On the Mechanism of the Molybdenum and Vanadium Catalyzed Epoxidation of Olefins by Alkyl Hydroperoxides

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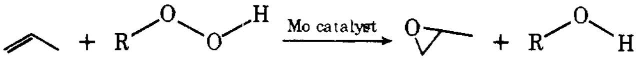
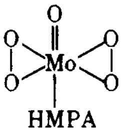
Epoxidations carried out in the presence of ^{18}O-enriched water provide evidence that the intact alkyl hydroperoxide is present in the activated complex responsible for oxygen transfer to the olefin. The literature mechanisms for these epoxidations are criticized, and a new mechanistic approach is presented.

On a worldwide basis almost a billion pounds of propylene oxide will be produced this year by the molybdenum catalyzed epoxidation of propylene with alkyl hydroperoxides (Halcon process[1]):



The by-product alcohol (ROH) is either converted to styrene (R = α-phenethyl) or used as an octane booster in gasoline (R = *tert*-butyl). In spite of the importance of this very efficient epoxidizing system some essential facts concerning the mechanism are missing.[2] For example, it is not known whether the alkyl hydroperoxide (or some coordinated version of it) is present in the activated complex which effects transfer of the oxygen atom to the olefin. A priori one cannot exclude initial reaction of the alkyl hydroperoxide with the metal producing the alcohol and a metal species which epoxidizes the olefin in a subsequent step. This latter possibility seemed especially worthy of consideration following the important discovery by Mimoun, de Roch, and Sajus that molybdenum(VI) peroxo compounds, such as **1**, stoichiometrically epoxidize olefins under anhydrous conditions in organic solvents.[3]



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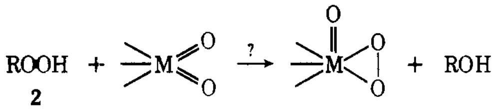


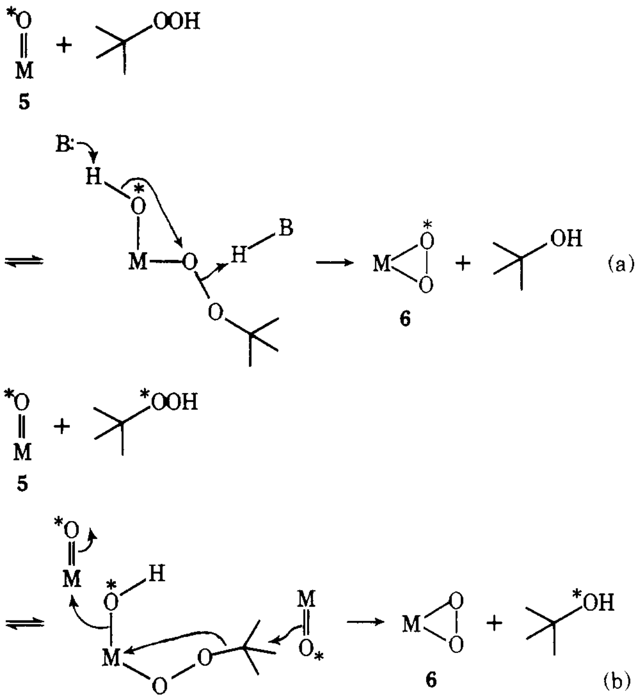
2 **3** **4**

Thus these French workers[3] and several other groups[2,5] including ourselves[4] speculated that the active oxidants in the catalytic systems might also be peroxo species (**4**, analogous to **1**) generated in situ by reaction of the alkyl hydroperoxide (**2**) with a metal oxo compound (**3**). There are reports, albeit under fairly drastic conditions, that molybdenum compounds react with alkyl hydroperoxides to give peroxo complexes.[5] We made numerous unsuccessful attempts to isolate peroxo complex **1**, under the normal (*tert*-butyl hydroperoxide, PhH, reflux) $Mo(CO)_6$ catalyzed reaction conditions, by adding HMPA at different stages. Promising-looking yellow mixtures (**1** is yellow) were sometimes obtained, but all efforts at purification failed.[6]

The issue of whether or not the alkyl hydroperoxide is directly involved in the epoxidation step is an important one. No serious mechanistic considerations can begin until this question is answered. It seemed that an ^{18}O-labeling experiment might provide useful information. We had previously shown that the oxo oxygen of peroxo complex **1** exchanged rapidly with ^{18}O-enriched water, and that there was no scrambling of the oxo and peroxo oxygens.[4] It was this selectively labeled specimen of **1** which enabled us to demonstrate that only the peroxo oxygens of **1** were transferred during epoxidation of olefins.[4]

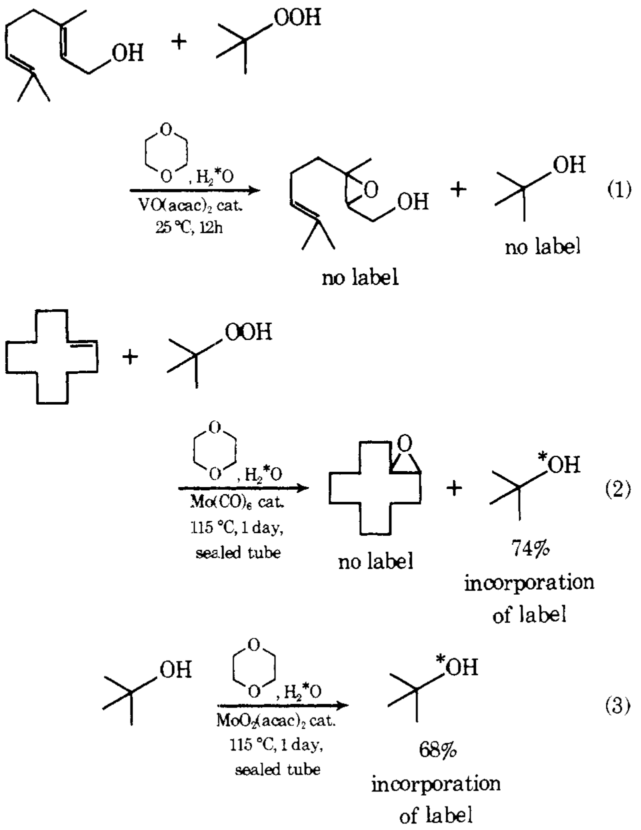
In order to speculate on how a peroxo–metal linkage might arise from interaction of an alkyl hydroperoxide and a metal species, one must know something about the nature of the metallic catalyst under the reaction conditions. Sheldon has made the important observation that the same *cis*-dioxomolybdenum(VI) diol complex is isolated from these epoxidations regardless of which molybdenum compound is initially added as catalyst.[7] For this and other reasons[8] it seems very likely that the active catalytic species bear oxometal groups. If peroxo species are formed from reaction of alkyl hydroperoxides with the oxometal groups on the catalyst, we feel that the two reaction paths shown in Scheme I are the most reasonable alternatives. Since these epoxidations proceed readily under anhydrous conditions, and since the alcohol is formed in essentially quantitative yield, path a appears more likely than path b. In path b the only oxygen nucleophile available, under the usual dry conditions, to capture the incipient tertiary cation would be a metal oxo group; it is not likely that this would be an efficient enough process to account for the high yields of *tert*-butyl alcohol observed.

Scheme I. Peroxo Mechanisms



The oxometal group **5** is shown as labeled in both pathways in Scheme I. It is apparent that if such labeling was possible, one could determine whether either of these peroxo paths were involved. Path a predicts ^{18}O incorporation into the epoxide (via the partially labeled peroxo species **6**) but none into the *tert*-butyl alcohol, and path b predicts label in the *tert*-butyl alcohol but none in the epoxide. Since oxo transition metal compounds are known to exchange readily with water,[9,4] we tested for the involvement of the peroxo paths in Scheme I by carrying out epoxidations in the presence of ^{18}O-enriched

Scheme II. $H_2{}^{18}O$ Incorporation Experiments

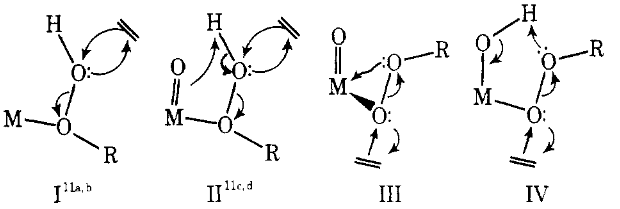


water. As shown in Scheme II, both the vanadium and the molybdenum systems were examined. The epoxidations were carried out in dioxane containing 10% by volume 66% ^{18}O-enriched water. Lucidol 90% *tert*-butyl hydroperoxide was dried by swirling with anhydrous magnesium sulfate prior to use. The reactions were performed using 1% of the metal catalyst, excess olefin (2 equiv), and 0.15 mmol of the hydroperoxide all in 0.5 mL of the dioxane–water (9:1) solvent. The reactions were continued until the *tert*-butyl hydroperoxide had been consumed. The ^{18}O content of the products was determined by mass spectrometry.

A crucial assumption underlying the interpretation of the experiments in Scheme II is that the rate of exchange of the oxometal groups (**5**, Scheme I) is faster than the rate of formation of the peroxo species (**6**, Scheme I). If, as seems likely,[4,9] this assumption is correct, then the results in Scheme II speak against the involvement of peroxo species (both paths a and b of Scheme I) in these oxidations. Although experiment 2 (Scheme II) reveals that the *tert*-butyl alcohol has exchanged extensively with the labeled water, the control experiment 3 indicates that, in the presence of a catalytic amount of a molybdenum(VI) compound, *tert*-butyl alcohol is itself extensively exchanged under these rather harsh conditions (115 °C, 1 day).[10] Note that in experiment 1 at room temperature the *tert*-butyl alcohol produced is unlabeled.

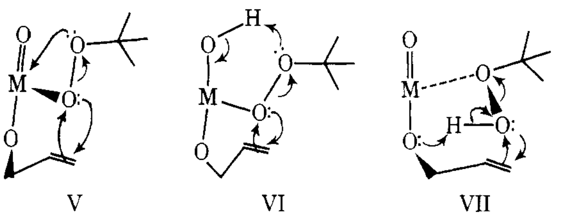
Thus it appears that the epoxidation of olefins by the molybdenum peroxo compound **1** is not directly related to the catalytic systems employing alkyl hydroperoxides. The catalytic epoxidations must proceed by a mechanism involving an intact alkyl hydroperoxide; actually all of the detailed mechanistic proposals in the literature fall into this category.[11] In Scheme III are shown the two published mechanisms (I and II) which are most often cited, along with the two new proposals (III and IV) which we feel are more consistent with the facts of these oxidations. Note that the new mechanisms III and IV are rather similar. In III the coordinated peroxide is polarized by a three-centered interaction with an empty coordination site on the Lewis acidic metal; thus the transition state resembles that which we favor[12] for epoxidations by the peroxomolybdenum substance **1**. In IV the peroxidic bond is polarized by an acidic hydrogen through a five-membered interaction. In both mechanisms III and IV the epoxide is initially produced coordinated to the metal. It must be emphasized that all of our mechanistic considerations are based on the assumption, which we feel is highly reasonable, that the optimum direction of approach of the olefin to the oxygen will be from the back side and roughly along the axis of the oxygen–oxygen bond.[13]

Scheme III. Mechanisms Involving Coordinated Alkyl Hydroperoxide



The previous mechanisms (I and II) are in our opinion less attractive than these new proposals. For one thing they require coordination of the metal to the more hindered hydroperoxide oxygen, but a much more serious shortcoming is their failure to account for the exceptional reactivity of allylic alcohols[14] in these systems. It is geometrically impossible for the double bond of an allylic alcohol to approach the oxidant as indicated in mechanisms I and II, and at the same time coordinate to the metal through its hydroxyl group. By contrast the direction of approach required in mechanisms III and IV is ideal for an allylic alcohol which is simultaneously coordinated through its hydroxyl group to the same[15] metal center. Approximate transition states for the epoxidation of coordinated allylic alcohols via mechanisms III and IV are indicated in V and VI, respectively, of Scheme IV.

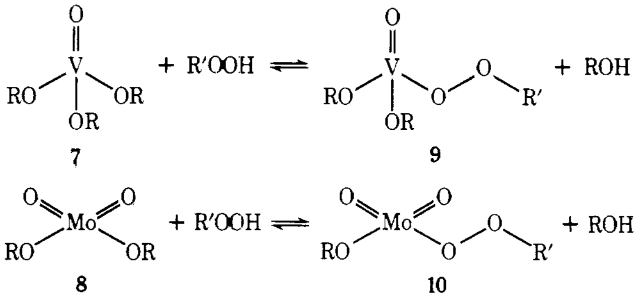
Scheme IV. Epoxidation of Allylic Alcohols



Although mechanisms I and II fail to account for the enhanced reactivity of allylic alcohols in these systems, we have noted a variant on this mechanistic theme which would be consonant with the special reactivity observed with allylic alcohols. This mechanism is shown in VII of Scheme IV, and, like the mechanisms in I and II of Scheme III, involves coordination of the hydroperoxide by the oxygen proximal to the alkyl group. A key feature of this process is the hydrogen transfer from the hydroperoxide oxygen to the oxygen of the coordinated allylic alcohol. Whatever objections might be raised to this mechanism, it at least meets our criterion of geometrical feasibility.

The present work has provided good evidence that the intact hydroperoxide is involved in the epoxidation step. As discussed above, we favor activation of the hydroperoxide by coordination to the metal through the oxygen distal to the alkyl group. Oxo alkoxides such as **7** and **8** are well known[16] for vanadium(V) and molybdenum(VI) and such species are substitution labile. Thus it seems logical to assume that in the presence of alkyl hydroperoxides equilibria such as those indicated in Scheme V would be set up. These equilibria would

Scheme V



generate the peroxidic species (e.g., **9** and **10**) which we believe to be responsible for these epoxidations.

In the process of designing chiral polydentate ligands for these epoxidation catalysts,[17] it is hoped that these mechanistic concepts can be further refined.

Experimental Section

Oxygen-18 enriched water (66 atom %) was procured from Miles Laboratories. The *tert*-butyl hydroperoxide (ca. 90%) was obtained from the Lucidol Division of the Pennwalt Corp.; it was dried over anhydrous magnesium sulfate just before use. Commercial samples of $Mo(CO)_6$ (Pressure Chemical Co.), $VO(acac)_2$ (Alfa), (*E*)-cyclododecene (Chemical Samples), and geraniol (Aldrich) were used as obtained. Dioxane was distilled from sodium metal under nitrogen just prior to use.

The "combustion tubes" were obtained from the Lab Crest Scientific Division of the Fischer and Porter Co. The combustion tube consisted of a thick-walled glass tube fitted with a Teflon-lined, screw-on metal cap.

Preparative GLC was performed on a Varian Model 920 instrument. Mass spectra were obtained on a Hitachi Perkin-Elmer RMU-6E spectrometer. Isotopic analysis of the *tert*-butyl alcohol was carried out by GC–MS using a 6 ft × 1 mm Porapak QS column.

Molybdenum Catalyzed Epoxidation of Cyclododecene in Oxygen-18 Enriched Water/Dioxane. To a solution of 25 mg (27 μL, 0.15 mmol) of (*E*)-cyclododecene in 0.5 mL of freshly distilled dioxane contained in a combustion tube (Fischer and Porter, 0.375 in. i.d., 3 in. length) were added 50 μL of 66 atom % oxygen-18 enriched water, 18 μL (18 mg, 0.18 mmol) of 90% *tert*-butyl hydroperoxide, and 0.4 mg (0.0015 mmol, 1% based on olefin) of molybdenum hexacarbonyl. The combustion tube was capped tightly and immersed in an oil bath at 115 °C for 24 h with periodic shaking. The blue reaction mixture was then cooled to room temperature and a small portion was reserved for GC–MS analysis of the *tert*-butyl alcohol formed. The solvent from the remaining portion of the reaction mixture was removed under reduced pressure and the residue was taken up in 15 mL of methylene chloride. The resultant solution was washed with 10% aqueous sodium bisulfite (1 × 15 mL) followed by water (1 × 15 mL), then dried ($MgSO_4$) and concentrated to give a light-yellow oil. Mass spectral analysis of the *trans*-cyclododecene epoxide, isolated from the oil by preparative GLC (a 15 ft × 0.25 in. column packed with 10% UCW-98 on 45/60 mesh Chromosorb W, 175 °C) indicated no incorporation of oxygen-18 into the epoxide. The mass spectra of the authentic unlabeled epoxide and the epoxide from this labeling experiment were identical. However, since the parent ion (*m/e* 182) was small the accuracy of the measurement was not great. For this reason the epoxide was opened ($HClO_4$, H_2O, THF) to the diol, which was further transformed (acetone, $HClO_4$) to the acetonide. The acetonide exhibited an intense $M^+ - CH_3$ ion at *m/e* 225 which was ideal for determination of the ^{18}O content. Again the acetonide derived from the labeling experiment and an authentic unlabeled specimen gave identical spectra, confirming the original conclusion that no ^{18}O had been incorporated.

GC–MS analysis (using a Porapak QS column) of the original crude reaction mixture indicated 74% incorporation of oxygen-18 into the *tert*-butyl alcohol formed. The $M^+ - CH_3$ ion (*m/e* 59) was used to calculate ^{18}O content.

Control. A control reaction was performed to indicate whether *tert*-butyl alcohol exchanges oxygen with water under the reaction conditions. To a solution of 25 mg (27 μL, 0.15 mmol) of (*E*)-cyclododecene in 0.5 mL of freshly distilled dioxane contained in a combustion tube were added 50 μL of 66 atom % oxygen-18 enriched water, 18 μL (18 mg, 0.18 mmol) of *tert*-butyl alcohol, and 0.4 mg (0.0015 mmol) of dioxobis(acetylacetonato)molybdenum(VI) $[MoO_2(acac)_2]$. The tube was capped tightly and immersed in an oil bath at 115 °C for 24 h with periodic shaking. GC–MS analysis of the reaction mixture indicated 68% incorporation of oxygen-18 in the *tert*-butyl alcohol.

Vanadium Catalyzed Epoxidation of Geraniol in Oxygen-18 Enriched Water/Dioxane. To a solution of 46 mg (52 μL, 0.3 mmol) of geraniol in 0.5 mL of freshly distilled dioxane and 50 μL of 66 atom % oxygen-18 enriched water were added 18 μL (18 mg, 0.18 mmol) of 90% *tert*-butyl hydroperoxide and 0.4 mg (0.0015 mmol) of vanadyl acetylacetonate $[VO(acac)_2]$. The initially red mixture was stirred in a small test tube (capped with a rubber septum) at 25 °C for 12 h, by which time the solution had become green-yellow. A small portion of this reaction mixture was reserved for GC–MS analysis of the *tert*-butyl alcohol formed. To the remaining portion of the reaction mixture were added 1.0 mL of pyridine and 0.5 mL of acetic anhydride and the mixture was stirred at 25 °C for 3 h. To this mixture was then added 0.5 mL of water and after stirring for a further 0.5 h, the mixture was taken up in 10 mL of chloroform and washed with water (3 × 10 mL). The chloroform layer was dried ($MgSO_4$) and concentrated to give a yellow oil. Mass spectral analysis of the 2,3-epoxygeranyl acetate, isolated from the oil by preparative GLC (a 20 ft × 0.375 in. column packed with 20% OV-17 on 45/60 mesh Chromosorb W, 180 °C) indicated no incorporation of oxygen-18 into the epoxide. The intense $M^+ - HOAc$ ion at *m/e* 152 was used to calculate the ^{18}O content. GC–MS analysis of the original crude reaction mixture revealed no ^{18}O incorporation into the *tert*-butyl alcohol formed.

Acknowledgment. We are indebted to Dr. Catherine Costello of Professor Biemann's laboratory for determining the isotopic composition of our products by GC–MS. A. O. Chong is grateful to the Upjohn Co. for a graduate fellowship, and we thank the National Science Foundation (MPS 74-21260) for supporting this research.

Registry No.—(*E*)-cyclododecene, 1486-75-5; *tert*-butyl hydroperoxide, 75-91-2; molybdenum hexacarbonyl, 13939-06-5; geraniol, 106-24-1; vanadyl acetylacetonate, 3153-26-2.

References and Notes

(1) J. Kollar, U.S. Patent 3 360 584 (1967) to Halcon International.

(2) R. Hiatt in "Oxidation", Vol. 2, R. L. Augustine and D. J. Trecker, Ed., Marcel Dekker, New York, N.Y., 1971, Chapter 3; this is a good review on these epoxidations but much has happened since it was written.

(3) H. Mimoun, I. Seree de Roch, and L. Sajus, *Tetrahedron*, **26**, 37 (1970).

(4) K. B. Sharpless, J. M. Townsend, and D. R. Williams, *J. Am. Chem. Soc.*, **94**, 295 (1972).

(5) J. Kaloustian, L. Lena, and J. Metzger, *Tetrahedron Lett.*, 599 (1975).

(6) K. B. Sharpless and J. M. Townsend, unpublished results.

(7) R. A. Sheldon, *Recl. Trav. Chim. Pays-Bas*, **92**, 367 (1973).

(8) Oxo groups are ubiquitous in the chemistry of d° vanadium and molybdenum compounds.

(9) The following references reveal that oxo transition metal compounds generally undergo exchange with $H_2{}^{18}O$ at reasonable rates even at 25 °C. Under the conditions of our experiments (Scheme II) we would expect at least partial exchange of any oxo groups to occur. Since *no ^{18}O incorporation* was observed in the epoxide and alcohol products (Scheme II), we feel that the peroxo mechanisms of Scheme I must be considered extremely unlikely. (a) R. K. Murmann and P. R. Robinson, *Inorg. Chem.*, **14**, 203 (1975); (b) H. Goff and R. K. Murmann, *J. Am. Chem. Soc.*, **93**, 6058 (1971); (c) R. K. Murmann, *J. Phys. Chem.*, **71**, 964 (1967); (d) R. K. Murmann, *J. Am. Chem. Soc.*, **96**, 7836 (1974); (e) R. K. Murmann, *Inorg. Chem.*, in press; (f) J. A. McClaskey and M. J. McClelland, *J. Am. Chem. Soc.*, **87**, 5090 (1965).

(10) Because of the inhibition by dioxane and water, these conditions were necessary for the reaction to proceed. Less severe conditions might have been possible with a more reactive olefin such as geraniol (used with vanadium in experiment 1, Scheme II); however, we wanted to know the outcome with both a simple olefin and an allylic alcohol to be sure that there were no differences between these two types of substrates.

(11) (a) M. N. Sheng and J. G. Zajacek, *J. Org. Chem.*, **35**, 1839 (1970); also M. N. Sheng and J. G. Zajacek, *Adv. Chem. Ser.*, **76**, 418 (1968); (b) E. S. Gould, R. Hiatt and K. C. Irwin, *J. Am. Chem. Soc.*, **90**, 4573 (1968); also C.-C. Su, J. W. Reed, and E. S. Gould, *Inorg. Chem.*, **12**, 337 (1973); (c) R. A. Sheldon, *Recl. Trav. Chim. Pays-Bas*, **92**, 253 (1973); (d) R. A. Sheldon and J. A. Von Doorn, *J. Catal.*, **31**, 427 (1973).

(12) This mechanism is indicated in a figure labeled IV in our earlier publication (ref 4). *IV is incorrect as it appears in that work;*[4] *an oxo group* (*Mo* = *O*) *is missing.* The similarity between peroxo species **1**, which is known to epoxidize olefins, and the putative active oxidants in mechanisms III and IV is another attractive feature of these new proposals.

(13) The approach of a nucleophile to a peroxide linkage has long been assumed to occur in this manner (see, e.g., J. O. Edwards in "Peroxide Reaction Mechanisms", J. O. Edwards, Ed., Wiley, New York, N.Y., 1962, pp 67–106. All the evidence is consistent with the proposal of backside attack, but to the best of our knowledge, no one has yet designed an experiment which would provide a rigorous test of this hypothesis. What is needed here is

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)].

(14) (a) F. List and L. Kuhnen, *Erdoel Kohle, Erdgas, Petrochem.,* **20,** 192 (1967); (b) ref 11a; (c) K. B. Sharpless and R. C. Michaelson, *J. Am. Chem. Soc.,* **95,** 6136 (1973); (d) S. Tanaka, H. Yamamoto, H. Nozaki, K. B. Sharpless, R. C. Michaelson, and J. D. Cutting, *ibid.,* **96,** 5254 (1974); (e) T. Itoh, K. Kaneda, and S. Teranishi, *J. Chem. Soc., Chem. Commun.,* 421 (1976).

(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.

(16) (a) R. J. H. Clark, "The Chemistry of Titanium and Vanadium", Elsevier, Amsterdam, 1968, Chapter 10; (b) ref 7; (c) K. M. Sarma and S. K. Anand, *J. Prakt. Chem.,* **317,** 540 (1975).

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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.