A Two-Phase Second-Order Reaction: Kinetics of Epoxidation of Methyl 12,13-Epoxyoleate[1]

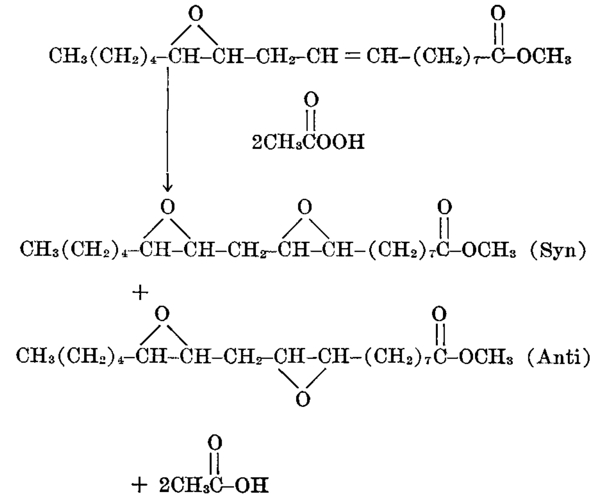
H. L. ROTHBART, M. E. SNOOK, J. F. RUSLING and W. E. SCOTT,
Eastern Utilization Research and Development Division, ARS, USDA, Philadelphia, Pennsylvania 19118

Abstract

The kinetics of epoxidation of methyl 12,13-epoxyoleate with peracetic acid have been studied. Chloroform and benzene solvents were used at 25, 30 and 40 C. A second-order equation was developed to determine the rate constants in this two-phase system. Variation of the relative phase volumes provides a convenient method for controlling the rate of reaction. Differences in the ΔS° of activation for the formation of the two isomeric diepoxides were greater than 1 eu in all cases. If the usual integrated second-order equation is used, the rate constant will be in error. The magnitude of the error is related to the partition coefficient of the species distributed between the phases and the volume ratios of the two phases. Other errors in the rate constant were determined by expressing K as a function of time, temperature and the concentration of reactants at any time in the reaction. The total differential of K divided by K, to get the relative error, was evaluated at various reaction times. The choice of best times for the determination of the rate constant was dictated from the error analysis.

Introduction

Methyl 12,13-epoxyoleate (methyl vernolate) is readily oxidized to methyl 9,10 : 12,13-diepoxystearate. Epoxidations of olefins have been shown to be second order when peracetic acid is the source of oxygen in liquid media (1). The kinetic picture is obscured somewhat since commercial peracetic acid solutions contain acetic acid, hydrogen peroxide, water and a trace of sulfuric acid in addition to the peracid. When this reagent is added to solutions of methyl vernolate in chloroform or benzene, a two-phase system results. The kinetic data obtained for such epoxidations must be corrected for partition of the reactants.



Ordinarily the acid is added to a solution of the ester. Since this takes a finite time there is often some doubt as to starting conditions. The effect of these and other experimental conditions on the apparent rate constant and on evaluation of errors is discussed in succeeding sections.

Experimental Procedures

A 40% solution (w/w) of peracetic acid in acetic acid was obtained from Becco Chemical, Buffalo, N.Y. Analysis of the reagent indicated 37–42% peracetic acid depending upon the time of storage. Three methods of analysis were tested (2–4). A modification of the method of Greenspan gave the most satisfactory results which had the highest precision. Duplicate 0.100 ml aliquots were taken and 50 ml of 4 N H_2SO_4 and 3 ml of saturated KI were added to one of these. The resulting solution was titrated to the starch endpoint with $Na_2S_2O_3$ in order to determine the total number of milliequivalents of HOOH and peracetic acid. The second aliquot was cooled to 0 C, 50 ml of 2 N H_2SO_4 (precooled to 0 C) and 0.1 ml of foerroin indicator (*o*-phenanthroline-ferrous sulfate complex) were added. The solution was titrated with $Ce(SO_4)_2$ solution to the disappearance of the salmon color of the indicator. The temperature was maintained at less than 5 C during the titration by the use of an ice bath. The datum was used to calculate the amount of HOOH present. Water (13%), acetic acid (40%), and H_2SO_4 (1%) are the other components in the reagent.

Methyl vernolate was prepared from naturally-occurring glyceryl trivernolate as described previously (5).

In a typical kinetic experiment 25 g (0.08051 moles) of pure methyl vernolate was dissolved in about 200 ml of solvent contained in a 500 ml flask. This was immersed in a constant temperature bath and the solution stirred. A quantity of reagent containing 0.1124 moles of peracetic acid was added to 0.015 moles of sodium acetate trihydrate. The resulting solution was added to the reaction vessel from a burette over a period of less than 2 min. The mixture was stirred vigorously throughout the experiment. During this procedure the temperature never rose more than 3 C above the desired reaction temperature. Ten-milliliter aliquots were removed at timed intervals and drained into approximately 50 ml of 20% (w/v) solution of Na_2SO_3 which contained ice. The low temperature and the destruction of peracetic acid effectively stopped the reaction with the ester.

The organic layer was then washed with 100 ml of a 10% (w/v) sodium bicarbonate solution. This was followed by three washings with 60 ml portions of water. The samples were dried with anhydrous sodium sulfate and the solvent was evaporated. The oil from each sample was analyzed by gas liquid chromatography (GLC) as described previously (6).

Three different mixtures of known proportions of pure methyl vernolate and the pure solid isomer of methyl 9,10 : 12,13-diepoxystearate (probably the anti-isomer (6)) were prepared for analysis by GLC. The peak areas, taken as weight per cent for each com-

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ponent, were within 1.5% of the true values. The liquid isomer of methyl 9,10: 12-13-diepoxystearate was assumed to behave similarly. The concentration of peracetic acid was not measured directly during the course of the reaction. Its concentration at any time was calculated from the number of equivalents of peracetic acid added initially minus the number of equivalents of the diepoxides formed.

The reaction mixture was observed to consist of two phases, a large organic phase and a small water- and HOOH-rich phase. These are in intimate contact as a suspension during the course of the reaction due to stirring. Error analysis indicated that if any of the species involved in the reaction were partitioned between the phases, its concentration would have to be determined in the organic phase at any time during the course of the reaction. Even though the water-rich phase was relatively small, it was found that considerable amounts of HOOH and peracid were dissolved within it. The partition coefficients of these species were determined for the $CHCl_3$ and C_6H_6 systems. No other reactants partitioned to any measurable extent. Partition coefficients were determined by simulating reaction conditions. The methyl vernolate was replaced by a typical mixture of both isomers of methyl 9,10: 12,13-diepoxystearate so that no reaction with peracetic acid occurred. The ester was dissolved in an appropriate solvent and placed in a calibrated graduated cylinder. The mixture was shaken several times, allowed to settle, aliquots were taken, and the mixture was allowed to stand (with repeated agitation) for time periods up to 20 hr. Equilibration occurred so rapidly that no differences could be found in aliquots taken after 0.5 to 20 hr. The volumes of each phase were measured at the desired temperatures. Determinations of HOOH and peracid in both phases were made by essentially the same techniques as were used in the determination of the reagent peracid.

Results and Discussion

Partition Studies

Partition coefficients, Kp, defined as the ratio of the molar concentration of species in the water-rich phase to that in the organic-rich phase, are listed in Table I. The total liquid volume of the system was either about 250 ml (essentially the reaction condition) or twice this amount. All data are corrected to the former condition. The volumes of each phase are listed in the table. The subscription "aq" refers to the water-rich phase while "or" refers to the organic-rich phase within which the reaction takes place. Probable errors in the volume determinations were 0.2 ml or 3% to 5% in the case of V_{aq}. These were determined from the standard error evaluated during the calibration of the graduated cylinder. The relative error in the determination of the concentration of peracid (HOOAc) is less than 1% (4) in the starting reagent and V_{aq}. Poor titration of HOOAc dissolved in aliquots of the organic phase made it practicable to determine its concentration in V_{aq} directly and calculate the amounts of both species in V_{or} by difference. This results in a 1% relative error in Kp for two or three determinations.

TABLE I

Partition Coefficients for Peracetic Acid

T° C	Solvent	KpHOOAc	V_{aq}	V_{or}
25	C_6H_6	10.2	5.0	244
30	C_6H_6	10.0	6.0	242
40	C_6H_6	9.5	7.5	243
25	$CHCl_3$	4.5	5.7	244
30	$CHCl_3$	4.2	5.4	245
40	$CHCl_3$	3.9	4.0	246

Rate Equations

A typical plot of the disappearance of methyl vernolate and the formation of the isomeric diepoxides as a function of time is represented by Figure 1. The data are most consistent with that for a second-order reaction described by equation 1. Here [MeV] refers to the methyl vernolate concentration and [HOOAc] refers to the peracetic acid concentration.

$$\frac{-d\,[\mathrm{MeV}]_{or}}{dt} = K\,[\mathrm{MeV}]_{or}\,[\mathrm{HOOAc}]_{or} \qquad [1]$$

Let A = mm HOOAc taken; P = mm HOOAc in the aqueous phase; R = mm HOOAc reacted; A′ = mm MeV taken; R′ = mm MeV reacted; and $\alpha = A/A'$. Methyl vernolate is essentially insoluble in the aqueous phase so P′ would be zero at all times.

Since the only reactions of HOOAc and MeV are with one another, in this system R′ = R. Thus equations 2–6 are obtained

$$[\mathrm{HOOAc}]_{or} = \frac{A - P - R}{V_{or}} \qquad [2]$$

$$[\mathrm{HOOAc}]_{o,or} = \frac{A - P_o}{V_{or}} \qquad [3]$$

$$[\mathrm{MeV}]_{or} = \frac{A' - R'}{V_{or}} \qquad [4]$$

$$[\mathrm{MeV}]_{o,or} = \frac{A'}{V_{or}} \qquad [5]$$

$$[\mathrm{HOOAc}]_{or} = \frac{(\alpha - 1)\,A' + (A' - R')}{V_{or} + Kp\,V_{aq}} \qquad [6]$$

If equations 4 and 6 are substituted into equation 1, the resulting expression may be integrated by the method of partial fractions to give equation 7.

$$\frac{V_{or} + Kp\,V_{aq}}{(\alpha - 1)\,A'} \ln \frac{\alpha A' - R'}{\alpha(A' - R')} = Kt \qquad [7]$$

The rate constant may be evaluated from equation 7 if the initial conditions are known and the amount of MeV present at any time is evaluated.

In other studies of similar epoxidations partition of the reactants was absent, not important or not considered (7). If no partition takes place, equation 7 may be written as equation 8.

$$\frac{V_{or}}{(\alpha - 1)A'} \ln \frac{\alpha A' - R'}{\alpha(A' - R')} = Kt \qquad [8]$$

The experimental data in this study fit a straight line if either equation is used but equation 8 results in an incorrect estimate of K.

A typical curve is shown in Figure 2 and may be compared with the curve obtained when partition is disregarded. The data are summarized in Table II. Apparent rate constants refer to those uncorrected for partition. Dielectric constants were determined for the reactants dissolved in the organic solvents at

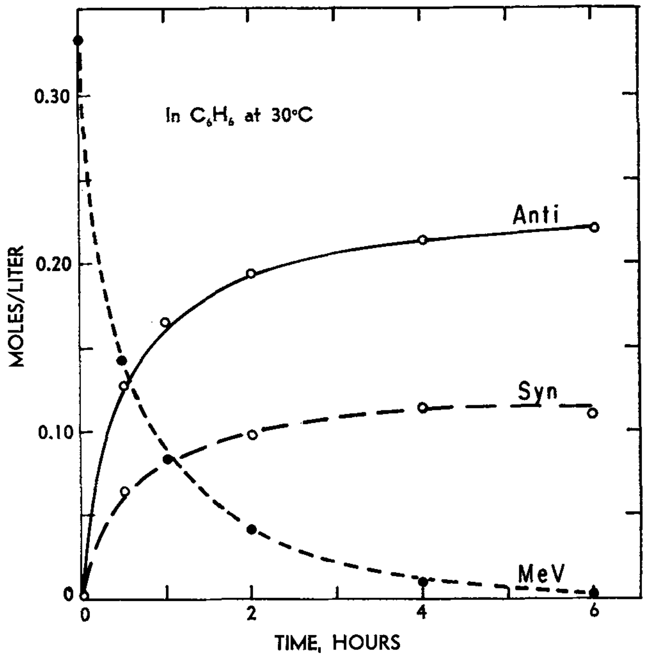

FIG. 1. The change in the concentration of methyl vernolate (MeV) and the isomeric methyl diepoxystearates (Syn and Anti) plotted as a function of time.

30 C at 1000 cycles/sec. The values were 2.9 and 5.5 for the C_6H_6 and $CHCl_3$ systems respectively.

Examination of equations 1 through 7 indicates how partition may be used to control the rate of reaction. It is apparent that the greater the concentration of reactants in the organic phase, the faster is the rate of reaction. Partition of peracetic acid into the aqueous phase lowers its concentration in the organic phase at any time. Although an excess of this acid may be used, its concentration in the reaction phase may be controlled by appropriate choice of relative volumes of the two phases.

Activation Parameters

Energies and entropies of activation may be calculated from equations 9 and 10. The former are listed in Table II. Values of these parameters are indicative of orders of magnitude when evaluated over so short a temperature range as in this study (8).

$$\frac{d \ln K}{dT} \cong \frac{Ea}{RT^2} \qquad [9]$$

$$\Delta S^{\circ\neq} = R \ln (Kh/\kappa Te) + Ea/T \qquad [10]$$

where h = Planck's constant, κ = the Boltzman Constant, T = degrees Kelvin, e = base of the natural logarithm, and the other terms have their usual significance. Since the rate of disappearance of methyl vernolate is equal to the sum of the rates of formation of the syn and anti isomers of methyl diepoxystearate, and the formation of both isomers may be described by second-order kinetics,

$$K = K_{syn} + K_{anti} \qquad [11]$$

and

$$K_{anti}/K_{syn} = [Anti]_{or}/[Syn]_{or} \qquad [12]$$

Where K_{syn} = rate constant for the formation of the syn isomer, and $[Syn]_{or}$ = the concentration of the syn isomer in the organic phase at $t > O$. If equation 11 is solved for either K_{syn} or K_{anti} through the use of equation 12 and substituted into equation 9, it becomes apparent that Ea is identical for the formation of both isomers and the disappearance of methyl vernolate. This occurs because K_{anti}/K_{syn} is essentially constant, within an experimental error of 4% over the aforementioned temperature range. Equations analogous to 10 may be written for $\Delta S^{\circ\neq}$ for the formation of the two isomers. Subtracting one from the other, equation 13 is obtained

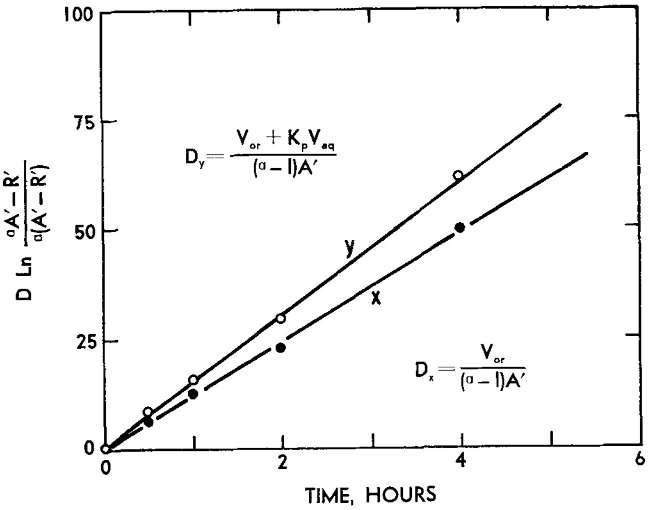

FIG. 2. Second-order plot of the epoxidation of methyl vernolate in benzene at 30 C. The data for curve x was not corrected for partition of peracetic acid. Curve y shows the same data corrected for partition.

$$\Delta S^{\circ\neq}_{anti} - \Delta S^{\circ\neq}_{syn} =$$

$$\Delta(\Delta S^{\circ\neq}) = R \ln \frac{K_{anti}}{K_{syn}} = R \ln \frac{[Anti]_{or}}{[Syn]_{or}} \qquad [13]$$

This is true since the ratio of rate constants of formation is approximately constant within an experimental-error range of 1–3%. Although the determination of the entropy of activation is not possible, in this case, differences in the entropies of activation are readily obtainable. These are listed in Table II.

Errors in K. The experimental values for the rate constant in this study depend upon the values for t, T and the original and reactant concentrations at any time which the experimenter believes to be the true value. If the experimental value of K is not very different from the true value, that is, if the errors are small, the error in K may be evaluated from the total differential of K, a function of the aforementioned variables. This may be divided by K to get the relative error in the rate constant. At this point it is worthwhile to rewrite equation 7 in terms of these variables and constants. This form [7a] makes

TABLE II
Rate Constants and Activation Parameters for the Epoxidation of Methyl Vernolate

Solvent	T° Kelvin	$10^4 \times K$ (1/mole-sec)		K_{Anti}/K_{Syn}	Ea- (Kcal/ mole)	$\Delta(\Delta S^{\circ\neq})$
		Apparent	Corrected			
C_6H_6	298	7.9	9.3	1.97	17	1.35
C_6H_6	303	12	15	1.94	12	1.33
C_6H_6	313	20	28	1.97		1.35
$CHCl_3$	298	16	17	1.84	12	1.21
$CHCl_3$	303	22	24	1.81	16	1.18
$CHCl_3$	313	52	54	1.72		1.08

$$\frac{1+\mathrm{Kp}\,\mathrm{V_{aq}}/\mathrm{V_{or}}}{[\mathrm{HOOAc}]^*_{\mathrm{o,or}}-[\mathrm{MeV}]_{\mathrm{o,or}}}\ \ln\frac{[\mathrm{MeV}]_{\mathrm{o,or}}\,[\mathrm{HOOAc}]_{\mathrm{or}}}{[\mathrm{HOOAc}]_{\mathrm{o,or}}\,[\mathrm{MeV}]_{\mathrm{or}}}=\mathrm{Kt} \qquad [7a]$$

$$[\mathrm{HOOAc}]^*_{\mathrm{o,or}}=\mathrm{A}/\mathrm{V_{or}} \qquad [14]$$

the discussion somewhat simpler and it points up the similarity of equation 7 to the more common forms of integrated second-order rate expressions. Then:

$$\frac{\mathrm{dK}}{\mathrm{K}}=\left(\frac{\partial \mathrm{K}}{\partial \mathrm{t}}\right)_{\mathrm{T},\,[\mathrm{MeV}]_{\mathrm{or}}}\cdots\frac{\mathrm{dt}}{\mathrm{K}}+\left(\frac{\partial \mathrm{K}}{\partial \mathrm{T}}\right)_{\mathrm{t},\,[\mathrm{MeV}]_{\mathrm{or}}}$$

$$\cdots\frac{\mathrm{dT}}{\mathrm{K}}+\left(\frac{\partial \mathrm{K}}{\partial[\mathrm{MeV}]_{\mathrm{o,or}}}\right)_{\mathrm{t,T}}\cdots\frac{\mathrm{d}[\mathrm{MeV}]_{\mathrm{o,or}}}{\mathrm{K}}$$

$$+\left(\frac{\partial \mathrm{K}}{\partial[\mathrm{MeV}]_{\mathrm{or}}}\right)_{\mathrm{t,T}}\cdots\frac{\mathrm{d}[\mathrm{MeV}]_{\mathrm{or}}}{\mathrm{K}}+\quad\cdots \qquad [15]$$

The first and second terms on the right-hand side of equation 15 may be evaluated from equations 7a and 9 respectively. The results of this are the first and second terms on the r.h.s. in equation 18. The other terms in equation 15 may be evaluated by differentiation of equation 7a and added to obtain equation 18. Two of these are given in equations 16 and 17. Similar equations may be written for $[\mathrm{HOOAc}]_{\mathrm{or}}$ and $[\mathrm{HOOAc}]_{\mathrm{o,or}}$.

$$\left(\frac{\partial \mathrm{K}}{\partial[\mathrm{MeV}]_{\mathrm{or}}}\right)_{\mathrm{t,T}}\cdots\frac{\mathrm{d}[\mathrm{MeV}]_{\mathrm{or}}}{\mathrm{K}}$$

$$=\frac{-\mathrm{d}[\mathrm{MeV}]_{\mathrm{or}}}{[\mathrm{MeV}]_{\mathrm{or}}\left(\ln\dfrac{[\mathrm{MeV}]_{\mathrm{o,or}}\,[\mathrm{HOOAc}]_{\mathrm{or}}}{[\mathrm{HOOAc}]_{\mathrm{o,or}}\,[\mathrm{MeV}]_{\mathrm{or}}}\right)} \qquad [16]$$

$$\left(\frac{\partial \mathrm{K}}{\partial[\mathrm{MeV}]_{\mathrm{o,or}}}\right)_{\mathrm{t,T}}\cdots\frac{\mathrm{d}[\mathrm{MeV}]_{\mathrm{o,or}}}{\mathrm{K}}=\frac{\mathrm{d}[\mathrm{MeV}]_{\mathrm{o,or}}}{[\mathrm{HOOAc}]^*_{\mathrm{o,or}}-[\mathrm{MeV}]_{\mathrm{o,or}}}$$

$$+\frac{\mathrm{d}[\mathrm{MeV}]_{\mathrm{o,or}}}{[\mathrm{MeV}]_{\mathrm{o,or}}\left(\ln\dfrac{[\mathrm{MeV}]_{\mathrm{o,or}}\,[\mathrm{HOOAc}]_{\mathrm{or}}}{[\mathrm{HOOAc}]_{\mathrm{o,or}}\,[\mathrm{MeV}]_{\mathrm{or}}}\right)} \qquad [17]$$

The relative error in K may be evaluated where absolute errors are equal to the true value subtracted from the experimental value. Consider the error in time. Time zero for the reaction was designated as the point when all of the peracid had just been added. Experimental determinations of t were made from this starting point. It took about 1.5 min to add all of the reagent; therefore, the experimental value of t was less than the true value. Similarly, the time needed for quenching the reaction in an aliquot of reaction mixture led to an error in t of about −0.5 min. The sum of these might have led to a large positive error in K; however, the important item here is the relative error both in t and in K. For reaction times greater than 65 min the relative error caused by this term is less than 3%.

This error in t is introduced by the requirement of a relatively slow addition of acid to the ester-containing solution. Under the conditions described above when the two reactant solutions are kept at the reaction temperature and mixed, the temperature rises 2–3 C and returns to the desired temperature in less than 30 min. If one or both reactants are cooled slightly, (2–5 C) below the reaction temperature, the temperature climbs to about that desired within the first half hour. Temperature control is critical as is demonstrated by equation 18. For an activation energy of 18 Kcal at a reaction temperature of about 300 K an error of 3 degrees (1% relative error in T) is propagated by Ea/RT or 30. This would lead to a 30% error in K if it were evaluated in the first half hour where temperature control is bad (9). After this first half hour, the temperature remained constant within less than a degree leading to an uncertainty in the rate constant, evaluated from data taken after an hour of reaction, of less than ±10%.

$$\frac{\mathrm{dK}}{\mathrm{K}}=\frac{-\mathrm{dt}}{\mathrm{t}}+\frac{\mathrm{dT}}{\mathrm{T}}\left(\frac{\mathrm{Ea}}{\mathrm{RT}}\right)+\frac{\mathrm{d}[\mathrm{MeV}]_{\mathrm{o,or}}-\mathrm{d}[\mathrm{HOOAc}]^*_{\mathrm{o,or}}}{[\mathrm{HOOAc}]^*_{\mathrm{o,or}}-[\mathrm{MeV}]_{\mathrm{o,or}}}$$

$$+\frac{\mathrm{AdP_o}-\mathrm{P_odA}}{(\mathrm{A}-\mathrm{P_o})^2+\mathrm{P_o}(\mathrm{A}-\mathrm{P_o})}$$

$$+\frac{\left(\dfrac{\mathrm{d}[\mathrm{HOOAc}]_{\mathrm{or}}}{[\mathrm{HOOAc}]_{\mathrm{or}}}\right)-\left(\dfrac{\mathrm{d}[\mathrm{MeV}]_{\mathrm{or}}}{[\mathrm{MeV}]_{\mathrm{or}}}\right)+\left(\dfrac{\mathrm{d}[\mathrm{MeV}]_{\mathrm{o,or}}}{[\mathrm{MeV}]_{\mathrm{o,or}}}\right)-\left(\dfrac{\mathrm{d}[\mathrm{HOOAc}]_{\mathrm{o,or}}}{[\mathrm{HOOAc}]_{\mathrm{o,or}}}\right)}{\ln\dfrac{[\mathrm{MeV}]_{\mathrm{o,or}}\,[\mathrm{HOOAc}]_{\mathrm{or}}}{[\mathrm{HOOAc}]_{\mathrm{o,or}}\,[\mathrm{MeV}]_{\mathrm{or}}}} \qquad [18]$$

Errors in the initial concentrations of peracetic acid and methyl vernolate could be highly significant as can be discerned from the third term on the r.h.s. of equation 18. This term may be evaluated by taking the total differentials of equations 14 and 4. Equations 19 and 20 are true at any time including t = o at which time $[\mathrm{MeV}]_{\mathrm{o,or}}=[\mathrm{MeV}]_{\mathrm{or}}$. Ordinarily at t = o the R and R′ terms are zero. However, t was defined experimentally as zero when all of the reagent peracid had been added.

$$\mathrm{d}[\mathrm{HOOAc}]^*_{\mathrm{o,or}}=\frac{\mathrm{dA}-\mathrm{dR}}{\mathrm{V_{or}}}-\frac{(\mathrm{A}-\mathrm{R})\,\mathrm{dV_{or}}}{\mathrm{V^2_{or}}} \qquad [19]$$

$$\mathrm{d}[\mathrm{MeV}]_{\mathrm{or}}=\frac{\mathrm{dA'}-\mathrm{dR'}}{\mathrm{V_{or}}}-\frac{(\mathrm{A'}-\mathrm{R'})\,\mathrm{dV_{or}}}{\mathrm{V^2_{or}}} \qquad [20]$$

The reaction had actually been under way for less than 2 min at this point. Since the methyl vernolate and peracetic acid react only with one another under the aforementioned conditions dR = dR′ at all times including t = o. Similarly, dA′ is negligible since methyl vernolate is essentially insoluble in $\mathrm{V_{aq}}$ and a highly purified sample of this compound was weighed out prior to its use. The error $\mathrm{dV_{or}}$ is less than 1 ml and since $\mathrm{V_{or}}$ is greater than 200 ml the last term in these equations is negligible. Thus,

$$\frac{\mathrm{d}[\mathrm{MeV}]_{\mathrm{o,or}}-\mathrm{d}[\mathrm{HOOAc}]^*_{\mathrm{o,or}}}{[\mathrm{HOOAc}]^*_{\mathrm{o,or}}-[\mathrm{MeV}]_{\mathrm{o,or}}}=\frac{-\mathrm{dA}}{(\mathrm{A}-\mathrm{A'})} \qquad [21]$$

The relative error in A was less than 1% or about ±1 mm while the denominator was 32 mm. The resulting contribution to the error in K is only ±3%. Accuracy in t = o may be sacrificed since $\mathrm{R_o}=\mathrm{R'_o}$ and this allows the experimenter to minimize temperature fluctuations in the early stages of the reaction. These temperature fluctuations have already been shown to lead to large errors in K.

The fourth term on the r.h.s. of equation 18 is in terms similar to those in equation 21. It originates in the numerator of equation 7a and is the sum of the partial derivatives of equation 22 with respect to A and P_o divided by K. The term contributes from ±2.2 to ±4.5% to the total relative error.

$$1 + KpV_{aq}/V_{or} = 1 + \frac{P_o}{A - P_o} \qquad [22]$$

The numerator of the last term on the r.h.s. of equation 18 may be evaluated from equations 2 and 4 to give equation 23. At t = o this whole last term is indeterminate, at t > o the last two terms may be evaluated if the value of each item is experimentally determined and the errors are estimated. The value of R′ was experimentally determined and P was calculated from knowledge of the starting conditions, stoichiometry and the experimentally determined partition data. The value of R'_o was estimated by extrapolating the plots of the rate of disappearance of methyl vernolate back to a true time where t = o. The steep slope and uncertainty in this approach required the large value of dR'_o which also was estimated from this curve. The values of the other terms have already been discussed.

$$\frac{d[HOOAc]_{or}}{[HOOAc]_{or}} - \frac{d[MeV]_{or}}{[MeV]_{or}} + \frac{d[MeV]_{o,or}}{[MeV]_{o,or}} - \frac{d[HOOAc]_{o,or}}{[HOOAc]_{o,or}}$$

$$= \frac{dA - dP - dR'}{A - P - R'} + \frac{dR'}{A' - R'} - \frac{d\,R'_o}{A'_{.} - R'_o} - \frac{dA - dP_o - dR'_o}{A - P_o - R'_o} \qquad [23]$$

Since there are five error terms, each of which was expressed as a range from (+) to (−), equation 23 has 32 solutions (16 ranges) at each time, t > o. The maximum and minimum ranges for representative experiments are reported in Table III. The sum of the last three terms on the r.h.s. in equation 18 also has been calculated. These values are reported as "range, per cent error in K." It is clear that these terms lead to large relative errors in K if it is estimated from data obtained in the late stages of the reaction. The first term in equation 18 leads to a large error in K determined at the start of the reaction. It appears that K is best determined from data obtained between 60% and 90% of completion. Since this was done, the actual value of the error is probably less than ±20%.

Actual values of the errors in this and other kinetic studies are unknown but may be estimated through the use of these techniques. This error estimation technique allows the experimenter to use data which are subject to the smallest errors.

TABLE III[a]

Relative Error in the Rate Constant

t, sec	R	P	d P	Range, eq (23)		Range, per cent error in K	
				max.	min.	max.	min.
In C_6H_6 at 30°[b]							
1,800	46	13	±.6	± .04	±.000	±10	± .7
3,600	60	10	±.5	± .06	±.007	±10	± .04
7,200	71	8	±.4	± .1	±.04	±10	± 2
14,400	78	7	±.4	± .5	±.4	±20	±20
21,600	79	7	±.4	±1	±.9	±30	±20
In $CHCl_3$ at 30°[c]							
1,188	51	5	±.1	± .04	±.000	±10	± .2
2,988	67	4	±.08	± .08	±.03	± 9	± 3
4,788	73	3	±.06	± .1	±.08	±10	± 5
6,588	77	3	±.06	± .3	±.3	±20	±10
8,388	78	3	±.06	± .5	±.4	±20	±20

[a] A = 112, A′ = 80 determined; dA = ±1, dR′ = ±1 estimated.
[b] P_o = 22, determined; dP_o = ±1, dR'_o ±2, R'_o = 3 estimated.
[c] P_o = 9.5, determined; dP_o = ±.2, dR'_o = ±3, R'_o = 6 estimated.

It has been assumed throughout that there are no surface or interface effects, that no significant volume changes occur during the reaction and that partition equilibrium exists throughout the experiment at t > O. Evidence for rapid attainment of partition equilibrium given in the Experimental Procedures section is further supported by comparisons of the slopes and linearity of the curves depicted in Figure 2. If the partition state were near but not at equilibrium, errors would be small, compared to errors from other sources; that is, in these systems where one of the phases is very small and the values of apparent and corrected K are not widely different. Diffusion controlled reaction would not fit the observed rate law.

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REFERENCES

1. Swern, D., "Encyclopedia of Polymer Science and Technology," Vol. 6, Interscience Publishers, Inc., New York, 1967, p. 83–102.
2. D'Ans, J., and W. Frey, Z. anorg. Chem. *84*, 145–164 (1914).
3. Sully, B. D., and P. L. Williams, Analyst *87*, 653–657 (1962).
4. Greenspan, F. P., and D. G. MacKellar, Anal. Chem. *20*, 1061–1063 (1948).
5. Riemenschneider, R. W., T. Zell and W. E. Scott, JAOCS *43*, 325–326 (1966).
6. Maerker, G., E. T. Haeberer and S. F. Herb, Ibid. *43*, 505–508 (1966).
7. Kwart, H., and D. M. Hoffman, J. Org. Chem. *31*, 419–425 (1966).
8. Purlee, E. L., R. W. Taft, Jr. and C. A. De Fazio, J. Am. Chem. Soc. *77*, 837–842 (1955).
9. Morse, B. K., in "Technique of Organic Chemistry," Vol. 8, A. Weissberger, Editor, Interscience Publishers, Inc., New York, 1961, p. 499–578.

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