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Kinetics of organometallic reactions: a quick method to obtain rate coefficients for complex reactions from 'pseudo-first-order' rate coefficients and related information

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Abstract

Kinetic data from reactions which are more complicated than simple first order processes can give linear plots of ln $|M_\infty - M_t|$ against time (where M is a physical property of the reacting solution, such as absorbance or conductance). It is shown how these linear plots arise, and how the correct rate coefficients for complex reactions can be calculated from the pseudo-first-order rate coefficients, together with reagent concentrations and related information. This approach is useful for organometallic reactions, where there are often severe limitations on the experimental data that can readily be obtained.

Introduction

Kinetic work with organometallic systems can be difficult. Side reactions, and reactions with the atmosphere can lead to 'noisy' concentration-time data. Although experiments over a wide range of concentrations are desirable, the availability of reactants and limitations of solubility or of sensitivity of monitoring equipment may severely limit this range. Often kinetic work is hurried in order to minimize deterioration of the solutions, and the results of one experiment are not processed fully before the next is attempted. This paper presents a new quick way of processing kinetic data from such experiments.

Reaction kinetics in solution are often studied under conditions in which the reaction can be treated as a first-order process, as represented by eq. 1 and 2.

$$A \xrightarrow{k_1} P_1 + P_2 + \dots P_i \tag{1}$$

$$d[P_i]/dt = -d[A]/dt = k_1[A] \tag{2}$$

There are good reasons for this. The reaction progress is commonly monitored by measurement of some physical property M (such as absorbance or conductance) which is linearly proportional to the concentrations of reactant A and products P_i at any time (eq. 3).

$$M_t = K + a[\mathrm{A}] + \sum b_i[\mathrm{P}_i] \tag{3}$$

The concentration of a product P_i at any time t is given by eq. 4 where M_0, M_∞, and M_t are the values of M at the start, end, and at time t respectively.

$$[\mathrm{P}_i] = [\mathrm{A}]_0(M_t - M_0)/(M_\infty - M_0) \tag{4}$$

Integration of rate equation 2 and expression of the concentrations in terms of M gives eq. 5.

$$\ln(M_\infty - M_t) = -k_1 t + \ln(M_\infty - M_0) \tag{5}$$

A plot of $\ln|M_\infty - M_t|$ against time is a straight line of slope $-k_1$. The value of M_0 is not needed to get k_1. This is convenient, since M_0 is often difficult to measure because mixing of solutions and thermostatting after initiation of the reaction can take some time. Even if M_∞ is not known there are several well documented ways of deriving k_1 [1–5]. All in all, the simple treatment of data together with this flexibility towards M_0 and M_∞ makes kinetic studies of reactions under first-order conditions very popular. In particular, stopped-flow absorbance-time data is often directly analysed with an 'on-board' microprocessor to give 'first-order' rate coefficients.

Consider a simple second-order reaction, eq. 6a.

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_2} \mathrm{C} + \mathrm{D} \tag{6a}$$

If the reaction is studied under pseudo-first-order conditions ($[\mathrm{B}]_0 \gg [\mathrm{A}]_0$) the true second-order rate coefficient is calculated from the pseudo-first-order rate coefficient, $k_1{}^{\mathrm{obs}}$, by use of the relationship $k_2 = k_1{}^{\mathrm{obs}}/[\mathrm{B}]_0$. If the k_2 values obtained from a series of experiments at different concentrations are not constant, one possibility is that there may be an equilibrium, as in eq. 6b.

$$\mathrm{A} + \mathrm{B} \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} \mathrm{C} + \mathrm{D} \tag{6b}$$

Can k_2 be simply calculated from k_1^{obs} to check on the existence of this equilibrium? This paper demonstrates that reaction schemes where there are first- or second-order rate laws, and which may involve equilibria lead to experimental data which give linear plots of $\ln|M_\infty - M_t|$ against time. It shows how to convert the 'first-order' rate coefficients into the rate coefficients appropriate to these other rate laws.

First-order with equilibrium

(a) Single product formed

A first-order reaction going to a position of equilibrium can be represented by eq. 7 and 8.

$$\mathrm{A} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} \tag{7}$$

$$\mathrm{d}[\mathrm{B}]/\mathrm{d}t = k_1[\mathrm{A}] - k_{-1}[\mathrm{B}] \tag{8}$$

As is well known, plots of $\ln|M_\infty - M_t|$ against time give straight lines of slope $-k_1^{\mathrm{obs}}$, where $k_1^{\mathrm{obs}} = k_1 + k_{-1}$. If we define a function β to be the fraction of reaction at equilibrium, i.e. $\beta = [\mathrm{B}]_e/[\mathrm{A}]_0$, then it is easy to calculate k_1 as $k_1 = \beta k_1^{\mathrm{obs}}$.

(b) Two products formed

When the reverse reaction is second order, we get eq. 9 and 10.

$$\mathrm{A} \underset{k_{-2}}{\overset{k_1}{\rightleftharpoons}} \mathrm{B} + \mathrm{C} \tag{9}$$

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = k_1[\mathrm{A}] - k_{-2}[\mathrm{B}][\mathrm{C}] \tag{10}$$

This often arises in studies of solvolyses when the solvent is in large excess. If the initial concentrations of A, B, and C are $[\mathrm{A}]_0$, 0, and 0 respectively, the integrated rate equation for this reaction is given in eq. 11, where $[\mathrm{A}]_e$ is the equilibrium concentration of A.

$$\ln \frac{[\mathrm{A}]_0^2 - [\mathrm{A}]_e[\mathrm{A}]_t}{([\mathrm{A}]_t - [\mathrm{A}]_e)[\mathrm{A}]_0} = k_1 \frac{[\mathrm{A}]_0 + [\mathrm{A}]_e}{[\mathrm{A}]_0 - [\mathrm{A}]_e} t \tag{11}$$

Plots of the left-hand side of eq. 11 against time will give a straight line, the slope of which when multiplied by $([\mathrm{A}]_0 - [\mathrm{A}]_e)/([\mathrm{A}]_0 + [\mathrm{A}]_e)$ gives k_1. This is quite a tedious calculation, especially if [A] is calculated from a physical property, M, such as absorbance or conductance, when good measurements of M_0 and M_∞ are required for each kinetic run. If we define β to be the fraction of reaction at equilibrium, i.e. $\beta = [\mathrm{B}]_e/[\mathrm{A}]_0 = [\mathrm{C}]_e/[\mathrm{A}]_0$, and reaction is followed until [B] reaches a fraction ϕ of its final concentration $[\mathrm{B}]_e$, plots of $\ln|M_\infty - M_t|$ against time are good straight lines (correlation coefficient $r > 0.999$ for 20 data points at equally spaced times) provided β and ϕ lie in the unshaded area in Fig. 1. The slope of

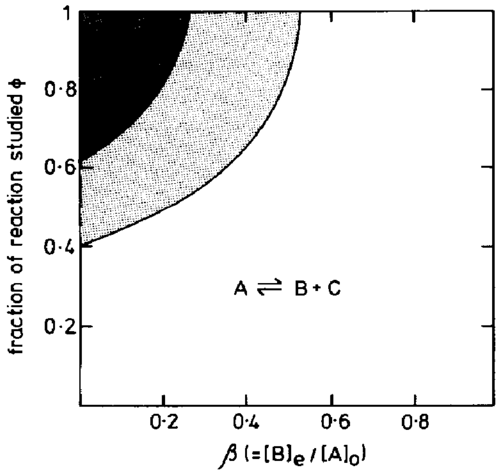

Fig. 1. A $\rightleftharpoons$ B + C. Clear area shows which values of ϕ (fraction of reaction followed) and β ($[\mathrm{B}]_e/[\mathrm{A}]_0$) would lead to linear plots of $\ln|M_\infty - M_t|$ against time with correlation coefficients, r, > 0.999 (20 data pairs); light shading $0.999 > r > 0.998$; heavy shading $r < 0.998$.

Table 1

Values of z (see eq. 13) for different fractions of reaction followed, ϕ.

Fraction of reaction, ϕ	z
0.25	0.131
0.3	0.159
0.4	0.217
0.5	0.279
0.6	0.345
0.75	0.459
0.85	0.552

these plots give a pseudo-first-order rate coefficient k_1^{obs}. To calculate the value of k_1 from this it is necessary to use eq. 12 and 13.

$$k_1^{\text{calc}} = \beta k_1^{\text{obs}} / [1 + z(1-\beta)] \tag{12}$$

$$z = 1 + \phi / \ln(1-\phi) \tag{13}$$

Table 1 shows values of z for various fractions of reaction. Examples of the accuracy of this approach are shown in Table 2. This compares values of the true rate coefficient k_1 with those calculated from the appropriate plots of "first-order" $\ln|M_\infty - M_t|$ against time. It can be seen that resultant rate coefficients, k_1^{calc}, calculated from k_1^{obs} using eq. 12 and 13 are within 1% of the correct value. Values of k_1^{obs} depend only slightly on ϕ. This leads to a very quick way of processing sets of results from kinetic experiments, e.g. from stopped-flow measurements. For a particular set of concentrations the $\ln|M_\infty - M_t|$ plots are drawn and k_1^{obs} calculated for each run. These are averaged for a set and k_1 calculated using eq. 12 and 13. The derivation of eq. 12 and 13 is given in the appendix.

Table 2

Correlation coefficients and rate coefficients for reaction $A \rightleftharpoons B + C$ calculated from $\ln|M_\infty - M_t|$ Plots.

β	r	k_1^{obs}/k_1	k_1^{calc}/k_1	
1	1	1	1	Reaction
0.8	> 0.999	1.366	1.001	followed
0.6	> 0.999	1.970	0.999	until
0.4	0.999	3.170	0.994	$\phi = 0.75$
0.2	0.998	6.760	0.989	
0.1	0.998	13.93	0.986	
0.05	0.998	28.27	0.984	
1	1	1	1	Reaction
0.8	> 0.999	1.320	1.000	followed
0.6	> 0.999	1.850	0.999	until
0.4	> 0.999	2.096	0.996	$\phi = 0.5$
0.2	0.999	6.069	0.993	
0.1	0.999	12.39	0.991	
0.05	0.999	25.03	0.990	

Second-order reactions going to completion

Second-order reactions going to completion are described by eq. 14 and 15.

$$\mathrm{A} + \mathrm{B} \xrightarrow{k_2} \mathrm{P} \tag{14}$$

$$-\mathrm{d}[\mathrm{A}]/\mathrm{d}t = -\mathrm{d}[\mathrm{B}]/\mathrm{d}t = \mathrm{d}[\mathrm{P}]/\mathrm{d}t = k_2[\mathrm{A}][\mathrm{B}] \tag{15}$$

Integrated rate equations can be found for the two conditions $[\mathrm{A}]_0 = [\mathrm{B}]_0$, or $[\mathrm{A}]_0 < [\mathrm{B}]_0$, ($[\mathrm{A}]_0$ and $[\mathrm{B}]_0$ are the initial concentrations of A and B). For the latter conditions the integrated rate expression is eq. 16.

$$k_2 t = \frac{1}{[\mathrm{B}]_0 - [\mathrm{A}]_0} \ln \frac{[\mathrm{A}]_0[\mathrm{B}]_t}{[\mathrm{A}]_t[\mathrm{B}]_0} \tag{16}$$

When $[\mathrm{A}]_t$ and $[\mathrm{B}]_t$ are expressed in terms of M we get a complicated function to calculate and plot. If the ratio of initial concentrations $[\mathrm{B}]_0/[\mathrm{A}]_0 = \alpha$, and reaction is studied up to the time when $[\mathrm{P}] = \phi[\mathrm{A}]_0$ good linear plots of $\ln|M_\infty - M_t|$ against time are found ($r > 0.999$ for 20 points) for the range of values of α and ϕ shown in Fig. 2. A similar analysis to that above shows that the value of k_2 can be calculated from k_1^{obs} by eq. 17, where z is given by eq. 13.

$$k_2^{\mathrm{calc}} = k_1^{\mathrm{obs}}/\{[\mathrm{A}]_0(\alpha - z)\} \tag{17}$$

Table 3 shows how second-order rate coefficients, k_2^{calc}, calculated from "first-order" plots using eq. 17 and 13 compare with the correct value k_2. If data points are taken over the first half of reaction, ($\phi = 0.5$), there is less than 1% error introduced provided $[\mathrm{B}]_0$ is greater than $2[\mathrm{A}]_0$.

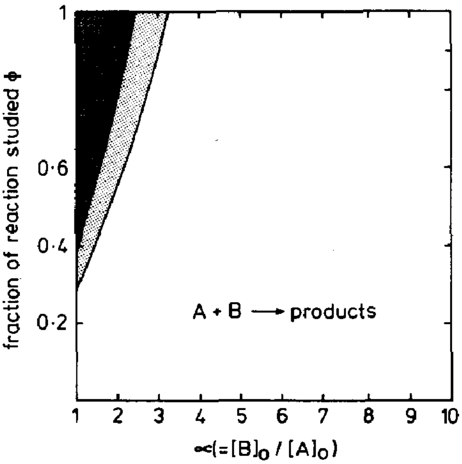

Fig. 2. A + B → products. Clear area shows which values of α ($[\mathrm{B}]_0/[\mathrm{A}]_0$) and ϕ (fraction of reaction followed) would lead to linear plots of $\ln|M_\infty - M_t|$ against time with correlation coefficients, r, > 0.999 (20 data pairs); light shading $0.999 > r > 0.998$; heavy shading $r < 0.998$.

Table 3

Correlation coefficients and rate coefficients calculated from $\ln|M_\infty - M_t|$ against time plots for second-order reactions $A + B \rightarrow$ products.

α	r	$k_1^{obs}/[A]_0$	k_2^{calc}/k_2	
50	> 0.999	49.52	1.000	Reaction followed until $\phi = 0.75$
10	> 0.999	9.520	0.998	
7	> 0.999	6.519	0.997	
5	> 0.999	4.516	0.994	
3	> 0.999	2.507	0.987	
2.5	0.999	2.003	0.981	
2.0	0.998	1.495	0.970	
50	> 0.999	49.72	1.000	Reaction followed until $\phi = 0.5$
10	> 0.999	9.714	0.999	
7	> 0.999	6.713	0.999	
5	> 0.999	4.711	0.998	
3	> 0.999	2.708	0.995	
2.5	> 0.999	2.206	0.993	
2.0	> 0.999	1.703	0.989	
1.6	0.999	1.300	0.983	
1.4	0.998	1.096	0.977	

Second-order with equilibrium

(a) Single product formed

This is described by eq. 18 and 19. The integrated rate equations are complex and given by Espenson [6]. They are not easy to use. For reaction 18 if $[A]_0 \neq [B]_0$ the kinetic case can be represented by two variables; (i) the fraction of reaction, β, which has taken place at equilibrium, i.e. $\beta = [C]_e/[A]_0$; (ii) the ratio of initial concentrations, α, $= [B]_0/[A]_0$. Good straight line plots ($r > 0.999$ for 20 points) of $\ln|M_\infty - M_t|$ against time are found for a wide ranges of α and β. Figure 3 shows the limits of α and β values where such linear plots are found when reaction is followed up to the time $[C] = 0.75[C]_e$ (i.e. $\phi = 0.75$). The required k_2 values can be found from k_1^{obs} using eq. 20 and 13.

$$A + B \underset{k_{-1}}{\overset{k_2}{\rightleftharpoons}} C \qquad (18)$$

$$d[C]/dt = k_2[A][B] - k_{-1}[C] \qquad (19)$$

$$k_2^{calc} = \frac{\beta k_{s1}^{ob}}{[A]_0(\alpha - z\beta^2)} \qquad (20)$$

Table 4 shows how second order rate coefficients, k_2^{calc}, calculated from "first-order" plots using eq. 20 and 13 compare with the correct value for the conditions $[A]_0 = [B]_0$.

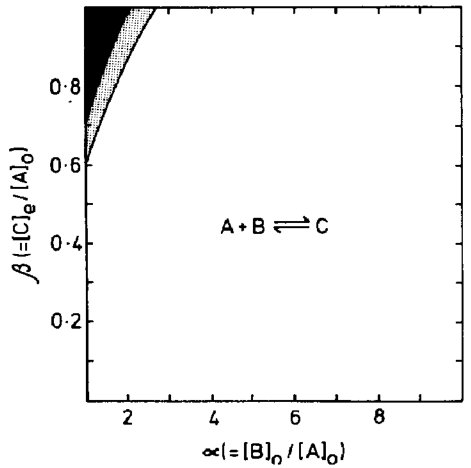

Fig. 3. $A+B \rightleftharpoons C$. Clear area shows range of values for α ($[B]_0/[A]_0$) and β ($[C]_e/[A]_0$) where plots of $\ln|M_\infty - M_t|$ against time over the first two half-lives are straight lines with correlation coefficients, r, > 0.999; light shading $0.999 > r > 0.998$; heavy shading $r < 0.998$.

(b) Two products formed

When two products are formed (eq. 21 and 22), we note that if the equilibrium

$$A + B \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} C + D \tag{21}$$

$$-d[A]/dt = -d[B]/dt = d[C]/dt = d[D]/dt = k_2[A][B] - k_{-2}[C][D] \tag{22}$$

constant K ($=k_2/k_{-2}$) for eq. 21 is equal to unity (eq. 23):

$$1 = ([A]_0 - [C]_e)([B]_0 - [C]_e)/[C]_e^2 \tag{23}$$

Table 4

Correlation coefficients and rate coefficients for reaction $A+B \rightleftharpoons C$ calculated from $\ln|M_\infty - M_t|$ plots [a]

β	r	$k_1^{obs}/[A]_0$	k_2^{calc}/k_2	
0.7	> 0.998	1.076	0.971	Reaction followed until $\phi = 0.75$
0.6	> 0.999	1.370	0.985	
0.5	> 0.999	1.756	0.992	
0.3	> 0.999	3.190	0.998	
0.1	> 0.999	9.925	1.000	
0.9	0.998	0.834	0.969	Reaction followed until $\phi = 0.5$
0.8	0.999	1.009	0.982	
0.7	> 0.999	1.221	0.990	
0.5	> 0.999	1.855	0.997	
0.3	> 0.999	3.248	0.999	
0.1	> 0.999	9.972	1.000	

[a] Equal concentrations of A and B.

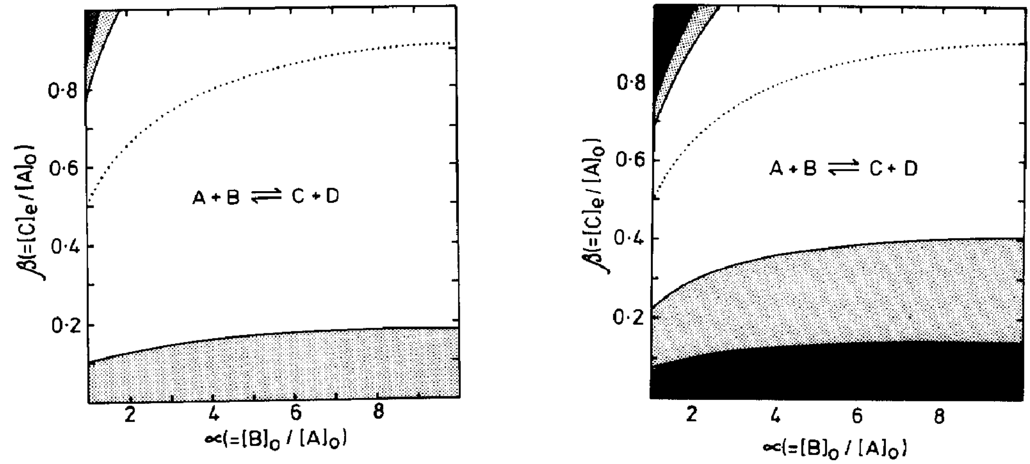

Fig. 4a and 4b. $A + B \rightleftharpoons C + D$. Clear area shows range of values for α ($[B]_0/[\alpha]_0$) and β ($[C]_e/[A]_0$) where plots of $\ln|M_\infty - M_t|$ against time over the first two half lives are straight lines with correlation coefficients, r, > 0.999; light shading $0.999 > r > 0.998$; heavy shading $r < 0.998$. Dotted line shows where $K = 1$, and kinetics show perfect first-order behaviour (see text). In Fig. 4a ϕ (= fraction of reaction studied) $= 0.5$; in Fig. 4b $\phi = 0.75$.

we can show that α and β are related by eq. 24.

$$\beta = \alpha/(1 + \alpha) \tag{24}$$

Under these conditions eq. 22 becomes eq. 25 and plots of $\ln|M_\infty - M_t|$ against time will be perfect straight lines. The slope of the lines will be $k_2[A]_0(1 + \alpha)$, which

$$d[C]/dt = ([C]_e - [C])k_2[A]_0(1 + \alpha) \tag{25}$$

can be written as $k_2\alpha[A]_0/\beta$ (from eq. 24). It is found that over wide ranges of the parameters α and β plots of $\ln|M_\infty - M_t|$ against time are good straight lines ($r > 0.999$ for 20 points). k_2^{calc} can be calculated from eq. 26 and 13.

$$k_2^{\text{calc}} = \frac{\beta k_1^{\text{obs}}}{[A]_0[\alpha - z(\alpha\beta + \beta - \alpha)]} \tag{26}$$

Figures 4a and 4b show the ranges over which these straight line plots are found. They have been calculated for reactions followed until $[C] = 0.5[C]_e$ (Fig. 4a) and $0.75[C]_e$ (Fig. 4b) (i.e. $\phi = 0.5$ and 0.75, respectively). The cases when $\beta = 1$ correspond to a second-order reaction going to completion. This has been treated above.

Example. The kinetics of hydrolysis of triphenylchlorogermane can be followed by stopped-flow conductance measurements [7]. A first-order plot of data over the first two half lives from the reaction of triphenylchlorogermane (2.47×10^{-3} mol dm^{-3}) in aqueous ether/acetone ($[H_2O] = 6$ mol dm^{-3}) gives a good 'first-order' plot with $k_1^{\text{obs}} = 3.35$ s^{-1}. However these hydrolyses are incomplete, and equilibrium conductance measurements show that for these concentrations $\beta = 0.166$. For the reaction scheme represented by eq. 9 and 10, the true first-order rate coefficient is given by eq. 12. For a reaction followed for two apparent half-lives, $\phi = 0.75$ and $z = 0.459$ (eq. 13). Thus $k_1 = 0.166 \times 3.35/[1 + 0.459(1 - 0.166)]$ which comes to

0.402 s^{-1}. This agrees well with the figure of 0.405 s^{-1} obtained by the full data treatment using eq. 11. It is much simpler to obtain the true rate coefficients from k_1^{obs} by eq. 12 than to use eq. 11 on the kinetic measurements.

Calculation. For each kinetic case the time, t_ϕ, at which the product reaches fraction ϕ of its concentration at the end of reaction, ($[\text{P}]_\infty$), was calculated from the appropriate integrated rate equation, assuming arbitrary values for the concentrations and rate coefficients. Then the concentration of product was calculated at 20 equally-spaced times from 0 to t_ϕ. These concentration-time pairs together with $[\text{P}]_\infty$, were used to calculate a pseudo-first-order rate coefficient, k_1^{obs}, from the slope of a plot of $\ln([\text{P}]_\infty - [\text{P}]_t)$ against time. Such plots are equivalent to plots of $\ln | M_\infty - M_t |$ against time, as M is related linearly to [P] (eq. 4). Suitable computer programs were written to perform these calculations.

Conclusions

Plots of $\ln | M_\infty - M_t |$ against time are usually only used to obtain rate coefficients for first-order reactions. Surprisingly, perhaps, such plots give good straight lines for many other common reaction schemes. This leads to a simple method of getting rate coefficients from time-concentration data for a variety of reaction schemes which have complicated integrated rate equations. It is especially useful if kinetic studies have been made and it is later realised that another rate law may be appropriate. The equations are summarised in Table 5. This novel treatment comes about because the integrated rate equations can be partitioned into an exponential part and a modifier. The surprising feature is the wide range of conditions over which the exponential part is approximately the same as for a first-order reaction.

Table 5

Summary of equations needed to calculate rate coefficients from k_1^{obs}, obtained from plots of $\ln | M | - M_{t\infty}$ against time

Reaction scheme	α	β	To obtain k_1 multiply k_1^{obs} by
First order			
$\text{A} \overset{k_1}{\rightleftharpoons} \text{B}$		$[\text{B}]_e/[\text{A}]_0$	β
$\text{A} \overset{k_1}{\rightleftharpoons} \text{B} + \text{C}$		$[\text{B}]_e/[\text{A}]_0$ $[\text{C}]_e/[\text{A}]_0$	$\beta/[1 + z(1 - \beta)]$
			To obtain k_2 multiply k_1^{obs} by
Second order			
$\text{A} + \text{B} \xrightarrow{k_2} \text{products}$	$[\text{B}]_0/[\text{A}]_0$		$1/\{[\text{A}]_0(\alpha - z)\}$
$\text{A} + \text{B} \overset{k_2}{\rightleftharpoons} \text{C}$	$[\text{B}]_0/[\text{A}]_0$	$[\text{C}]_e/[\text{A}]_0$	$\beta/\{[\text{A}]_0(\alpha - z\beta^2)\}$
$\text{A} + \text{B} \overset{k_2}{\rightleftharpoons} \text{C} + \text{D}$	$[\text{B}]_0/[\text{A}]_0$	$[\text{C}]_e/[\text{A}]_0$ $[\text{D}]_e/[\text{A}]_0$	$\beta/\{[\text{A}]_0[\alpha - z(\alpha\beta + \beta - \alpha)]\}$

$z = 1 + \phi/\ln(1 - \phi)$ where ϕ = fraction of reaction studied ($= x_{(\text{last point})}/x_\infty$)

Appendix - Derivation

Consider the equilibrium described by eq. 9 and 10. Let $a = [\mathrm{A}]_0$, $x = [\mathrm{B}]_t = [\mathrm{C}]_t$, and $x_e = [\mathrm{B}]_e = [\mathrm{C}]_e$. When straight line "first-order" plots of $\ln|M_\infty - M_t|$ against time are found we can write eq. A1.

$$d(\ln|M_\infty - M_t|)/dt = -k_1^{obs} \tag{A1}$$

Using eq. 4 this leads to eq. A2.

$$d[\ln(x_e - x)]/dt = k_1^{obs} \tag{A2}$$

This can be rewritten as eq. A3.

$$\frac{d[\ln(x_e - x)]}{dx} \cdot \frac{dx}{dt} = k_1^{obs} \tag{A3}$$

When βa is substituted for x_e and the first term differentiated we obtain eq. A4.

$$\frac{1}{a\beta} \cdot \frac{1}{(1 - x/a\beta)} \cdot \frac{dx}{dt} = k_1^{obs} \tag{A4}$$

Now for equilibrium 9 dx/dt can be obtained from eq. 10. As $k_1/k_{-2} = x_e^2/(a - x_e)$ we can substitute for k_{-2} in eq. 10 to get get eq. A5.

$$dx/dt = ak_1[1 - (x/a\beta)][1 + (1 - \beta)(x/a\beta)] \tag{A5}$$

When combined with eq. A4 this gives eq. A6.

$$[1 + (1 - \beta)(x/a\beta)]k_1/\beta = k_1^{obs} \tag{A6}$$

This rearranges to eq. A7.

$$k_1 = \beta k_1^{obs}/[1 + (1 - \beta)(x/a\beta)] \tag{A7}$$

The concentration-time curve can be written as eq. A8.

$$x = a\beta[1 - \exp(-k_1^{obs}t)] \tag{A8}$$

If reaction is studied until $x = \phi x_e$ the value of x to use in eq. A7 is an average x value up to the time when $x = \phi x_e$. This can be written as eq. A9 where t_ϕ is the time when $x = \phi x_e$.

$$x_{av} = \left(\int_0^{t_\phi} x \, dt\right) \Big/ \left(\int_0^{t_\phi} dt\right) \tag{A9}$$

After integration we get x_{av} as $a\beta[1 + \phi/\ln(1 - \phi)]$. When this is substituted into eq. A7 we get eq. 12 and 13.

Equations 17, 20, and 26 can be obtained similarly by substitution of the appropriate dx/dt, eq. 15, 19 or 22, into eq. A4.

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