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THE INFLUENCE OF AN INTERMEDIATE ON REACTION KINETICS IN ORGANOMETALLIC SYSTEMS: SECOND-ORDER CONDITIONS

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Summary

In a spectrophotometric study of the kinetics of a bimolecular reaction proceeding via an intermediate, A + B → C → D, the kinetic results can appear to fit the rate equation for the simpler bimolecular process A + B → D. The conditions for this to occur are discussed and are illustrated with data from the reaction of $[M(cp)(CO)_3(SnMe_3)]$ with iodine (M = Mo, W).

Introduction

In an earlier paper [1] it was shown that when the kinetics of reactions are followed by spectrophotometry it is possible for the kinetics of consecutive first-order reactions (eq. 1) to appear

$$A \xrightarrow{k_{AB}} B \xrightarrow{k_{BC}} C \qquad (1)$$

as if they arise from a simple first-order process (eq. 2).

$$A \xrightarrow{k_1^{obs}} C \qquad (2)$$

The apparent first-order rate coefficient, k_1^{obs}, calculated from experimental data can be both higher or lower than k_{AB}, depending on the species whose concentration is measured during reaction. A bimolecular reaction proceeding through an intermediate (eq. 3) can give rise to the same behaviour when

$$A + B \overset{k_1}{\rightarrow} C \overset{k_2}{\rightarrow} D \qquad (3)$$

studied under pseudo-first-order conditions (i.e. with an excess of either A or B). In this paper the theory is developed to show how similar features can be observed under second-order conditions, and these effects are demonstrated in kinetic studies of the reactions of $[M(cp)(CO)_3(SnMe_3)]$ with iodine (M = Mo, W).

Calculations

The integrated rate equations for a second-order reaction followed by a first-order step (eq. 3) have been discussed by Emanuel and Knorre [2], and Kelen [3]. If A and B both have an initial concentration a_0 the time dependences of the concentrations of A, B, and C are given by equations 4 to 6. The integral in

$$[\mathrm{A}] = a_0/(1 + a_0 k_1 t) \tag{4}$$

$$[\mathrm{C}] = \exp(-k_2 t) \int_0^t k_1 a_0^2 \exp(k_2 u)\, \mathrm{d}u/(1 + a_0 k_1 u)^2 \tag{5}$$

$$[\mathrm{D}] = a_0 - [\mathrm{A}] - [\mathrm{C}] \tag{6}$$

eq. 5 cannot be evaluated explicitly. For any particular case it can be evaluated numerically using Simpson's Rule and a suitable computer program [4], and Emanuel and Knorre have shown how the logarithmic integral, li(x), can be used to calculate this term [2].

If the kinetics of a second-order reaction (eq. 7) starting with equal concentrations of A and B are studied by measuring absorbances (A) at different times, a plot of F (eq. 8) against time should be linear with slope k^{obs}. (A_∞, A_0, A_t are

$$\mathrm{A} + \mathrm{B} \xrightarrow{k^{\mathrm{obs}}} \mathrm{D} \tag{7}$$

$$F = \frac{1}{a_0} \frac{A_t - A_0}{A_\infty - A_t} \tag{8}$$

measured absorbances at times ∞, 0, and t; a_0 = initial concentration of A and B).

If reaction proceeds via an intermediate (eq. 3) a plot of F against time may still be linear, depending on the relationship between k_1, k_2, and the molar absorptivities of A, B, C, and D. For instance, if A and/or B absorb and C and D do not, a plot of F against time will be a straight line with slope k_1, as only the first step is detected.

For the case where A and B do not absorb, but C and D do, the absorbance A_t is given by eq. (9) (if pathlength = 1 cm). As A_0 will be zero and $A_\infty = a_0 \epsilon_\mathrm{D}$

$$A_t = [\mathrm{C}]\epsilon_\mathrm{C} + [\mathrm{D}]\epsilon_\mathrm{D} \tag{9}$$

(ϵ_C and ϵ_D are the molar absorptivities of C and D) eq. 8 can be rewritten as eq. 10.

$$F = \frac{[\mathrm{C}]\dfrac{\epsilon_\mathrm{C}}{\epsilon_\mathrm{D}} + [\mathrm{D}]}{a_0\left(a_0 - [\mathrm{C}]\dfrac{\epsilon_\mathrm{C}}{\epsilon_\mathrm{D}} - [\mathrm{D}]\right)} \tag{10}$$

For each of a series of second-order conditions (chosen ratios of $\epsilon_\mathrm{C}/\epsilon_\mathrm{D}$ and $k_2/a_0 k_1$) values of F at times corresponding to a series of 20 intervals up to two apparent half-lives (i.e. when $A_t = 0.75 A_\infty$) were calculated using equations 4, 5, 6, and 10. The integral in eq. 5 was evaluated numerically using Simpson's Rule [4]. The slopes ($=k^{\mathrm{obs}}$) and correlation coefficients r, for the least-squares

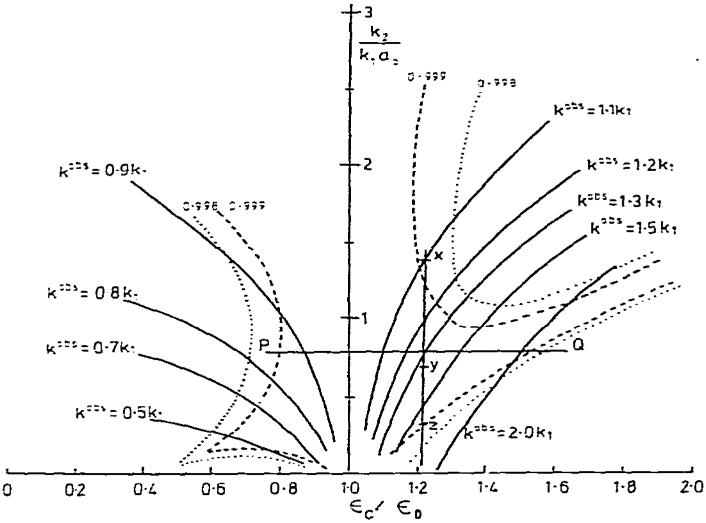

Fig. 1. Plot showing dependence of k^{obs} upon k_2/k_1a_0 and ϵ_C/ϵ_D. The coordinates of any point within the dashed lines describe a system where a plot of F (eq. 8 see text) against time is approximately linear ($r > 0.999$) giving rate coefficients k^{obs} which are greater than k_1 (if $\epsilon_C/\epsilon_D > 1$) or less than k_1 (if $\epsilon_C/\epsilon_D < 1$). Solid lines link points where k^{obs} is constant. For lines X, Y, Z, and PQ see text. (Within the dotted lines $r > 0.998$.)

plots of F against time were then calculated. Figure 1 shows the range of ϵ_C/ϵ_D and k_2/a_0k_1 where such plots are good straight lines ($r > 0.999$). Unlike the analogous system of two consecutive first-order reactions [1] there are no conditions where plots of F against time are exactly linear, but most workers would readily accept a line with 20 points with a correlation coefficient of 0.999 or more as satisfactorily linear. It is often very difficult to get even this degree of linearity when using hard-to-handle, air-sensitive organometallic compounds. From Fig. 1 it can be seen that the apparent rate coefficient, k^{obs}, can be greater than, equal to, or less than k_1, the second-order rate coefficient, which would be obtained if only A and B absorbed and C and D did not, or if there were no intermediate C.

For a reaction following eq. 3 with unequal initial concentrations a_0' and b_0 of A and B, respectively, equations 4 to 6 are replaced by 11 to 13 [2]. For second-order conditions (eq. 7) with unequal initial concentrations of reactants

$$[A] = a_0'(b_0 - a_0')/\{b_0 \exp[k_1(b_0 - a_0')t] - a_0'\} \tag{11}$$

$$[C] = k_1(b_0 - a_0')^2 b_0 a_0' \exp(-k_2 t) \times \int_0^t \exp\{[k_1(b_0 - a_0') + k_2]u\}\, du/\{b_0 - a_0')u] - a_0'\}^2 \tag{12}$$

$$[D] = a_0' - [A] - [C] \tag{13}$$

a plot of F' (eq. 14) [where $x = a_0'(A_t - A_0)/(A_\infty - A_0)$ if $b_0 > a_0'$] against time

$$F' = \frac{1}{(b_0 - a_0')} \ln\left[\frac{a_0'(b_0 - x)}{b_0(a_0' - x)}\right] \tag{14}$$

is linear with slope k^{obs}. In a similar way to that discussed above, plots of F' against time can be linear if reaction proceeds via an intermediate. Values of F' were calculated using equations 11, 12, 13 and 9 in a similar way to that described above and values of k^{obs} evaluated. The results show that provided a'_0 and b_0 do not differ by more than 10%, linear plots of F' against time are obtained under the conditions shown in Fig. 1 if a_0 is replaced by $(b_0 + a'_0)/2$. If $b_0/a'_0 > 10$ the system can be regarded as one with consecutive first-order reactions as previously described [1]. It is difficult to show graphically the conditions where all such linear plots of F' against time would be obtained as three variables are involved (b_0/a'_0, ϵ_C/ϵ_D, and k_2/k_1).

Results and discussion

The reaction of $[Cr(cp)(CO)_3(SnMe_3)]$ with iodine (eq. 15, M = Cr) has been shown to take place via an intermediate [5].

$$[M(cp)(CO)_3(SnMe_3)] + I_2 \xrightarrow[\substack{\text{cyclohexane} \\ 30.0^\circ C}]{CCl_4 \text{ or}} [M(cp)(CO)_3(I)] + Me_3SnI \qquad (15)$$

When the kinetics of the iodination of the analogous molybdenum and tungsten derivatives were studied (eq. 15, M = Mo, W) under pseudo-first-order conditions the observed second-order rate coefficient varied according to whether the disappearance of iodine or the appearance of product was being monitored [1,6]. This is consistent with reaction via an intermediate. The kinetics of these reactions have now been studied under second-order conditions (concentration of complex about 10% greater than the concentration of iodine). Under these second-order conditions it is possible to use conventional methods rather than stopped-flow to monitor absorbance changes with time.

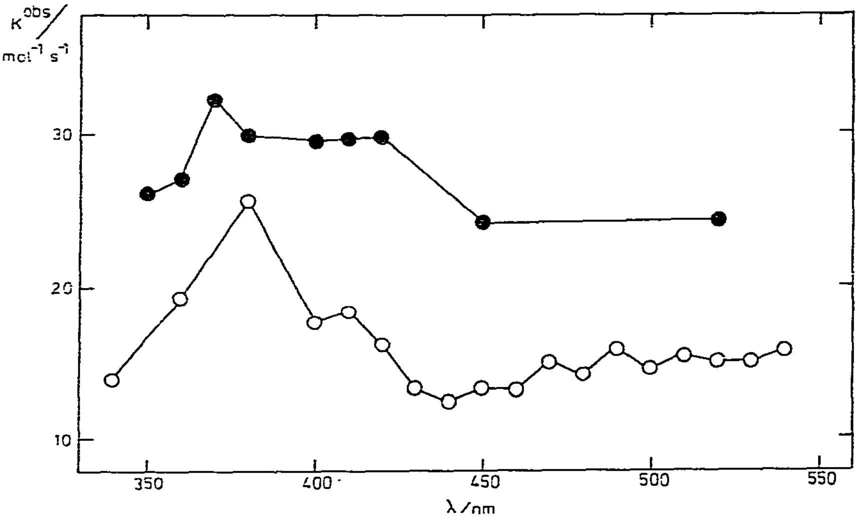

Fig. 2. Apparent second order rate coefficients, k^{obs}, for reactions of $[M(cp)(CO)_3(SnMe_3)]$ with iodine in cyclohexane at 30.0°C plotted against wavelengths used to monitor reaction ● M = Mo; ○ M = W. Initial concentrations $[M(cp)(CO)_3(SnMe_3)] = 6.3 \times 10^{-4}$ mol dm^{-3}., $[I_2] = 5.8 \times 10^{-4}$ mol dm^{-3}.

TABLE I

RATE COEFFICIENTS k^{obs} FOR REACTION OF [W(cp)(CO)$_3$(SnMe$_3$)] WITH I_2 IN CYCLOHEXANE AT 30°C, λ = 380 nm

10^3 × concn. [a] (mol l^{-1})	k^{obs}(l mol^{-1} s^{-1}) [b]	k^{obs}/k_1 [c]
3.26	18.9(5)	1.26
6.39	23.7(9)	1.58
12.54	44.6(8)	2.97

[a] Average concentration given. [W(cp)(CO)$_3$(SnMe$_3$)] 10% higher than [I_2]. [b] Number of separate runs in parentheses. [c] k_1 = 15.0 l mol^{-1} s^{-1} from experiment at 520 nm.

Absorbance changes were followed for up to two half-lives and apparent second-order rate coefficients, k^{obs}, were calculated from the plots of F' (eq. 14) against time, which were good straight lines. Fig. 2 shows that these rate coefficients varied with the wavelength of light used to monitor reaction. This variation of k^{obs} with wavelength arises as reaction 15 is not a simple second order process (eq. 7) but a two-stage reaction (eq. 3). The molar absorptivities of A, B, C, and D will all vary with wavelength so that although k_1 and k_2 are fixed for each compound, k^{obs} will depend on the molar absorptivities of the species present. For any system at constant initial concentration k^{obs} must lie on a horizontal line on Fig. 1 such as PQ. Exactly where on the line depends on the molar absorptivities.

Good confirmation of this comes from studies at a fixed wavelength when the starting concentrations are changed. Consider a reaction system described by point X. A good second-order plot would be obtained with $k^{obs} = 1.1k_1$. If the initial concentrations of reactants are doubled the reaction would be described by point Y (as k_1, k_2, ϵ_C, and ϵ_D are constant) and k^{obs} would increase to ca $1.35k_1$. A further doubling of the initial concentration of reactants would give point Z with k^{obs} even larger at $1.7k_1$. This behaviour is found for the reaction of [W(cp)(CO)$_3$(SnMe$_3$)] with iodine at 380 nm, (Table 1). The k^{obs} values in Table 1 do not change exactly as predicted in Fig. 1 as the latter is calculated on the assumption that the reactants do not absorb, whereas at 380 nm [W(cp)(CO)$_3$(SnMe$_3$)] does absorb somewhat. To show the effect on k^{obs} of reactant absorbance as well as intermediate and product is difficult on a two-dimensional graph.

Conclusion

Kinetic studies of reactions which proceed via an intermediate can give misleading results if the presence of an intermediate is ignored. The kinetic data can appear to fit the appropriate integrated second-order equation to give a second-order rate coefficient. However, the presence of the intermediate will cause the value of this apparent rate coefficient to vary with the wavelength of light used to monitor the reaction, and it will also vary with the initial concentrations of the reactants.

Experimental

[Mo(cp)(CO)$_3$(SnMe$_3$)] and [W(cp)(CO)$_3$(SnMe)] were prepared and purified as previously described [6]. A 0.1 cm^3 portion of I$_2$ was quickly added and mixed with 3.0 cm^3 of a solution of the appropriate organometallic compound contained in a thermostatted cuvette at 30.0°C. The absorbances were measured with a Unicam SP500 spectrophotometer in the 'direct-read out' mode, and transmittances recorded on a chart recorder.

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