d_{m_2}) + f(1 + d_{e_2})], \qquad (10)$$

which at zero conversion reduces to

$$C_{NaOH:\,Initial} = C_m[1 + d_{m_2}]. \qquad (11)$$

Thus, from the equivalents of NaOH necessary to raise the pH of an aqueous solution of maleic acid to 5.0 and Eq. (11), d_{m_2} is found to be $(1.1234 - 1) = 0.1234$. Similarly, at complete conversion of H_2M to H_2E, $f = 1$ so from Eq. (10)

$$C_{NaOH\cdot Final} = C_m[1 + d_{e2}],$$

$$\text{or} \quad d_{e_2} = (C_{NaOH:Final}/C_m) - 1. \qquad (12)$$

Analogously, from the equivalents of NaOH necessary to raise the pH of an aqueous solution of *cis*-epoxysuccinic acid to 5.0 and Eq. (12), d_{e_2} is found to be $(1.9440 - 1) = 0.9440$. Rearranging Eq. (10) and substituting for d_{m_2} and d_{e_2} gives the fractional conversion in terms of C_m and C_{NaOH} so that at pH 5

$$f = [(C_{NaOH}/C_m) - (1 + d_{m_2})]/(d_{e_2} - d_{m_2}) = [(C_{NaOH}/C_m) - 1.1234]/0.8206. \qquad (13)$$

Thus the fractional conversion can be simply determined from the amount of NaOH added and Table 1 shows that Eq. (13) is valid for the analysis of known mixtures of maleic and *cis*-epoxysuccinic acid and that the error is within ±1%.

TABLE 1

EVALUATION OF THE ALKALI TITRATION METHOD FOR THE ANALYSIS OF MALEIC-*cis*-EPOXYSUCCINIC ACID MIXTURES

cis-Epoxysuccinic acid (%) in admixture with maleic acid	
Added	Found
100.00	100.00
87.64	87.37
77.22	77.36
69.84	70.01
60.09	60.05
00.00	00.00

RESULTS AND DISCUSSION

The reactions which occur on dissolution of the three catalysts are summarized in Eqs. (14)–(16).

$$Na_2WO_4 \overset{H_2O}{\rightleftharpoons} NaHWO_4 + NaOH, \qquad (14)$$

$$Na_2MoO_4 \overset{H_2O}{\rightleftharpoons} NaHMoO_4 + NaOH, \qquad (15)$$

$$Na_3VO_4 \overset{H_2O}{\rightleftharpoons} Na_2HVO_4 + NaOH \overset{H_2O}{\rightleftharpoons} NaH_2VO_4 + 2NaOH, \qquad (16)$$

Each of the acid anion species is capable of combination with hydrogen peroxide to afford the corresponding peroxyacid anion as in Eqs. (17)–(24).

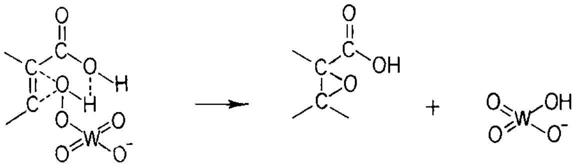
$$HWO_4^- + H_2O_2 \rightleftharpoons HWO_5^- + H_2O, \quad (17)$$

$$HMoO_4^- + H_2O_2 \rightleftharpoons HMoO_5^- + H_2O, \quad (18)$$

$$HVO_4^{2-} + H_2O_2 \rightleftharpoons HVO_5^{2-} + H_2O, \quad (19)$$

$$H_2VO_4^- + H_2O_2 \rightleftharpoons H_2VO_5^- + H_2O. \quad (20)$$

These peroxyacid anions are the epoxidizing agents though other peroxyacid species may also be present (*28–31*). The probable oxidation mechanism (*15*) is exemplified by the peroxytungstate ion in Eq. (21).



(21)

Eq. (21) can be written in kinetic terms so that

$$H_2M + HWO_5^- \underset{k_2}{\overset{k_1}{\rightleftharpoons}} \begin{bmatrix}\text{Intermediate}\\ \text{complex of}\\ H_2M \text{ and } HWO_5^-\end{bmatrix} \overset{k_3}{\rightleftharpoons} H_2E + HWO_4^-,$$

and the rate of formation of H_2E is therefore

$$r_{H_2E} = k_3[A^*], \quad (22)$$

where A^* is the intermediate complex of H_2M and HWO_5^-. If the complex A^* is always in equilibrium then its rate of formation is

$$r_{A^*} = k_1[H_2M][HWO_5^-] - k_2[A^*] - k_3[A^*] = 0,$$

and $[A^*] = k_1[H_2M][HWO_5^-]/[k_2 + k_3]$.

Hence from Eq. (22) the rate of epoxidation

$$r_{H_2E} = k_1k_3[H_2M][HWO_5^-]/[k_2 + k_3] = k[H_2M][HWO_5^-], \quad (23)$$

if $k = k_1k_3/(k_2 + k_3)$. Since in each set of experiments the concentration of catalyst added is a constant, as is pH, the rate equation (23) can be rewritten as

$$r_{H_2E} = k[\text{Maleic Acid}] \times [Na_2WO_4 \text{ or } Na_2MoO_4 \text{ or } Na_3VO_4]. \quad (24)$$

However the concentration of the peroxyacid anion is pH dependent and therefore k should change with pH variation. Then

$$r_{H_2E} = -\frac{d}{dt}[H_2M] = k[H_2M]C_c,$$

and $$[H_2M] = C_m(1 - f),$$

so $$-\frac{d}{dt}C_m(1 - f) = kC_m(1 - f)C_c = C_m\frac{df}{dt}.$$

Thus $$\frac{df}{1 - f} = kC_c\,dt,$$

and $$\int_{f_1}^{f_2}\frac{df}{1 - f} = k\int_{t_1}^{t_2}C_c\,dt,$$

or $$\ln\frac{1 - f_1}{1 - f_2} = kC_c(t_2 - t_1) = kC_c\Delta t.$$

A plot of $(1/C_c)[\ln(1 - f_1)/(1 - f_2)]$ against time should therefore be a straight line of slope k, and Figs. 1–3 shows data in accord with this prediction for several tungstate catalyst concentrations and reaction temperatures. Similarly Fig. 4 con-

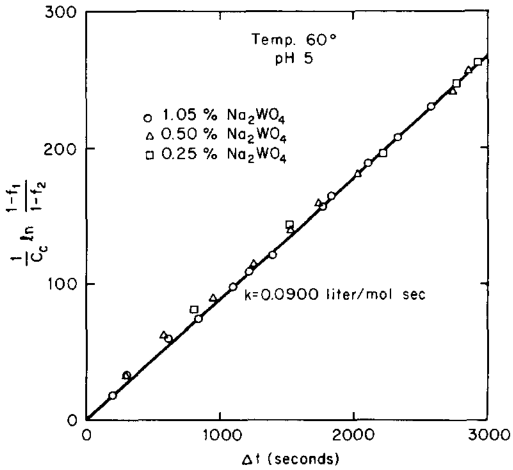


FIG. 1. Epoxidation of maleic acid at 60° by hydrogen peroxide in the presence of sodium tungstate as catalyst.

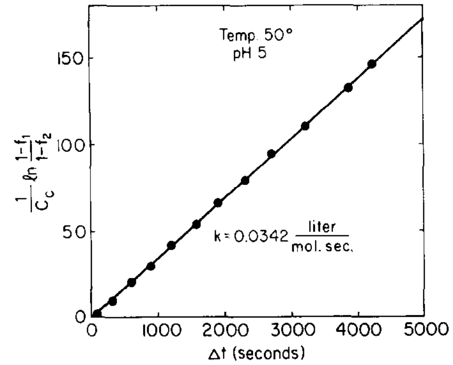


FIG. 2. Epoxidation of maleic acid at 50° by hydrogen peroxide in the presence of sodium tungstate as catalyst.

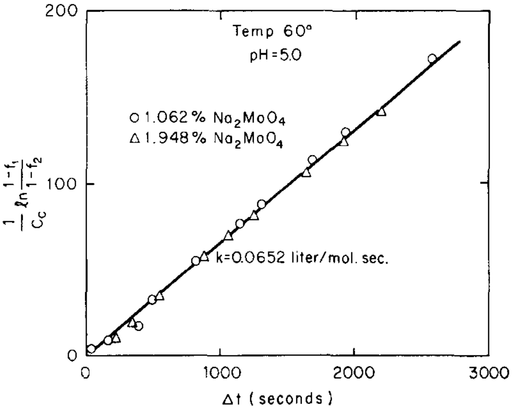


FIG. 4. Epoxidation of maleic acid by hydrogen peroxide in the presence of sodium molybdate as catalyst.

tains the corresponding data for the molybdate catalyst.

The pH-dependency of the peroxytungstate catalysis is illustrated by the data in Figs. 1 and 5 which is collected in Table 2. This apparent change in the magnitude of the rate constant is due to the fact that in the rate equation (24), $[HWO_5^-]$ should be substituted for $[Na_2WO_4]$ because the latter does not reflect the changes in actual catalyst species concentration with pH. Thus, for example, at pH 13 all the tungsten is in the WO_4^{2-} form and no HWO_5^- is available for catalysis. As the pH is decreased WO_4^{2-} ions are converted to HWO_4^- ions and the apparent rate constant increases. Continued pH reduction eventually suppresses the ionization of the tungstic acid and so the apparent rate constant drops as the HWO_5^- ions become unavailable. Hence there will be an optimum pH for epoxidation at which the catalytic activity of Na_2WO_4 is maximized and Table 2 shows that this maximum lies between pH 4.5 and 5. The same considerations apply to molybdate but not to vanadate catalysis. Peroxyvanadic acid is tribasic and appears to be effective only at low pH values where the intermediate oxiranes are subject to facile ring opening (*1, 16*). Among the three catalyst systems the tungstate is therefore clearly superior for the epoxidation of maleic acid. This may be a reflection of the greater stability of

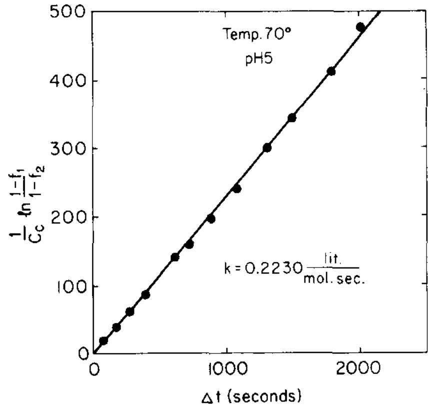


FIG. 3. Epoxidation of maleic acid at 70° by hydrogen peroxide in the presence of sodium tungstate as catalyst.

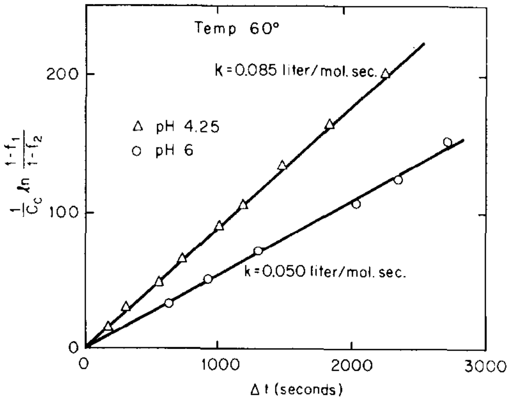


FIG. 5. Epoxidation of maleic acid by hydrogen peroxide in the presence of sodium tungstate as catalyst.

TABLE 2
VARIATION OF TUNGSTATE CATALYZED EPOXIDATION REACTION RATE CONSTANT WITH pH

Epoxidation pH	Reaction rate constant (liter/mole sec × 10^2)
4.25	8.5
5.0	9.0
6.0	5.0

the peroxytungstic acid and the consequent greater concentration of peroxyanions since within a group of the Periodic Table these increase with increasing molecular weight (*29, 32*). Some further characterization of this system was therefore undertaken. Thus Figs. 4 and 5 consist of plots of $(1/C_c)\ln[(1-f_1)/(1-f_2)]$ against Δt for temperatures other than 60°. The gradients of the lines give the magnitude of the rate constants at pH 5 for these temperatures and this data is summarized in Table 3. The data in Table 3 also permitted the determination of the activation energy (ΔE) of the epoxidation reaction. Thus a plot of ln k against $1/T$, where T is the reaction temperature (°K) afforded the straight line shown in Fig. 6. From the Arrhenius equation the slope of this line is $-\Delta E/T$ and since R is the universal gas constant, $\Delta E = 20.641$ kcal.

TABLE 3
VARIATION OF TUNGSTATE CATALYZED EPOXIDATION REACTION RATE CONSTANT WITH TEMPERATURE

Epoxidation temp. (°C)	Reaction rate constant (liter/mole sec × 10^2)
50	3.4
60	9.0
70	22.3

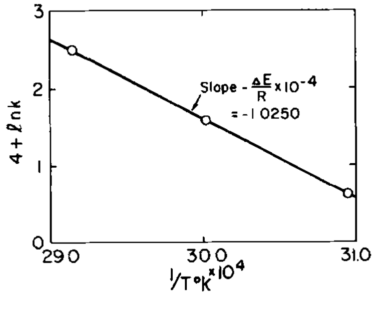


FIG. 6. Effect of temperature on the reaction rate constant of epoxidation.

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