On the Calculation of the Rate Constant Ratio in Consecutive Reactions

SIGVARD WIDEQVIST

Department of Organic Chemistry, University of Uppsala, Sweden

Submitted in honour of the sixtieth birthday of my teacher, Professor *Arne Fredga*

The calculations of the rate constants for consecutive second-order reactions has been discussed, and a method of calculation has been suggested. The method which makes use of numerical or graphical integration has been tested against the data given by Regna and Caldwell for the conversion of a ketopolyhydroxy acid to furfural via ascorbic acid.

Recently Mc Millan [1] published a paper on the calculation of the rate constant ratio in consecutive second-order reactions:

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

$$A + C \xrightarrow{k_2} D + F$$
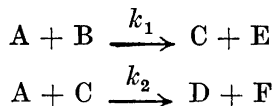
The statement of Mc Millan that the problem of determining the rate constants k_1 and k_2 has been solved in detail only for the case of equivalent initial reactant concentrations (*i.e.* $B_o = 2A_o$) or for a limited range of the extent of the reaction is not correct (Wideqvist [2]).

The extent of the reaction is usually determined by measuring the concentration of A. From this concentration the rate constants are calculated in some way (Frost and Schwemer [3], Wideqvist [2,4]).

Mc Millan points out that it is a much simpler problem to obtain the ratio $\varkappa = k_2/k_1$ of the two rate constants from a knowledge of the concentrations of *two components* of the reacting system at *the same time*. According to Mc Millan this case assumes greater relevance in view of the increasingly powerful analytical methods, whereby one can often directly determine the concentrations of products and reactants other than A.

The rates of change of the concentrations B and C are

$$dB/dt = -k_1 AB \tag{1}$$

$$dC/dt = k_1 A(B - \varkappa C) \tag{2}$$

In terms of the reduced concentrations, defined by

$$\beta = B/B_0 \tag{3a}$$

$$\gamma = C/B_0 \tag{3b}$$

the ratio of eqn. (2) to (1) becomes

$$d\gamma/d\beta = (\varkappa\gamma - \beta)/\beta \tag{4}$$

On integrating we obtain

$$\varkappa \ln\beta = \ln[\beta + (1-\varkappa)\gamma] \tag{5}$$

or

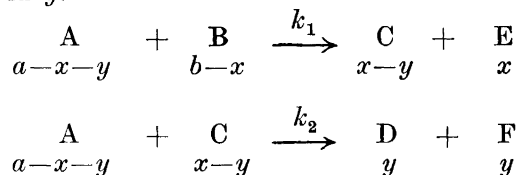$$\gamma = \beta(1 - \beta^{\varkappa-1})/(\varkappa - 1) \tag{6}$$

For any measured pair (β,γ) of experimental concentrations the value of $\varkappa$ which satisfies eqn. (5) is calculated by determination of the intersection of the left and right hand sides, considered as functions of $\varkappa$ for the given values of the parameters (β,γ). This procedure, recommended by Mc Millan, is, however, very cumbersome. For values of $\varkappa$ less than 0.05 it should be possible to use eqn. (5) in the explicit approximate form

$$\varkappa \approx [\ln(\beta + \gamma)]/[\ln\beta + \gamma/(\beta + \gamma)] \tag{7}$$

Finally Mc Millan states that although the procedure above "is much simpler than in the general case, it also accomplishes less in providing only the ratio $\varkappa$ rather than the values of the individual rate constants k_1 and k_2".

It seems, however, as Mc Millan has overlooked two important facts, namely (1) that $\varkappa$ is already explicitly expressed in eqn. (4) and, (2) that a knowledge of the concentrations B and C also gives the remaining concentration A and thus k_1 and k_2.

The discussion is considerably facilitated by introduction of the reaction variables x and y:

$$\underset{a-x-y}{A} \quad + \quad \underset{b-x}{B} \quad \xrightarrow{k_1} \quad \underset{x-y}{C} \quad + \quad \underset{x}{E}$$

$$\underset{a-x-y}{A} \quad + \quad \underset{x-y}{C} \quad \xrightarrow{k_2} \quad \underset{y}{D} \quad + \quad \underset{y}{F}$$

We thus have

$$A_0 = a \text{ and } A = a - x - y$$
$$B_0 = b \text{ and } B = b - x$$
$$C = x - y$$

and then

$$x = B_o - B$$
$$y = B_o - B - C$$
$$A = A_o - 2(B_o - B) + C$$

Every pair of concentrations B and C thus gives a corresponding value of A. By use of the reaction variables we obtain

$$dx/dt = k_1(a-x-y)(b-x) \qquad (8)$$

$$dy/dt = k_2(a-x-y)(x-y) \qquad (9)$$

By division we get

$$dy/dx = \varkappa(x-y)/(b-x) \qquad (10)$$

and on integrating

$$y = \varkappa \int_0^x \frac{x-y}{b-x} \, dx = \varkappa U \qquad (11)$$

Thus we get

$$\varkappa = y/U \qquad (12)$$

The integral U is easily obtained as the area between the curve $(x-y)/(b-x) = f(x)$ and the x-axis.

Eqn. (8) may be written

$$dx/(b-x) = k_1(a-x-y)dt = k_1 d\Theta \qquad (8a)$$

By integration we obtain

$$\frac{1}{\Theta} \ln \frac{b}{b-x} = k_1 \qquad (13)$$

where

$$\Theta = \int_0^t (a-x-y)dt \qquad (14)$$

A second-order reaction can thus be converted into a first-order reaction by changing the time-variable (Wideqvist [5]). The new time-variable Θ is obtained as the area between the curve $(a-x-y) = f(t)$ and the t-axis. From the knowledge of k_1 and $\varkappa$ we may obtain k_2 from the relation $k_2 = k_1\varkappa$.

It is thus evident that a determination of the reaction variables x and y permits a very simple calculation of the rate constants.

EXAMPLE

Mc Millan gives no example of a reaction which can be treated by his method or by the method described above. However, Regna and Caldwell [6] have described a reaction which can be treated in a similar, although somewhat

simpler way. They have investigated the conversion of a 2-ketopolyhydroxy acid (B) to furfural (F). This is a consecutive first-order process, where ascorbic acid (C) is the intermediate product.

$$B \xrightarrow{k_1} C \xrightarrow{k_2} F$$
$$b-x \qquad x-y=z \qquad y$$
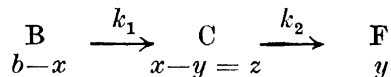
The progress of the reaction was followed by determining the concentration $(x-y)$ of the intermediate product ascorbic acid. Analyses were made by titrating samples of the reaction mixture with an iodine solution of approximately 0.025 N. This gives a quantitative indication of the ascorbic acid present, since iodine oxidizes ascorbic acid to its first oxidation product, dehydro-ascorbic acid.

For the rate of the reactions we get the equations

$$dx/dt = k_1(b-x) \tag{15}$$

$$dy/dt = k_2(x-y) \tag{16}$$

The rate constant k_2 which evaluates the rate of decomposition of the ascorbic acid was determined directly by measurements on the free ascorbic acid and calculated from the reaction

$$k_2 t = \ln \, c_0/(c_0-y) \tag{17}$$

where c_0 is the initial concentration of ascorbic acid in the separate experiment. Integration of the equation system (15, 16) gives the final equations

Table 1. The conversion of a 2-ketopolyhydroxy acid to furfural *via* ascorbic acid (According to Regna and Caldwell).

t_{min}	$x-y$	Q	$k_2 Q = y$	$b-x$	$k_1 \times 10^3$ W	R & C
0				42.17		
43.6	4.28	93.30	0.046	37.84	2.49	2.53
77.6	7.42	292.2	0.143	34.61	2.54	2.55
114.7	10.32	621.3	0.305	31.54	2.53	2.53
166.0	13.45	1 231	0.604	28.12	2.44	2.44
208.7	16.58	1 872	0.919	24.67	2.57	2.57
278.3	19.89	3 141	1.542	20.74	2.55	2.55
361.9	22.73	4 923	2.417	17.02	2.51	2.50
442.3	25.11	6 846	3.361	13.70	2.54	2.55
480.9	25.98	7 832	3.846	12.34	2.56	2.56
516.8	26.41	8 772	4.307	11.45	2.52	2.53
556.1	27.14	9 825	4.824	10.21	2.55	2.56
602.7	27.56	11 099	5.450	9.16	2.53	2.53
658.0	27.98	12 635	6.204	7.99	2.53	2.53
742.8	28.30	15 021	7.375	6.50	2.52	2.51
770.7	28.04	15 807	7.761	6.37	2.45	2.41
802.1	27.82	16 684	8.192	6.16	2.40	2.34
843.8	27.65	17 841	8.760	5.76	2.36	2.27

$$k_1 t = \ln b/(b-x) \tag{18}$$

and

$$x - y = \frac{k_1 b}{[k_2 - k_1} \; (e^{-k_1 t} - e^{-k_2 t}) \tag{19}$$

From eqn. (19) Regna and Caldwell calculated k_1 by a time-consuming itera-
tion process. The knowledge of the rate constant k_2 and the intermediate
concentration $(x-y)$ permits, however, a very simple calculation of k_1. From
eqn. (16) we get on integration

$$y = k_2 \int_0^t (x-y)\mathrm{d}t = k_2 Q \tag{20}$$

where Q is the area between the curve $(x-y) = \mathrm{f}(t)$ and the t-axis. As k_2
is known before, we thus also know y. During the reaction the concentration
$(x-y) = z$ is measured. Thus we get $x = (y + z) = (z + k_2 Q)$ and
$(b-x) = (b - k_2 Q - z)$. The rate constant k_1 is then calculated from eqn. (18).

The results of the calculations are recorded in Table 1. All the concentra-
tions are expressed in "ml of 0.025 N iodine solution". For k_2 Regna and
Caldwell obtained the value 4.91×10^{-4}. In Table 1 the values of k_1 calculated
in this paper are indicated with (W) and those given by Regna and Caldwell
with (R & C).

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