

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, UNIVERSITY OF MARYLAND, COLLEGE PARK, MD.]

The Kinetics of Four-Step Competitive-Consecutive Second-Order Reactions. The Alkaline Hydrolysis of Pentaerythritol Tetraacetate

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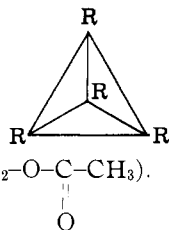
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The rate equations for a four-step competitive, consecutive second-order reaction of the type $A + B \xrightarrow{k_1} C + M$, $A + C \xrightarrow{k_2} D + M$, $A + D \xrightarrow{k_3} E + M$, $A + E \xrightarrow{k_4} F + M$ have been solved in terms of the variable λ where $\lambda = \int_0^t A dt$ and when $A_0 = 4B_0$. The solution is of the form $A/B_0 = G_1 e^{-k_1 \lambda} + G_2 e^{-k_2 \lambda} + G_3 e^{-k_3 \lambda} + G_4 e^{-k_4 \lambda}$ where the G 's are constants involving various combinations of k_1, k_2, k_3 , and k_4 . Using procedures similar to those developed previously for a three-step reaction of similar kinetic type, a least square solution based on first approximations of ${}^0k_1, {}^0k_2, {}^0k_3$, and 0k_4 and utilizing all time-concentration data has been developed. A second method based upon the expansion of A/B_0 into a fourth-degree power series of λ was developed. For the alkaline hydrolysis of pentaerythritol tetraacetate at 4.1° in various dioxane-water media the second procedure was considerably more successful than the first method in obtaining the four rate constants of the reaction. The fit of the time-concentration data from the derived rate constants and the calculated standard deviation of the individual rate constants are very satisfactory.

Introduction

Our success in handling the kinetics of three-step competitive consecutive second-order processes²⁻⁴ encouraged us to investigate the kinetics of four-step processes of the same kinetic type. A search of the literature⁵ indicated that the saponification of pentaerythritol tetraacetate had been studied with the conclusion that the statistical ratio of $k_1:k_2:k_3:k_4 = 4:3:2:1$ was maintained. In light of our experience with molecules where interaction occurs because of the proximity of the groups, this conclusion was rather disturbing.

This molecule is a symmetrical tetraester whose structural formula is

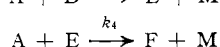
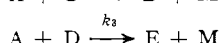
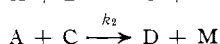
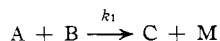


where R is $(-\text{CH}_2-\text{O}-\text{C}-\text{CH}_3)$.

The residual group after R reacts with the hydroxide ion is $(-\text{CH}_2\text{OH})$. Thus each step of this reaction should be between an ion and a neutral molecule. Because of the small size of this molecule relative to the size of the substituents one would expect some interaction between the groups and one would not expect that a statistical ratio of the rate constants could be maintained. Consequently, after the mathematical analysis was made, a study of the alkaline hydrolysis of pentaerythritol tetraacetate was made in various dioxane-water mixtures at 4.1°.

Mathematical Analysis

The reactions to be considered are



In our reaction A, B, C, D, E, F, and M are OH^- , $\text{C}(\text{CH}_2\text{OCOCH}_3)_4$, $\text{C}(\text{CH}_2\text{OH})(\text{CH}_2\text{OCOCH}_3)_3$, $\text{C}(\text{CH}_2-$

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(2) W. J. Svirbely, *J. Am. Chem. Soc.*, **81**, 255 (1959).

(3) W. J. Svirbely and H. E. Weisberg, *ibid.*, **81**, 257 (1959).

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$\text{OH})_2(\text{CH}_2\text{OCOCH}_3)_2$, $\text{C}(\text{CH}_2\text{OH})_3(\text{CH}_2\text{OCOCH}_3)$, $\text{C}(\text{CH}_2\text{OH})_4$, and CH_3COO^- , respectively.

The pertinent rate equations for the above steps in terms of the molar concentrations of A, B, C, D, and E are

$$dA/dt = -k_1AB - k_2AC - k_3AD - k_4AE \quad (1)$$

$$dB/dt = -k_1AB \quad (2)$$

$$dC/dt = k_1AB - k_2AC \quad (3)$$

$$dD/dt = k_2AC - k_3AD \quad (4)$$

$$dE/dt = k_3AD - k_4AE \quad (5)$$

Let us define a new variable λ , so that

$$\lambda = \int_0^t A dt \quad (6)$$

It follows that

$$d\lambda = A dt \quad (7)$$

On substituting eq. 7 into eq. 1 through 5, the resulting five new equations can be integrated. Constants of integration are evaluated in each case from the appropriate boundary conditions which are: $\lambda = C = D = E = 0, A = A_0, B = B_0$ at $t = 0$; and $A_0 = 4B_0$ (equivalent amounts). The results of the integrations are given by eq. 8-12. The concentration of each of the various reacting species can be calculated by use of the appropriate equation.

$$B = B_0 e^{-k_1 \lambda} \quad (8)$$

$$C = B_0 k_1 e^{-k_2 \lambda} \frac{[e^{(k_2 - k_1) \lambda} - 1]}{k_2 - k_1} \quad (9)$$

$$D = B_0 k_1 k_2 e^{-k_3 \lambda} \frac{[e^{(k_3 - k_1) \lambda} - 1] - [e^{(k_3 - k_2) \lambda} - 1]}{k_3 - k_1} \quad (10)$$

$$E = B_0 k_1 k_2 k_3 e^{-k_4 \lambda} \frac{[e^{(k_4 - k_1) \lambda} - 1] - [e^{(k_4 - k_2) \lambda} - 1] - [e^{(k_4 - k_3) \lambda} - 1]}{k_4 - k_1} \quad (11)$$

$$A = 4B + 3C + 2D + E \quad (12)$$

Rewriting eq. 12 yields eq. 13, namely

$$S = \frac{A}{B_0} = G_1 e^{-k_1 \lambda} + G_2 e^{-k_2 \lambda} + G_3 e^{-k_3 \lambda} + G_4 e^{-k_4 \lambda} \quad (13)$$

where

$$G_1 = 4 + \frac{k_1}{k_2 - k_1} \left[3 + \frac{k_2}{k_3 - k_1} \left(2 + \frac{k_3}{k_4 - k_1} \right) \right] \quad (14)$$

$$G_2 = - \frac{k_1}{k_2 - k_1} \left[3 + \frac{k_2}{k_3 - k_2} \left(2 + \frac{k_3}{k_4 - k_2} \right) \right] \quad (15)$$

$$G_2 = \frac{k_2}{k_3 - k_2} \frac{k_1}{k_3 - k_1} \left[2 + \frac{k_3}{k_4 - k_3} \right] \quad (16)$$

$$G_4 = - \frac{k_1}{k_4 - k_1} \frac{k_2}{k_4 - k_2} \frac{k_3}{k_4 - k_3} \quad (17)$$

Method 1.—A procedure for evaluating the rate constants through direct use of eq. 13 has been described under method 1, ref. 4. It is based upon first estimates of the k 's, expansion of eq. 13 about the first estimates *via* Taylor's series expansion, least squares solution for the correction terms for the first-estimates, and repetition of the process using the corrected k 's as new first estimates.

Method 2.—Let us expand eq. 13 in a power series involving λ and let us use all terms through the 4th power as shown by eq. 18

$$S = G_1(1 - k_1\lambda + (k_1\lambda)^2/2! - (k_1\lambda)^3/3! + (k_1\lambda)^4/4! + G_2(1 - k_2\lambda + \dots) + G_3(1 - k_3\lambda + \dots) + G_4(1 - k_4\lambda + \dots) \quad (18)$$

Equation 18 can be rearranged to give eq. 19, namely

$$S = (G_1 + G_2 + G_3 + G_4) - \lambda(k_1G_1 + k_2G_2 + k_3G_3 + k_4G_4) + \frac{\lambda^2}{2!}(k_1^2G_1 + k_2^2G_2 + k_3^2G_3 + k_4^2G_4) - \frac{\lambda^3}{3!} \times (k_1^3G_1 + k_2^3G_2 + k_3^3G_3 + k_4^3G_4) + \frac{\lambda^4}{4!}(k_1^4G_1 + k_2^4G_2 + k_3^4G_3 + k_4^4G_4) + \dots \quad (19)$$

Through use of eq. 13-17 one can obtain identities for the coefficients of the λ terms of eq. 19. The results are

$$k_1G_1 + k_2G_2 + k_3G_3 + k_4G_4 = k_1 \quad (20)$$

$$k_1^2G_1 + k_2^2G_2 + k_3^2G_3 + k_4^2G_4 = k_1(k_1 - k_2) \quad (21)$$

$$k_1^3G_1 + k_2^3G_2 + k_3^3G_3 + k_4^3G_4 = k_1[k_1(k_1 - k_2) - k_2(k_2 - k_3)] \quad (22)$$

$$k_1^4G_1 + k_2^4G_2 + k_3^4G_3 + k_4^4G_4 = k_1[k_1^2(k_1 - k_2) - k_2^2(k_2 - k_3) - k_1k_2 \times (k_2 - k_3) + k_2k_3(k_3 - k_4)] \quad (23)$$

Equation 19 now becomes eq. 24, namely

$$S = 4 - k_1\lambda + k_1(k_1 - k_2) \frac{\lambda^2}{2!} - k_1[k_1(k_1 - k_2) - k_2(k_2 - k_3)] \frac{\lambda^3}{3!} + k_1[(k_1^2(k_1 - k_2) - k_2^2(k_2 - k_3) - k_1k_2(k_2 - k_3) + k_2k_3(k_3 - k_4))] \frac{\lambda^4}{4!} + \dots \quad (24)$$

For brevity, eq. 24 can be written as

$$S = 4 + J_1\lambda + J_2\lambda^2 + J_3\lambda^3 + J_4\lambda^4 + \dots \quad (25)$$

We have thus reduced our exact solution as represented by eq. 13 to a power series expressed by eq. 25. It should now be possible to determine the coefficients (J 's) by the method of least squares using the experimental S and λ values. The evaluation of the k 's from the J 's then follows quite easily. Programs for carrying out such operations were developed.

Remarks.—The exact solution represented by eq. 13 will fail to describe the data if any two of the rate constants approach each other in value. In such a case there exist rather complicated indeterminate forms as reference to eq. 8-11 shows and the use of the iterative procedure leads to difficulties. Such a situation does not arise on using eq. 25. The validity of the series as a good approximation will have to be established by comparing the experimental data with the derived data obtained through the use of the calculated rate constants.

If in a reaction of this kinetic type, the rate constants are in the statistical ratio of $k_1:k_2:k_3:k_4 = 4:3:2:1$, then eq. 13 reduces to eq. 26, namely

$$A = 4B_0e^{-k_4\lambda} \quad (26)$$

If one now makes use of eq. 7 and the fact that $A_0 = 4B_0$, then eq. 26 reduces to eq. 27, namely

$$\frac{1}{A} - \frac{1}{A_0} = k_4t \quad (27)$$

In such a case the over-all reaction will look like a simple second-order process and the slope of a $1/A$ vs. t plot will be equal to k_4 . The calculation of k_1 , k_2 , and k_3 from k_4 is obvious.

Materials and Apparatus

Pentaerythritol Tetraacetate.—The ester was Eastman's "best" grade. It was recrystallized from hot water and leached with cold water until no odor of acetic acid was evidenced. The saponification equivalent indicated a purity of 100.04%. The m.p. was 78-79°.

Other Details.—The apparatus, procedure, and other pertinent facts have already been described.⁴ The only variation in the experimental procedure was that the starting concentrations of the tetraester and sodium hydroxide were adjusted so that equivalent amounts were used (*i.e.*, $A_0 = 4B_0$, where A_0 and B_0 were the initial concentrations in moles/liter of hydroxide and tetraester, respectively).

Calculations and Discussion

Evaluation of Rate Constants.—Before using a computer program for evaluating rate constants from experimental data, it is essential to show that the program is correct. This was done by arbitrarily generating a test set of A -values for various times t through the use of eq. 27 which assumes that $k_1:k_2:k_3:k_4 = 4:3:2:1$. We assigned a value of 6.51 to k_4 and 0.0300 to A_0 . The resulting test values of A were transformed into test values of λ by graphical integration in accordance with eq. 6. The program developed for method 1 was used and values of k_1 , k_2 , k_3 , and k_4 were generated by the iterative procedure. The results were 25.97 ± 0.05 , 19.77 ± 0.10 , 12.88 ± 0.08 , 6.57 ± 0.04 , to be compared with the assumed values of 26.04, 19.53, 13.02, and 6.51 for k_1 , k_2 , k_3 , and k_4 , respectively.

The data for all of our runs were handled by the above procedure. However, convergence to a solution occurred only for the duplicate runs 2 and 3. Thus the iterative procedure failed in most of our cases which could only mean that in the balance of our work indeterminacy was in evidence. Recourse was then made to method 2 which gives values of k_1 , k_2 , k_3 , and k_4 directly. In order to determine the standard deviations of the individual rate constants we proceeded in the following manner. Let the experimental k 's be considered as a set of initial estimates 0k_1 , 0k_2 , 0k_3 , and 0k_4 of the actual rate constants k_1 , k_2 , k_3 , and k_4 . Equation 25 may be expanded around these initial estimates *via* a Taylor's series expansion to give

$$S = S|_0 + \frac{\partial S}{\partial k_1} (k_1 - {}^0k_1) + \frac{\partial S}{\partial k_2} (k_2 - {}^0k_2) + \frac{\partial S}{\partial k_3} (k_3 - {}^0k_3) + \frac{\partial S}{\partial k_4} (k_4 - {}^0k_4) + H \quad (28)$$

H represents higher order partial derivatives which may be neglected. Equation 28 may be rewritten as

$$S - S|_0 = \frac{\partial S}{\partial k_1} \Delta k_1 + \frac{\partial S}{\partial k_2} \Delta k_2 + \frac{\partial S}{\partial k_3} \Delta k_3 + \frac{\partial S}{\partial k_4} \Delta k_4 \quad (29)$$

where

$$\frac{\partial S}{\partial k_i} = \frac{\partial J_1}{\partial k_i} \lambda + \frac{\partial J_2}{\partial k_i} \lambda^2 + \frac{\partial J_3}{\partial k_i} \lambda^3 + \frac{\partial J_4}{\partial k_i} \lambda^4 \quad (30)$$

On differentiating the definitions of the J 's given in eq. 24 one obtains the values of the partials of the J 's. The value of $\partial S/\partial k_1|_0$ for each experimental value of λ is determined from eq. 30 on using the experimentally determined value of λ and the values of the ∂J 's/ ∂k_i evaluated by using the outstanding estimates 0k_1 , 0k_2 , 0k_3 , and 0k_4 . Similarly one obtains values for $\partial S/\partial k_2|_0$, $\partial S/\partial k_3|_0$, and $\partial S/\partial k_4|_0$; $S|_0$ is the value of A/B_0 calculated *via* eq. 25 when 0k_1 , 0k_2 , 0k_3 , and 0k_4 are substituted for the actual rate constants.

The problem now becomes one of the evaluation of Δk_1 , Δk_2 , Δk_3 , and Δk_4 . Once these values have been

TABLE I
DATA FOR RUN 9

Time, min.	A (exptl.), mole/l.	λ , mole min./l.	A exptl. - A calcd.
2.5	0.01806	0.04841	-0.00005
3.5	.01714	.06589	-.00001
5.25	.01557	.09430	-.00002
7	.01422	.12040	-.00003
9	.01286	.14734	-.00006
11	.01163	.17192	-.00004
15	.009619	.21426	-.00006
19	.008218	.24975	-.00003
26	.006514	.30085	-.00003
28	.006116	.31342	-.00001
30	.005719	.32540	-.00004
34	.005151	.34696	-.00003
42	.004355	.38480	-.00009
49	.003636	.41275	-.00002
56.25	.003124	.43750	-.00002
61.25	.002840	.45254	.00000

TABLE II
RATE CONSTANTS OBTAINED BY BOTH METHODS 1 AND 2

	Run 2		Run 3	
	Method 1	Method 2	Method 1	Method 2
k_1	13.32	13.39	13.19	13.33
k_2	11.71	12.01	12.66	12.31
k_3	11.08	9.93	10.19	10.29
k_4	6.75	6.94	7.24	7.10

TABLE III
SUMMARY OF RATE CONSTANTS WITH THEIR QUADRATIC^c MEAN ERRORS AT 4.1°

Run	Di-oxane, wt. %	D	A_0 , mole/l.	Input rate constants, ^c l./mole min.				Output rate constants, ^d l./mole min.				Quadratic mean error of fit, mole/l. $\times 10^5$
				k_1	k_2	k_3	k_4	k_1	k_2	k_3	k_4	
2	20	67.7	0.02038	13.32	11.71	11.08	6.75	13.39 \pm 0.25	12.01 \pm 0.17	9.93 \pm 0.29	6.94 \pm 0.18	7.34
3	20	67.7	.02038	13.19	12.66	10.19	7.24	13.33 \pm .26	12.31 \pm .18	10.29 \pm .30	7.10 \pm .23	9.0
4	40	48.26	.02075	12.63	13.20	11.66	8.40	12.63 \pm .26	13.20 \pm .24	11.66 \pm .29	8.40 \pm .20	8.17
5	40	48.26	.02075	12.35	13.17	11.81	8.77	12.35 \pm .28	13.17 \pm .26	11.81 \pm .31	8.77 \pm .22	8.80
6 ^a	40	48.26	.02074	11.00	12.23	10.75	7.43	11.00 \pm .24	12.23 \pm .35	10.75 \pm .30	7.43 \pm .15	6.19
9 ^b	40	48.26	.02074	10.16	11.92	10.51	7.21	10.16 \pm .17	11.92 \pm .26	10.51 \pm .22	7.21 \pm .11	4.56
7	60	29.14	.02097	11.65	13.18	12.18	9.48	11.65 \pm .35	13.18 \pm .53	12.18 \pm .45	9.48 \pm .20	8.61
8	60	29.14	.02097	12.01	12.81	11.81	9.39	12.01 \pm .38	12.81 \pm .51	11.81 \pm .47	9.39 \pm .21	9.00

^a KCl added, 0.1 mole/l.; ionic strength, 0.10. ^b BaCl₂ added, 0.0333 mole/l.; ionic strength, 0.10. ^c Input rate constants for runs 2 and 3 were obtained by method 1 and for the remainder of the runs by method 2. ^d Output rate constants for all runs were obtained by the iteration procedure using eq. 29.

obtained, the first estimates 0k_1 , 0k_2 , 0k_3 , and 0k_4 may be corrected for the error terms and the process repeated with new estimates of k_1 , k_2 , k_3 , and k_4 . In the evaluation of eq. 25 we are solving for four unknowns, Δk_1 , Δk_2 , Δk_3 , and Δk_4 . While there are only four unknowns, a run may provide as many as 16 experimental points, *i.e.*, 16 sets of S and λ values. The problem therefore becomes one of using all sixteen equations in the total solution for Δk_1 , Δk_2 , Δk_3 , and Δk_4 . The solution was accomplished by a method of least squares using all experimental points. The standard deviations of the individual rate constants were assumed to be the standard deviations of the correctional terms in the last cycle of the iteration.

Our results are shown in Tables I, II, and III. Table I shows a typical time-concentration set of data. The values of λ in the third column were obtained by a graphical integration of a plot of A vs. t in accordance with eq. 6.

Discussion.—Table II compares methods 1 and 2 for the duplicate runs 2 and 3. One cannot select between the methods on the basis of those results even if the agreement is somewhat better when method 2 is

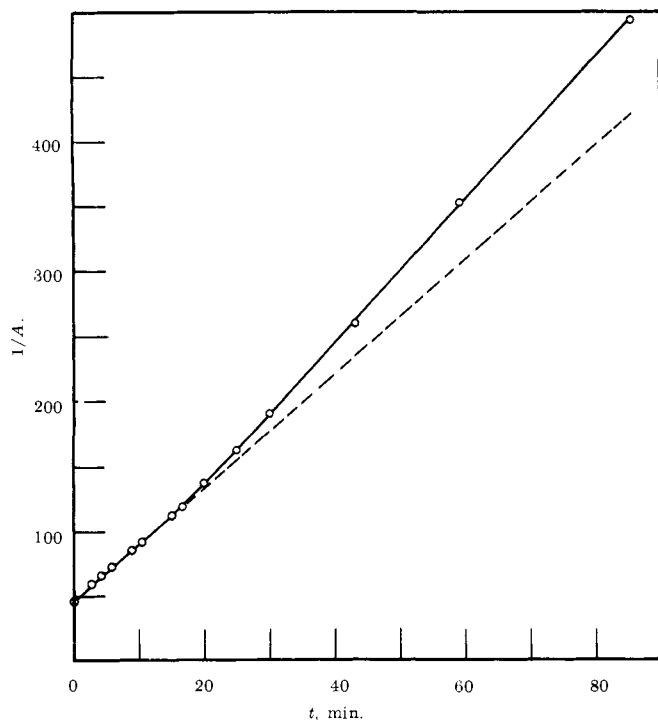
used. Inasmuch as method 1 worked very well on the test set of data and inasmuch as convergence occurred when the data of runs 2 and 3 were used, one must accept the validity of method 1. Table III lists under "input rate constants" for runs 4 through 9 the results which were obtained through the use of eq. 25. Reference to those figures will show that some of the succeeding rate constants are larger than some of the preceding rate constants. This fact provides the answer as to why method 1 did not work for runs 4 through 9. The column headed "output rate constants" was determined through use of eq. 29 along with their standard deviations. It is observed that when the input data were the results of the quartic equation, no correction was made in the k 's (runs 4 to 9). However, when the "input data" were the results of the exact solution, then those values were corrected and one now obtained the same results as were obtained by the quartic equation for runs 2 and 3. We can only conclude that because of the closeness of some of the k 's to each other the quartic equation gives better final results than does the exact solution. The quadratic mean error of the k 's indicates that the reliability of the values listed is between 2 and 4%.

The last column of Table I for run 9 shows the reproducibility of the concentration data calculated through use of the rate constants in Table III. While the results are all off in the same direction, the discrepancy is so small that one can claim that the "fit" is

excellent. The last column of Table III gives the quadratic mean error of fit for all of the runs. We believe that we have demonstrated conclusively the validity of the quartic equation in obtaining the rate constants recorded. It should be noted that the presence of initial impurities and possible side reactions would lead to unreliable rate constants. However, the purity of our material in terms of the saponification equivalent certainly indicates the absence of impurities.

Figure 1 is a plot of $1/A$ vs. t for run 2. As explained earlier, if the rate constants were in the statistical ratio of 4:3:2:1, such a plot would be linear. Such linearity might be said to exist for the first 58% of the reaction. However, it is clearly evident that the linearity does not exist over the whole range of the reaction. Thus this reaction could not have the statistical ratio sequence as claimed by Skrabal and Zlatewa.⁵ This conclusion is also supported by the actual rate constants of Table III.

Furthermore, changes in the rate constants in any fixed medium cannot be due to ionic strength changes as the reaction proceeds, since the ionic strength is constant during a run. However, the rate constants

Fig. 1.— $1/A$ vs. t for run 2.

are affected by the addition of an inert electrolyte as can be seen by reference to the data of runs 6 and 9 in comparison to those of the duplicate runs 4 and 5 which were carried out in the same solvent mixture. Potassium chloride and barium chloride at the same ionic strength were used to produce the salt effects observed. All rate constants in a similar solvent environment were lowered as the result of added electrolyte. However, the effect of barium chloride on k_1 is markedly larger than is the effect of potassium chloride. Nevertheless, one cannot distinguish within experimental error as to a difference between the effects of the two salts on k_2 , k_3 , and k_4 .

Figure 2 is a plot of the $\log k$'s vs. $1/D$. It shows quite clearly the behavior of the rate constants as the solvent composition is changed. The behavior of the $\log k_1$ vs. $1/D$ curve is at variance with the behavior of the $\log k_2$, $\log k_3$, and $\log k_4$ vs. $1/D$ curves. In this multistep reaction both statistical and stereochemical considerations must be considered. From purely statistical considerations, one would expect k_1 to be always the largest of the four rate constants. However, steric hindrance of the large ester groups could outweigh the statistical factors with the result that a following rate constant could be larger than a preceding one. Examination of the data in the different mixtures indicates that the order of sequence in the magnitudes of the rate constants is also influenced by the solvent. For example, in the solvent where $D = 67.7$ one observes that $k_1 > k_2 > k_3$; in the solvent where $D = 48.26$ one observed that $k_2 > k_1 > k_3$; and in the solvent where $D = 29.14$ one observes that $k_2 > k_1 \approx k_3$. It

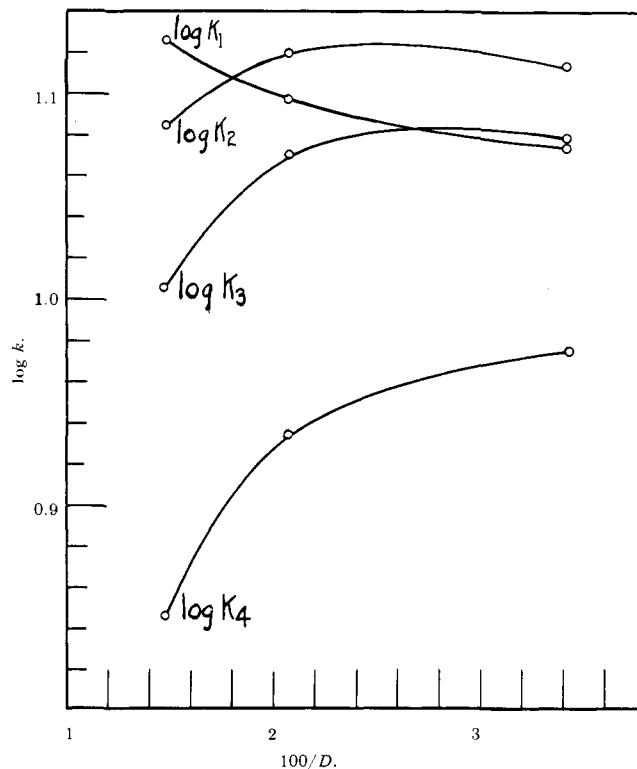


Fig. 2.—Effect of medium on rate constants.

is also interesting to compare the behavior of the $\log k$ vs. $1/D$ curves for esters which on hydrolysis furnish ionic intermediates^{6,7} with those esters which furnish nonionic intermediates as in this research. In both cases the $\log k_1$ vs. $1/D$ curves behave quite similarly. One would expect this since the mechanisms of both reactions in the first step are similar. However, the $\log k_2$ vs. $1/D$ curves for ionic intermediates in the diester hydrolyses at first decreased with decreasing dielectric constant and then increased with a minimum occurring in a dielectric range between 25 and 33. It was postulated that the minimum could be in the region at which an ion-ion reaction was changing to one involving ion-pairs. In this research using similar plots none of the last three steps of the reaction has gone through a minimum. In fact, the $\log k_4$ vs. $1/D$ curve of the last step (which is the comparable curve) has increased with decreasing dielectric constant in a manner similar to the one observed for the second step of the diester hydrolysis where ion-pair formation is postulated. This fact supports the argument for the ion-pair formation.

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