

CONTRIBUTION TO THE KINETICS OF THE SECOND-ORDER COMPETITIVE CONSECUTIVE REACTIONS*

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Received March 12th, 1974

Transformation of variables in differential equations describing the kinetics of second-order competitive consecutive reactions was used to derive relationships which must be satisfied by the concentrations of reaction components. A procedure has been outlined which allows the above relationships to be used for an effective determination of the rate constants of elementary reactions by minimalizing an appropriately chosen objective function without the necessity of solving numerically the respective set of differential equations. The procedure has been applied to published kinetic data of two- and three-step reactions of this type. The results have been compared with other methods.

Second-order competitive consecutive reactions involving two or more steps are of considerable practical importance: they include *e.g.* saponification of symmetric diesters^{1,2} and triesters^{3,4}, reactions of monoorganosilanes with alcohols⁵ or carboxylic acids⁶, *etc.* The corresponding kinetic schemes are rather complex and the respective differential equations cannot be solved by conventional methods. Approximative methods for the evaluation of the rate constants from kinetic data for two-step reactions have been suggested by Ingold¹ and Widequist⁷. Frost and Schwemer² have investigated this case extensively; on a simplifying assumption that the intermediate is absent at the beginning of the reaction and that the initial concentrations of both remaining reaction components are stoichiometrically equivalent, they suggested an approximative graphic numerical procedure for the determination of both rate constants. McMillan⁸ has shown how the ratio of the rate constants can be calculated if the concentrations of two reaction components are measured simultaneously. Recently, Wen⁹ has generalized the procedure suggested by Frost and Schwemer to include the case of a nonstoichiometric initial ratio of concentrations of the two reaction components. A corresponding three-step reaction scheme has been studied by Svrbely and coworkers^{3,4} on the example of saponification of symmetric triesters; they described two approximative procedures for determining the three rate constants.

In an earlier paper one of the present authors¹⁰ suggested a general procedure for the kinetic solution of complex reaction schemes in which rate constants of elementary reactions are determined by minimalizing a suitably chosen objective function. The latter is defined so as to be a measure of the deviation of calculated conversion curves from the experimental course. The method is quite general but its demands on computer time are considerable because the calcula-

* Part III in the series Model Compounds of Hydrophilic Gels; Part II: This Journal 37, 2009 (1972).

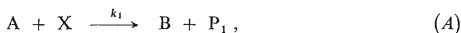
tion of "theoretical" conversion curves with the instantaneous values of the rate constants necessitates a repeated numerical solution of the corresponding set of differential equations.

In connection with our study of the hydrolytic stability of low-molecular weight compounds modelling various structural units of hydrophilic gels, we present in this paper relationships which must be satisfied by the time-dependent concentrations of the reacting components; these relationships have been derived for several types of second-order competitive consecutive reactions by a suitable transformation of variables in the initial differential equations. It has been shown how these relationships may be employed for an effective treatment of kinetic data by minimalization of an objective function without solving numerically the basic set of differential equations. The suggested procedure has been applied to experimental data taken from the literature, and the results compared with other methods.

THEORETICAL

Two-Step Reaction

This simplest case of second-order competitive consecutive reactions is represented by the scheme



where P_1 denotes products which do not further participate in the reaction; k_1 and k_2 are the respective rate constants ($1 \text{ mol}^{-1} \text{ min}^{-1}$). The corresponding system of differential equations for the three relevant components then is

$$-d\alpha/dt = k_1\alpha\xi, \quad (1)$$

$$-d\beta/dt = k_2\beta\xi - k_1\alpha\xi, \quad (2)$$

$$-d\xi/dt = k_1\alpha\xi + k_2\beta\xi; \quad (3)$$

α , β and ξ are the instantaneous concentrations of the components A, B and X, and t is time. In most cases the reaction course is followed by measuring the time dependence of the concentration of the component X (which is alkali in alkaline hydrolysis of symmetric diesters), so that the quantity $\xi(t) \equiv \xi_{\text{ex}}(t)$ may be regarded as a known function of time. Following Widequist⁷ we define a new variable $I(t)$ as

$$I(t) = \int_0^t \xi_{\text{ex}}(\tau) d\tau; \quad (4)$$

this quantity is easy to determine from experimental data by graphic or numerical integration of the smoothed experimental dependence $\xi_{\text{ex}}(t)$. The solution of Eq. (1)

can then be written as

$$\alpha = A_0 \exp[-k_1 I(t)], \quad (5)$$

where A_0 is the initial concentration of the component A , $A_0 = \alpha(0)$. By substituting Eq. (5) into Eq. (2) we obtain a simple differential equation having the solution

$$\beta = \exp[-k_2 I(t)] \left\{ B_0 + \frac{A_0 k_1}{k_1 - k_2} \left[1 - \exp[-(k_1 - k_2) I(t)] \right] \right\}, \quad (6)$$

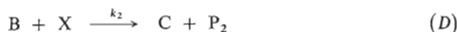
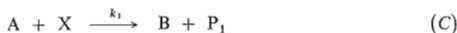
where B_0 again is the initial concentration of the component B , $B_0 = \beta(0)$. Finally, by substituting (5) and (6) into (3) we obtain a differential equation with the solution

$$\begin{aligned} \xi(k_1, k_2, t) = & X_0 - B_0 \left[1 - \exp[-k_2 I(t)] \right] - A_0 \left[1 - \exp[-k_1 I(t)] \right] - \\ & - \frac{A_0 k_1 k_2}{k_1 - k_2} \left\{ \frac{1}{k_2} \left[1 - \exp[-k_2 I(t)] \right] - \frac{1}{k_1} \left[1 - \exp[-k_1 I(t)] \right] \right\}; \quad (7) \end{aligned}$$

X_0 is the initial concentration of the component X , $X_0 = \xi(0)$. (Eq. (7) is a more general form of the relationship derived by Widequist⁷.) Here, the quantity I is of course defined by expression (4), so that the right-hand side of Eq. (7) implicitly contains the function $\xi_{\text{ex}}(t)$. Hence, if we calculate $I(t)$ from the smoothed experimental dependence $\xi_{\text{ex}}(t)$ according to (4) and substitute into the right-hand side of Eq. (7) together with the correct values of the rate constants k_1, k_2 , we obtain on the left-hand side a function ξ which is identical with the experimental reaction course, $\xi(k_1, k_2, t) = \xi_{\text{ex}}(t)$. If, however, other than the correct values of the rate constants are substituted, the time dependence of the concentration of the component X thus calculated will differ from the experimental data. Thus, a suitably defined deviation of the experimental data from the quantity $\xi(k_1, k_2, t)$ calculated from Eq. (7) may be employed as a criterion of the correctness of the chosen values of the unknown rate constants. Details of the calculation will be given below.

Three-Step Reaction

In this case three rate constants k_1, k_2 and k_3 are to be found in the reaction scheme



differing from the preceding one only in that it contains one additional reaction step.

The corresponding set of differential equations is

$$-d\alpha/dt = k_1\alpha\xi, \quad (8)$$

$$-d\beta/dt = k_2\beta\xi - k_1\alpha\xi, \quad (9)$$

$$-d\gamma/dt = k_3\gamma\xi - k_2\beta\xi, \quad (10)$$

$$-d\xi/dt = k_1\alpha\xi + k_2\beta\xi + k_3\gamma\xi; \quad (11)$$

γ is the instantaneous concentration of the component C, and the other symbols retain the original meaning. If we assume again that ξ is the measured value, we may employ a similar procedure as before to derive the equation

$$\begin{aligned} \xi(k_1, k_2, k_3, t) = & X_0 - A_0 \alpha_1(t) - B_0 \alpha_2(t) - C_0 \alpha_3(t) - \\ & - \frac{k_1 k_2 A_0}{k_1 - k_2} \left[\frac{\alpha_2(t)}{k_2} - \frac{\alpha_1(t)}{k_1} \right] - \frac{k_2 k_3}{k_2 - k_3} \left[B_0 + \frac{k_1 A_0}{k_1 - k_2} \right] \left[\frac{\alpha_3(t)}{k_3} - \frac{\alpha_2(t)}{k_2} \right] + \\ & + \frac{k_1 k_2 k_3 A_0}{(k_1 - k_2)(k_1 - k_3)} \left[\frac{\alpha_3(t)}{k_3} - \frac{\alpha_1(t)}{k_1} \right], \end{aligned} \quad (12)$$

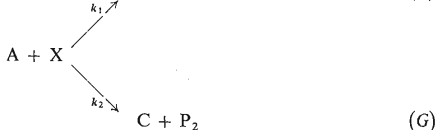
where C_0 denotes the initial concentration of the component C, $C_0 = \gamma(0)$,

$$\alpha_i(t) = 1 - \exp[-k_i I(t)], \quad i = 1, 2, 3 \quad (12a)$$

and $I(t)$ is again defined by expression (4). (A special case of Eq. (12) for a situation when at a time $t = 0$ only stoichiometric concentrations of components A and X are present, i.e. $X_0 = 3A_0$, $B_0 = C_0 = 0$, was derived by Svirbely and Blauer⁴.) Also in this case the deviation of the quantity $\xi(k_1, k_2, k_3, t)$ (calculated from Eq. (12)) from the experimental data can be used as a criterion of the correctness of the chosen rate constants k_1 , k_2 , and k_3 .

Two pairs of competitive consecutive reactions

In this case we have the reaction scheme



in which P_i again denote reaction products which do not further participate in the reaction. This sequence of reactions which *e.g.* described the hydrolysis of unsymmetric diesters was investigated by Chao-Tung¹¹. The set of differential equations to be solved is

$$-d\alpha/dt = k\alpha\xi, \quad (13)$$

$$-d\beta/dt = k_3\beta\xi - k_1\alpha\xi, \quad (14)$$

$$-d\gamma/dt = k_4\gamma\xi - k_2\alpha\xi, \quad (15)$$

$$-d\xi/dt = k\alpha\xi + k_3\beta\xi + k_4\gamma\xi; \quad (16)$$

α , β , γ and ξ are the instantaneous concentrations of the components A, B, C, and X, $k = k_1 + k_2$, and t is time. By employing the same procedure as before, *i.e.* by transforming the variables according to Eq. (4), and by solving the differential equations in the order (13), (14) and (15), and finally (16), the following relationship is obtained for the concentration of the component X

$$\begin{aligned} \xi(k_1, k_2, k_3, k_4, t) = & X_0 - A_0 x(t) - B_0 x_3(t) - C_0 x_4(t) - \\ & - \frac{k_1 k_3 A_0}{k - k_3} \left[\frac{x_3(t)}{k_3} - \frac{x(t)}{k} \right] - \frac{k_2 k_4 A_0}{k - k_4} \left[\frac{x_4(t)}{k_4} - \frac{x(t)}{k} \right], \end{aligned} \quad (17)$$

where

$$x(t) = 1 - \exp[-kI(t)] \quad (17a)$$

and the quantities x_i are again defined by Eqs (12a).

RESULTS AND DISCUSSION

The relationships derived above were used to calculate the rate constants of two- and three-step consecutive competitive second-order reactions on the basis of kinetic data taken from the literature. (No experimental data have been published so far for the scheme consisting of two pairs of competitive consecutive reactions.)

A program has been devised which calculates those components of the vector of the rate constants, \mathbf{k} , which minimize¹⁰ the objective function

$$R(\mathbf{k}) = \sum_i |\xi_{\text{ex}}(t_i) - \xi(\mathbf{k}, t_i)|; \quad (18)$$

here \mathbf{k} is the vector of the rate constants ($\mathbf{k} \equiv (k_1, k_2)$ for the two-step and $\mathbf{k} \equiv (k_1, k_2, k_3)$ for the three-step reaction scheme), $\xi_{\text{ex}}(t_i)$ is the smoothed value of the experimentally determined concentration of the component X measured at a time t_i , $\xi(\mathbf{k}, t_i)$ is the value calculated from Eq. (7) (or (12) for three-step reactions) for a corresponding time; the summation in Eq. (18) is carried out over all experimental points.

To find the minimum of function (18) Dickinson's method of steepest descent¹² was adapted. Prior to the actual minimalization, the program smoothed the experimental data piecewise by cubic polynomials with coefficients calculated by the least-squares method from the coordinates of the nearest eight experimental points, and then calculated the quantities $I(t_i)$ from their definition (Eq. (4)), where the integral was approximated by Gaussian quadrature formula of fifth order.

The form of Eq. (7) seems to suggest that the method for the determination of $\xi(k_1, k_2, t)$ will fail if during the calculation a situation arises when $k_1 = k_2$, because

TABLE I

Comparison of the Rate Constants of Two- and Three-Step Second-Order Competitive Consecutive Reactions Determined by the Proposed Procedure with the Results of Other Authors

Reaction	Rate constants, $1 \text{ mol}^{-1} \text{ min}^{-1}$					
	new method			published values		
	k_1	k_2	k_3	k_1	k_2	k_3
Two-step reaction						
Alkaline hydrolysis of diethyl adipate	5.107	1.870	—	5.136	1.842	—
Alkaline hydrolysis of dimethyl glutarate	7.086	2.483	—	7.24 ^a	1.12 ^{a,b}	—
				7.277 ^c	1.12 ^{c,b}	—
				7.334 ^d	1.107 ^d	—
Three-step reaction						
Alkaline hydrolysis of 1,3,5-tris[4-(methoxycarbonyl)phenyl]benzene	4.328	3.238	2.252	5.34 ^e	3.56 ^e	1.78
Alkaline hydrolysis of 1,3,5-tris(methoxycarbonyl)benzene ^f	13.366	1.624	0.288	14.69	1.558	0.290
Reaction of <i>p</i> -chlorophenylsilane with benzoic acid ^g	3.592	5.081	2.052	3.514	5.297	1.887

^a Kinetic data¹ evaluated by Ingold. ^b An independent kinetic measurement was necessary for the determination of k_2 . ^c Ingold's data evaluated by Widequist⁷. ^d Ingold's data evaluated by Wen⁹. ^e Calculated³ from the determined value of k_3 assuming that the three ester groups behave independently during the hydrolysis. ^f Investigated by Svirbely and Weisberg³. ^g The original authors⁶ do not give the volume of the system and take into account only mol of reacting compounds: a volume of 1 litre was assumed here for comparison's sake.

in such case the last term in the right-hand side of Eq. (7) will remain undefined. It is easy to demonstrate, however, that this term has a finite limit for $k_1 \rightarrow k_2$:

$$\lim_{k_1 \rightarrow k_2} A_0 k_1 k_2 [(1 - e^{-k_2 t})/k_2 - (1 - e^{-k_1 t})/k_1] / (k_1 - k_2) = A_0 k_1^2 t^2 \sum_{i=0}^{\infty} \lambda_i, \quad (19)$$

where

$$\lambda_i = (-1)^i \frac{(I k_1)^i (i + 1)}{(i + 2)!} \quad (19a)$$

and the series in Eq. (19) converges very rapidly. This relationship was always used in the actual calculations when $|k_1 - k_2| \leq 5 \cdot 10^{-3}$. A similar method was employed for a similar situation in the calculations according to Eq. (12). The program was written in FORTRAN IV and a Tesla 200 computer was used in the calculations.

Table I offers a comparison of the rate constants, calculated by the above procedure from published experimental data for two- and three-step reaction schemes, with values determined by various approximative methods.

Fig. 1 shows a plot of the experimental data (time dependence of the instantaneous alkali concentration – component X) for the alkaline hydrolysis of diethyl adipate² along with a theoretical curve calculated from differential equations (1)–(3) with the values $k_1 = 5.107$, $k_2 = 1.870$ determined by means of the new method. The Figure demonstrates the excellent fit between the calculated curve and the experimental points, which confirms the correctness of the constants thus determined.

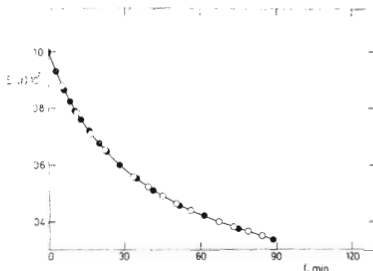


FIG. 1

Time Dependence of the Alkali Concentration $\xi(t)$ (mol/l) During the Alkaline Hydrolysis of Diethyl Adipate According to Frost and Schwemer²

● Experimental values, ○ calculated from differential equations (1)–(3) for rate constants $k_1 = 5.107$, $k_2 = 1.870$.

Practically identical values for k_1 and k_2 were also obtained by Frost and Schwemer² — cf. Table I — by using a graphical numerical approximative procedure.

Kinetic data for the alkaline hydrolysis of dimethyl glutarate¹ were analyzed by a number of authors^{1,7,9}; some approximative procedures^{1,7} required independent kinetic data for the determination of the rate constant k_2 . It can be seen from the results in Table I that in this case there exists a rather pronounced difference between the rate constant k_1 , and especially k_2 , as determined by our procedure, and the values found by other authors. The reason for such discrepancy is seen in Fig. 2 which shows plots of the theoretical concentration curves of the component X (alkali) for our values of the rate constants (curve 2, $k_1 = 7.086$, $k_2 = 2.483$), on the one hand, and for the values calculated by Wen⁹ ($k_1 = 7.334$, $k_2 = 1.107$, curve 1), on the other. Experimental points as determined by Ingold¹ are also plotted. In the region of low conversion which was examined experimentally (up to conversion of about 30%) both curves coincide and correspond equally well to the experimental course. This Figure also shows that for an accurate determination of the rate constant k_2 in particular it is necessary, in the case of the two-step reaction scheme, to measure the reaction course at least up to a 70–75% conversion.

The three-step reaction scheme, namely, the alkaline hydrolysis of 1,3,5-tris[4-(methoxycarbonyl)phenyl]benzene was experimentally investigated by Svrbely and Weisberg³; they suggested an approximative procedure for the determination of the rate constant k_3 from the course of the last reaction stages at a high conversion.

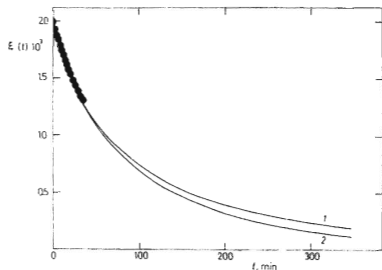


FIG. 2

Time Dependence of the Alkali Concentration $\xi(t)$ (mol/l) During the Alkaline Hydrolysis of Dimethyl Glutarate According to Ingold¹

● Experimental points; 2 calculated from differential equations (1)–(3) for $k_1 = 7.086$, $k_2 = 2.483$, determined by the proposed method; 1 calculated for $k_1 = 7.334$, $k_2 = 1.107$ as determined by Wen⁹.

The value thus determined was $k_3 = 1.78$ which was then used for calculating the rate constants k_1, k_2 (Table I) assuming that the ester groups of this symmetrical molecule are so far apart that they do not interact during the hydrolysis. (It then holds that $k_2 = 2k_3, k_1 = 3k_3$.) Fig. 3 shows the experimental data³ together with the theoretical course of NaOH conversion (full line) calculated from differential equations (8)–(11) with the rate constants (Table I) determined by our procedure based on Eq. (12). The same Figure also shows the theoretical curve corresponding to the rate constants according to ref.³ (broken line). The values calculated by employing the new procedure give a much better agreement with the experiment; consequently, under the given experimental conditions the assumed independence of the reaction centres is not fully justified even for the bulky molecule of 1,3,5-tris[4-(methoxycarbonyl)phenyl]benzene.

Later, Svrbely and Blauer⁴ suggested two approximative methods for the determination of the rate constants of three-step reactions and analyzed the data obtained in the alkaline hydrolysis of 1,3,5-tris(methoxycarbonyl)benzene. This procedure was afterwards applied by Reichsfeld and coworkers⁶ to the reaction of *p*-chlorophenylsilane with benzoic acid which proceeded by the same mechanism. The results obtained by these authors are compared in the last two lines of Table I with the rate constants determined by our procedure. In both cases the agreement was very good,

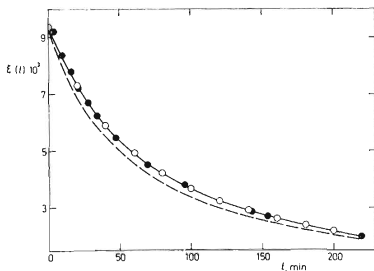


FIG. 3

Time Dependence of the Alkali Concentration $\xi(t)$ (mol/l) During the Alkaline Hydrolysis of 1,3,5-Tris[4-(methoxycarbonyl)phenyl]benzene³

● Experimental points; — smoothed experimental course; ○ calculated from differential equations (8)–(11) using $k_1 = 4.382, k_2 = 3.238, k_3 = 2.252$ determined by the proposed procedure; - - calculated using $k_1 = 5.34, k_2 = 3.56, k_3 = 1.78$ determined by the authors³ assuming that the reaction centres are completely independent.

and the theoretical conversion curves calculated with one or the other set of constants were practically undistinguishable and in a very good agreement with the experimental data.

The advantages of this new procedure consist in its general character and in the possibility of treating experimental data obtained at nonstoichiometric concentrations of the reaction components for both the two- and three-step reaction scheme; the preparation of stoichiometric initial concentrations may prove difficult in some cases¹³. The relationships corresponding to Eqs (7) and (12) may be derived also for four- and multistep reaction schemes and for more complicated cases of second-order competitive consecutive reactions, for instance for pairs of multistep reactions. The method also offers a possibility to evaluate kinetic data obtained by measuring the rate of disappearance of the common reaction component X in those cases when one or more intermediates are initially present in a known concentration. This may be particularly important in the investigation of branched reactions (*e.g.* in the scheme of two pairs of competitive consecutive reactions): if only components A and X are initially present, it is impossible to decide which pair of the rate constants (k_1 , k_3 and k_2 , k_4 , respectively) is to be ascribed to the given branch (to the given intermediate). This can be solved by adding one of the intermediates (B or C) in a known concentration to the starting reaction mixture.

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Translated by L. Kopecká.