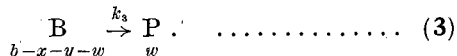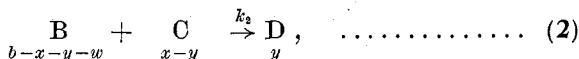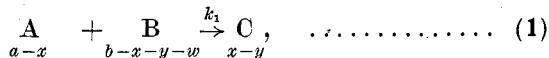# KINETIC TREATMENT OF CONSECUTIVE SECOND–ORDER REACTIONS WITH A CONCURRENT REACTION*

By R. D. Brown† and B. A. W. Coller†

The problem of calculating reaction rate constants from experimental data for consecutive second-order reactions has been solved in detail by Wideqvist (1950, 1955). We wish to point out that Wideqvist's method can be extended to the case where there is further kinetic competition from a concurrent reaction, that is, to the scheme :

$$\underset{a-x}{A} \;+\; \underset{b-x-y-w}{B} \;\overset{k_1}{\to}\; \underset{x-y}{C}\,, \quad \dots\dots\dots\dots \textbf{(1)}$$

$$\underset{b-x-y-w}{B} \;+\; \underset{x-y}{C} \;\overset{k_2}{\to}\; \underset{y}{D}\,, \quad \dots\dots\dots\dots \textbf{(2)}$$

$$\underset{b-x-y-w}{B} \;\overset{k_3}{\to}\; \underset{w}{P}\,. \quad \dots\dots\dots\dots \textbf{(3)}$$

Such a reaction scheme occurs where a reagent B, reacts twice with a substrate A, and simultaneously is decomposing ; for example, it has arisen in some diazonium coupling reactions (Brown, Coller, and Heffernan 1958, in press). One of several cases may arise depending on the kinetics of the concurrent reaction (3).

Zero-Order Concurrent Reaction

When stage (3) is a zero-order reaction the kinetic equations become :

$$\mathrm{d}x/\mathrm{d}t = k_1(a-x)(b-x-y-w), \quad \dots\dots\dots\dots \textbf{(4)}$$
$$\mathrm{d}y/\mathrm{d}t = k_2(x-y)(b-x-y-w), \quad \dots\dots\dots\dots \textbf{(5)}$$
$$\mathrm{d}w/\mathrm{d}t = k_3. \quad \dots\dots\dots\dots\dots\dots \textbf{(6)}$$

If we substitute

$$(b-x-y-w)\mathrm{d}t=\mathrm{d}T, \quad \dots\dots\dots\dots\dots \quad (7)$$

then equations (4) and (5) become

$$\mathrm{d}x/\mathrm{d}T=k_1(a-x), \quad \dots\dots\dots\dots \quad (8)$$
$$\mathrm{d}y/\mathrm{d}T=k_2(x-y). \quad \dots\dots\dots\dots \quad (9)$$

As Wideqvist has indicated, these equations may be integrated directly to give

$$x+y=a[2(k_1-k_2)+(2k_2-k_1)\exp(-k_1T)-k_1\exp(-k_2T)]/(k_1-k_2)$$
$$=aF(T), \text{ say. } \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots \quad (10)$$

Thus, after integration of (6),

$$[B]=b-w-x-y=b-k_3t-aF(T),$$

that is,

$$F(T)=(b-k_3t-[B])/a, \quad \dots\dots\dots\dots\dots \quad (11)$$

where

$$T=\int_0^t [B]\mathrm{d}t. \quad \dots\dots\dots\dots\dots \quad (12)$$

To evaluate k_1 and k_2, k_3 is evaluated from separate experiments in which A was absent, then the quantity T is evaluated for each experimental point by numerical integration (the trapezium rule is convenient). Next the quantity $(b-k_3t-[B])/a$ is plotted against T. It is then easy to determine by trial and error the values of k_1 and k_2 necessary to make $F(T)$ fit the curve so plotted. Alternatively, the statistical method of fitting described by Wideqvist (1955) may be used but we have found this to be more time-consuming than trial and error methods.

First-Order Concurrent Reaction

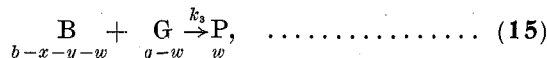When stage (3) is first-order with respect to B, equation (6) is replaced by

$$\mathrm{d}w/\mathrm{d}t=k_3(b-x-y-w). \quad \dots\dots\dots\dots \quad (13)$$

The substitution (7) again facilitates integration of the equations and in this case we find:

$$F(T)=(b-k_3T-[B])/a. \quad \dots\dots\dots\dots \quad (14)$$

The procedure for determining k_1 and k_2 is the same as before although the quantity plotted as a function of T, that is, the right-hand side of (14), is slightly different from that plotted for case 1.

If stage (3) is also first-order with respect to some other reactant, that is,

$$\underset{b-x-y-w}{B} + \underset{g-w}{G} \overset{k_3}{\to} \underset{w}{P}, \quad \dots\dots\dots\dots \quad (15)$$

then equation (6) is replaced by

$$\mathrm{d}w/\mathrm{d}t=k_3(g-w)(b-x-y-w). \quad \dots\dots\dots\dots \quad (16)$$

Using the same substitution as before, we find:

$$F(T)=\{b-g[1-\exp(-k_3T)]-[B]\}/a, \quad \dots\dots\dots \quad (17)$$

and the procedure for finding k_1 and k_2 is as before.

Second-Order Concurrent Reaction

When stage (3) is second-order with respect to B, that is, when equation (6) is replaced by

$$dw/dt = k_3(b - x - y - w)^2, \quad \ldots\ldots\ldots\ldots\ldots (18)$$

the equations again may be integrated by use of (7) but the resultant equation is more complicated:

$$F(T) - G(T) = \{b \exp(-k_3 T) - [B]\}/a, \quad \ldots\ldots\ldots (19)$$

where

$$G(T) = 2[1 - \exp(-k_3 T)] + \frac{k_3(2k_2 - k_1)}{(k_1 - k_2)(k_3 - k_1)}[\exp(-k_1 T) - \exp(-k_3 T)]$$

$$- \frac{k_1 k_3[\exp(-k_2 T) - \exp(-k_3 T)]}{(k_1 - k_2)(k_3 - k_2)}. \quad \ldots\ldots\ldots\ldots (20)$$

It will be noticed that equations (10) and (20), defining $F(T)$ and $G(T)$, have been written under the assumption that $k_1 \neq k_2$. However, it is simple to obtain the corresponding functions for the special case of $k_1 = k_2 = k$, say. For example, $F(T)$ then becomes $2 - (2 + kT)\exp(-kT)$. When k_1 and k_2 are similar it may be expedient to regard $F(T)$ and $G(T)$ as functions of k_2 and $\delta = k_1 - k_2$ when the trial-and-error fitting of (11), (14), or (19) is in progress.

References

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