Methanolysis of the Oxyphosphorane IV. A solution of the oxyphosphorane (6.8 g.) in methanol (15 ml.) was kept at 0°. The infrared spectrum of aliquots of this solution were examined in CCl_4 solution after removal of the methanol. Spectra were taken after 5 min., 90 min. and 6, 25, 31, 97, 121, 147, 173, and 202

hr. The methanolysis at 20° was very slow and after 202 hr. the solvent was removed. The residue was the diketo phosphonate VII, 4.0 g., m.p. 106–108°.

Kinetics and Mechanism of Pertungstic Acid Epoxidations. II. The Methyl-Substituted Allyl Alcohols[1]

H. C. Stevens and A. J. Kaman

Contribution from the Pittsburgh Plate Glass Company, Chemical Division, Barberton, Ohio. Received October 7, 1964
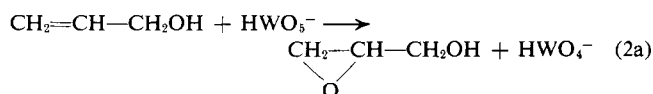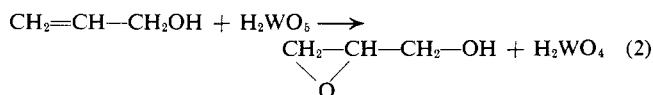
The epoxidation of primary and secondary allylic alcohols by hydrogen peroxide in the presence of tungstic acid appears to involve the formation of a pertungstate ester followed by a rate-determining rearrangement. Based on substituent, solvent, and salt effects, the mechanism of the epoxidation step is believed concerted with considerable polar (electrophilic) character.

Introduction

In a previous paper from this laboratory[2] we reported on the kinetics of epoxidizing allyl alcohol in buffered aqueous hydrogen peroxide containing tungstic acid as catalyst. The rate was found to be first order in both substrate and catalyst but independent of the hydrogen peroxide concentration. Since tungstic oxide was found to be completely oxidized in the presence of excess hydrogen peroxide, it was surmised that the reacting species was pertungstic acid or a closely related anionic species. Their formation is most simply represented by the following equilibria.

$$H_2WO_4 + H_2O_2 \rightleftharpoons H_2WO_5 + H_2O \quad (1)$$

$$H_2WO_5 + H_2O \rightleftharpoons HWO_5^- + H_3O^+ \quad (1a)$$
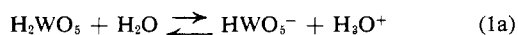
Catalyst regeneration was assumed to be the result of the subsequent epoxidation step

$$CH_2{=}CH{-}CH_2OH + H_2WO_5 \longrightarrow$$
$$CH_2{-}CH{-}CH_2{-}OH + H_2WO_4 \quad (2)$$

$$CH_2{=}CH{-}CH_2OH + HWO_5^- \longrightarrow$$
$$CH_2{-}CH{-}CH_2OH + HWO_4^- \quad (2a)$$

Suggestions concerning mechanisms of oxidations by pertungstate species have been advanced by Mugdan and Young,[3] Payne,[4] Saegebarth,[5] and Raciszewski.[2] However, no mechanistic study of the epoxidation

reaction with a selected group of substrates has been reported.

Two critical approaches were taken in our work to elucidate the mechanism of the epoxidation reaction. First, to assess polar effects in the addition, the substitution of methyl groups onto the three carbon atoms of allyl alcohol was investigated kinetically. Secondly, the importance of the relative proximity of the olefinic and hydroxylic functions upon the reactivity of the substrate was examined with a number of cyclic and acylic olefin alcohols. This paper pertains to the first of the two objectives.

Experimental

A. Materials. The unsaturated alcohols were commercial samples redistilled before use. Center cuts were collected and assayed by v.p.c. and unsaturation equivalent. The values were recorded in Table I.

Table I

Alcohol	Assay, % V.p.c.	Assay, % Unsatd.	$n^{20}D$
Allyl	99.6	100.0	1.4150
α-Methallyl	97.2	100.1	1.4147
β-Methallyl	99.9	100.2	1.4267
Crotyl	99.3	...	1.4289
α,α-Dimethallyl	98.1	...	1.4168

B. Kinetic Experiments. In a typical run 0.324 g. (1.3 mmoles) of tungstic acid (Baker analyzed reagent), 23.5 g. (0.339 mole) of 49.01% aqueous hydrogen peroxide (Pittsburgh Plate Glass, Chem. Div.), and 14.9 g. of distilled water were added to a 500-ml., four-necked flask equipped with a Trubone stirrer and immersed in a thermostated water bath controlled at 20 ± 0.1°. The mixture was stirred for 30 min. resulting in a pale blue, turbid solution. Immediately afterwards 0.1–0.2 g. of triethylamine (Eastman Kodak) was introduced to adjust the pH from 2.2 to 4.8–5.0. In the course of 15 sec. 0.300 mole of olefin alcohol freshly dissolved was added in 184.1 g. of distilled water precooled to 20°. This was followed by a 5.0-ml. rinse. A total charge of 249.7 g

(1) Presented in part at the 137th National Meeting of the American Chemical Society, Cleveland, Ohio, April 1960.
(2) Z. Raciszewski, *J. Am. Chem. Soc.*, **82**, 1267 (1960).
(3) M. Mugdan and D. P. Young, *J. Chem. Soc.*, 2988 (1949).
(4) G. B. Payne, Fifth Petroleum Congress, Section IV, Paper 16, New York, N. Y., 1959.
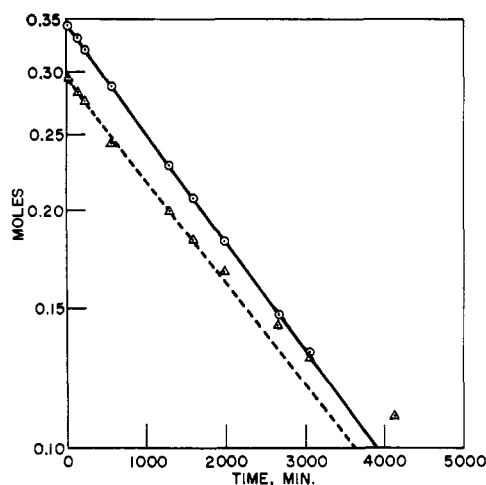(5) K. A. Saegebarth, *J. Org. Chem.*, 24, 1214 (1959).

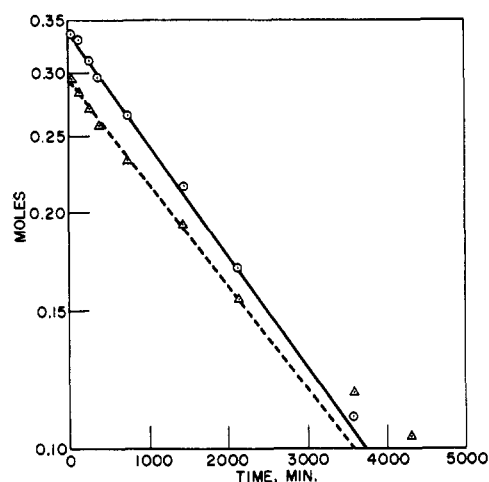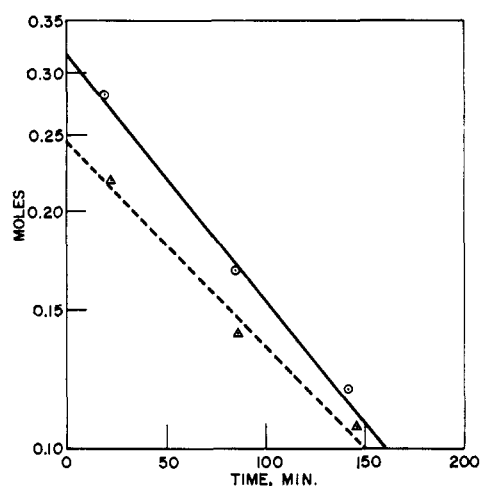Figure 1. First-order plots for the epoxidation of allyl alcohol: -○- by [H₂O₂], -△- by [Epoxide].

Figure 2. First-order plots for the epoxidation of crotyl alcohol: -○- by [H₂O₂], -△- by [Epoxide].

Figure 3. First-order plots for the epoxidation of α-methallyl alcohol: -○- by [H₂O₂], -△- by [Epoxide].

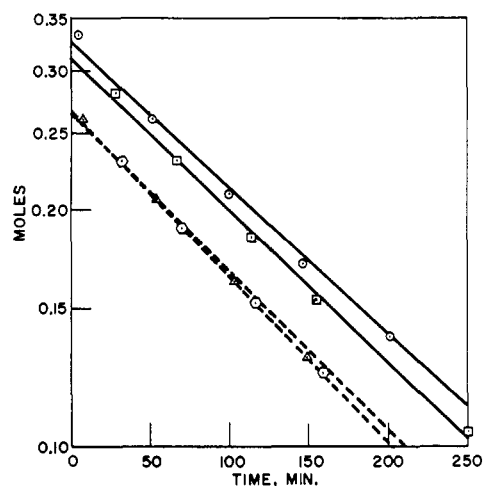Figure 4. First-order plots for the epoxidation of β-methallyl alcohol: -□- by [H₂O₂], -○- by [Epoxide]; in the presence of added KClO₄: -○- by [H₂O₂], -△- by [Epoxide].

was maintained with all substrates by addition of the required amount of water. The mixture was stirred continuously and at suitable time intervals duplicate 1- or 2-ml. aliquots were removed for hydrogen peroxide and oxirane oxygen analyses. The pH was determined periodically and maintained at 5.0 ± 0.2 by occasional addition of small amounts of triethylamine.

C. Product Isolation. The epoxy alcohols were isolated from preparative runs, first by removal of water under reduced pressure not allowing the pot temperature to rise above 50°. This was followed by vacuum fractionation. Results are summarized in Table II.

D. Analytical Procedures. The methods of analysis employed were reported in the previous paper.[2] Vapor phase chromatographic analyses were performed in a Perkin-Elmer instrument (154B) employing a column of didecyl phthalate on Celite.

Results

The kinetics of epoxidizing the lower olefinic alcohols in aqueous solution could be followed by monitoring the disappearance of hydrogen peroxide or the development of oxirane oxygen. The *initial slopes* from

first-order plots based on the two measurements were usually in good agreement, so that reliable rate comparisons could be based on either analytical approaches (see Figures 1–5).[6] In several instances good straight-

Table II. Product Study

Alcohol	B.p., °C. (mm)	n^{20}D	Epoxide Yield, %[a]	Assay, %[b]
Allyl	36 (2)	1.4312	46 (70)	102.3
α-Methallyl	47 (7)	1.4291	34 (90)	100.4
β-Methallyl	42 (6)	1.4288	56 (96)	95.9
Crotyl	48 (5)	1.4276	83 (97)	100.3
2-Cyclopentenyl	77 (4)	1.4750	80 (90)	100.0
3-Cyclohexenyl-methyl	102 (2)	1.4867	22 (48)	85.0

[a] Values in parenthesis refer to oxirane analysis of the crude reaction mixtures. [b] By oxirane analysis.

(6) To permit convenient comparisons, the kinetic data are plotted on a common ordinate representing the hydrogen peroxide concentration [H₂O₂] on one hand, and the difference [substrate]₀ − [epoxide] on the other.
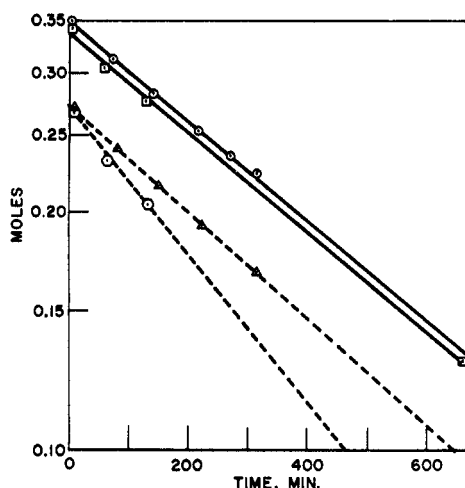
Figure 5. First-order plots for the epoxidation of β-methallyl alcohol in aqueous ethyl alcohol: $-\bigcirc-$ by $[H_2O_2]$, $-\triangle-$ by [Epoxide]; in aqueous t-butyl alcohol: $-\square-$ by $[H_2O_2]$, $-\ominus-$ by [Epoxide].

line fits were obtained well past the half-lives of the reaction.

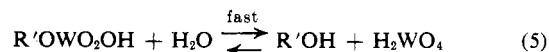**Table III.** Substituent Effect

| R_3 | R_2 | R_1 | R_1' | First-order rate const., $k_1 \times 10^4$ min.$^{-1}$ | |
				H_2O_2	Oxirane
H	H	H	H	3.2	3.0
CH$_3$	H	H	H	71	59
H	CH$_3$	H	H	45	48
H	H	CH$_3$	H	3.2	3.0
H	H	CH$_3$	CH$_3$	0.5^a	...

^{a} Since oxirane levels were too low for accurate analyses, this figure should be considered as an upper limit approximation.

The data in Table III illustrate a number of findings significant to the mechanism of the epoxidation reaction. Clearly, the presence of methyl groups at the site of the double bond was strongly rate enhancing. This would be expected from an electrophilic addition and is generally observed in the corresponding reaction of olefins with organic peracids and in other three-center-type additions.[7] The lack of rate change resulting from substitution of one methyl group in the α-position and the large reduction shown by the tertiary α,α-dimethallyl alcohol, however, needed to be interpreted in terms of steric effects at the hydroxylic function of the molecule. Thus, an interaction of the primary and secondary alcohols with the pertungstic acid (eq. 3), if rapid and reversible, could be followed by a rate-determining rearrangement to the epoxy tungstate ester (eq. 4). A hydrolysis step (eq. 5) analogous to the reverse of (3) could then complete the reaction cycle in which the catalyst is finally regenerated.

(7) (a) D. Swern, *Org. Reactions*, **7**, 378 (1957); (b) P. Skell and A. Garner, *J. Am. Chem. Soc.*, **78**, 5430 (1956).

$$H_2WO_5 + ROH \underset{}{\overset{fast}{\rightleftharpoons}} ROWO_3OH + H_2O \quad (3)$$

$$ROWO_3OH \overset{slow}{\longrightarrow} R'OWO_2OH \quad (4)$$

$$R'OWO_2OH + H_2O \underset{}{\overset{fast}{\rightleftharpoons}} R'OH + H_2WO_4 \quad (5)$$

R = alkenyl
R' = apoxyalkyl

In the case of the tertiary alcohol, equilibrium step 3 would appear unfavorable, so that the rate of epoxidation should more nearly correspond to that of an unaided olefin case.[8]

The kinetics of the reaction were indeed consistent with the scheme shown, provided that the pertungstate and tungstate esters were present at low steady-state concentrations and the equilibrium 3 established rapidly in relation to the rate of step 4.

A brief study of solvent and salt effects was indicated to gain an insight into the nature of the transition state of the oxygen transfer from the peracid to the olefin. The data shown in Figures 4 and 5 as well as Table IV

Table IV. Solvent and Salt Effects (β-Methallyl Alcohol)

| | —First-order rate const.— $k_1 \times 10^4$ min.$^{-1}$ | |
	H_2O_2	Oxirane
Water	45	48
Water, 0.1 M KClO$_4$	43	46
Ethyl alcohol, 44.5%^{a}	15	16
t-Butyl alcohol, 50.0%^{a}	15	21

^{a} By weight basis water present.

indicated the absence of a salt effect and a moderate rate reduction in water–alcohol solvent systems. The results would appear to discredit any polar, stepwise addition mechanisms involving charge-separated intermediates visualized from an attack by an OH$^+$ fragment.[9] The results would be in accord with an intramolecular, concerted reaction progressing at a rate subject to the nucleophilic reactivity of the double bond and the equilibrium concentration of allylic pertungstate ester present. A transition state may be visualized


(6)
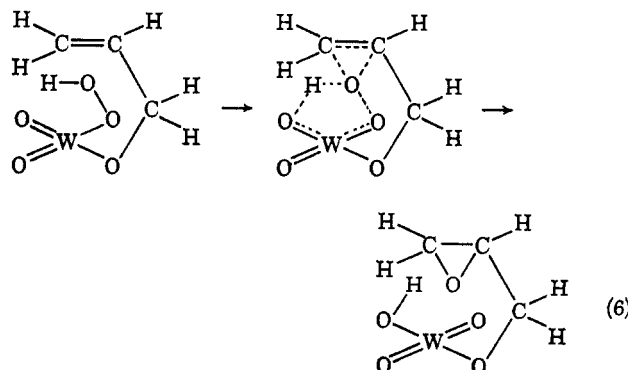
(8) Direct rate comparisons with olefins could not be made because of solubility limitations. Extrapolation of the rates observed with cyclohexene at 30 and 70° in aqueous t-butyl alcohol would indicate an approximate rate constant in water at 20° of the order of 0.2 × 10^{-4} min.$^{-1}$

(9) The occurrence of a Wagner–Meerwein rearrangement in the hydroxylation of bicyclo[2.2.1]-2-heptene[5] need not require an intermediate carbonium ion *arising from the addition of OH$^+$*. Formation of an epoxide which is protonated in the acidic medium is believed a more plausible course leading to the rearrangement.

as involving a concerted delivery of the peroxy oxygen with coordination of the hydroxyl hydrogen by one of the W=O bonds (eq. 6).[10,11]

A precedent for the facile formation of esters from oxides of transition elements could be found in published work on chromic acid oxidations.[12] The ester formation in the present case was preferred over an

$$CH_2=CH$$

(7)
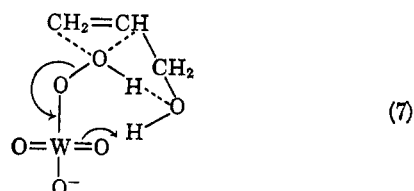
(10) P. D. Bartlett was the first to suggest a cyclic concerted mechanism for the epoxidation of olefins with perbenzoic acid; cf. *Record Chem. Progr.* (Kresge-Hooker Sci. Lib.), **11**, 51 (1950).

(11) The polycyclic nature of the transition state pictured receives support from a highly negative entropy of activation (H. C. Stevens and J. C. Cook, Jr., paper presented at the 143rd National Meeting of the American Chemical Society, Atlantic City, N. J., Sept. 1962).

(12) F. Holloway, M. Cohen, and F. H. Westheimer, *J. Am. Chem. Soc.*, **73**, 65 (1951), and references cited therein.

earlier interpretation[4] postutating merely hydrogen bonding in the intermediate or transition state (eq. 7). Intuitively, an interaction between the peracid hydrogen and the alcohol oxygen would appear to be opposed to the required electron deficiency of the peroxy oxygen. Furthermore, the mechanism would appear to be less consistent with the steric inhibition observed in the case of the tertiary pentenol.

It is concluded that the epoxidation of primary and secondary allylic alcohols involves an interaction of a pertungstic acid species with the hydroxyl function prior to a rate-determining delivery of the peroxy oxygen to the olefinic site. Although showing electrophilic character, the reaction appears to be concerted rather than stepwise. Further evidence bearing on the postulated mechanism is contained in the following paper of this series dealing with the effect of hydroxyl group double bond proximity upon substrate reactivity.

The Mechanism of Ozonolysis.
Formation of Cross Ozonides

L. D. Loan, R. W. Murray, and P. R. Story

Contribution from the Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey. Received September 23, 1964

The ozonolysis of pure pentene-2 at −70° has been shown to give butene-2 ozonide and hexene-3 ozonide in addition to the normal pentene-2 ozonide. N.m.r. spectra of the ozonides have been obtained and used to show that each ozonide exists as a cis–trans pair. Ozonolyses of pentene-2 in pentane as solvent and in the presence of excess aldehyde have permitted an evaluation of the extent of a cage mechanism.

Introduction

The ozonolysis of olefins is generally interpreted in terms of a mechanism provided by Criegee.[1] This mechanism (Figure 1) postulates that ozone reacts with the unsaturated bond to form an initial unstable ozonide (primary ozonide, I) which readily decomposes to give a zwitterion (II) and a carbonyl fragment (III). These fragments can then combine to give the normal ozonide (IV). Alternatively, the zwitterion may dimerize to a diperoxide (V) or polymerize to a higher molecular weight peroxide (VI). In reactive solvents the zwitterion may react with the solvent to give other products; as an example, a methoxyhydroperoxide (VII) is formed in the presence of methanol. This scheme is consistent with most of the known experimental facts but recent observations of a number of workers suggest that further refinement is required.

The existence of a primary ozonide has been confirmed in the case of *trans*-di-*t*-butylethylene by Criegee and Schröder,[2] but these authors further found no evidence for the formation of such a primary ozonide from the *cis* compound. Recently, Greenwood[3] has found that this difference between *cis* and *trans* isomers with respect to the formation of a primary ozonide may be a general phenomenon, that is, *trans*-olefins give primary ozonides while *cis*-olefins do not give primary ozonides of sufficient lifetime to be characterized. Another important observation from the standpoint of a complete mechanistic picture is that made by Schröder[4] who found that the *cis*- and *trans*-ozonides obtained from the ozonolysis of the *cis* and *trans* isomers of di-*t*-butylethylene could be separated by gas phase chromatography (g.p.c.). Use of this technique yielded the surprising result that the *trans* isomer gave a single ozonide, which Schröder formulated as the *trans*-ozonide, while the *cis* olefin gave an ozonide distribution of 70:30, which Schröder formulated as the *cis* to *trans* ratio. Taken together the results of Greenwood and Schröder suggest that *cis*-olefins are able to form the normal ozonide *via* a path which may not involve a primary ozonide but which can be largely stereoselective. Another aspect of the Criegee mechanism which is intimately con-

(1) For a thorough discussion of the mechanism of ozonolysis see P. S. Bailey, *Chem. Rev.*, **58**, 925 (1958).

(2) R. Criegee and G. Schröder, *Chem. Ber.*, **93**, 689 (1960).

(3) F. L. Greenwood, *J. Org. Chem.*, **29**, 1321 (1964).

(4) G. Schröder, *Chem. Ber.*, **95**, 733 (1962).