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The Kinetics of Three-step Competitive Consecutive Second-order Reactions[1]

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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 have been analyzed in terms of dimensionless variables. Although the general equation obtained is, in principle, solvable it was more convenient and equally instructive to solve the equation for the special case where $k_2 = 2k_3$.

Frost and Schwemer[2] have succeeded in solving the rate equations for competitive consecutive second-order reactions of the type A + B $\xrightarrow{k_1}$ C + E, A + C $\xrightarrow{k_2}$ D + E in terms of general variables.

The purpose of this investigation was to analyze the rate equations in terms of general variables for three-step competitive consecutive second-order reactions.

The application of the resulting analysis to the alkaline hydrolysis of 1,3,5-tri-(4-carbomethoxyphenyl)-benzene will appear in another paper.

Mathematical Analysis

The reactions to be considered are

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_1} \mathrm{C} + \mathrm{E}$$

$$\mathrm{A} + \mathrm{C} \xrightarrow{k_2} \mathrm{D} + \mathrm{E}$$

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

The pertinent rate equations for the above steps are

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

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

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

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

where A, B, C and D are the molar concentrations at any time t, of the corresponding chemical species. If the initial concentrations of the species A and B are A_0 and B_0 respectively, and those of C and D are zero, then combination of equations 1–4 and integration between limits leads to the material balance equation 5, namely

$$A - 3B - 2C - D = A_0 - 3B_0 \qquad (5)$$

If the initial concentrations of species A and B are so adjusted that $A_0 = 3B_0$ (equivalent amounts) then equation 5 leads to

$$C = \frac{A - D - 3B}{2} \qquad (6)$$

combination of equations 6 and 1 leads to equation 7, namely

$$\frac{\mathrm{d}A}{\mathrm{d}t} = \left(\frac{3}{2}k_2 - k_1\right)AB + \left(\frac{k_2}{2} - k_3\right)AD - \frac{k_2}{2}A^2 \qquad (7)$$

By use of the dimensionless variables α, β and τ and the parameter K, where

$$\alpha = \frac{A}{A_0};\ \beta = \frac{B}{B_0};\ \tau = B_0k_1t;\ K = \frac{k_2}{k_1} \qquad (8)$$

equations 7 and 2 become

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\tau} = \left(\frac{3}{2}K - 1\right)\alpha\beta + \left(\frac{K}{2} - \frac{k_3}{k_1}\right)\alpha\frac{D}{B_0} - \frac{3}{2}K\alpha^2 \qquad (9)$$

$$\frac{\mathrm{d}\beta}{\mathrm{d}\tau} = -3\alpha\beta \qquad (10)$$

On dividing equation 9 by equation 10 one obtains

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\beta} = \left(\frac{2 - 3K}{6}\right) - \frac{D}{3\beta B_0}\left(\frac{K}{2} - \frac{k_3}{k_1}\right) + \frac{K}{2}\frac{\alpha}{\beta} \qquad (11)$$

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[1] Presented in part at the Chicago Meeting of the American Chemical Society, September, 1958.

[2] A. A. Frost and W. C. Schwemer, THIS JOURNAL, **74**, 1268 (1952).

Recently,[3] a procedure was described for evaluating the concentration of the D species for this series of reactions. The pertinent equation is

$$D = B_0\left[\frac{-K}{(K-1)}\,\frac{\beta}{(1-JK)} + \frac{\beta^K}{(K-1)(1-J)} + \frac{\beta^{JK}}{(1-JK)(1-J)}\right] \quad (12)$$

where $J = k_3/k_2$. Substituting equation 12 into equation 11 yields

$$\frac{\mathrm{d}\alpha}{\mathrm{d}\beta} = \frac{(2-3K)}{6} - \frac{1}{3}\left(\frac{K}{2} - JK\right)\left[\frac{-K}{(K-1)(1-JK)} + \frac{\beta^{K-1}}{(K-1)(1-J)} + \frac{\beta^{JK-1}}{(1-JK)(1-J)}\right] + \frac{K}{2}\,\frac{\alpha}{\beta} \quad (13)$$

The solution of equation 13 is given by

$$\alpha = \frac{(2-3K)\beta}{3(2-K)} + \frac{1}{3}\left[\frac{-K^2\beta(2\,J-1)}{(K-1)(1-JK)(2-K)} + \frac{\beta^K(2J-1)}{(K-1)(1-J)} + \frac{\beta^{JK}}{(1-JK)(1-J)}\right] \quad (14)$$

where the constant of integration is determined by the initial condition that when $\alpha = 1, \beta = 1$.

On substituting equation 14 into equation 10 one obtains an equation for $\mathrm{d}\beta/\mathrm{d}\tau$, which on integration (when $\tau = 0, \beta = 1$) yields

$$\tau = \int_\beta^1 \frac{\mathrm{d}\beta}{\beta^2\left\{\frac{(2-3K)}{(2-K)} + \frac{-K^2(2J-1)}{(K-1)(1-JK)(2-K)} + \frac{(2J-1)\beta^{K-1}}{(K-1)(1-J)} + \frac{\beta^{JK-1}}{(1-JK)(1-J)}\right\}} \quad (15)$$

The solution of the problem now involves the evaluation of the integral in equation 15 for various values of the parameters K and J and the limit β. The computations required so that the result would be applicable to all future experimental data are too involved to be practical. Each situation must be handled separately. For the sake of convenience, instruction and later application to our reaction we have solved the equation for the parameter value of J equal to 1/2. This is tantamount to saying that we are interested in a reaction in which $k_2 = 2k_3$. So, if $J = 1/2$, equations 14 and 15 became equations 16 and 17, respectively.

$$\alpha = \frac{(2-3K)}{3(2-K)}\beta + \frac{4}{3(2-K)}\beta^{K/2} \quad (16)$$

$$\tau = \frac{(2-K)}{(2-3K)}\int_\beta^1 \frac{\mathrm{d}\beta}{\beta^2\left(1 + \frac{4\beta^{K/2-1}}{(2-3K)}\right)} \quad (17)$$

The solution of this problem now involves the evaluation of the integral in equation 17 for various values of the parameter K and the limit β. The integral may be evaluated for certain ranges of K as

Case I. $0 < K < 2/3$.—Let $K = m/n$, where m and n are both integers and $n > 3/2\,m$. Also, let

$$x = \left(\frac{n}{2n-3m}\right)^{2/(2n-m)}\beta^{-1/n} \quad (18)$$

By use of the above definitions, equation 17 can be transformed into equation 19, namely

$$\tau = (2-K)(2-3K)^{K/(2-K)}\,n\int_{x_0}^{x}\frac{x^{n-1}\,\mathrm{d}x}{(4x^{(n-m/2)}+1)} \quad (19)$$

where

$$x_0 = \left(\frac{n}{2n-3m}\right)^{2/(2n-m)} \quad (20)$$

The integral over x is of the general form

$$\int\frac{x^P\mathrm{d}x}{ax^q+1}$$

If $P > q$ then

$$\int\frac{x^P\mathrm{d}x}{ax^q+1} = \frac{1}{a(P-q+1)}x^{P-q+1} - \frac{1}{a}\int\frac{x^{(P-q)}\,\mathrm{d}x}{ax^q+1} \quad (21)$$

If the integral on the right side of equation 21 is of a lower degree in the numerator than in the denominator, then it will be of the general form

$$\int\frac{x^s\mathrm{d}x}{ax^\eta+b}$$

where $\eta > S$. The solution[4] for this integral is

$$\int\frac{x^s\mathrm{d}x}{ax^\eta+b} = \frac{1}{b}\left(\frac{b}{a}\right)^{s+1/\eta}\int\frac{y^s\mathrm{d}y}{y^\eta+1} \text{ with } y = \sqrt[\eta]{\frac{a}{b}}\,x \quad (22)$$

$$\int\frac{y^s\mathrm{d}y}{y^\eta+1} = (-1)^s\frac{j}{\eta}\ln(y+1) - \frac{2}{\eta}\sum_{\nu=0}^{\eta-1}\left[P_\nu\cos\frac{(2\nu+1)(s+1)\pi}{\eta} - Q_\nu\sin\frac{(2\nu+1)(s+1)\pi}{\eta}\right] + C$$

$$\text{with } \eta = 2r + j;\ j = 0 \text{ or } 1;\ s = 0,1\cdots\eta-1 \quad (23)$$

$$P_\nu = \frac{1}{2}\ln\left[y^2 - 2y\cos\frac{(2\nu+1)\pi}{\eta} + 1\right];$$

$$Q_\nu = \operatorname{arc\,tg}\left[\frac{y - \cos\frac{(2\nu+1)\pi}{\eta}}{\sin\frac{(2\nu+1)\pi}{\eta}}\right]$$

Assuming values of K = 6/10, 10/18, 2/4 and 4/9, values of P and q were calculated since $P = n - 1$, $q = n - m/2$ and $K = m/n$. For each value of K at values of α = 0.9, 0.8, 0.7, 0.6, 0.5, 0.4, 0.3 and 0.2, respectively, corresponding values of β were obtained by the use of equation 16. For each value of β, corresponding values of x and x_0 were obtained by use of equations 18 and 20. Successive application of equations 21, 22, 23 and 19 for each value of x gave corresponding values of τ. For $K = 2/3$, equation 29 was used to obtain values of τ. The calculated values of τ for each value of α were plotted against $1/K$ and an interpolation was made for various values of $1/K$. Some of the results are listed in Table I.

Case II. $2/3 < K < \infty$; $K \neq 2$.— Let $K = m/n$ but let

$$x = \left(\frac{n}{3m-2n}\right)^{2/(2n-m)}\beta^{-1/n} \quad (24)$$

and

$$x_0 = \left(\frac{n}{3m-2n}\right)^{2/(2n-m)}$$

Equation 17 now becomes

$$\tau = (2-K)(3K-2)^{K/(2-K)}\eta\int_{x_0}^{x}\frac{x^{n-1}}{4x^{n-m/2}-1} \quad (25)$$

The integral over x is of the general form

$$\int\frac{x^P\mathrm{d}x}{ax^q-1}$$

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(3) W. J. Svirbely, *J. Phys. Chem.*, **62**, 380 (1958), equation 8.

(4) W. Gröbner and N. Hofreiter, "Integraltafel," Vol. I, Springer-Verlag, Vienna, 1949.

TABLE I

τ AS A FUNCTION OF K AND α

$1/K \downarrow$	$\alpha \rightarrow 0.9$	0.8	0.7	0.6	0.5	0.4	0.3	0.2
1.4	0.1105	0.2470	0.4212	0.6475	0.9710	1.438	2.223	3.800
1.5	.1110	.2500	.4286	.6667	1.000	1.500	2.3333	4.000
1.6	.1117	.2530	.4370	.6845	1.033	1.560	2.442	4.205
1.7	.1121	.2560	.4450	.7010	1.064	1.620	2.550	4.405
1.8		.2590	.4523	.7177	1.0985	1.682		
1.9		.2615	.4604	.7343	1.128	1.743		
2.0		.2642	.4669	.7494	1.1609	1.802		

If $P > q$, then

$$\int \frac{x^P \mathrm{d}x}{ax^q - 1} = \frac{1}{a(P - q + 1)} x^{P-q+1} + \frac{1}{a} \int \frac{x^{P-q}}{ax^q - 1} \mathrm{d}x \qquad (26)$$

The integral on the right side of equation 26 is of the general form

$$\int \frac{x^s \mathrm{d}x}{ax^\eta - b}$$

where $\eta > S$. The solution[4] for this general integral is

$$\int \frac{x^s \mathrm{d}x}{ax^\eta - b} = \frac{1}{b}\left(\frac{b}{a}\right)^{s+1/\eta} \int \frac{y^s \mathrm{d}y}{y^\eta - 1} \text{ with } y = \sqrt[\eta]{\frac{a}{b}}\,x \qquad (27)$$

$$\int \frac{y^s \mathrm{d}y}{y^\eta - 1} = \frac{1}{\eta} \ln (y - 1) + \frac{(1 - j)(-1)^{s+1}}{\eta} \ln (y + 1) + \frac{2}{\eta} \sum_{\nu=1}^{r-1} \left[R_\nu \cos \frac{2\nu(s + 1)\pi}{\eta} - S_\nu \sin \frac{2\nu(s + 1)\pi}{\eta}\right] + C$$

with

$\eta = 2r - j;\ j = 0 \text{ or } 1;\ \eta > 2;\ s = 0,1 \cdots \eta - 1$

$$R_\nu = \frac{1}{2} \ln \left[y^2 - 2y \cos \frac{2\nu\pi}{\eta} + 1\right];$$

$$S_\nu = \text{arc tg} \left[\frac{y - \cos \frac{2\nu\pi}{\eta}}{\sin \frac{2\nu\pi}{\eta}}\right] \qquad (28)$$

Tables of calculated values can be prepared for Case II in an analogous manner to Case I.

Case III. Solution Only.—For $K = 2/3$, *i.e.*, $k_1 = 3/2\,k_2$

$$\tau = \left(\frac{1}{\alpha} - 1\right) \text{ and } \alpha = \beta^{1/3} \qquad (29)$$

The application of the data in Table I will be demonstrated in a later paper.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF MARYLAND]

The Kinetics of the Alkaline Hydrolysis of 1,3,5-Tri-(4-carbomethoxyphenyl)-benzene[1]

BY W. J. SVIRBELY AND HAROLD E. WEISBERG

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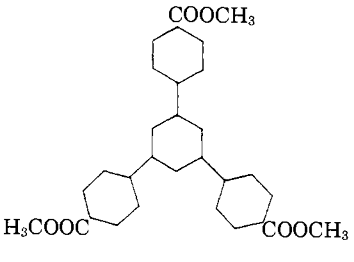
The compounds 1,3,5-tri-(4-carbomethoxyphenyl)-benzene, (4-carbomethoxyphenyl) (4-carbomethoxy-β-methyl-styryl) ketone, 1,3,5-tri-(4-carboxyphenyl)-benzene and 1,3-di-(4-carboxyphenyl)-5-(4-carbomethoxyphenyl)-benzene disodium salt have been prepared. The three step alkaline hydrolysis of 1,3,5-tri-(4-carbomethoxyphenyl)-benzene has been studied in dioxane–water mixtures over a temperature range. The three rate constants have been determined in isocomposition and isodielectric media using a procedure developed for the determination of the rate constants for a three-step consecutive-competitive second-order reaction involving a symmetrical molecule where there is no interaction among the reaction sites. The rate constant of the third step was also determined independently by the alkaline hydrolysis of the monoester ion and it was in good agreement with the result obtained in the three-step case. The various thermodynamic activation values have been calculated in isocomposition and isodielectric media. The data have been examined statistically for their significance and a statistical adjustment of data analysis supports the conclusion that the rate constants are in the statistical ratio $k_1:k_2:k_3 = 3:2:1$. We concluded that not only are the succeeding steps of the reaction independent of each other but that each step behaves like a dipole–dipole reaction probably because of ion-association effects in our low dielectric media.

Introduction

Recently,[2] 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. However, the labor involved in making the computations so that the resulting tables would be generally applicable was too involved. So, for the sake of convenience and instruction, the resulting equation was solved for the case of a reaction where $k_2 = 2k_3$ in which k_2 and k_3 are the rate constants for the second and third steps of the three-step reaction. In this paper we shall report on an application of the above analysis to the alkaline hydrolysis of 1,3,5-tri-(4-carbomethoxyphenyl)-benzene, a triester whose structural formula is



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[1] (a) Abstracted from a thesis submitted by Harold E. Weisberg to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the degree of Doctor of Philosophy. (b) Presented in part at the Chicago Meeting of the American Chemical Society, September, 1958.

[2] W. J. Svirbely, THIS JOURNAL, **81**, 255 (1959).