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Macromolecular Organometallic Catalysis

II. Epoxidation Using a Polymeric Quaternary Ammonium Hydrogen Tungstate Catalyst*

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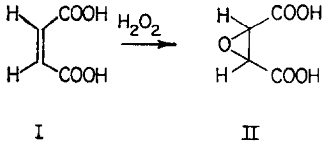
The concept of heterogeneous catalysis by organometallic polymers is presented. These macromolecules are insoluble and contain as an integral part moieties normally recognized as soluble catalysts. The utility of such systems is discussed and demonstrated by a comparison of the efficiency of an insoluble and soluble tungsten catalyst in the epoxidation of maleic acid with hydrogen peroxide. A *pseudo*homogeneous rate equation is proposed for this new type of catalysis and the reaction rate constants and the kinetics are established in terms of a diffusion-controlled catalyst-lined pore model.

INTRODUCTION

The epoxidation and hydroxylation of alkenes can be accomplished by hydrogen peroxide in concert with a variety of catalysts (*1*) the choice of which is often dictated by the structure of the oxidizable substrate. Thus, although unsubstituted hydrocarbons and comparable oils can be smoothly oxidized using a simple aliphatic carboxylic acid as the catalyst, double bonds having electronegative substituents are not susceptible to this treatment (*2*). In these cases, inorganic compounds of metals such as W, Mo, V, Os, Ti, Zr, Th, Nb, Ta, Cr, Ru, and Se have been employed as the catalyst and tungsten in particular is especially effective (*3*) for the conversion of maleic acid (I) to the corresponding *cis*-epoxide (II).



(1)

This unusual functionally substituted epoxide has a potential commercial utility since accessible derivatives are plasticizer-stabilizers for polyvinyl chloride (*4*) and also epoxy resin precursors (*5*).

However, the use of these inorganic catalysts in general and tungsten in particular has not been extensive for a number of reasons. First, catalyst costs are high and adventitious losses must therefore be minimized. Catalyst recovery is clearly mandatory and recovery processes are generally cumbersome and expensive especially when relatively high catalyst concentrations have been required. Secondly, product contamination by traces of the catalyst is often detrimental to product stability, and toxicity (*6*) has been a troublesome problem.

It could therefore be of considerable

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* Part I. Epoxidation. A comparative kinetic study of tungstate, molybdate and vanadate ions as catalysts for the epoxidation of maleic acid at pH 5 (*1*).

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practical importance if these disadvantages were to be overcome by the conversion of these *soluble* catalysts to *insoluble* derivatives which still retained the structural integrity of the catalytic moiety and hence, the catalytic activity. Such a transformation might be achieved by making the catalytic site a pendant or integral part of a polymeric chain or network. The use of polymeric insoluble catalysts has, of course, been recognized for some time (*7–14*), and ion exchange resins have been used as catalysts for arylation, alkylation, acetalization, cyanoethylation, dehydration, dehydrochlorination, esterification, and hydrolysis, as well as for a variety of other synthetic procedures including aldol, Knoevenagel, Pechmann, and Mannich condensations and the Michael addition and Hofmann degradation sequences.

Although in all of these cases the ion exchange resins function only as an insoluble acid or base, it is clear that molecules in solution can diffuse up to an active site on an insoluble polymer, react, and then diffuse away. Support for the applicability of this concept to more sophisticated oxidation reaction systems is provided by the observations that the benzoin condensation and the hydration of alkynes are catalyzed by polymeric cyanide (*15*) and mercuric salts (*16*), respectively. This research is therefore concerned with the demonstration and evaluation of the concept of oxidation catalysis by an insoluble polymeric organometallic catalyst.

The fundamental advantage of such catalysts is that by virtue of their insolubility separation from the reaction mixture by filtration, decantation, or other mechanical methods can readily be achieved. This ease of separation greatly simplifies the problem of securing product uncontaminated by catalyst which is then immediately available for reuse. Furthermore, the insoluble form of the catalyst can be employed in large amounts or concentrations where it is necessary to increase the reaction rate without creating any special or burdensome problem of catalyst separation.

The particular soluble oxidation system selected for demonstration of the insoluble catalyst concept was the tungstate catalyzed epoxidation of maleic acid (I) because Allan and Neogi (*1,2*) had already reported a kinetic study of this reaction and convenient analytical methods had been developed.

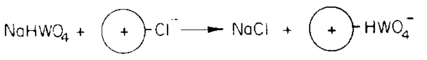
This paper will therefore describe the synthesis of insoluble tungsten-containing catalysts, the kinetics and rate constants of epoxidations using such a catalyst, and a comparison with the corresponding soluble catalyst.

EXPERIMENTAL METHODS

Catalyst Preparation

A solution of sodium tungstate dihydrate ($Na_2WO_42H_2O$) in water (200 ml) was adjusted to pH 5 by the addition of a commercial sulfonic acid ion exchange resin (Dowex 50, Dow Chem. Co.) in the hydrogen form. The solution was filtered, and the filtrate was stirred overnight with the chloride form of a commercial quaternary ammonium ion exchange resin (Amberlite IRA 400, Rohm & Haas Co.) which had previously been adjusted to pH 5 using hydrochloric acid, and exhaustively washed. The resin was then collected and washed with distilled water until the washing gave a negative test for tungsten. This residue was the solid catalyst. The reaction which takes place is as shown in Eqs. (2) and (3).

(2)



(3)

The solid catalyst is thus the hydrogen tungstate form of the resin. Four such catalysts were prepared, and their tungsten trioxide content, which ranged from 4 to 20%, was determined by ignition to WO_3 at 400° for 5 hr.

Epoxidation Procedure

A spoutless beaker (800 ml) fitted with a rubber bung and equipped with stirrer, thermometer, and dropping funnel was charged with maleic anhydride (9.8 g, 0.1 mole) and distilled water (100 ml). A 2 *N* sodium hydroxide solution (~50 ml) 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 and a water suspension of the solid catalyst (consistency ~12%) was added. The pH of the solution was then adjusted to 5 using 2 *N* sodium hydroxide solution (5 ml). A 20% excess of aqueous hydrogen peroxide (30%, 15 ml) was then added. The reaction starts with the evolution of heat, and the temperature tends to increase but is maintained at 60 ± 0.5° by the intermittent removal of the reaction vessel from the heating bath. Moreover, as maleic acid is converted to *cis*-epoxysuccinic acid, the pH of the solution 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 to determine the conversion of the maleic acid to *cis*-epoxysuccinic acid. Each catalyst was recovered by filtration and repeatedly used.

RESULTS AND DISCUSSION

The epoxidation experiments at pH 5 and 60° determined the conversion of maleic to *cis*-epoxysuccinic acid with respect to time and the insoluble catalyst concentrations used. Assuming that heterogeneous reaction follows a *pseudo*homogeneous rate equation the conversion of maleic acid (H_2M) can be written as

$$-\frac{d[\mathrm{H_2M}]}{dt} = kC_c[\mathrm{H_2M}], \qquad (4)$$

where C_c is the catalyst concentration and k is the *pseudo*homogeneous rate constant.

Then, if C_0 is the initial concentration (moles/liter) of maleic acid in a solution of average volume V(liter) and f is the fractional conversion to *cis*-epoxysuccinic acid realized by a polymeric catalyst containing W moles of hydrogen tungstate ions, Eq. (4) can be written as

$$C_0Vdf = kC_0(1-f)Wdt, \qquad (5)$$

and since ϕ and ρ are the bulk volume and density of the catalyst and α is the tungsten trioxide content (g/g) of the catalyst

$$W = \phi\alpha\rho/\mathrm{MW\ of\ WO_3} = \phi\alpha\rho/235. \qquad (6)$$

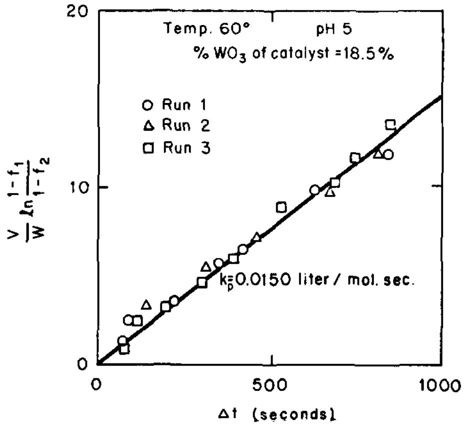


FIG. 1. Epoxidation of maleic acid by hydrogen peroxide using a macromolecular tungstate catalyst.

Rearrangement of Eq. (5) yields

$$k(W/V)\Delta t = \int_{f_1}^{f_2} \frac{df}{1-f} = \ln\frac{1-f_1}{1-f_2},$$

or

$$k\Delta t = \frac{V}{W}\ln\frac{1-f_1}{1-f_2}.$$

Since plots of Δt against $(V/W)\ln[(1-f_1)/(1-f_2)]$ constructed in Figs. 1–4 from the conversion (f) — time (Δt) data collected in Table 1 afford straight lines, the foregoing assumptions are valid and the

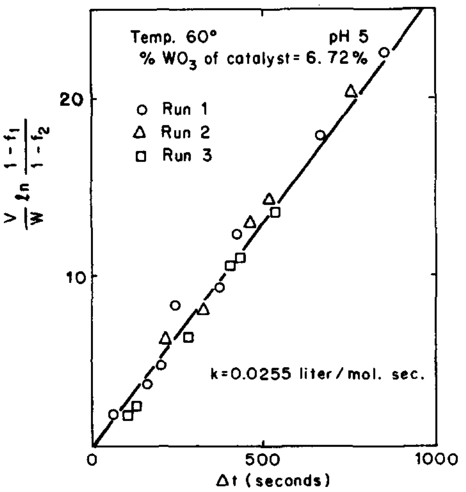


FIG. 2. Epoxidation of maleic acid by hydrogen peroxide using a macromolecular tungstate catalyst.

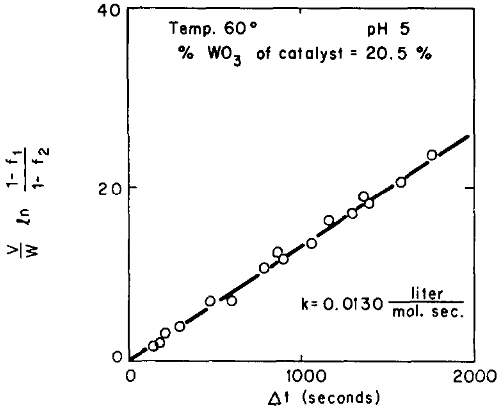


FIG. 3. Epoxidation of maleic acid by hydrogen peroxide using a macromolecular tungstate catalyst.

slope of the lines furnishes the magnitude of the rate constants (k) for the various catalysts. The magnitude of the rate constant for a particular catalyst was found to remain constant even after repeated reuse (as many as 15 times), and this coupled with the fact that the reaction does not proceed in the absence of catalyst demonstrates that it is the organometallic macromolecule which functions as the catalyst. A striking visual endorsement of this conclusion is provided by the corresponding vanadium-containing polymer which turns a brilliant red during oxidation while the surrounding solution remains colorless. The variation of k with the tungsten content of

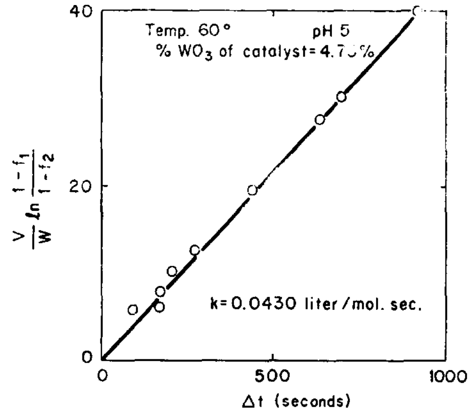


FIG. 4. Epoxidation of maleic acid by hydrogen peroxide using a macromolecular tungstate catalyst.

TABLE 1
EPOXIDATION[a] OF MALEIC ACID BY HYDROGEN PEROXIDE USING A MACROMOLECULAR CATALYST

Expt. no.	WO$_3$ in catalyst (%)	V/W[b]	Elapsed reaction time (Δt) (sec)	Fractional conversion (f)
1	18.50	18.1	0	0.0000
2			85	0.1344
3			230	0.1762
4			345	0.2684
5			425	0.2953
7			536	0.3528
8			865	0.4456
1	18.50	19.7	0	0.0331
2			137	0.1772
3			315	0.2470
4			400	0.3033
5			670	0.3812
6			838	0.4322
1	18.50	20.7	0	0.0322
2			115	0.1476
3			198	0.1825
4			300	0.2335
5			392	0.2738
6			521	0.3597
7			696	0.4080
8			845	0.5637
1	6.72	59.5	0	0.0000
2			58	0.0725
3			255	0.1503
4			430	0.2067
5			665	0.2792
6			859	0.3382
1	6.72	53.8	0	0.0000
2			215	0.1586
3			450	0.2899
4			676	0.3703
5			975	0.4503
1	6.72	60	0	0.1274
2			143	0.1640
3			275	0.2034
4			435	0.2691
5			550	0.2953
1	20.50	28.5	0	0.0000
2			215	0.1109
3			400	0.1591
4			600	0.2127
5			324	0.3200
6			1070	0.3575
7			1310	0.4272

TABLE 1 (*Continued*)

Expt. no.	WO_3 in catalyst (%)	V/W^b	Elapsed reaction time (Δt) (sec)	Fractional conversion (f)
8			1403	0.4540
9			1586	0.5076
10			1788	0.5613
1	4.75	74.4	0	0.1430
2			100	0.2127
3			270	0.2771
4			444	0.3441
5			699	0.4300
6			920	0.5023

[a] Epoxidation carried out at 60° and pH 5.

[b] V is the average volume of the solution and W is the moles of HWO_4^- present in the added macromolecular catalyst.

the catalyst is summarized in Table 2 and Fig. 5.

It is apparent that the reaction rate constant is inversely proportional to the tungsten content of the polymer and extrapolation of the plot of these quantities at low tungsten levels gives the value of the reaction rate constant when all the hydrogen tungstate ions are at the surface of the polymer bead and are readily accessible to the reactant molecules in solution. However, as the tungsten content of the catalyst is increased, the additional hydrogen tungstate ions are accommodated in the interior of the polymer network, and the soluble reactants have to diffuse into this microporous structure in order to reach these sites. The reaction products also have to diffuse out before the peroxidation sites again become available. Both of these diffusion processes contribute to the decrease in the reaction rate constant.

TABLE 2

VARIATION OF REACTION RATE CONSTANT WITH TUNGSTEN CONTENT OF THE MACROMOLECULAR ORGANOMETALLIC CATALYST

Tungsten content of the polymeric catalyst (% WO_3)	Reaction rate constant (liter/mole sec)
4.75	43.0×10^{-3}
6.72	25.5
18.50	15.0
20.50	13.0

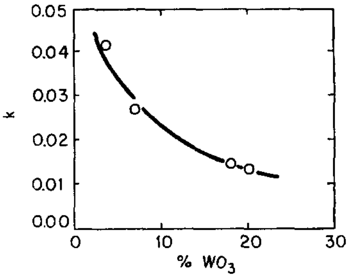


FIG. 5. Variation of the reaction rate constant for the epoxidation of maleic acid with the tungsten trioxide content of the macromolecular catalyst.

Assuming that Thiele's porous catalyst model (*17*) can be applied to this system.

$$\frac{\partial C_t}{\partial t} = D_L \frac{\partial^2 C_t}{\partial x^2} - \frac{2k_a C_t}{r}, \tag{9}$$

where C_t is the concentration at time t at a distance x within the pore of radius r; D_L is the diffusivity of the maleic acid within the catalyst of net cross-sectional area of pores Ψ; and k_a is the reaction rate constant based on pore surface area. Moreover,

$$V \frac{\partial C_m}{\partial t} = D_L \Psi \left. \frac{\partial C_t}{\partial x} \right|_{x=0}. \tag{10}$$

Since C_m is the concentration of H_2M outside the catalyst at any time t, the boundary conditions for Eqs. (9) and (10) are $C = C_m$ when $x = 0$ and $\partial C / \partial x = 0$ when $x = L$ the pore length. Also at zero time, $C = 0$ for $x > 0$. Therefore, if s is the parameter, taking the Laplace Transform of both sides of Eq. (9) yields

$$sC(s) = D_L \frac{d^2 C(s)}{dx^2} - \frac{2k_a}{r} C(s),$$

solution of which gives

$$C(s) = A \sinh px + B \cosh px,$$

where

$$p = [(2k_a / rD_L) + (s/D_L)]^{1/2}$$

and A and B are constants.

Since at $x = 0$, $C = C_m$ and therefore $C(s) = C_m(s)$, $B = C_m(s)$.

Also at $x = L$, $\partial C/\partial x = 0$ for all values of t and so $\partial C(s)/\partial x|_{x=L} = 0$.
Thus,

$pA \cosh pL - pB \sinh pL = 0$ or $A = B \tanh pL$ and

$$C(s) = C_m(s) \cosh p(L - x)/\cosh/pL. \quad (11)$$

Since experimentally t is relatively large and the mathematical solution must be for finite time, s/D_L is negligibly small in comparison to $2k_a/rD_L$ and therefore

$$p^2 = 2k_a/rD_L.$$

Returning to Eq. (10) and taking the Laplace Transform affords

$$V[sC_m(s) - C_0] = D_L\Psi \left.\frac{dC(s)}{dx}\right|_{x=0} \cdot \quad (12)$$

Combination of Eqs. (11) and (12) and substitution of Ψ by $n\pi r^2$, where n is the number of pores in the catalyst gives

$$V[sC_m(s) - C_0] = -D_L(n\pi r^2)p \tanh pLC_m(s). \quad (13)$$

Multiplication of Eq. (13) by pL/pL furnishes

$$V[sC_m(s) - C_0] = -D_L(n\pi r^2 L)p^2 \left(\frac{\tanh pL}{pL}\right),$$

and substitution of $2k_a/rD_L$ for p^2 affords

$$[sC_m(s) - C_0] = -\frac{(2n\pi rL)}{V} k_a \left(\frac{\tanh pL}{pL}\right) C_m(s) \cdot \quad (14)$$

Rearrangement of Eq. (14) yields

$$[sC_m(s) - C_0] = -\frac{(2n\pi rL)}{V} k_a \left(\frac{\tanh pL}{pL}\right) C_m(s) \cdot \quad (15)$$

Since the concentration of catalyst,

$$C_c = 2n\pi rL\gamma/V = W/V,$$

where γ is the surface density of hydrogen tungstate ions (moles/cm^2) and $k_a/\gamma = k_0$, then Eq. (15) can be rewritten so that

$$C_m(s)\left[s + k_cC_c\left(\frac{\tanh pL}{pL}\right)\right] = C_0,$$

or

$$C_m(s) = C_0 \Big/ \left[s + k_0C_c\left(\frac{\tanh pL}{pL}\right)\right].$$

Taking the inverse of both sides

$$C_m(t) = C_0 \exp\left[-k_0C_c\left(\frac{\tanh pL}{pL}\right)t\right],$$

which is equivalent to

$$\ln\frac{1 - f_1}{1 - f_2} = k_0C_c\left(\frac{\tanh pL}{pL}\right)\Delta t. \quad (16)$$

Combinations of Eqs. (8) and (16) gives

$$\frac{V}{W}\ln\frac{1 - f_1}{1 - f_2} = k_0\left(\frac{\tanh pL}{pL}\right)\Delta t, \quad (17)$$

which can be rewritten as

$$\frac{V}{W}\ln\frac{1 - f_1}{1 - f_2} = k_0E\,\Delta t, \quad (18)$$

where $E = \tanh pL/pL$ is a Thiele type catalyst effectiveness factor. Moreover, Eq. (18) suggests that a plot of $V/W. \ln[(1 - f_1)/(1 - f_2)]$ against Δt will be a straight line for a particular catalyst having a defined tungsten content. Equation (18) is therefore identical with Eq. (7) when $k = k_0E$. However, as the tungsten content approaches zero, the length of the active catalyst pore L also approaches zero and the effectiveness factor $E = \tanh pL/pL$ will approach unity. On the other hand, if the distribution of HWO_4^- ions is uniform over the entire carrier surface then γ should vary proportionately with the tungsten content; i.e., as $k_a \rightarrow 0$, E will approach a value of unity. Since $E = 1$ for a homogeneous epoxidation (*1*) the corresponding rate constant (0.09 liter mole^{-1} sec^{-1}) can be substituted for k_0. Since by definition the effectiveness factor E for any catalyst containing ω moles of tungsten is k/k_0, values of E can be calculated from the experimentally determined values of the reaction rate constants, and these are summarized in Table 3.

Moreover, since during the preparation of the catalyst, each resin bead is uniformly immersed in the sodium hydrogen tungstate solution, and since the beads are of rather uniform size and spheroidal shape, it can be assumed that the catalytic

TABLE 3

VARIATION OF THE EFFECTIVENESS FACTOR WITH THE TUNGSTEN CONTENT OF THE MACROMOLECULAR ORGANOMETALLIC CATALYST

Expt. no.	Tungsten content of the polymeric catalyst (% WO_3)	$E = k/k_0$
1	4.75	0.48
2	6.72	0.28
3	18.50	0.17
4	20.50	0.14

length of the pores, L, is proportional to the tungsten content. Further, if $pL > 3$, $E = \tanh pL/pL \simeq 1/pL$ and, therefore, from Expt. 4 in Table 2, $(pL)_4 = (1/E) = 6.94$.

It also follows that for any catalyst containing ω moles of tungsten $(pL)_\omega = (pL)_4$ [$\text{Tungsten}_\omega/\text{Tungsten}_4$] and the various values of pL corresponding to the tungsten contents of the catalysts used are calculated and collated in Table 4. The theoretical value of the effectiveness factor E_{theo} is determined from a standard plot (*18*) of E against (pL) for $(pL) < 3$.

However the effectiveness factor can also be calculated on the basis that the catalyst ions are distributed uniformly over the entire pore surface. Under this circumstance γ varies directly with the tungsten content of the catalyst, L being constant, so that $(pL)_\omega = (pL)_4(\gamma_\omega/\gamma_4)^{1/2} = (pL)_4[(WO_3 \text{ content})_\omega/(WO_3 \text{ content})_4]^{1/2}$.

TABLE 4

COMPARISON OF CATALYSIS EFFECTIVENESS FACTOR E DETERMINED FROM THEORETICAL CONSIDERATIONS (pore length variable) AND EXPERIMENT

Expt. no.	Tungsten content of the polymeric catalyst (% WO_3)	pL	E_{theo}	$E_{\text{exp}} = k/k_0$
1	4.75	1.61	0.57	0.48
2	6.72	2.27	0.40	0.28
3	18.50	6.26	0.16	0.17
4	20.50	6.94	0.14	0.14

TABLE 5

COMPARISON OF CATALYSIS EFFECTIVENESS FACTOR E DETERMINED FROM THEORETICAL CONSIDERATIONS (pore length constant) AND EXPERIMENT

Expt. no.	Tungsten content of the polymeric catalyst (% WO_3)	pL	E_{theo}	$E_{\text{exp}} = k/k_0$
1	4.75	3.34	0.30	0.48
2	6.72	3.97	0.25	0.28
3	18.50	6.60	0.15	0.17
4	20.50	6.94	0.14	0.14

The values of $(pL)_\omega$ and the corresponding theoretical values of the effectiveness factor are shown in Table 5.

It is noteworthy that the experimentally determined values of E fall between the two theoretically calculated values. This is attributed to the nonexistence of either a uniform distribution of catalyst ions over the entire surface or of sharp catalytic surface boundaries within the partially catalyst-lined pores. The preferred physical picture of the macromolecular catalyst is therefore one in which there is a nonuniform distribution of catalyst ions over the entire surface of the pores with a maximum concentration near the exterior and a minimum at the interior of the pore.

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