an approach modeled after the elegant work of Eschenmoser and coworkers, wherein they demonstrate the angular dependence of displacements at saturated carbon [L. Tenud, S. Faroog, J. Seible, and A. Eschenmoser, *Helv. Chim. Acta,* **53,** 2059 (1970)].

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(15) It must be pointed out that all our mechanistic considerations, as well as those of others (ref 11), are predicated on the assumption that a single metal center is acting as the catalyst. This is by no means a foregone conclusion, especially in the case of high valent V, Mo, and W oxo species which are well known for their tendencies to form exotic oligomers. Even if metal clusters do turn out to play a role in these oxidations, we feel that the results with allylic alcohols would support the involvement of only one metal center at a time. Unless the allylic alcohol and the hydroperoxide coordinate to the same metal, it is, in our opinion, difficult to rationalize the exceptional syn selectivities observed[13c,e] in epoxidations of cyclic allylic alcohols.

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Kinetics and Mechanism of the Epoxidation of Maleic and Fumaric Acids by Hydrogen Peroxide in the Presence of Sodium Orthovanadate as Catalyst

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The kinetics and mechanism of epoxidation of maleic and fumaric acids by hydrogen peroxide in the presence of sodium orthovanadate have been studied. The epoxidation rate of fumaric acid into *trans*-epoxysuccinic acid is faster than that for the epoxidation of maleic acid into *cis*-epoxysuccinic acid. The reaction is first order with respect to unsaturated acid and catalyst and zero order with respect to hydrogen peroxide. Based on substituent, solvent, and salt effects, the mechanism of the epoxidation step is believed concerted with considerable polar (electrophilic) character.

Although organic peracids[1] are generally used for the epoxidation of alkenes, compounds having strong electron-withdrawing substituents adjacent to the double bonds are not readily epoxidized by them.[2] More recently hydroperoxides[3–7] 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[5–7] bring about epoxidation through metal–hydroperoxide–olefin complexes, whereas aqueous hydrogen peroxide in the presence of tungstate or molybdate epoxidizes through peroxy acid.[8–10] And contrary to expectation, the pH dependence of the epoxidation rate shows that vanadate-catalyzed epoxidation by aqueous hydrogen peroxide is still different from the molybdate- or the tungstate-catalyzed process.

The epoxydicarboxylic acids should be of potential commercial interest because of their easy conversion into dialkyltin epoxysuccinates which are important plasticizer-stabilizers for polyvinyl chlorides[11] as well as for cross-linkable epoxy-containing film-forming polyamides.[12] This paper, therefore, presents a quantitative and comparative kinetic study of the epoxidation of maleic and fumaric acids by hydrogen peroxide in the presence of sodium orthovanadate as catalyst.

Experimental Section

All the chemicals used were reagent (B. D. H.) grade. Maleic and fumaric acid solutions were standardized using the bromate–bromide procedure.[13] The ionic strength of the reaction mixture was maintained by the addition of sodium perchlorate solution. The progress of the reaction was followed spectrophotometrically as detailed elsewhere.[10] Triethanolamine was used to adjust the pH of the reaction mixture. Every run was followed until reaction was at least 75% complete. The plots of concentration of hydrogen peroxide vs. time were good straight lines, and the rates were obtained from the slopes of these lines. No plot contained less than ten points. Pseudo-zero-order rates are reported here as k_{obsd}.

Decomposition of Hydrogen Peroxide by Sodium Orthovanadate. Aqueous solutions of hydrogen peroxide, catalyst, and hydrochloric acid were mixed under experimental conditions and hydrogen peroxide was estimated after 4 h. In the presence of vanadate, the decomposition of hydrogen peroxide was negligible between pH 4 and 7 and significant at about pH 7.

Identification of Products. The epoxysuccinic acid formed in the reaction was measured quantitatively by the pyridinium chloride–pyridine method described by Jungnickel et al.[14] Instead of methanolic sodium hydroxide, an aqueous solution was used for the titration. Maleic and fumaric acids, at pH 6.0, gave their corresponding epoxides in 93 and 86% yields, respectively. No tartaric acid could be detected in the reaction mixture above pH 5. However, below pH 5 the test for tartaric acid[15] was positive and its form was identified by Buchanan's chromatographic method.[16] The R_f values suggest that maleic and fumaric acids give *dl* and meso forms of tartaric acid, respectively.

Results and Discussion

Straight line plots of hydrogen peroxide concentration against time with identical slopes (Table I) indicated zero-order dependence of rate on the hydrogen peroxide concentration. k_{obsd} (Tables II and III) is directly proportional to the concentrations of substrate and catalyst. The standard deviation of k_{obsd} is 0.02.

Preliminary studies have shown that under our experimental conditions, hydrogen peroxide does not bring about epoxidation of maleic and fumaric acids without the catalyst (vanadate) and also the catalyst alone (without the oxidant) fails to bring about the epoxidation. This clearly suggests the involvement of some more oxygenated form of vanadium in the process as oxygen carrier. Jander and Jahr[17] have shown that in the acidic medium, orthovanadate changes into vanadium pentoxide, which according to Flood and co-workers[18] dissolves in aqueous hydrogen peroxide giving peroxyvanadic acid. It is thus presumed here that in the system under investigation, peroxyvanadic acid is the epoxidizing species and in a 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.

Table I. Pseudo-Zero-Order Rates for the Epoxidation of Maleic and Fumaric Acids with Hydrogen Peroxide in the Presence of Sodium Orthovanadate[a]

$[H_2O_2] \times 10^4$, M	Maleic acid $k_{obsd} \times 10^7$, mol L^{-1} min^{-1}	Fumaric acid $k_{obsd} \times 10^6$, mol L^{-1} min^{-1}
6.00	8.35	3.14
8.00	8.33	3.16
10.00	8.36	3.17
12.50	8.34	3.16
15.00	8.32	3.18
20.00	8.33	3.19
25.00	8.30	3.18
30.00	8.32	3.16
35.00	8.34	3.19
40.00	8.33	3.17

[a] $[Na_3VO_4] = 2.00 \times 10^{-4}$ M; [maleic acid] = [fumaric acid] = 6.00×10^{-2} M; temp, 40 °C; pH 6.0.

Table II. First-Order Dependence of Vanadate Catalyzed Epoxidation Rates of Maleic and Fumaric Acids on the Concentration of Unsaturated Acid[a]

[Maleic acid] $\times 10^2$, M	$k_{obsd} \times 10^7$, mol L^{-1} min^{-1}	[Fumaric acid] $\times 10^2$, M	$k_{obsd} \times 10^6$, mol L^{-1} min^{-1}
6.00	8.33	6.00	3.18
8.00	11.50	8.00	4.28
10.00	14.01	10.00	5.10
12.00	16.23	12.00	6.78
14.00	19.85	14.00	7.35

[a] $[H_2O_2] = 2.50 \times 10^{-3}$ M; $[Na_3VO_4] = 2.00 \times 10^{-4}$ M; temp, 40 °C; pH 6.0.

Table III. First-Order Dependence of Vanadate-Catalyzed Epoxidation Rate of Maleic and Fumaric Acids on Catalyst Concentration[a]

$[Na_3VO_4] \times 10^4$, M	Maleic acid $k_{obsd} \times 10^7$, mol L^{-1} min^{-1}	Fumaric acid $k_{obsd} \times 10^6$, mol L^{-1} min^{-1}
2.00	8.33	3.19
4.00	15.78	6.20
6.00	24.01	9.89
8.00	34.35	12.40
10.00	41.02	16.35

[a] $[H_2O_2] = 2.50 \times 10^{-3}$ M; [maleic acid] = [fumaric acid] = 6.00×10^{-2} M; temp, 40 °C; pH 6.0; $\mu = 60.0 \times 10^{-4}$ M.

$$H_3VO_5 \overset{K_1}{\rightleftharpoons} H_2VO_5^- + H^+ \quad (1)$$

$$H_2M \text{ or } H_2F + H_3VO_5 \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \text{(intermediate complex)} \quad (2)$$

$$\text{(intermediate complex)} \xrightarrow{k_3} H_2E + H_3VO_4 \quad (3)$$

H_2M, H_2F, and H_2E are maleic, fumaric, and epoxysuccinic acid, respectively.

Assuming steady state for the complex concentration,

$$\text{epoxidation rate} = k'[H_2M \text{ or } H_2F][H_3VO_5] \quad (4)$$

where

$$k' = \frac{k_2k_3}{k_{-2} + k_3}$$

Table IV. Dependence of Vanadate-Catalyzed Epoxidation Rate of Maleic and Fumaric Acids on the pH of the Medium[a]

	Maleic acid		Fumaric acid	
Epoxidation pH	$k_{obsd} \times 10^7$ (calcd), mol L^{-1} min^{-1}	$k_{obsd} \times 10^7$ (exptl), mol L^{-1} min^{-1}	$k_{obsd} \times 10^7$ (calcd), mol L^{-1} min^{-1}	$k_{obsd} \times 10^6$ (exptl), mol L^{-1} min^{-1}
4.00	—	—	4.98	4.98
5.00	9.31	9.32	4.76	4.77
5.50	9.07	9.09	4.32	4.35
6.00	8.37	8.33	3.33	3.19
6.50	6.73	6.62	1.93	1.88
7.00	4.15	4.16	0.83	0.83

[a] [Maleic acid] = [fumaric acid] = 6.00×10^{-2} M; $[Na_3VO_4] = 2.00 \times 10^{-4}$ M; $[H_2O_2] = 2.50 \times 10^{-3}$ M; temp, 40 °C.

Table V. Dependence of Vanadate-Catalyzed Epoxidation Rate of Maleic or Fumaric Acid in Ethanol–Water Mixture on the Composition of the Solvent[a]

% of ethanol	Dielectric constant[b]	Maleic acid $k_{obsd} \times 10^7$, mol L^{-1} min^{-1}	Fumaric acid $k_{obsd} \times 10^6$, mol L^{-1} min^{-1}
0	78.5	8.32	3.19
15.4	69.5	6.93	2.76
31.5	60.0	5.20	2.35
50.0		2.74	1.08

[a] [Maleic acid] = [fumaric acid] = 6.00×10^{-2} M; $[Na_3VO_4] = 2.00 \times 10^{-4}$ M; $[H_2O_2] = 2.50 \times 10^{-3}$ M; pH 6.0; temp, 40 °C. [b] The dielectric constant values have been taken from A. A. Frost and R. G. Pearson, "Kinetics and Mechanism", 2nd ed, Wiley, New York, N.Y., 1961, p 146.

The catalyst (Na_3VO_4), at any stage in the process, is distributed in three forms according to eq 5.

$$[Na_3VO_4] = [H_3VO_5] + [H_2VO_5^-] + \text{[intermediate complex]} \quad (5)$$

The concentration of the intermediate complex in eq 5 is negligible in comparison to other terms of eq 5. Hence,

$$[Na_3VO_4] = [H_3VO_5] + [H_2VO_5^-] \quad (6)$$

Substituting for $[H_3VO_5]$ from eq 1 and 6 in eq 4, we get

$$\text{epoxidation rate} = \frac{k'[H^+][Na_3VO_4][H_2M \text{ or } H_2F]}{K_1 + [H^+]} \quad (7)$$

This explains the order of the reaction with respect to the substrate, catalyst, and hydrogen peroxide. The pH dependency of the process (Table IV) is also very well explained by eq 7. The straight-line plot between inverse of epoxidation rate and inverse of $[H^+]$ is in agreement with eq 7. Using the measured epoxidation rate values at pH 5.0 and 7.0 (Table IV) and eq 7, pK_1 and k' were calculated both for maleic and fumaric acids. For maleic acid pK_1 is 6.90 and k' is 0.08, and for fumaric acid pK_1 is 6.30 and k' is 0.42. The two values of pK_1 are different due to the large difference in the dissociation constants of maleic and fumaric acids. Substituting these values of K_1 and k' in eq 7, epoxidation rates at different pH's were calculated. The calculated epoxidation rates compare well (Table IV) with the observed ones. The un-ionized substrate maleic or fumaric acid will no doubt be in equilibrium with its ionized forms. But as reaction 2 involves only the double bond, k_2 for the ionized and un-ionized forms will not be different and the same will be true for k_{-2}. Hence, H_2M or

Table VI. Dependence of Vanadate-Catalyzed Epoxidation Rate of Maleic and Fumaric Acid on the Ionic Strength of the Medium[a]

Ionic strength, $\mu \times 10^4$ M	Maleic acid $k_{obsd} \times 10^7$, mol L^{-1} min^{-1}	Fumaric acid $k_{obsd} \times 10^6$, mol L^{-1} min^{-1}
12.0	8.33	3.19
16.0	8.32	3.18
20.0	8.29	3.19
24.0	8.34	3.20
36.0	8.33	3.19

[a] [Maleic acid] = [fumaric acid] = 6.00×10^{-2} ; M; [Na_3VO_4] = 2.00×10^{-4} M; [H_2O_2] = 2.50×10^{-3} M; temp, 40 °C; pH 6.0.

Table VII. The Substituent Effect on the Epoxidation of Maleic and Fumaric Acid by Hydrogen Peroxide[a]

[H_2O_2] $\times 10^3$, M	Citraconic acid $k_{obsd} \times 10^7$, mol L^{-1} min^{-1}	Mesoconic acid $k_{obsd} \times 10^6$, mol L^{-1} min^{-1}
2.00	16.52	6.32
2.50	16.51	6.35
3.00	16.52	6.33
3.50	16.53	6.32

[a] [Citraconic acid] = [mesoconic acid] = 6.00×10^{-2} M; [Na_3VO_4] = 2.00×10^{-4} M; temp, 40 °C; pH 6.0.

H_2F in eq 7 stand for the total concentration of the ionized and un-ionized acid.

Above pH 5, *cis*- and *trans*-epoxysuccinic acids are stable, but below pH 5 they change into *dl*- and *meso*-tartaric acids, respectively. The *dl* form reacts with the catalyst[19] whereas the meso form does not. Hence, in the case of maleic acid, epoxidation kinetics were not studied below pH 5.

Increase in ionic strength did not affect the rate. The faster epoxidation rate of citraconic acid as compared to that of maleic acid and of mesaconic acid as compared to that of fumaric acid under identical conditions show 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-center-type additions.[20,21] The epoxidation rate decreased as the percentage of water in alcohol–water mixture decreased (dielectric constant lowered) but no linear relation between 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 bond of the olefinic substrate as described elsewhere.[10]

The two carboxylic groups on the same side of the double bond offer hindrance in the formation of the intermediate complex and this explains why the epoxidation rate of maleic acid is slower than that of fumaric acid.

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Registry No.—Maleic acid, 110-16-7; fumaric acid, 110-17-8; H_2O_2, 7722-84-1; Na_3VO_4, 13721-39-6.

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