JOURNAL OF THE
AMERICAN CHEMICAL SOCIETY

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VOLUME 82 MARCH 31, 1960 NUMBER 6

PHYSICAL AND INORGANIC CHEMISTRY

[CONTRIBUTION FROM THE BARBERTON RESEARCH LABORATORY, COLUMBIA-SOUTHERN CHEMICAL CORPORATION]

Kinetics and Mechanism of the Epoxidation of Allyl Alcohol with Aqueous Hydrogen Peroxide Catalyzed by Tungstic Acid[1]

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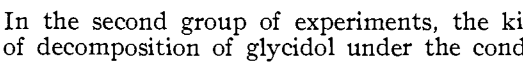
RECEIVED OCTOBER 14, 1959

The kinetics of a novel method of epoxidation of allyl alcohol (AA) to glycidol (G) with aqueous hydrogen peroxide in the presence of tungstic acid catalyst was studied. The changes in the concentration of glycidol were determined analytically and were found to follow the kinetics of two consecutive pseudo-first order reactions. $d[G]/dt = k_1[AA] - k_2[G]$. The coefficients k_1 and k_2 were calculated by means of the time-ratio method and the effect of several reaction variables on both coefficients was studied. An increase in temperature affects k_1 to a lesser degree than k_2; the respective energies of activation are 15 and 19 kcal. mole^{-1}. Both coefficients are proportional to the concentration of tungstic acid and increase with the decreasing *p*H of the reaction medium, although not in a uniform fashion. It was concluded that most probably the anion of pertungstic acid, which is produced rapidly from tungstic acid, oxidizes allyl alcohol. The addition of this anion to the double bond appears to be facilitated by the inductive effect of the hydroxy group, or perhaps the protonated hydroxy group, and possibly by the delocalization of the electron pair, with the accompanying negative charge, *via* the incipient formation of the oxirane-ring. The analogy between this mechanism and the S$_N$2′ substitutions in the allylic systems is pointed out. An alternative mechanism, specific for allylic alcohols and consisting of a rapid esterification of the hydroxy group prior to the attack on the double bond is also considered. The anion of pertungstic acid was found to participate in the opening of the oxirane-ring.

Introduction

During the course of the investigation of the hydroxylation of olefins to the corresponding α,β-glycols, by the direct addition of hydrogen peroxide in the presence of inorganic catalysts, Mugdan and Young observed that pertungstic acid yields exclusively *trans*-glycols.[2] In order to explain this stereospecificity the authors suggested, as one possible reaction path, the formation of the intermediate epoxide. The failure to isolate the epoxide was ascribed to its high reactivity under the conditions of hydroxylation. However, recently several reports were published in which the successful epoxidation of olefins by the hydrogen peroxide–tungstic acid system was described.[3] Quite independently a similar method has been developed in this Laboratory.[4]

One phase of the investigation carried out in this Laboratory concerned the kinetics of epoxidation of an aqueous solution of allyl alcohol by the hydrogen peroxide–tungstic acid system. Two groups of experiments were performed. In the experiments of the first group, allyl alcohol, diluted aqueous hydrogen peroxide and a catalytic amount of tungstic acid were brought together, the *p*H of the mixture was suitably adjusted by the addition of triethylamine, and the reaction was followed by the periodical determination of the concentration of glycidol. From the changes in the concentration of glycidol, the rate equation was derived and the pseudo-first order rate coefficients, k_1 and k_2, for the formation and for the decomposition of glycidol, respectively, were calculated.



$$CH_2{=}CHCH_2OH \xrightarrow{k_1} \overset{O}{CH_2{-}CHCH_2OH} \xrightarrow{k_2} \text{final products} \quad (1)$$

In the second group of experiments, the kinetics of decomposition of glycidol under the conditions of epoxidation, but in the absence of allyl alcohol, were studied. In both groups of experiments the

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(1) Presented at the 136th American Chemical Society Meeting, Atlantic City, September, 1959.

(2) M. Mugdan and D. P. Young, *J. Chem. Soc.*, 2988 (1949).

(3) (a) P. G. Sergeev and L. M. Bukreeva, *Zhur. Obshchei Khim.*, **28**, 101 (1958), *C. A.*, **52**, 12758j (1958); (b) G. B. Payne and P. H. Williams, *J. Org. Chem.*, **24**, 54 (1959); (c) G. B. Payne and C. W. Smith, U. S. Patent 2,776,301 (1957); (d) C. W. Smith and G. B. Payne, U. S. Patent 2,786,854 (1957); (e) G. J. Carlson, J. R. Skinner, C. W. Smith and C. H. Wilcoxen, U. S. Patent 2,833,787 (1958); (f) J. R. Skinner, C. H. Wilcoxen and G. J. Carlson, U. S. Patent 2,833,788 (1958).

(4) A. Kaman and H. C. Stevens, unpublished data.

TABLE I

EPOXIDATION OF ALLYL ALCOHOL

Expt. no.	Initial composition, mmole/1000 g.				pH		Temp., °C.	Rate coefficients			Max. yield of glycidol[a]	t_{max},[a] hr.
	Et_3N[d]	H_2WO_4	H_2O_2	C_3H_6O	Init.	After $2/k_1$ hr.		$k_1 \times 10^6$, sec.$^{-1}$	$k_2 \times 10^6$, sec.$^{-1}$	k_2/k_1		
A. Effect of the *p*H of the reaction mixture												
1	7.9	8.57	2240	1940	3.0	3.1	30	19.8	7.9	0.400	54.5	21.4
2	9.8	8.57	2240	1940	3.9	3.7	30	19.6	3.2	.163	70.0	30.6
3	11.7	8.57	2240	1940	4.9	4.7	30	18.2	2.2	.121	75.0	37.0
4	13.1	8.61	2110	1930	5.4	5.3[b]	30	14.7	1.9	.129	73.5	44.3
5	17.7	8.57	2250	1940	6.0	5.6	30	14.5	1.7	.117	75.0	46.4
6	>17.7	8.57	2240	1940	7.0	6.6[b]	30	4.8	..	..	..	..
7	26.3	8.59	2110	1930	7.1	6.9[b]	30	5.8	..	..	..	..
B. Effect of tungstic acid concentration												
5	17.7	8.57	2250	1940	6.0	5.6	30	14.5	1.7	0.117	75.0	46.4
8	43.1	25.72	2240	1940	5.4	6.0	30	33.7	4.1	.122	75.0	19.9
9	61.5	42.86	2110	1980	5.4	6.3[b]	30	66.5	8.0	.120	75.0	10.1
10	105.9	68.57	2240	1940	5.4	7.0	30	87.3	9.4	.108	76.5	7.9
11	9.8[c]	4.29	2240	1940	5.6	5.1[c]	40	17.1	3.9	.228	64.5	31.1
12	13.7[c]	8.57	2240	1940	5.4	5.0[c]	40	33.7	5.1	.151	71.5	18.3
13	7.9[c]	4.29	2240	1940	5.4	5.2[c]	50	36.7	10.8	.294	60.0	13.1
14	13.7[c]	8.57	2240	1940	5.4	5.5[c]	50	64.7	11.5	.178	69.0	9.0
C. Effect of the initial concentration of hydrogen peroxide and allyl alcohol												
4	13.1	8.61	2110	1980	5.4	5.3[b]	30	14.7	1.9	0.129	73.5	44.3
15	19.6[c]	8.57	6710	1940	5.4	5.1[c]	30	7.3	1.5	0.205	66.0	70.3
16	11.3	8.60	2110	3970	5.4	6.3[b]	30	11.3	..	..	..	..
D. Effect of temperature												
5	17.7	8.47	2250	1940	6.0	5.6	30	14.5	1.7	0.117	75.0	46.4
4	13.1	8.61	2110	1980	5.4	5.3[b]	30	14.7	1.9	.129	73.5	44.3
12	13.7[c]	8.57	2240	1940	5.4	5.0[c]	40	33.7	5.1	.151	71.5	18.3
17	13.8	8.61	2120	1980	5.3	4.8	40	34.4	5.3	.154	71.0	17.9
14	13.7[c]	8.57	2240	1940	5.4	5.5[c]	50	64.7	11.5	.178	69.0	9.0
18	13.8	8.61	2120	1980	5.2	4.6	50	76.1	14.4	.190	68.0	7.5

[a] Calculated from the rate coefficients. [b] After $1/k_1$ hours. [c] An additional small amount of triethylamine was introduced during the course of the reaction. [d] Estimated error ±1.0.

effect of the *p*H of the reaction mixture, the concentration of the reactants and the temperature were investigated.

Experimental

Epoxidation of Allyl Alcohol.—In a typical experiment 0.540 g. of tungstic acid (Baker Analyzed Reagent), 37.8 g. of 50.7% solution of hydrogen peroxide (Columbia-Southern) and 24.0 g. of water were introduced into a four-necked, 300-ml. flask equipped with a Teflon Tru-Bore stirrer and immersed in a thermostated bath, maintained at a desired temperature (30, 40 or 50°) with a tolerance of less than 0.25°. The mixture was stirred, and after 30 min. a solution of 29.0 g. of allyl alcohol (Shell, purified by fractional distillation, assay: 99.75%) in 158 g. of water, freshly made and preheated to the desired temperature, was added. The time of the addition of allyl alcohol was regarded as zero time. Immediately afterwards triethylamine (Eastman Kodak) was introduced in an amount necessary to bring the *p*H of the mixture to the desired level. (The weight of the added amine was roughly determined.) An additional portion of preheated water was added to bring the total weight of the reaction mixture to 252.0 g. The mixture was stirred continuously and at suitable time intervals aliquots were taken and analyzed for glycidol and hydrogen peroxide contents. The *p*H and, in several experiments, the density of the mixture were determined periodically; also the acidity was checked by titration of the aliquots with 0.1 *N* sodium hydroxide. The initial compositions of the reaction mixtures are listed in Table I.

The products of the reaction, glycidol and glycerol, were isolated in two experiments and a representative example is given. After completing the kinetic experiment (No. 3) 161.5 g. of the reaction mixture (containing, by analysis, 14.73 g. of glycidol) was passed through 10 ml. of Amberlite IRA-400 (OH^-) and washed with water, giving 195.8 g. of the solution free from tungstic acid. A portion of this solution, 192.1 g., was distilled through an 8-cm. Vigreux column. Glycidol was collected in two fractions: b.p. 34° (3.0 mm.) to 45° (1.8 mm.), $n^{20}D$ 1.4213, 4.3 g., assay 86.4% and b.p. 45° (1.8 mm.) to 31° (0.7 mm.); $n^{20}D$ 1.4319, 4.3 g. assay 96.3%; lit.[7] b.p. 56–56.5° (11 mm.), $n^{16}D$ 1.4293. The next fraction constituted glycerol: b.p. 130° (0.65 mm.) to 126° (0.55 mm.), $n^{20}D$ 1.4722, 5.7 g.; lit. b.p. 125.5° (1 mm.),[5] $n^{20}D$ 1.47399.[6,7] A viscous residue (3.5 g.) remained in the distilling flask. The fraction preceding glycidol (166.0 g.) was analyzed and found to contain 3.45 g. of glycidol.

Decomposition of Glycidol.—The equipment and the procedure was the same as in the experiments on the epoxidation of allyl alcohol except that instead of allyl alcohol an equivalent amount of glycidol (b.p. 65° (13 mm.), $n^{20}D$ 1.4314, assay 99.2%) was used. The initial compositions of the reaction mixtures are listed in Table II.

Analytical Methods.—The concentration of glycidol was determined by the pyridinium chloride-pyridine method described by J. L. Jungnickel, *et al.*[8] however, instead of methanolic sodium hydroxide, an aqueous solution was used for titration. Additional tests were performed to establish if allyl alcohol consumed hydrogen chloride under the conditions of the determination. The consumption, if any, was found not to exceed the usual experimental error. The concentration of hydrogen peroxide was determined by titration of the acidified solution of the sample with ceric sulfate, according to the procedure of F. P. Greenspan and D. G.

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(5) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

(6) L. F. Hoyt, *ibid.*, **26**, 329 (1934).

(7) J. C. Snowden and H. O. L. Fischer, THIS JOURNAL, **64**, 1291 (1942).

(8) J. L. Jungnickel, *et al.*, in J. Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer and A. Weissberger, "Organic Analysis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1953, p. 136.

TABLE II

DECOMPOSITION OF GLYCIDOL IN THE ABSENCE OF ALLYL ALCOHOL

Expt. no.	Initial composition, mmole/1000 g.				pH		Temp., °C.	$k \times 10^6$, sec.$^{-1}$
	Et_3N [b]	H_2WO_4	H_2O_2	$C_3H_6O_2$	Init.	After 0.2/k hr.		
A. Effect of the pH of the reaction mixture								
19	2.5	8.35	2050	1910	3.1	3.9	30	2.6
20	9.7	8.34	2050	1900	5.3	4.8	30	1.7
21	17.9	8.34	2050	1890	7.3	6.7[a]	30	1.0
B. Effect of tungstic acid concentration								
20	9.7	8.34	2050	1900	5.3	4.8	30	1.7
22	56.9	41.52	2040	1910	5.1	5.3	30	4.2
23	100.3	82.74	2040	1880	5.1	5.1	30	8.5
C. Effect of the initial concentration of hydrogen peroxide								
20	9.7	8.34	2050	1900	5.3	4.8	30	1.7
24	0.8	8.35	0	1920	5.5	5.2[a]	30	0.8
25	19.0	8.32	6180	1910	5.3	5.5	30	1.5
D. Effect of temperature								
20	9.7	8.34	2050	1900	5.3	4.8	30	1.7
26	11.4	8.34	2050	1910	5.3	5.4	40	3.7
27	11.4	8.34	2050	1890	5.3	5.4	50	8.6

[a] After 0.1/k hours. [b] Estimated error ±1.0.

MacKellar.[9] Additional experiments showed that the presence of tungstic acid, allyl alcohol and a relatively short storage of the acidified solution at room temperature did not affect the results of the hydrogen peroxide determination beyond the limits of experimental error. Johnson and Clark's modification of Francis' bromate–bromide method was used for allyl alcohol assays.[10] The pH of the reaction mixtures was determined by means of the Beckman Zeromatic pH-Meter, Model 9600, with the General Purpose Glass Electrode, No. 4990–83, and the fiber-type Reference Electrode, No. 1170.

Rate Equations and Calculation of the Rate Coefficients.—The experimental results indicate that the changes in the concentration of glycidol during the course of epoxidation of allyl alcohol follow the kinetics of two consecutive pseudo-first order reactions

$$\frac{d\,[G]}{dt} = k_1[AA] - k_2[G] \qquad (2)$$

and in the integrated form

$$[G] = [AA]_0 \frac{k_1}{k_2 - k_1} (e^{-k_1t} - e^{-k_2t}) \qquad (3)$$

Here [G] is the concentration of glycidol, [AA] the concentration of allyl alcohol, $[AA]_0$ the initial concentration of allyl alcohol and k_1 and k_2 the pseudo-first order rate coefficients for the formation and the decomposition of glycidol during the course of epoxidation, respectively. The remaining symbols have their usual meaning. The rate law was established in the following way. From the changes in the concentration of glycidol observed in a given experiment and from the initial concentration of allyl alcohol, the rate coefficients k_1 and k_2 were calculated (*vide infra*). The coefficients, together with the initial concentration of allyl alcohol, were substituted into eq. 3 and the concentrations of glycidol at different times t were calculated. A satisfactory agreement between the calculated and observed values was found. This agreement is illustrated in Figs. 1, 2 and 3 where the results obtained in several typical experiments are presented.[11] Here the per cent. yields of glycidol, based on the initial concentration of allyl alcohol, are plotted *versus* the reaction time. The points represent the yields determined analytically and the curves illustrate the calculated values.

The coefficients k_1 and k_2 were calculated by means of a suitably modified time-ratio method.[12] The useful initial information was obtained from the maximum concentration of glycidol and the time at which it occurred.

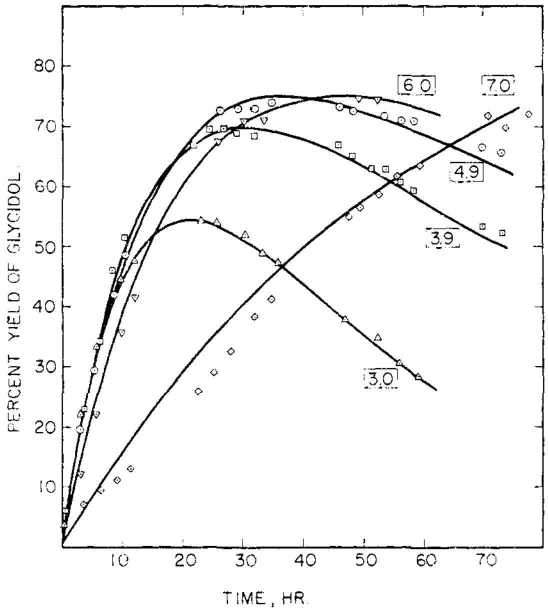

Fig. 1.—Epoxidation of allyl alcohol: dependence of the changes in the concentration of glycidol on the initial pH of the reaction mixtures. The numbers denote the pH values of these experiments: 3.0, expt. 1; 3.9, expt. 2; 4.9, expt. 3; 6.0, expt. 5; 7.0, expt. 6.

For the presentation of both methods it is convenient to transform eq. 3 into eq. 5 by the introduction of the substituents

$$\beta = [G]/[AA]_0,\ \tau = k_1t,\ \kappa = k_2/k_1 \qquad (4)$$

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(9) F. P. Greenspan and D. G. MacKellar, *Anal. Chem.*, **20,** 1061 (1948).

(10) A. Polgar and J. L. Jungnickel, in J. Mitchell, Jr., I. M. Kolthoff, E. S. Proskauer and A. Weissberger, "Organic Analysis," Vol. III, Interscience Publishers, Inc., New York, N. Y., 1956, p. 246.

(11) Curve 7.0 in Fig. 1 (expt. 6) was calculated by means of eq. 11.

(12) The time-ratio method was originally used by Swain[13] for the treatment of data in the special case of two consecutive first- or pseudo-first order reactions where the rate was measured by the determination of the concentration of a product common to the first and second step; *cf.* also ref. 14.

(13) C. G. Swain, THIS JOURNAL, **66,** 1696 (1944).

(14) A. A. Frost and R. G. Pearson, "Kinetics and Mechanism," John Wiley and Sons, Inc., New York, N. Y., 1953, p. 153–159.

TABLE III

RELATION BETWEEN VARIOUS RELATIVE RATE CONSTANTS FOR TWO CONSECUTIVE FIRST ORDER REACTIONS

$\beta_{\max}$	0.95455	0.92327	0.85413	0.81860	0.77426	0.66874	0.56819	0.5000	0.46476
κ	0.01	0.02	0.05	0.07	0.10	0.20	0.35	0.50	0.60
$\tau_{\max}$	4.6525	3.9926	3.1540	2.8599	2.5589	2.0122	1.6154	1.3865	1.2771

$$\beta = \frac{1}{\kappa - 1}\left(e^{-\tau} - e^{-\kappa\tau}\right) \qquad (5)$$

Eqs. 5 and 3 hold for $\kappa \neq 1$; for $\kappa = 1$ eq. 6 is valid.

$$\beta = \tau e^{-\tau} \qquad (6)$$

With the increasing τ, β increases, passes through a maximum and decreases. The equations for the maximum value of β and the corresponding τ can be derived easily

$$\text{For } \kappa \neq 1: \quad \beta_{\max} = \kappa^{\kappa/(1-\kappa)} \qquad (7)$$

$$\tau_{\max} = \ln \kappa/(\kappa - 1) \qquad (8)$$

$$\text{For } \kappa = 1: \quad \beta_{\max} = 1/e \qquad (9)$$

$$\tau_{\max} = 1 \qquad (10)$$

From eqs. 7 to 10 the values of $\beta_{\max}$ and $\tau_{\max}$ corresponding to a series of arbitrary selected κ's were calculated. A portion of these data is presented in Table III. These data were used for relating, by a graphical interpolation, of the experimentally observed maximum yield of glycidol, $\beta_{\max}$ with the κ and $\tau_{\max}$. From $\tau_{\max}$ and the recorded time at which $\beta_{\max}$ occurred, $t_{\max}$, the coefficient k_1 was calculated. Since K was already known the calculation of k_2 was a matter of simple arithmetic.

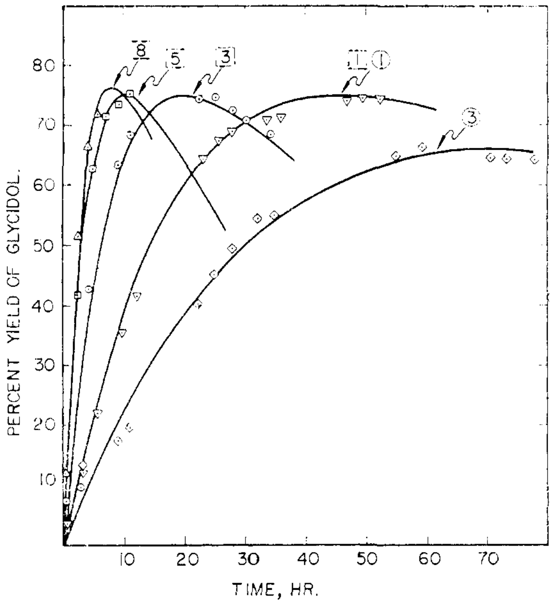

Fig. 2.—Epoxidation of allyl alcohol: dependence of the changes in the concentration of glycidol on the concentration of tungstic acid and hydrogen peroxide. The numbers in the squares denote the relative concentration of tungstic acid; the numbers in the circles denote the relative concentration of hydrogen peroxide and these experiments are represented: 8, expt. 10; 5, expt. 9; 3, expt. 8; 1, expt. 5; 3, expt. 15.

Because of the difficulty in the accurate experimental determination of $\beta_{\max}$ and $t_{\max}$, the coefficients k_1 and k_2 were associated with an uncertainty which in some cases was of considerable magnitude. Therefore, it was necessary to supplement this procedure with the more accurate time-ratio method.

The time-ratio method requires the introduction of the symbols τ_{30}, τ_{40}, τ_{50} . . . and t_{30}, t_{40}, t_{50} . . . They signify the values of τ, or t, for which β is equal to 0.30, 0.40, 0.50 . . ., respectively. Eqs. 5 and 6 demonstrate that the values of τ_{30}, τ_{40}, τ_{50}, . . . depend solely on κ. Hence, the ratios τ_{50}/τ_{40}, τ_{40}/τ_{30} . . . are also characteristic of a given κ. From the definition of τ follows that when k_1 is constant, the ratios of τ's are equal to the ratios of the corresponding t's. Since the latter are experimentally determinable the calculation of κ is possible.

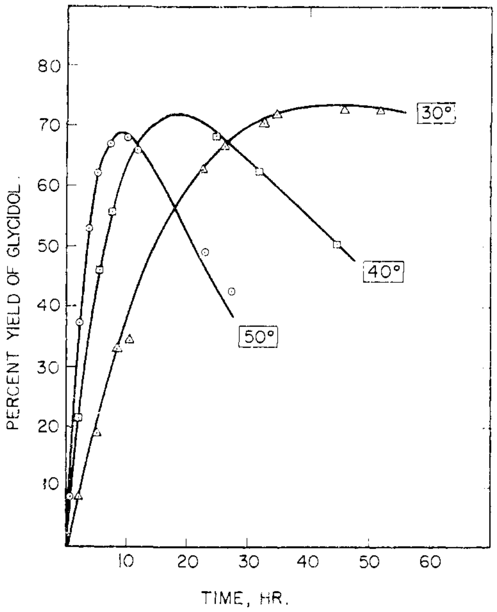

Fig. 3.—Epoxidation of allyl alcohol: dependence of the changes in the concentration of glycidol on temperature: these experiments are represented: 50°, expt. 14; 40°, expt. 17; 30°, expt. 4.

A series of selected κ's was substituted into eq. 5 and for each κ the τ_{15}, τ_{30}, τ_{40} . . . were calculated. The results are listed in Table IV. Since for a given κ there are two values of τ_β corresponding to two identical β, one on each side of $\beta_{\max}$, the τ's (and t's) of the diminishing values of β are marked with an apostrophe. From the data in Table IV the ratios of τ's, equal to the ratios of the corresponding t's, were calculated; a portion of the results is listed in Table V.

The experimentally determined β's were plotted *versus* reaction time and from this graph the t_{30}, t_{40}, t_{50} . . . were read. The ratios t_{40}/t_{30}, t_{50}/t_{40} . . . were calculated and used for the determination of the κ by a graphical interpolation utilizing the data in Table V.

For the determination of the individual rate coefficients a graph was prepared relating the τ's and κ's listed in Table IV. From this graph the τ_{30}, τ_{40}, τ_{50} . . . corresponding to the already found κ were read. Since the t_{30}, t_{40}, t_{50} . . . were already known a simple division yielded k_1 and k_2.

In three experiments, Nos. 6, 7 and 16, the time-ratio method could not be applied,[15] and the coefficients k_1 were calculated by the method of least squares from the changes in the concentration of glycidol in the initial stages of the reaction.

$$[G] = [AA]_0(1 - e^{-k_1 t}) \qquad (11)$$

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[15] In expts. 6 and 7 the reactions were very slow, and the experiments were terminated before the decomposition of glycidol achieved measurable proportions. In expt. 16 allyl alcohol was in excess, in contrast to the remaining experiments where the concentration of hydrogen peroxide *always exceeded* that of allyl alcohol. Hence, there was no simple, common way of expressing the per cent. yield of glycidol.

TABLE IV

RELATION BETWEEN EXTENT OF REACTION AND VARIOUS RELATIVE RATE CONSTANTS FOR TWO CONSECUTIVE FIRST ORDER REACTIONS[a]

κ	0.01	0.02	0.05	0.07	0.10	0.20	0.35	0.50
τ_{15}	0.1626	0.1628	0.1633	0.1635	0.1640	0.1655	0.1679	0.1704
τ_{30}	.3575	.3583	.3608	.3625	.3651	.3741	.3891	.4061
τ_{40}	.5127	.5146	.5203	.5243	.5305	.5528	.5933	.6470
τ_{45}	.6005	.6033	.6118	.6177	.6270	.6615	.7294	.8368
τ_{50}	.6971	.7010	.7134	.7222	.7360	.7900	.9120	1.386
τ_{55}	.8050	.8100	.8280	.8410	.8617	.9490	1.224	
τ_{60}	.9243	.9326	.9593	.9787	1.011	1.163	....	....
τ_{65}	1.061	1.074	1.114	1.114	1.197	1.532	....	....
τ_{70}	1.221	1.240	1.302	1.352	1.447	....	....	....
τ_{75}	1.413	1.441	1.546	1.640	1.866	....	....	....
τ_{80}	1.652	1.700	1.902	2.153	.....	....	....	....
τ_{85}	1.975	2.070	2.745	.....	.....	....	....	....
τ_{90}	2.470	2.738	.....	.....	.....	....	....	....
τ_{95}	3.810	.....	.....	.....	.....	....	....	....
τ'_{95}	5.820	.....	.....	.....	.....	....	....	....
τ'_{90}	11.55	6.156	.....	.....	.....	....	....	....
τ'_{85}	17.26	9.130	3.615	.....	.....	....	....	....
τ'_{80}	23.32	12.17	5.366	3.805	.....	....	....	....
τ'_{75}	.....	15.39	6.746	5.010	3.487	....	....	....
τ'_{70}	.....	18.84	8.150	6.082	4.433	....	....	....
τ'_{65}	.....	22.55	9.639	7.173	5.274	2.606	....	....
τ'_{60}	.....	.....	11.23	8.330	6.120	3.300	....	....
τ'_{55}	.....	.....	12.98	9.579	7.014	3.874	2.090	....
τ'_{50}	.....	.....	14.89	10.94	7.978	4.435	2.648	1.386
τ'_{45}	.....	.....	17.00	12.44	9.036	5.019	3.105	2.146
τ'_{40}	.....	.....	19.35	14.13	10.215	5.643	3.550	2.572
τ'_{35}	.....	.....	22.02	16.04	11.55	6.333	4.011	2.979
τ'_{30}	.....	.....	.....	18.24	13.09	7.119	4.515	3.888

[a] The τ-values corresponding to the diminishing values of β are marked with an apostrophe.

TABLE V

RELATION BETWEEN EXTENT OF REACTION AND VARIOUS RELATIVE RATE CONSTANTS FOR TWO CONSECUTIVE FIRST ORDER REACTIONS[a]

κ	0.01	0.02	0.05	0.07	0.10	0.20	0.35	0.50
t'_{50}/t_{50}	...	....	20.87	15.15	10.84	5.614	2.903	1.000
t'_{50}/t_{45}	...	....	24.34	17.71	12.72	6.704	3.630	1.656
t'_{50}/t_{40}	...	....	28.62	20.87	15.04	8.023	4.463	2.142
t'_{55}/t_{55}	...	....	15.68	11.39	8.140	4.082	1.707	...
t'_{55}/t_{50}	...	....	18.19	13.26	9.530	4.904	2.292	...
t'_{55}/t_{45}	...	....	21.22	15.51	11.19	5.856	2.865	...
t'_{55}/t_{40}	...	....	24.95	18.27	13.22	7.008	3.523	...
t'_{60}/t_{60}	...	....	11.71	8.511	6.053	2.837	...	...
t'_{60}/t_{55}	...	....	13.56	9.905	7.102	3.477	...	...
t'_{60}/t_{50}	...	....	15.75	11.53	8.315	4.177	...	...
t'_{60}/t_{45}	...	....	18.36	13.48	9.761	4.989	...	...
t'_{60}/t_{40}	...	....	21.58	15.89	11.54	5.970	...	...
t'_{65}/t_{65}	...	21.00	8.653	6.270	4.406	1.701	...	...
t'_{65}/t_{60}	...	24.18	10.05	7.329	5.217	2.241	...	...
t'_{65}/t_{55}	...	27.84	11.64	8.529	6.120	2.746	...	...
t'_{65}/t_{50}	...	32.17	13.51	9.932	7.166	3.299	...	...
t'_{65}/t_{45}	...	37.38	15.75	11.61	8.411	3.939	...	...
t'_{65}/t_{40}	...	43.82	18.53	13.68	9.942	4.714	...	...
t_{65}/t_{55}	1.318	1.326	1.345	1.360	1.389	1.614	...	...
t_{65}/t_{50}	1.522	1.532	1.561	1.584	1.626	1.939	...	...
t_{65}/t_{45}	1.767	1.780	1.821	1.852	1.909	2.316	...	...
t_{65}/t_{40}	2.069	2.087	2.141	2.182	2.256	2.771	...	...
t_{65}/t_{30}	2.968	2.997	3.088	3.156	3.278	4.095	...	...
t_{65}/t_{15}	6.525	6.597	6.822	6.997	7.299	9.257	...	...

[a] The t-values corresponding to the diminishing values of β are marked with an apostrophe.

The decomposition of glycidol in the second group of experiments, *i.e.*, under the conditions of epoxidation but in the absence of allyl alcohol, followed the simple pseudo-first order kinetics. The rate coefficients k were calculated by the method of least squares.

$$-\frac{d[G]}{dt} = k[G] \qquad (12)$$

Results

The experimental data pertinent to the epoxidation of allyl alcohol are listed in Table I. With the exception of the component of the reaction mixture whose effect was investigated, the variations in the concentration of the remaining components are minor. In addition to the initial pH of the reaction mixtures, the values recorded after $2/k_1$ or, in a few cases after $1/k_1$ hours, are listed. Except for the experiments performed at a pH of about 3 and at higher than the usual concentrations of tungstic acid or allyl alcohol, a small decrease in the pH of the mixture was observed during the course of the reaction. In most cases these drifts amounted to no more than a few tenths of a unit and probably had little effect on the values of the rate coefficients. The extent of the drifts appears to be related to the extent of the reaction and, as an arbitrary indication of its magnitude the pH values recorded after $2/k_1$, or if this was impossible after $1/k_1$ hr., are reported. In some experiments a small amount of triethylamine was added during the course of the reaction in order to prevent large variations in the pH. In the last two columns of Table I are listed the maximum yields of glycidol and the times required to reach them. Both sets of values were calculated from the respective rate coefficients by means of eqs. 7 and 8.

The data pertinent to the experiments on the decomposition of glycidol in the absence of allyl alcohol are summarized in Table II. The comparison of Tables I and II reveals that the differences in the concentration of tungstic acid, hydrogen peroxide and both alcohols in the comparable experiments of both groups are minor. As an illustration of the variation in the pH during the course of the reaction the initial values and the values recorded after $0.2/k$ hr. are listed. The time of $0.2/k$ hr. is roughly comparable to $1/k_1$ or $2/k_1$.

The data in section A of Table I indicate that the rate coefficients, k_1 and k_2, increase with the decreasing pH of the reaction mixture but not in a uniform fashion. The ratio k_2/k_1 is the largest and the maximum yield of glycidol is the lowest at a pH of about 3. Both the maximum yield and $t_{\max}$ increase with the increasing pH, although the former appears to remain stationary in the pH region of about 5 to 6. Section A of Table II reveals that at a pH of about 5.5 the replacement of allyl alcohol with glycidol does not affect perceptibly the magnitude of the rate coefficients for the decomposition of glycidol. However, in the pH range of about 3 to 4 the coefficient k is somewhat smaller than the corresponding k_2. One cannot decide on the basis of a single experiment, *n.b.* characterized by a large pH drift, if this difference is significant.

The data in sections B, Tables I and II, indicate that an increase in the concentration of tungstic acid results in the increase of k_1, k_2 and k, but the ratio k_2/k_1 does not change appreciably.

In Figs. 4 and 5 the pseudo-first order rate coefficients, k_1, k_2 and k, are plotted *versus* the concentration of tungstic acid. The points appear to follow straight lines although the fit is not the best. From the slopes the second order rate coefficients for the formation of glycidol and from the slopes and intercepts the second- and the first order rate coefficients for the decomposition of glycidol were calculated[16]; they are listed in Table VI.

TABLE VI

EFFECT OF TUNGSTIC ACID. FIRST AND SECOND ORDER RATE COEFFICIENTS AT A pH OF ABOUT 5.5

		Decomposition of glycidol			
	Formation of glycidol $k_1 = k_1''\cdot[H_2WO_4]_0$	During the epoxidation $k_2 = k_2' + k_2''[H_2WO_4]_0$		In the absence of allyl alcohol $k = k' + k''[H_2WO_4]_0$	
Temp., °C.	$k_1'' \times 10^3$ l. mole^{-1} sec.$^{-1}$	$k_2' \times 10^6$ sec.$^{-1}$	$k_2'' \times 10^3$ l. mole^{-1} sec.$^{-1}$	$k' \times 10^6$ sec.$^{-1}$	$k'' \times 10^3$ l. mole^{-1} sec.$^{-1}$
30	1.33	0.82	0.14	0.74	0.09
40	3.95	2.6	.30	..	..
50	8.21	8.6	.50	..	..

At 30° the second order rate coefficient k'' is smaller than the corresponding constant k_2''. The dispersion of the experimental points in Fig. 5 indicates that the values of k'' and k_2'' at 30° are associated with an appreciable uncertainty, yet it appears that the relative order of magnitude of k'' and k_2'' has to be accepted. Thus tungstic acid, or its derivative, appears to be more reactive with respect to glycidol during the course of epoxidation of allyl alcohol than in the experiments where allyl alcohol was absent.

All three coefficients, k_1 and k_2 and k, are decreased by the increase in the concentration of hydrogen peroxide, but k_1 is affected to a larger extent than k_2 or k (sections C, Tables I and II). The coefficient k in the absence of hydrogen peroxide (expt. 24, Table II) is about the same as the coefficients k_2' and k' at 30° (Table VI). Thus tungstic acid appears to react with glycidol only in the presence of hydrogen peroxide. At the increased concentration of allyl alcohol (expt. 16, Table I) the coefficient k_1 was calculated from the concentration changes in the initial stages of the reaction. This method tends to give lower values; it is not clear how much of the observed change in k_1 is due to the method rather than the high concentration of allyl alcohol.

From the data listed in sections D in Tables I and II the following Arrhenius energies of activation were found: formation of glycidol, 15 kcal. mole^{-1}; decomposition of glycidol during the course of epoxidation, 19 kcal. mole^{-1}; decomposition of glycidol in the absence of allyl alcohol, 16 kcal. mole^{-1}. These values are valid only for the reaction conditions specified in pertinent sections of Tables I and II. More general are the results based on the second- and first order rate coefficients from Table VI.

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(16) The method of least squares was used but it was assumed that in Fig. 4 all lines pass through the origin of the coördinates.

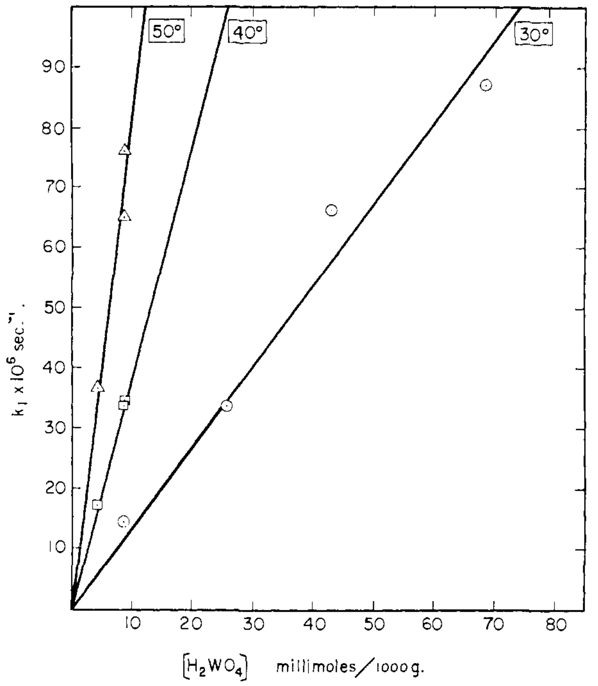


Fig. 4.—Dependence of the pseudo-first order rate coefficient for the formation of glycidol on the concentration of tungstic acid at 30, 40 and 50°.

Discussion

The accumulated experimental evidence supports the assertion that the changes in the concentration of glycidol during the course of epoxidation of allyl alcohol are satisfactorily described by eq. 2 which attributes them to two reactions: the formation of glycidol from allyl alcohol and the simultaneous decomposition of the former. The solution of eq. 2 and the calculation of the rate coefficients k_1 and k_2 under a variety of conditions provided enough information to justify the speculation about the mechanism of the reactions involved.

TABLE VII

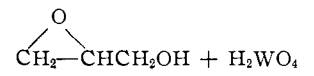
FREQUENCY FACTORS AND THE ARRHENIUS ENERGIES OF ACTIVATION AT A pH OF ABOUT 5.5[a]

Reaction	Z		E_a, kcal. mole^{-1}
Formation of glycidol	0.92×10^{-10}	l. mole^{-1} sec.$^{-1}$	18
Decomp. of glycidol during epoxidation			
Catalyzed by tungstic acid	1.3×10^{5}	l. mole^{-1} sec.$^{-1}$	12
Independent of tungstic acid	2.5×10^{10}	sec.$^{-1}$	23

[a] Calculated from the data in Table VI.

The experimental evidence clearly indicates that hydrogen peroxide does not oxidize allyl alcohol directly. It suggests that hydrogen peroxide rapidly and completely oxidizes tungstic acid to pertungstic acid, and the latter, in a rate-controlling step, reacts with allyl alcohol giving glycidol and regenerating tungstic acid.

$$H_2WO_4 + H_2O_2 \rightleftarrows H_2WO_5 + H_2O \qquad (13)$$



$$H_2WO_5 + CH_2{=}CHCH_2OH \longrightarrow \overset{\displaystyle O}{CH_2{-}CHCH_2OH} + H_2WO_4 \qquad (14)$$

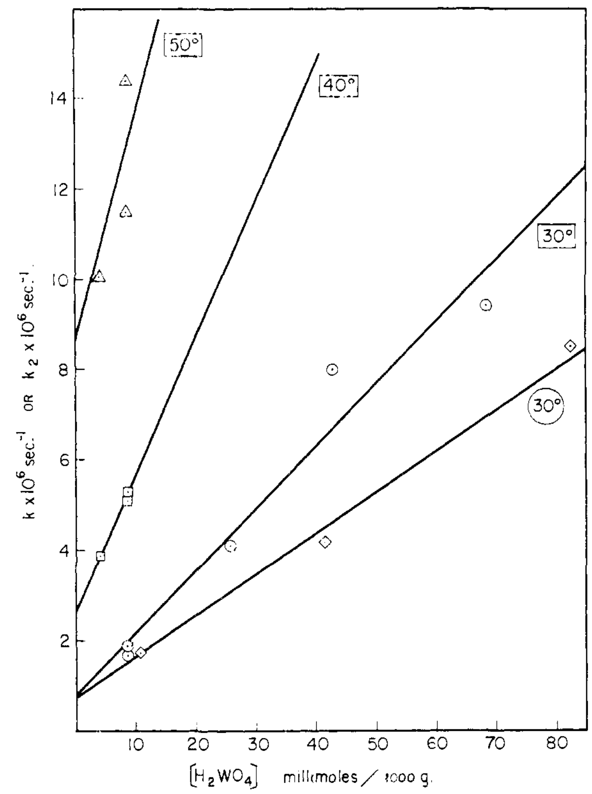


Fig. 5.—Dependence of the pseudo-first order rate coefficient for the decomposition of glycidol on the concentration of tungstic acid at 30, 40 and 50°; ◇, decomposition of glycidol in the absence of allyl alcohol; ○, □, △, decomposition of glycidol during the course of epoxidation of allyl alcohol.

It is known that tungstic acid is capable of forming peroxy acids,[17] and it is believed that the pertungstic acid was formed when the yellow, slightly soluble in water, tungstic acid was treated with hydrogen peroxide and converted into a white, soluble substance.[18] The conclusion concerning the rate-controlling step and the equilibrium in the oxidation of tungstic acid is based on the observation that at a constant pH the rate of formation of glycidol is proportional to the concentration of allyl alcohol and tungstic acid and does not increase with the increase in the concentration of hydrogen peroxide.[19] If the oxidation of tungstic acid to pertungstic acid were rate-controlling, then the rate of formation of glycidol (and k_1) should be proportional to the concentration of hydrogen peroxide. Conversely, a slow epoxidation step

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[17] (a) N. V. Sidgwick, "The Chemical Elements and Their Compounds," Vol. II, Oxford University Press, 1950, p. 1045; (b) H. Remy, "Treatise on Inorganic Chemistry," English Translation, Vol. II, Elsevier Publishing Company, 1956, p. 179.

[18] The discussion of the structure of pertungstic acid is beyond the scope of this paper. The formula H_2WO_5 was taken from ref. 17b and is used in eq. 13 and subsequently in the text since it can be reconciled with the requirements of the proposed mechanism.

[19] A decrease in the coefficients k_1, k_2 and k accompanying an increase in the concentration of hydrogen peroxide may be caused by its lower solvating power although another explanation also is available. It has been found that the pH-meter readings in aqueous solutions of hydrogen peroxide are lower than the "real pH" (ref. 22). Thus it appears that, in spite of similar pH-readings, the experiments differing in the concentration of hydrogen peroxide differed also in the acidity of the reaction media.

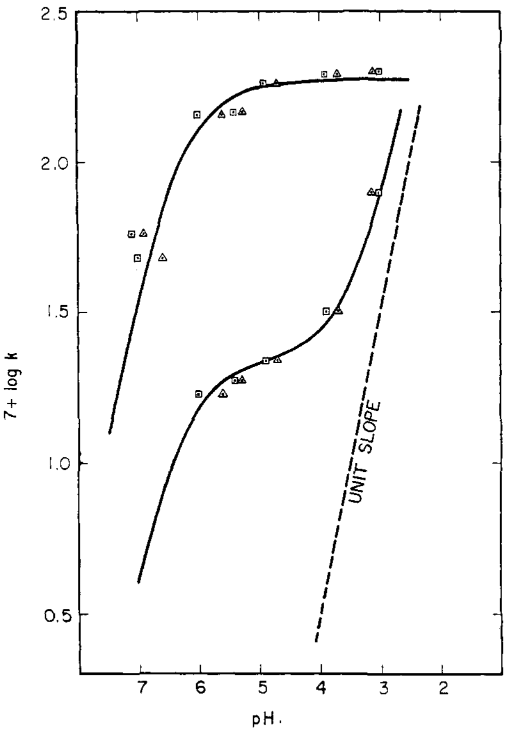

Fig. 6.—Epoxidation of allyl alcohol: dependence of the logarithms of the pseudo-first order rate coefficients for the formation of glycidol ($k = k_1$, the upper curve) and for its decomposition ($k = k_2$, the lower curve) on the *p*H of the reaction mixture: □, initial *p*H; △, *p*H recorded during the course of the experiment and listed in column 7 in Table I. The curves illustrate eqs. 16 and 30.

would be consistent with the observed effect of hydrogen peroxide concentration if all, or almost all, tungstic acid were oxidized to pertungstic acid.[20]

The speculation concerning the mechanism of the oxidation of allyl alcohol by pertungstic acid is based mainly on the dependence of the rate coefficients on the *p*H. In contrast to dilute aqueous solutions where the recorded *p*H-values can be used for the calculation, with moderate accuracy, of the kinetic and equilibrium constants, the *p*H, in the strict sense, has no meaning in the nonaqueous solutions.[21] However, in partially aqueous media or in water-like solvents, in some cases, a certain amount of fundamental meaning can be ascribed to the results of the *p*H-measurements.[22] Even if the *p*H-values reported in this paper could not serve as a quantitative measure of acidity, relative to that of the solutions with which the instrument was calibrated, they offered a reproducible and apparently reliable index of the changes in acidity, at least in these experiments where the concentration of allyl alcohol and hydrogen peroxide was similar and the proportion of tungstic acid and triethylamine was changed. The regularity in the variation of the coefficients k_1 and k_2 with the increasing *p*H values, which in turn reflect the increase in the concentration of triethylamine, supports this contention.

In Fig. 6 the logarithms of the pseudo-first order rate coefficients, k_1 and k_2, are plotted against the *p*H of the reaction mixtures. At high *p*H values the changes in k_1 are proportional, or approach this relation, to the apparent hydrogen ion concentration, which is defined in eq. 15, since the plot appears to follow a line of unit slope.

$$[H^+]^a = 10^{-pH} \tag{15}$$

At low *p*H value k_1 appears to be independent of $[H^+]^a$ whereas k_2 approaches the relation of simple proportionality.

The changes in log k_1 are described reasonably well by the curve which represents eq. 16.[24]

$$k_1 = \frac{1.84 \times 10^{-5} \times [H^+]^a}{4.54 \times 10^{-7} + [H^+]^a} \tag{16}$$

$$\frac{1}{[H^+]^a} = -22.0 \times 10^5 + 4.74 \times 10^3 \frac{[H_2WO_4]_0}{k_1} \tag{17}$$

Four mechanisms can be reconciled with eq. 16. In mechanism I it is assumed that pertungstic acid reacts with allyl alcohol giving an intermediate which, in a proton-catalyzed reaction, disproportionates to glycidol and tungstic acid. In the reaction media of low acidity the proton-catalyzed step is rate determining, whereas at high acidity, when the availability of protons is high, the formation of the intermediate controls the rate of epoxidation. The remaining three mechanisms are based on the assumption that pertungstic acid exists in the reaction mixtures in two forms, as a singly charged anion and as an un-ionized acid; their relative concentrations are a function of the acid ionization constant.

$$K = \frac{[^-HWO_5][H^+]}{[H_2WO_5]} \tag{18}$$

In mechanism II the epoxidation is accomplished by the un-ionized pertungstic acid. In mechanisms III and IV the anion acts as an oxidizing agent, and either the slow oxidation is preceded by a fast reversible protonation of allyl alcohol or the fast reversible addition of the anion to allyl alcohol is followed by a slow proton-catalyzed

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(20) The concentration of pertungstic acid could be taken as equal to the initial concentration of tungstic acid if, of course, the concentration of the reaction intermediate represented by the adduct of pertungstic acid to allyl alcohol (*vide infra*) were small relative to $[H_2WO_4]_0$.

(21) R. G. Bates, "Electrometric *p*H Determinations," John Wiley and Sons, Inc., New York, N. Y., 1954, Chapters 2, 6 and p. 243.

(22) Kolczynski, Roth and Shanley[23] investigated the behavior of the glass electrode in aqueous solutions of hydrogen peroxide of all strengths and found that the apparent *p*H values, as read from the *p*H-meter, are lower than the real *p*H values which have the same significance as in ordinary water solutions. The difference increases with the increasing concentration of hydrogen peroxide. A set of corrections was calculated to convert the apparent *p*H to the real values. (For the initial composition of the reaction mixtures in most of the experiments described in this paper, the real *p*H should be higher than the apparent one by about 0.25 unit, if the presence of allyl alcohol could be ignored.) The authors ascribe the difference between the apparent and real *p*H values to a shift in the E_0 for the electrode system in the new environment which, in addition to the small difference in the liquid-junction potentials, probably reflects the difference in free energy of solvation of the proton in water and nearly anhydrous hydrogen peroxide (about 9 kcal./mole).

(23) J. R. Kolczynski, E. M. Roth and E. Shanley, THIS JOURNAL, **79**, 531 (1957).

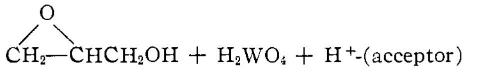
(24) Eq. 16 was derived from eq. 17 by substituting the value of 8.57×10^{-3} for the initial concentration of tungstic acid. Equation 17 indicates that a plot of $1/[H^+]^a$ *versus* $1/k_1$ should give a straight line. Indeed, except for expt. 7, a reasonably good linearity was obtained. Expt. 7 was discarded and the parameters of eq. 17 were calculated by the method of least squares.

disproportionation of the adduct to glycidol and tungstic acid. By applying the principle of the steady state and making few additional assumptions, four rate equations for the formation of glycidol can be obtained. From these equations the expressions for the coefficient k_1 can be easily derived.

Mechanism I:

$$CH_2{=}CHCH_2OH + H_2WO_5 \underset{k_{-1}^*}{\overset{k_1^*}{\rightleftharpoons}} \text{intermediate} \quad (19)$$

$$\text{Intermediate} + H^+\text{-(donor)} \xrightarrow{k_2^*}$$

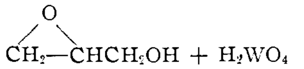


$$CH_2{-}CHCH_2OH\ (\text{O bridge}) + H_2WO_4 + H^+\text{-(acceptor)} \quad (20)$$

$$k_1 = \frac{k_1^* k_2^*}{k_{-1}^* + k_2^*[H^+]} [H^+][H_2WO_4]_0 \text{ if } [H_2WO_4]_0 = [H_2WO_5] \quad (21)$$

Mechanism II:

$$CH_2{=}CHCH_2OH + H_2WO_5 \xrightarrow{k_1^*}$$



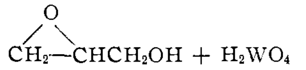
$$CH_2{-}CHCH_2OH + H_2WO_4 \quad (22)$$

$$k_1 = \frac{k_1^*}{K + [H^+]} [H^+][H_2WO_4]_0 \text{ if } [H_2WO_4]_0 = [{}^-HWO_5] + [H_2WO_5] \quad (23)$$

Mechanism III:

$$CH_2{=}CHCH_2OH + H^+\text{-(donor)} \underset{k_{-1}^*}{\overset{k_1^*}{\rightleftharpoons}} CH_2{=}CHCH_2OH_2^+ \quad (24)$$

$$CH_2{=}CHCH_2OH_2^+ + {}^-HWO_5 \xrightarrow{k_2^*}$$



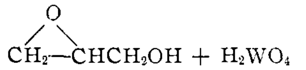
$$CH_2{-}CHCH_2OH + H_2WO_4 \quad (25)$$

$$k_1 = \frac{k^*K}{K + [H^+]} [H^+][H_2WO_4]_0 \text{ if } k_2^*[{}^-HWO_5] \ll k_{-1}^* \text{ and } [H_2WO_4]_0 = [{}^-HWO_5] + [H_2WO_5] \quad (26)$$

Mechanism IV:

$$CH_2{=}CHCH_2OH + {}^-HWO_5 \underset{k_{-1}^*}{\overset{k_1^*}{\rightleftharpoons}} \text{intermediate} \quad (27)$$

$$\text{Intermediate} + H^+\text{-(donor)} \xrightarrow{k_2^*}$$



$$CH_2{-}CHCH_2OH + H_2WO_4 \quad (28)$$

$$k_1 = \frac{k^*K}{K + [H^+]} [H^+][H_2WO_4]_0 \text{ if } k_2^*[H^+] \ll k_{-1}^* \text{ and } [H_2WO_4]_0 = [{}^-HWO_5] + [H_2WO_5] \quad (29)$$

The four rate equations, 21, 23, 26 and 29, are identical with the empirically established eq. 16, if the initial concentration of tungstic acid is taken as equal to 8.57×10^{-3} mole l.$^{-1}$ and the term $[H^+]$ is substituted with $[H^+]^a$. Hence, the determination of the parameters in these four equations, k_2^*/k_{-1}^*, k_1^*, k^* and K, is simple. It should be noted that the mechanisms II, III and IV lead to the same value of the *apparent ionization constant of pertungstic acid:* $K = 4.5 \times 10^{-7}$ mole l.$^{-1}$.

Before discussing the four mechanisms in greater detail, it is expedient to examine the effect of pH on the coefficient k_2 since the conclusions are helpful in clarifying some points pertinent to the epoxidation of allyl alcohol.[25] The curve in Fig. 6 which describes rather well the changes in log k_2 represents eq. 30.

$$k_2 = (k_W[{}^-HWO_5]^a + k_H)[H^+]^a \quad (30)$$

Here k_W and k_H are two constants equal to 0.569×10^3 l. mole^{-2} sec.$^{-2}$ and 5.62×10^{-3} l. mole^{-1} sec.$^{-1}$, respectively. The term $[H^+]^a$ is defined by eq. 15 and the apparent concentration of the pertungstate anion, $[{}^-HWO_5]^a$, is defined by eq. 31 where K is the apparent acid ionization constant

$$[{}^-HWO_5^-]^a = \frac{K[H_2WO_4]_0}{K + [H^+]^a} \quad (31)$$

of pertungstic acid calculated from the epoxidation data. The initial concentration of tungstic acid, $[H_2WO_4]_0 = 8.57 \times 10^{-3}$ mole l.$^{-1}$, was assumed to be equal to the sum of the concentration of the pertungstic anion and the un-ionized pertungstic acid.[26] Thus two parallel reaction paths appear to be responsible for the decomposition of glycidol *in the investigated region of pH.* One is the reaction of the protonated glycidol with the pertungstate anion. The other path probably involves several reactions: the pseudo-first order reaction of the protonated glycidol with various nucleophiles present in the reaction mixture in an approximately stationary concentration[27] and perhaps the unimolecular ring opening preceded by protonation.[28] The reactions of the unprotonated glycidol appear to be negligible in the investigated pH region. In fact, the introduction of a $[H^+]^a$ - independent term into eq. 30 does not improve the fit illustrated in Fig. 6.

It is remarkable that the dependence of both rate coefficients, k_1 and k_2, on the pH can be explained in terms of the pertungstic anion and the un-ionized acid and that the apparent ionization constant calculated from the epoxidation data is equally applicable to the decomposition of glycidol. Even if the apparent ionization constant and the equations correlating the rate coefficients with the pH were regarded, and quite justly, as approxima-

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[25] The investigation of the effect of pH on the rate of decomposition of glycidol in the absence of allyl alcohol comprises three experiments only. They are characterized by rather large drifts in the pH during the course of the experiments. For these reasons their value for the quantitative correlations is very limited.

[26] The combination of eqs. 30 and 31 gives

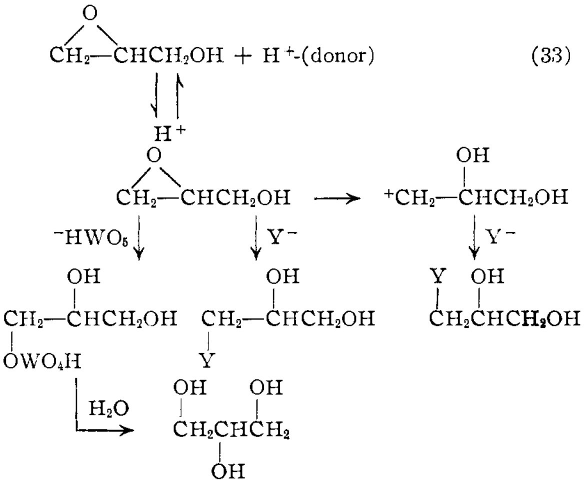
$$\frac{k_2(K + [H^+]^a)}{[H^+]^a} = (k_W[H_2WO_4]_0 + k_H)K + k_H[H^+]^a \quad (32)$$

A plot of the left-side term *versus* $[H^+]^a$ gave a reasonably straight line; from its slope and intersection the coefficients k_H and k_W were calculated by the method of least squares.

[27] For a review of the reactions of epoxides see: (a) S. Winstein and R. B. Henderson, "Heterocyclic Compounds," Ed. R. C. Elderfield, Vol. I, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 22 and ff., (b) R. E. Parker and N. S. Isaacs, *Chem. Revs.*, **59**, 737 (1959).

[28] The hydrolysis of certain epoxides and trimethylene oxide *via* the rate-controlling rearrangement of the protonated epoxide to a highly reactive carbonium ion was established by Pritchard and Long.[29] This reaction path is probably of minor importance in hydrolysis of glycidol because of the destabilizing effect of the hydroxymethyl group and the competition of the bimolecular ring-opening under the conditions of epoxidation of allyl alcohol.

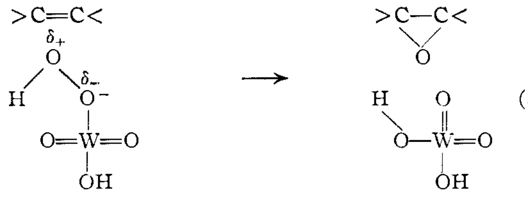
[29] J. G. Pritchard and F. A. Long, THIS JOURNAL, **78**, 2663 2667 (1956); *ibid.*, **78**, 6008 (1956); *ibid.*, **80**, 4162 (1958); F. A. Long, J. G. Pritchard and F. E. Stafford, *ibid.*, **79**, 2362 (1957).


(33)

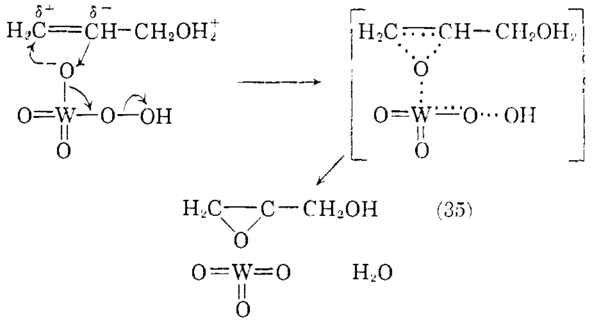
tions, the presence of the pertungstate ion under the conditions of epoxidation of allyl alcohol cannot be ignored. Hence, mechanism I has to be discarded. The question then arises which species, the un-ionized pertungstic acid or its anion, acts as an epoxidizing agent, *i.e.*, whether mechanism II or III and IV are the correct ones. This question cannot be answered on the basis of the kinetic data presented in this paper since all three mechanisms are compatible with the experimental results.

However, the data contained in the literature, although of a qualitative nature, are sufficiently informative to supplement the conclusions based on the kinetic study. The examination of the epoxidations, and of the hydroxylations *via* the epoxidation, performed in aqueous solutions with the hydrogen peroxide–tungstic acid system reveals two significant facts: the success in epoxidizing negatively substituted olefins as maleic, fumaric and crotonic acids, and the particular facility with which allylic alcohols are epoxidized.[2,3a,b,4,30] These facts are in a marked contrast to the epoxidations accomplished with organic peracids, which are believed to involve an electrophilic attack on the double bond and are retarded or inhibited by the electron-withdrawing substituents.[31]

The epoxidation by the un-ionized pertungstic acid, as in mechanism II, can be interpreted most reasonably as resembling the reactions of organic peracids and consequently cannot provide a satisfactory explanation for the specific behavior of the aqueous hydrogen peroxide–tungstic acid system.


(34)

It appears that a more satisfactory explanation can be provided by assuming that in aqueous media the pertungstate anion acts as an oxidant. The addition of the nucleophilic reagents to α,β-unsaturated carbonyl and related compounds is a well-known reaction and, therefore, it is not surprising that the pertungstate anion is capable of reacting with maleic, fumaric and crotonic acids.[3b] The course of the reaction of the pertungstate ion with allyl alcohol is less obvious. A rationalization can be offered by assuming that the hydroxymethyl substituent, or perhaps the protonated hydroxymethyl, sufficiently polarizes the ethylenic bond to permit the addition of the pertungstate anion and that the resulting intermediate is stabilized by the delocalization of the electron pair, with the accompanying negative charge, *via* the incipient formation of the oxirane ring. Hence the


(35)

proposed mechanism resembles the SN2′ substitutions in the allylic systems except that instead of the cleavage of the carbon–oxygen bond, the oxygen–tungsten bond is broken.[32] If the neutral allyl alcohol were subjected to the attack of the pertungstate anion then, for the consistency with the kinetic results, it would be necessary to postulate the acid-catalyzed disproportionation of the intermediate adduct.

Two variants in the epoxidation mechanism are conceivable. They are: (a) the formation of the allylic carbonium ion prior to the attack of the pertungstate anion and (b) the formation of allyl pertungstate either by the attack of the pertungstate anion on the α-carbon of allyl alcohol or *via* the "normal" SN2′ substitution. On the basis of the available kinetic evidence the first possibility cannot be dismissed. The second possible path, the formation of allyl pertungstate, may lead to two reactions. The ester may undergo a hydrolysis regenerating allyl alcohol and pertungstic acid, thus inducing no change in the composition of the reaction mixture, or it may undergo an intramolecular rearrangement giving glycidol tungstate and, upon hydrolysis, glycidol and tungstic acid. The epoxidation *via* the ester would be specific for allylic alcohols and perhaps the related compounds as cyclohexene-4-ol. The SN2′-like mechanism of eq. 35 appears to be more general; it could take place whenever an anionic addition to a double bond is possible. The observed second order kinetics of epoxidation would not contradict the ester hypothesis provided that the concentration of allyl pertungstate were low relative to the initial concentration of tungstic acid and one of the

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(32) For a review of the SN2′ mechanism see: R. H. DeWolfe and W. G. Young, *Chem. Revs.*, **56**, 769 (1956).

steps in the reaction sequence were acid-catalyzed. The support for the ester hypothesis could be found in the similarity between tungsten and chromium: the facility with which chromic acid esterifies alcohols is well known.[33] The ester hypothesis could perhaps explain why tungstic acid appears to catalyze the opening of the oxirane ring more efficiently during the course of epoxidation of allyl alcohol than in the absence of the latter. Were the path of eq. 35 the correct one, then a "cage effect" might be invoked.

Acknowledgments.—The author wishes to express his appreciation to Prof. P. D. Bartlett of Harvard University and Drs. P. L. Dietz and H. C. Stevens of this Laboratory for stimulating discussions. Thanks are also due to Mr. E. M. Pflueger who performed part of the experimental work.

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[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Dead-end Radical Polymerization. II

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RECEIVED AUGUST 13, 1959

In the absence of retardation of the termination reaction, the radical initiated polymerization of vinyl monomers ceases short of complete conversion, a phenomenon that has been termed dead-end radical polymerization. The modified kinetic expression describing the polymerization may be used with experimentally determined conversion–time data to calculate simultaneously the specific rate of initiator decomposition k_d and the kinetic constant $f^{1/2}k_p/k_t^{1/2}$. If the quantity $k_p/k_t^{1/2}$ is known for the monomer, the initiator efficiency f may be found. If k_d and $f^{1/2}k_p/k_t^{1/2}$ for the system are known, the course of conversion with time may be accurately predicted. When the theoretical value for the dead-end conversion is fairly high, acceleration of polymerization to nearly complete conversion may occur due to the retardation of the termination step; in such cases, the dead-end theory is inapplicable. Data for the bulk polymerization of styrene at several temperatures with 2,2′-azobisisobutyronitrile as initiator illustrate the application of the dead-end theory for kinetic measurements and also the limitations imposed by the "gel" effect.

Introduction

In the previous article,[1] it was shown that the limiting fractional conversion at infinite time of a radical initiated vinyl polymerization is less than unity (neglecting thermal polymerization) and can be predicted if the kinetic constants describing the system are known accurately. Under certain conditions of temperature and initiator concentration the limiting conversion may in fact be very low. This situation applies only in the absence of such complicating features at high conversion as the retardation of the termination step, the so-called Tromsdorff–Norrish[2,3] "gel" effect.

This present work shows experimental conditions where the dead-end theory appears to apply exactly and other conditions where the "gel" effect invalidates the theory. Where the theory is valid, it has been used to obtain values for the specific rate constant of initiator decomposition and for the initiator efficiency.

Theoretical

The rate of radical initiated vinyl polymerization, assuming a steady-state radical concentration, is

$$-\frac{d[M]}{dt} = \frac{k_p}{k_t^{1/2}} k_d^{1/2} f^{1/2} [Cat]^{1/2}[M] \qquad (1)$$

This disregards the polymer produced by purely thermal polymerization concurrent with the catalyzed polymerization. In this equation, [M] represents the concentration of unreacted monomer, [Cat] the concentration of unreacted catalyst and f the catalyst efficiency, that is, the fraction of radicals produced by the primary cleavage of catalyst that actually start polymer chains. The quantity k_d is the specific rate constant for the first-order primary cleavage of catalyst, k_p is the specific rate of propagation, $k_t = k_{tc} + k_{td}$ is the sum of the specific rates of combination and disproportionation, respectively.

If the catalyst is such as 2,2′-azobisisobutyronitrile, the rate of disappearance of catalyst is

$$\frac{-d[Cat]}{dt} = k_d\,[Cat] \qquad (2)$$

If the initial catalyst concentration is $[Cat]_0$ and if the catalyst is all added at the beginning of the polymerization, one obtains

$$[Cat] = [Cat]_0\, e^{-k_d t} \qquad (3)$$

As the polymerization proceeds, there is a net volume shrinkage of the system as monomer is converted into polymer of lesser specific volume. This results in an effective increase of the initial catalyst and monomer concentrations so that at a fractional conversion x

$$x = ([M]_0 - [M])/[M]_0 \qquad (4)$$

the effective unreacted catalyst and monomer concentrations are

$$[Cat] = \frac{[Cat]_0}{(1 - \alpha x)}\, e^{-k_d t} \qquad (5)$$

$$[M] = \frac{[M]_0}{(1 - \alpha x)}\,(1 - x) \qquad (6)$$

where $[M]_0$ is the initial monomer concentration and α is the total volume shrinkage for the complete conversion of monomer to polymer.

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