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The Kinetics of Three-step Competitive Consecutive Second-order Reactions. II[1,2]

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The rate equations for a three-step competitive consecutive second-order reaction of the type $A + B \xrightarrow{k_1} C + E$, $A + C \xrightarrow{k_2} D + E$, $A + D \xrightarrow{k_3} F + E$ has been solved in terms of a variable λ where $\lambda = \int_0^t A\mathrm{d}t$. When $A_0 = 3B_0$, the solution is $A = G_1e^{-k_1\lambda} + G_2e^{-k_2\lambda} + G_3e^{-k_3\lambda}$ where G_1, G_2 and G_3 are constants involving various combinations of k_1, k_2, k_3 and B_0. Taylor's theorem was used to expand the function A about the first approximations of k_1, k_2 and k_3 (*i.e.*, ${}^0k_1$, ${}^0k_2$ and ${}^0k_3$). If all higher order partials are neglected, then the equation in A becomes; $A = f({}^0k_1, {}^0k_2, {}^0k_3) + \left.\frac{\partial f}{\partial k_1}\right|_0 \Delta k_1 + \left.\frac{\partial f}{\partial k_2}\right|_0 \Delta k_2 + \left.\frac{\partial f}{\partial k_3}\right|_0 \Delta k_3$. The problem of evaluating Δk_1, Δk_2 and Δk_3 was accomplished by a least squares solution utilizing all experimental time-concentration data. An iterative procedure was developed for carrying out the operations on the I.B.M. 704 electronic computer. On multiplying the equation for A by $e^{k_1\lambda}$, differentiating the resulting equation and repeating the process using $e^{k_2\lambda}$ and $e^{k_3\lambda}$ successively, a third order differential equation in A and λ was obtained which, after several successive integrations, leads to: $A - A_0 + (k_1 + k_2 + k_3)A^* + (k_1k_3 + k_2k_3 + k_1k_2)A^{**} + k_1k_2k_3A^{***} = ({}^1/_2k_1k_2 + k_1k_3 + {}^3/_2k_2k_3)\lambda^2B_0 + (2k_1 + 3k_2 + 3k_3)\lambda B_0$ where $A^* = \int_0^\lambda A\mathrm{d}\lambda$, $A^{**} = \int_0^\lambda A^*\mathrm{d}\lambda$, $A^{***} = \int_0^\lambda A^{**}\mathrm{d}\lambda$. Taylor's theorem was used to expand this function of A about first approximations of k_1, k_2 and k_3 and an iterative procedure was developed to solve for Δk_1, Δk_2 and Δk_3 utilizing all experimental time-concentration data.

Introduction

Recently,[3] the kinetics of three-step competitive-consecutive second-order reactions was investigated mathematically in terms of general variables which in principle would apply to any reaction of that kinetic type. The resulting analysis was applied to the alkaline hydrolysis of 1,3,5-tri-(4-carbomethoxyphenyl)-benzene which, because of its size and corresponding absence of interaction between the carbomethoxy groups, led to the result that the rate constants are in the statistical ratio $k_1:k_2:k_3 = 3:2:1$. However, the above procedure becomes too involved to be practical when there is no criterion for determining beforehand what relationship, if any, exists between k_2 and k_3 for a particular reaction. This is the situation which exists when interaction between groups does occur or when the k's for a given reaction vary as the result of changing the solvent composition. Therefore, it becomes necessary for us to reconsider the problem and see whether a more practical solution can be obtained.

(1) Abstracted from a thesis submitted by Jay A. Blauer to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Presented in part at the New York City Meeting of the American Chemical Society, September, 1960.

(3) (a) W. J. Svirbely, *J. Am. Chem. Soc.*, **81**, 255 (1959); (b) W. J. Svirbely and H. E. Weisberg, *ibid.*, **81**, 257 (1959).

Mathematical Analysis

The reactions to be considered are

$$A + B \xrightarrow{k_1} C + F$$

$$A + C \xrightarrow{k_2} D + F$$

$$A + D \xrightarrow{k_3} E + F$$

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

$$\frac{\mathrm{d}A}{\mathrm{d}t} = -k_1AB - k_2AC - k_3AD \qquad (1)$$

$$\frac{\mathrm{d}B}{\mathrm{d}t} = -k_1AB \qquad (2)$$

$$\frac{\mathrm{d}C}{\mathrm{d}t} = k_1AB - k_2AC \qquad (3)$$

$$\frac{\mathrm{d}D}{\mathrm{d}t} = k_2AC - k_3AD \qquad (4)$$

$$\frac{\mathrm{d}E}{\mathrm{d}t} = k_3AD \qquad (5)$$

Let us define a new variable, λ, so that

$$\lambda = \int_0^t A\mathrm{d}t \quad (6)$$

it follows then that

$$\mathrm{d}\lambda = A\mathrm{d}t \quad (7)$$

On substituting equation 7 into equations 1 through 5, we obtain equations 8, 9, 10, 11 and 12.

$$\frac{\mathrm{d}A}{\mathrm{d}\lambda} = -k_1B - k_2C - k_3D \quad (8)$$

$$\frac{\mathrm{d}B}{\mathrm{d}\lambda} = -k_1B \quad (9)$$

$$\frac{\mathrm{d}C}{\mathrm{d}\lambda} = k_1B - k_2C \quad (10)$$

$$\frac{\mathrm{d}D}{\mathrm{d}\lambda} = k_2C - k_3D \quad (11)$$

$$\frac{\mathrm{d}E}{\mathrm{d}\lambda} = k_3D \quad (12)$$

Equations 9, 10, 11 and 8 are integrated in that order. Constants of integration are evaluated in each appropriate case from the boundary conditions, which are: $\lambda = C = D = 0$, $A = A_0$, and $B = B_0$ at $t = 0$. If the initial concentrations of species A and B are adjusted so that $A_0 = 3B_0$, then one obtains

$$\frac{A}{B_0} = \left[3 + \frac{2k_1}{(k_2 - k_1)} + \frac{k_1k_2}{(k_2 - k_1)(k_3 - k_1)}\right] e^{-k_1\lambda} - \left[\frac{2k_1}{(k_2 - k_1)} + \frac{k_1k_2}{(k_2 - k_1)(k_3 - k_2)}\right] e^{-k_2\lambda} + \left[\frac{k_1k_2}{(k_3 - k_1)(k_3 - k_2)}\right] e^{-k_3\lambda} \quad (13)$$

While we now have a solution for A in terms of the rate constants, it is in an impossible form for the direct evaluation of the rate constants. Ultimately, three different procedures were developed (two of which are described).

Method 1.—On rewriting equation 13 for simplification only, equation 14 is obtained

$$S = G_1e^{-k_1\lambda} + G_2e^{-k_2\lambda} + G_3e^{-k_3\lambda} \quad (14)$$

The definitions of S, G_1, G_2 and G_3 are obvious on reference to equation 13. If we let ${}^0k_1$, ${}^0k_2$ and ${}^0k_3$ be a set of initial estimates of the actual rate constants k_1, k_2 and k_3, equation 13 may be expanded about these initial estimates *via* a Taylor's series expansion to give

$$S = S|_0 + \left.\frac{\partial S}{\partial k_1}\right|_0 (k_1 - {}^0k_1) + \left.\frac{\partial S}{\partial k_2}\right|_0 (k_2 - {}^0k_2) + \left.\frac{\partial S}{\partial k_3}\right|_0 (k_3 - {}^0k_3) + H \quad (15)$$

$S|_0$ is the value of A/B_0 calculated *via* equation 13 when ${}^0k_1$, ${}^0k_2$ and ${}^0k_3$ are substituted for the actual rate constants k_1, k_2 and k_3. $\partial S/\partial k_1|_0$, $\partial S/\partial k_2|_0$ and $\partial S/\partial k_3|_0$ are the partial derivatives of A/B_0 with respect to the three rate constants. These partial derivatives are evaluated from equation 13 when the rate constants k_1, k_2 and k_3 are replaced by the estimates ${}^0k_1$, ${}^0k_2$ and ${}^0k_3$. H represents all higher order partial derivatives. On neglecting H and replacing $(k_1 - {}^0k_1)$, $(k - {}^0k_2)$ and $(k_3 - {}^0k_3)$ by Δk_1, Δk_2 and Δk_3, equation 15 becomes

$$S - S|_0 = \left.\frac{\partial S}{\partial k_1}\right|_0 \Delta k_1 + \left.\frac{\partial S}{\partial k_2}\right|_0 \Delta k_2 + \left.\frac{\partial S}{\partial k_3}\right|_0 \Delta k_3 \quad (16)$$

In the evaluation of $\partial S/\partial k_1|_0$, differentiation of equation 14 with respect to k_1 yields

$$\frac{\partial S}{\partial k_1} = \left(\frac{\partial G_1}{\partial k_1} - G_1\lambda\right) e^{-k_1\lambda} + \left(\frac{\partial G_2}{\partial k_1}\right) e^{-k_2\lambda} + \left(\frac{\partial G_3}{\partial k_1}\right) e^{-k_3\lambda} \quad (17)$$

On differentiating the definitions of G_1, G_2 and G_3, one obtains

$$\frac{\partial G_1}{\partial k_1} = \left[\frac{k_2(k_3 - k_1)^2 + k_2k_3(k_2 + k_3 - 2k_1)}{(k_2 - k_1)^2(k_3 - k_1)^2}\right] \quad (18)$$

$$\frac{\partial G_2}{\partial k_1} = \left[\frac{k_2(k_2 - 2k_3)}{(k_2 - k_1)^2(k_3 - k_2)}\right] \quad (19)$$

$$\frac{\partial G_3}{\partial k_1} = \left[\frac{k_2k_3}{(k_3 - k_1)^2(k_3 - k_2)}\right] \quad (20)$$

The value of $\partial S_1/\partial k_1|_0$ for each experimental value of A is determined from equation 17 on using the corresponding experimentally determined value of λ and the outstanding estimates ${}^0k_1$, ${}^0k_2$ and ${}^0k_3$ of the rate constants k_1, k_2 and k_3.

Similarly one obtains equations for evaluating $\left.\frac{\partial S}{\partial k_2}\right|_0$ and $\left.\frac{\partial S}{\partial k_3}\right|_0$.

The problem now becomes one of the evaluation of Δk_1, Δk_2 and Δk_3. Once these values have been obtained, the first estimates ${}^0k_1$, ${}^0k_2$ and ${}^0k_3$ may be corrected for the error terms and the process repeated with new estimates of k_1, k_2 and k_3. As the process is repeated the Δk_1 terms will become increasingly smaller. In the evaluation of equation 16, we are solving for the three unknowns Δk_1, Δk_2 and Δk_3. Therefore, we need at least three simultaneous equations, *i.e.*, three different sets of values of A and λ. The values of λ are obtained from the graphical integration of an A *vs.* t plot. Actually a run may provide as many as 15 experimental points, *i.e.*, 15 sets of values of A and λ. The problem therefore becomes one of using all fifteen equations in the total solution for Δk_1, Δk_2 and Δk_3.

The solution of equation 16 for the correction terms is accomplished by the method of least squares using all fifteen equations. For simplification, we make the following definitions

$$J = S - S|_0 \quad (21)$$

$$X_1 = \left.\frac{\partial S}{\partial k_1}\right|_0 \quad (22)$$

$$X_2 = \left.\frac{\partial S}{\partial k_2}\right|_0 \quad (23)$$

$$X_3 = \left.\frac{\partial S}{\partial k_3}\right|_0 \quad (24)$$

On substituting these definitions into equation 16, we obtain

$$J = X_1\Delta k_1 + X_2\Delta k_2 + X_3\Delta k_3 \quad (25)$$

The system of determinants arising from the solution of equation 25 is

$$\begin{vmatrix} \Sigma JX_1 \\ \Sigma JX_2 \\ \Sigma JX_3 \end{vmatrix} = \begin{vmatrix} \Sigma X_1^2 & \Sigma X_1X_2 & \Sigma X_1X_3 \\ \Sigma X_2X_1 & \Sigma X_2^2 & \Sigma X_2X_3 \\ \Sigma X_3X_1 & \Sigma X_3X_2 & \Sigma X_3^2 \end{vmatrix} \quad (26)$$

The iterative procedure described above was programmed for the use of an IBM 704 electronic computer.

Reference to equation 13 shows that if any two of the three rate constants are identical then equation 13 will fail to describe the data since two of the coefficients of the exponentials become indeterminate. As a result, the iterative procedure just described will fail. Such situations actually existed in some of our experimental work on the alkaline hydrolysis of 1,3,5-tricarbomethoxybenzene in low dielectric media. Accordingly, another procedure is required. This new procedure is described in method #2.

Method 2.—Start with equation 13 and for simplification write it as

$$A = G_1^*e^{-k_1\lambda} + G_2^*e^{-k_2\lambda} + G_3^*e^{-k_3\lambda} \quad (27)$$

In equation 27 we have redefined G_1B_0, G_2B_0 and G_3B_0 as G_1^*, G_2^* and G_3^*, respectively.

Upon multiplying equation 27 by $e^{k_1\lambda}$ and then differentiating the resulting equation with respect to λ, we obtain

$$\frac{\mathrm{d}A}{\mathrm{d}\lambda} + k_1A = G_2^*(k_1 - k_2)e^{-k_2\lambda} + G_3^*(k_1 - k_3)e^{-k_3\lambda} \quad (28)$$

Two repetitions of the above process of multiplication and subsequent differentiation using, however, $e^{k_2\lambda}$ and $e^{k_3\lambda}$ successively as multipliers leads to equation 29, namely

$$\frac{\mathrm{d}^3A}{\mathrm{d}\lambda^3} + (k_1 + k_2 + k_3)\frac{\mathrm{d}^2A}{\mathrm{d}\lambda^2} + (k_1k_2 + k_1k_3 + k_2k_3)\frac{\mathrm{d}A}{\mathrm{d}\lambda} + k_1k_2k_3A = 0 \quad (29)$$

For simplification we write equation 29 as

$$\frac{d^3A}{d\lambda^3} + J_1\frac{d^2A}{d\lambda^2} + J_2\frac{dA}{d\lambda} + J_3A = 0 \quad (30)$$

On multiplying equation 30 by $d\lambda$ and then integrating between limits, we obtain

$$\int_0^\lambda \frac{d^3A}{d\lambda^3}d\lambda + J_1\int_0^\lambda \frac{d^2A}{d\lambda^2}d\lambda + J_2\int_0^\lambda \frac{dA}{d\lambda}d\lambda + J_3\int_0^\lambda A d\lambda = 0 \quad (31)$$

The reduction of equation 31 leads to

$$\frac{d^2A}{d\lambda^2} + J_1\frac{dA}{d\lambda} + J_2A + J_3\int_0^\lambda A d\lambda = \left.\frac{d^2A}{d\lambda^2}\right|_0 + J_1\left.\frac{dA}{d\lambda}\right|_0 + J_2A_0 \quad (32)$$

The complete solution of equation 32 requires an evaluation of the limits $\left.\frac{d^2A}{d\lambda_2}\right|_0$ and $\left.\frac{dA}{d\lambda}\right|_0$. If the kinetic run is designed so that at $\lambda = 0$; $C = D = 0$ and $B = B_0$; then a $\lambda = 0$, equation 8 reduces to

$$\left.\frac{dA}{d\lambda}\right|_0 = -k_1B_0 \quad (33)$$

The differentiation of equation 8 with respect to λ and the substitution of equations 9, 10 and 11 into the resulting equation leads to equation 34 when $\lambda = 0$.

$$\left.\frac{d^2A}{d\lambda^2}\right|_0 = (k_1^2 - k_1k_2)B_0 \quad (34)$$

On the substitution of the limits defined by equations 33 and 34 into equation 32, one obtains an equation which in turn can be integrated. The process is repeated once more and equation (35) is obtained.

$$A - A_0 + J_1A^* + J_2A^{**} + J_3A^{***} = J_4/2\ \lambda^2 + J_5\lambda \quad (35)$$

where

$$A^* = \int_0^\lambda A d\lambda;\ A^{**} = \int_0^\lambda A^* d\lambda;\ A^{***} = \int_0^\lambda A^{**}d\lambda$$

$$J_4 = k_1k_2B_0 + 2k_1k_3B_0 + 3k_2k_3B_0$$

$$J_5 = 2k_1B_0 + 3k_2B_0 + 3k_3B_0$$

Although equation 35 involves four graphical integrations, it does have an advantage over equation 13. It will not break down if any two rate constants are equal. Equation 35 offers a means by which the rate constants may be evaluated by a method of least squares without the use of an iterative procedure. However, such a procedure is possible only with the aid of an electronic computer. Since we wished to use a method adaptable to a desk calculator, we developed a satisfactory solution for equation 35 through use of an iterative procedure.

For simplification, equation 35 is rewritten as equation 36, namely

$$S = J_1X_1 + J_2X_2 + J_3X_3 - \frac{J_4}{2}X_4 - J_5X_5 \quad (36)$$

where

$$S = A_0 - A;\ X_1 = A^*;\ X_2 = A^{**};\ X_3 = A^{***};\ X_4 = \lambda^2;\ X_5 = \lambda$$

Equation 36 may be expanded about first estimates of the three rate constants by means of Taylor's theorem. The starting equation is thus equation 37, namely

$$S - S|_0 = \left.\frac{\partial S}{\partial k_1}\right|_0 \Delta k_1 + \left.\frac{\partial S}{\partial k_2}\right|_0 \Delta k_2 + \left.\frac{\partial S}{\partial k_3}\right|_0 \Delta k_3 \quad (37)$$

$S|_0$ is the value of S evaluated by substituting values of X_1, X_2, X_3, X_4, X_5 and the estimates ${}^0k_1$, ${}^0k_2$ and ${}^0k_3$ into equation 36. $\left.\frac{\partial S}{\partial k_1}\right|_0$, $\left.\frac{\partial S}{\partial k_2}\right|_0$ and $\left.\frac{\partial S}{\partial k_3}\right|_0$ are the values of $\frac{\partial S}{\partial k_1}$, $\frac{\partial S}{\partial k_2}$ and $\frac{\partial S}{\partial k_3}$ evaluated from equation 36 using the estimates ${}^0k_1$, ${}^0k_2$, ${}^0k_3$ in place of the actual rate constants. Δk_1, Δk_2 and Δk_3 are the correction terms to be added to the estimates ${}^0k_1$, ${}^0k_2$ and ${}^0k_3$ to obtain an improved set of estimates. All higher order partials are neglected. The solution is a three-dimensional iteration. The solution of equation 37 is by the method of least squares. The partial derivatives must be evaluated for each datum point and have the following definitions (only $\left.\frac{\partial S}{\partial k_1}\right|_0$ is given, the other two are obtained in a similar fashion)

$$\left.\frac{\partial S}{\partial k_1}\right|_0 = \left.\frac{\partial J}{\partial k_1}\right|_0 X_1 + \left.\frac{\partial J_2}{\partial k_1}\right|_0 X_2 + \left.\frac{\partial J_3}{\partial k_1}\right|_0 X_3 - \frac{1}{2}\left.\frac{\partial J_4}{\partial k_1}\right|_0 X_4 - \left.\frac{\partial J_5}{\partial k_1}\right|_0 X_5 \quad (37)$$

Three equations involving $\left.\frac{\partial S}{\partial k_1}\right|_0$, $\left.\frac{\partial S}{\partial k_2}\right|_0$ and $\left.\frac{\partial S}{\partial k_3}\right|_0$ have fifteen constants of the form $\left.\frac{\partial J_1}{\partial k_j}\right|_0$. These constants must be evaluated. These constants are defined as

$$\left.\frac{\partial J_1}{\partial k_1}\right|_0 = 1.0000 \quad \left.\frac{\partial J_1}{\partial k_2}\right|_0 = 1.0000 \quad \left.\frac{\partial J_1}{\partial k_3}\right|_0 = 1.0000$$

$$\left.\frac{\partial J_2}{\partial k_1}\right|_0 = {}^0k_2 + {}^0k_3 \quad \left.\frac{\partial J_2}{\partial k_2}\right|_0 = {}^0k_1 + {}^0k_3 \quad \left.\frac{\partial J_2}{\partial k_3}\right|_0 = {}^0k_1 + {}^0k_2$$

$$\left.\frac{\partial J_3}{\partial k_1}\right|_0 = {}^0k_2{}^0k_3 \quad \left.\frac{\partial J_3}{\partial k_2}\right|_0 = {}^0k_1{}^0k_3 \quad \left.\frac{\partial J_3}{\partial k_3}\right|_0 = {}^0k_1{}^0k_2 \quad (38)$$

$$\left.\frac{\partial J_4}{\partial k_1}\right|_0 = ({}^0k_2 + 2{}^0k_3)B_0 \quad \left.\frac{\partial J_4}{\partial k_2}\right|_0 = ({}^0k_1 + 3{}^0k_3)B_0 \quad \left.\frac{\partial J_4}{\partial k_3}\right|_0 = (2{}^0k_1 + 3{}^0k_2)B_0$$

$$\left.\frac{\partial J_5}{\partial k_1}\right|_0 = 2B_0 \quad \left.\frac{\partial J_5}{\partial k_2}\right|_0 = 3B_0 \quad \left.\frac{\partial J_5}{\partial k_3}\right|_0 = 3B_0$$

For simplification we made the following definitions

$$R_1 = \left.\frac{\partial S}{\partial k_1}\right|_0 \quad (39)$$

$$R_2 = \left.\frac{\partial S}{\partial k_2}\right|_0 \quad (40)$$

$$R_3 = \left.\frac{\partial S}{\partial k_3}\right|_0 \quad (41)$$

$$H = S - S_0 \quad (42)$$

Equation 37 now becomes

$$H = R_1\Delta k_1 + R_2\Delta k_2 + R_3\Delta k_3 \quad (43)$$

The system of determinants arising from the solution of equation 43 is

$$\begin{vmatrix} \Sigma HR_1 \\ \Sigma HR_2 \\ \Sigma HR_3 \end{vmatrix} = \begin{vmatrix} \Sigma R_1^2 & \Sigma R_1R_2 & \Sigma R_1R_3 \\ \Sigma R_2R_1 & \Sigma R_2^2 & \Sigma R_2R_3 \\ \Sigma R_3R_1 & \Sigma R_3R_2 & \Sigma R_3^2 \end{vmatrix} \quad (44)$$

Discussion

The application of both methods to the alkaline hydrolysis of 1,3,5-tricarbomethoxybenzene is given in another paper. However, it is appropriate to show in this paper the validity of the analysis leading to equation 13 and the subsequent testing of the programming developed for Method 1.

In the special case where the relationship between the three rate constants is purely statistical, *i.e.*, in which $k_1 = 3/2\ k_2 = 3k_3$, the rate equation[3] reduces to

$$\frac{A_0 - A}{AA_0} = \frac{k_2}{2}t = k_3t \quad (45)$$

On solving equation 45 for A, one obtains

$$A = \frac{A_0}{1 + k_3A_0t} \quad (46)$$

It follows that

$$\int_0^\lambda A dt = \int_0^\lambda \frac{A_0 dt}{1 + k_3A_0t} = \frac{1}{k_3}\ln(1 + A_0k_3t) \quad (47)$$

Through use of equation 6, equation 47 becomes

$$\lambda = \frac{1}{k_3}\ln(1 + k_3A_0t) \quad (48)$$

A combination of equations 46 and 48 leads to eq. 49

$$k_3\lambda = \ln \frac{A_0}{A} \qquad (49)$$

On assigning values to the constants A_0 and k_3, we may arbitrarily generate a test set of A values for various times t through use of equation 46. This test set of A values can be used to generate a test set of λ values through use of equation 49. Both sets of test values are independent of any equations derived in this paper and apply to the situation where the rate constants are in the ratio of $k_1:k_2:k_3 = 3:2:1$.

On assigning a value of 6.51 to k_3 and 0.03000 to A_0, values of λ and A were generated and are listed in Table I. Also listed in Table I, column 3, are the values of A later calculated using the values of k_1, k_2 and k_3 generated by the iterative procedure. The initial estimates of the three rate constants and the values given by the iterative procedure are summarized below Table I. The iteration was stopped when Δk_1 became smaller than 1% of the outstanding value of k_1. Three cycles through the iterative procedure were required in this test case. Close estimates of the rate constants were chosen as a measure of economy. The calculations were done by an IBM-704 electronic computer.

In the application to experimental data, initial estimates of k_1 were found by plotting A *vs.* λ and estimating the slope at $\lambda = 0$ in accordance with the equation 33. If k_3 is much smaller than both k_1 and k_2, equation 14 reduces to equation 50 for large values of λ

$$\lim_{\lambda \to \infty} A/B_0 = G_3 e^{-k_3\lambda} \qquad (50)$$

The logarithmic form of equation 50 is

$$\lim_{\lambda \to \infty} \left(\log \frac{A}{B_0}\right) = \log G_3 - \frac{k_3}{2.303}\lambda \qquad (51)$$

The initial estimates of k_3 were found by plotting log A *vs.* λ and estimating the slope at large values of λ. The initial estimates of k_2 were found by simply guessing the values, it being assumed that $k_3 < k_2 < k_1$.

TABLE I

FIT OF THE TEST DATA AS CALCULATED BY THE MACHINE ITERATION

λ, mole min./l.	A, mole/l.	$A_{calcd.}$ mole/l.	$A - A_{calcd.}$ mole/l.
0.01437	0.02733	0.02732	0.000010
.03909	.02325	.02325	.000000
.06226	.01999	.01999	.000000
.08034	.01777	.01777	.000000
.09959	.01567	.01567	.000000
.11689	.01400	.01400	.000000
.12590	.01320	.01320	.000000
.15239	.01111	.01111	.000000
.20914	.007672	.007671	.000001
.26716	.005256	.005256	.000000
.33698	.003333	.003335	− .000002
k_i	Actual value	Initial estimate	Calcd. value
k_1	19.53	20.0	19.53
k_2	13.02	15.0	13.07
k_3	6.51	6.5	6.51

Our experience is that the iterative procedure will not converge unless the estimate ${}^0k_3$ is within 100% of the actual value of k_3, whereas ${}^0k_2$ and ${}^0k_1$ can be at variance more than 300% from the actual values of k_1 and k_2. Furthermore, we observed that in duplicate runs, reproducible values for k_3 will result only if the reaction is carried out until the plot of log A *vs.* λ approaches linearity. This usually occurred at about 75% completion of the reaction.

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

The Kinetics of the Alkaline Hydrolysis of 1,3,5-Tricarbomethoxybenzene[1,2]

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The three step alkaline hydrolysis of 1,3,5-tricarbomethoxybenzene has been studied in dioxane–water mixtures over a temperature range. The three rate constants have been determined using procedures developed for the determination of the rate constants for a three-step consecutive-competitive second-order reaction involving a symmetrical molecule where there may be interaction among the reaction sites. The various thermodynamic activation values have been calculated. The data have been examined statistically for their significance. It was observed that the k_2/k_3 ratio approached unity in the low dielectric media. The experimental observations can be explained on the basis of the formation of ion-pairs or aggregates.

Introduction

A recent[3] study of the alkaline hydrolysis of 1,3,5-tri-(4-carbomethoxyphenyl)-benzene showed that under the conditions of the experiment, *i.e.* dielectric constant ~9, the ratio of the rate con-

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(2) Presented in part at the New York City Meeting of the American Chemical Society, September, 1960.

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