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THE INFLUENCE OF AN INTERMEDIATE ON REACTION KINETICS IN ORGANOMETALLIC SYSTEMS: FORMATION OF PRODUCTS APPARENTLY FASTER THAN THE DISAPPEARANCE OF REACTANTS

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Summary

In a spectrophotometric study of the kinetics of reactions in solution it is possible to find that products are apparently formed faster than the reactants are used up. This can arise when reaction proceeds *via* an intermediate in a two-step mechanism as found in many organometallic systems.

Introduction

During a study of the kinetics of the cleavage of the metal—metal bonds in $[Mo(cp)(CO)_3(SnMe_3)]$ (cp = η-cyclopentadienyl) by iodine in solution (tetrachloromethane, 30°C, eq. 1) [1] we measured absorbance (A) changes at two

$$[Mo(cp)(CO)_3(SnMe_3)] + I_2 \xrightarrow{k_2^{Mo}} [Mo(cp)(CO)_3I] + SnMe_3I \qquad (1)$$

wavelengths (*a*) where only iodine absorbs (540 nm) and (*b*) where $[Mo(cp)(CO)_3I]$ absorbs (430 nm), and the other species in eq. 1 do not absorb. In the presence of a tenfold excess of $[Mo(cp)(CO)_3(SnMe_3)]$ pseudo-first-order kinetics were found, and the rate coefficients, k_1^{obs}, were calculated from the slope of linear plots of $\ln(A_\infty - A_t)$ against time where measurements extended to about two half-lives. However at the same concentration of $[Mo(cp)(CO)_3(SnMe_3)]$ k_1^{obs} values from the rate of appearance of product [absorbances at wavelength *b*] were 33% greater than those found from the rate of disappearance of the reactants (using absorbances taken at wavelength *a*). Either series of k_1^{obs} values when divided by the concentration of $[Mo(cp)(CO)_3(SnMe_3)]$ give constant values for k_2^{Mo}, 226 l mol^{-1} s^{-1} (at 540 nm) and 301 l mol^{-1} s^{-1} (at 430 nm).

At first sight it appears impossible that products can appear faster than the reactants are used up. We suggested [1] that these results could be explained if the reaction path included an intermediate, and I present here an analysis of this behaviour and show that it could arise in many other systems.

Calculation and results

For a reaction in solution taking place by two consecutive first-order steps (eq. 2) the absorbance A_t at any time t will be given by eq. 3 where ϵ_A, ϵ_B, and

$$A \xrightarrow{k_1} B \xrightarrow{k_2} C \tag{2}$$

$$A_t = \epsilon_A l[A] + \epsilon_B l[B] + \epsilon_C l[C] \tag{3}$$

ϵ_C are the molar absorptivities of A, B, and C respectively, and l is the spectrophotometric cell length. Buckingham, Francis and Sargeson [2] have recently shown that the function $(A_\infty - A_t)$, the logarithm of which is plotted against time to obtain first-order rate coefficients, is given by eq. 4, where A_0 is the

$$A_\infty - A_t = l\,A_0\{[(k_2 - k_1)(\epsilon_A - \epsilon_C) - k_1(\epsilon_C - \epsilon_B)]\exp(-k_1 t) + k_1(\epsilon_C - \epsilon_B)\exp(-k_2 t)\}/(k_1 - k_2) \tag{4}$$

initial concentration of A. A linear plot of $\ln(A_\infty - A_t)$ will be obtained if (*a*) $k_1 << k_2$, (b) $k_2 << k_1$, (c) $\epsilon_B = \epsilon_C$, or (d) $k_2/k_1 = (\epsilon_B - \epsilon_A)/(\epsilon_C - \epsilon_A)$. Conditions a, b, and c lead to observed rate coefficients equal to k_1, k_2, and k_1 respectively and are well understood. Condition d can lead to rate coefficients which are less easy to interpret.

If the formation of products is being followed at a wavelength where the reactant does not absorb ($\epsilon_A = 0$) condition d simplifies to eq. 5. Provided eq. 5

$$k_2/k_1 = \epsilon_B/\epsilon_C \tag{5}$$

is true eq. 4 reduces to eq. 6 where $\phi = \epsilon_B/\epsilon_C$ and the reaction is observed as a

$$A_\infty - A_t = \epsilon_C l\,A_0 \exp(-\phi k_1 t) \tag{6}$$

first-order process. A rate coefficient, k_1^P, for the apparent rate of formation of product C calculated from the usual plot of $\ln(A_\infty - A_t)$ against time will equal ϕk_1.

Even if the rate and absorbance coefficients do not exactly satisfy eq. 5 (which is likely in practice) it is still possible to get A changing with time in a way which is almost exponential. Although there are no hard and fast rules, first-order plots of $\ln(A_\infty - A_t)$ against time are usually regarded as satisfactory if the data consist of about twenty absorbance—time pairs extending over two half lives, and the correlation coefficients for the plots are greater than 0.999. In kinetic studies on many organometallic reactions it is difficult to achieve this standard. Figure 1 shows which values of k_2/k_1 and ϕ give absorbances which give such satisfactory 'first-order' plots. To draw Fig. 1 (a) values of k_2/k_1 and ϕ were chosen, (b) values of $A_\infty - A_t$ were calculated at twenty equally spaced times in the first two apparent half-lives (i.e. up to the time when $A_t = 0.75A_\infty$), and (c) k_1^P and a correlation coefficient were calculated from a least-squares plot of $\ln(A_\infty - A_t)$ against time.

A similar analysis applies for a bimolecular reaction involving an intermediate (eq. 7) such as the reaction between [Mo(cp)(CO)$_3$(SnMe$_3$)] and iodine. When

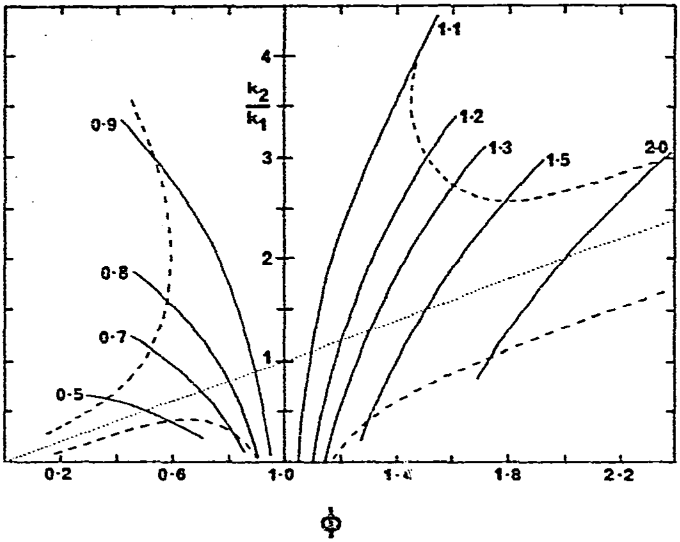

Fig. 1. The coordinates of any point inside the dashed lines describe a system where a plot of $\ln(A_\infty - A_t)$ against time is approximately linear with a correlation coefficient > 0.999 giving rate coefficients k_1^P greater than k_1 (if $\phi > 1$) or less than k_1 (if $\phi < 1$). Solid lines link points which give a constant value of k_1^P/k_1 as marked. The dotted line is where $k_2/k_1 = \phi$ and exact first-order plots are found.

the kinetics are studied under pseudo-first-order conditions (at least a tenfold

$$A + D \xrightarrow{k_3} B \xrightarrow{k_2} C \tag{7}$$

excess of D) the equations are as above with $k_3[D]$ replacing k_1.

Discussion

It is common to determine the kinetics of a reaction by following the increase of absorbance at a wavelength where the product absorbs and the reactants do not absorb. If plots of $\ln(A_\infty - A_t)$ against time are linear it is tempting to infer that a single step is rate-limiting. However if reaction proceeds *via* an intermediate (eq. 2) there are many possible values for the ratio of the rate coefficients of formation and decomposition of the intermediate (k_1/k_2) which will result in approximately linear first-order plots if the ratio of the extinction coefficients of intermediate and product (ϕ) is suitable. The rate coefficient k_1^P obtained from these plots can be less than, equal to, and even greater than k_1, the rate coefficient for the decomposition of reactant. It is easy to accept that formation of an intermediate can cause the rate of formation of products to appear to be slower than the rate of disappearance of reactant. What has not been recognised before is that formation of an intermediate can result in the anomaly of *products apparently being formed faster than reactants are used up*. Figure 1 shows that there is a considerable range of values for k_2/k_1 and ϕ for which it is possible to get values for the apparent rate of product formation, k_1^P, up to at least twice that of the rate of disappearance of reactants, k_1. For values of k_2/k_1 and extinction coefficients which satisfy eq. 5 an *exact* first-order plot will be found (dotted line on Fig. 1).

If both k_1 and k_1^{P} are measured for a reaction it is not possible to calculate the separate values of k_2/k_1 and ϕ. For a given ratio of k_1^{P}/k_1 such as the value of 1.33 found for the reaction of $[\mathrm{Mo(cp)(CO)_3(SnMe_3)}]$ with iodine there is a range of possible values for k_2/k_1 and ϕ shown by the solid lines in Fig. 1. Only if the kinetics deviate considerably from first order is it possible to obtain both k_2/k_1 and ϕ by suitable curve fitting as has been done for the kinetics of the reactions between iodine and $[\mathrm{Cr(cp)(CO)_3(SnMe_3)}]$ [3] and $[\mathrm{Re(CO)_5(SnMe_3)}]$ [4]. Figure 1 shows that in order for k_1^{P} to differ from k_1 the value of ϕ (i.e. $\epsilon_{\mathrm{B}}/\epsilon_{\mathrm{C}}$) will usually lie within an order of magnitude of unity. In a reaction the product C and a preceding intermediate B are quite likely to have a fairly similar molecular structure, and consequently their extinction coefficients are likely to be similar to each other.

It follows that in studies of a reaction which appears to be first order it is desirable to check for the presence of an intermediate either by comparing k_1^{P} with k_1 or, if the reactants do not absorb at a suitable wavelength, by checking the constancy of k_1^{P} by following the kinetics at a number of wavelengths. However in many organometallic systems it is not possible to take kinetic measurements at more than one wavelength and consequently it is easy to overlook the formation of an intermediate and from the 'first-order' kinetics observed to ascribe a simple one-step mechanism to the reaction.

The above treatment will apply if the kinetics are determined from measurements of a physical property other than absorbance (e.g. conductance) where an intermediate can make a contribution to the measurement.

Weighting of absorbances. Many UV spectrophotometers have a linear transmittance (T) scale with a constant precision (ca. 0.01) over the whole scale. If the standard deviation of transmittance is σ_T the corresponding standard deviation of an absorbance reading, σ_A, is given by eq. 8, and the appropriate standard

$$\sigma_A = (10^A/2.303)\,\sigma_T \qquad (8)$$

deviation, $\sigma_{\ln}$, of a point on a $\ln(A_\infty - A_t)$ plot is given by either eq. 9 (if $\sigma_{T_\infty} = 0$) or eq. 10 (if $\sigma_{T_\infty} = \sigma_T$).

$$\sigma_{\ln} = \sigma_T\ 10^{A_t}/[2.303(A_\infty - A_t)] \qquad (9)$$

$$\sigma_{\ln} = \sigma_T(10^{2A_t} + 10^{2A_\infty})^{1/2}/[2.303(A_\infty - A_t)] \qquad (10)$$

Points on the $\ln(A_\infty - A_t)$ plot where $A_\infty - A_t$ is small will be less accurate (although all T readings have the same precision) and should be weighted appropriately when calculating the slope of the line [5]. Fortunately k_1^{P} values calculated using the correct weighting factors are quite close to those obtained without weighting [e.g. for $k_2/k_1 = 3$ and $\phi = 1.4$, $k_1^{\mathrm{P}}/k_1 = 1.15$ (unweighted) and 1.18 (weighted); and for $k_2/k_1 = 0.01$ and $\phi = 1.1$, $k_1^{\mathrm{P}}/k_1 = 1.21$ (unweighted) and 1.18 (weighted)]. Figure 1 was drawn using k_1^{P} values calculated without weighting as most workers calculate rate coefficients this way. Weighted values would not change Fig. 1 by very much, and would not affect any of the other arguments.

Conclusions

In a study of a reaction where the rate of formation of products is being measured under first-order conditions it is possible that formation of an intermediate will affect the measurements. Although satisfactory 'first-order' plots may be obtained the rate coefficients calculated will not be a true measure of either the rate of disappearance of the reactants or the rate of formation of the products. The anomaly can arise where the products appear to be formed faster than the reactants are consumed. Under certain conditions perfect 'first-order' plots will be obtained and the kinetics completely mask the complexity of the reaction.

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