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A Possible Mechanism for the Reaction Between 2,2′-Bipyridyl and Di-μ-chlorobis(cycloocta-1,5-diene)dirhodium(I) in Dimethylformamide

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The unusual dependence of the rate constant for the slow step on the initial concentration of dimer $[(COD)RhCl]_2$ *can be explained if the reactive intermediate is the ion pair* $[(COD)Rh(Bipy)]^+[(COD)RhCl_2]^-$.

Introduction

A kinetic study of the reaction between 2,2′-bipyridyl and a series of neutral rhodium(I) amine complexes, [(COD)RhCl(Am)], was reported [1] by Robb and Nicholson. They found that, in methanol, the reactions follow a two-term rate law of the form:

$$k_{obs} = k_s + k_y[\text{Bipy}]$$

In a subsequent paper [2] they described the reactions between various amines and the neutral complex [(COD)RhCl(Piperidine)]. These reactions also obey a two-term rate law:

$$k_{obs} = k_1 + k_y\,[\text{Amine}]$$

They also referred to the reaction between bipyridyl and [(COD)RhCl(Pip)] in methanol, but these results have not yet been published. Details are given in Nicholson's dissertation [3] together with the results of a study of the reactions in dimethylformamide (DMF) between bipyridyl and $[(COD)RhCl]_2$, and between bipyridyl and [(COD)RhCl(Pip)]. Several aspects of the results are unusual. Firstly, both dimer and monomer yield essentially the same rate constants for the reaction. Secondly, the reaction obeys a two-part rate law, the first step being relatively fast while the second is slow, the two steps being consecutive.

$$k_{overall} = k_{fast} + k_{slow};$$

$$k_{fast} = k_2[\text{Bipy}];$$

k_{slow} is independent of [Bipy]

where k_{fast} and k_{slow} are pseudo first order rate constants (the concentration of bipyridyl was far greater than that of the complex). Thirdly, and of most interest, k_{slow} is proportional to the *initial* total concentration of rhodium, C_o

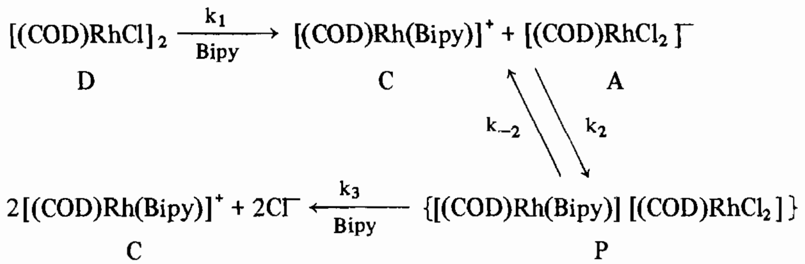
$$k_{slow} = k_1C_o$$

Lastly, the fast reaction stops well before all rhodium is converted to product.

It is possible to explain these results in terms of the reaction scheme outlined below.

Theoretical

Before one can postulate a plausible scheme for any complicated reaction, it is necessary to establish what the likely transient species will be. In the present case, the product of the reaction is $[(COD)Rh(Bipy)]^+$ independent of whether the starting material is $[(COD)RhCl]_2$ or [(COD)RhCl(Pip)]. While it has been established [1, 2] that a solvated speces [(COD)RhCl(S)] is formed from [(COD)RhCl(Pip)] in methanol, the formation of chloro-bridged dimeric species is commonly found for platinum-group metals in non-polar or non-coordinating solvents. For example, the complexes $[Pt_2Cl_4L_2]$ are stable in DMF and nitrobenzene [4, 5]. Thus one may justifiably assume that all rhodium is initially present as the dimer $[(COD)RhCl]_2$ in DMF. There are several possible intermediates: singly-bridged or partly solvated dimeric species [6], the anion $[(COD)RhCl_2]^-$ [7], or an ion pair $[(COD)Rh(Bipy)]^+[(COD)RhCl_2]^-$ [8]. Of these, the anion may be expected to be relatively inert to substitution by amines because the analogous dicarbonyl compound $[(CO)_2RhCl_2]^-$ is not attacked by amines [7, 9] and is sufficiently stable to be isolated as a crystalline salt and have its structure determined by X-ray diffraction [10, 11]. The formation of the ion pair is favoured in non-coordinating solvents but it is difficult to obtain pure [8], presumably because of its reactivity. In addition, attack by the lone pairs of the bipyridyl will be facilitated because the negative charge of the $[(COD)RhCl_2]^-$ is neutralised. For these reasons, the ion-pair is chosen as the reacting species in the slow step of the reaction scheme between bipyridyl and $[(COD)RhCl]_2$



The rate law is derived as follows:

Assume that the bipyridyl attacks only the dimer D and the ion-pair P to yield the cationic product C, and that the anion A is relatively inert to attack by the bipyridyl. Since bipyridyl is present in excess (pseudo first order conditions), it is clear that the first (fast) step is a first order reaction with respect to product formation, and that the pseudo first order rate constant is proportional to the concentration of bipyridyl:

$$k_{fast} = k_1 [Bipy]$$

This was observed experimentally [3]. It is also evident that the fast reaction stops when D is depleted.

If the steady-state approximation is applied to the ion-pair

$$d[P]/dt = 0,$$

then the following is obtained

$$[P] = \frac{k_2 [C] [A]}{k_{-2} + k_3 [Bipy]} \qquad (1)$$

The rate of production of product in the slow step is given by

$$d[C]/dt = k_3 [P] [Bipy] \qquad (2)$$

and hence

$$\frac{d[C]}{dt} = \frac{k_3 k_2 [C] [A] [Bipy]}{k_{-2} + k_3 [Bipy]} \qquad (3)$$

Since the concentration of bipyridyl is very large, it is assumed that the rate of attack on P by bipyridyl is greater than the rate of dissociation of the ion pair, *i.e.* $k_3 [Bipy] \gg k_{-2}$.

As a consequence, equation (3) reduces to

$$d[C]/dt = k_2 [C] [A] \qquad (4)$$

By the time the fast reaction is complete and the slow reaction is observable, D has disappeared and all rhodium (except for the negligible amount in P) is in the form of A or C. Therefore

$$[A] = C_0 - [C] \qquad (5)$$

and the rate equation becomes

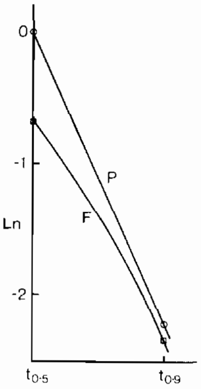


Figure 1. Graphical illustration of the rate laws: $d\ln(1/\alpha - 1)/dt = -C_0 k_2$, straight line P and $d\ln(1 - \alpha)/dt$, curved line F. These are obtained by calculating $\ln(1/\alpha - 1)$ and $\ln(1 - \alpha)$ for $\alpha = 0.5$ (points at $t_{0.5}$) and $\alpha = 0.9$ (points at $t_{0.9}$), the points ○ on curve P were joined by a straight line, the values of t for $\alpha = 0.6, 0.7, 0.8$ were calculated and the values of $\ln(1 - \alpha)$ were then plotted for the appropriate value of t. The curve F runs through these calculated points.

$$d[C]/dt = k_2 [C](C_0 - [C]) \qquad (6)$$

or

$$\frac{d[C]}{[C](C_0 - [C])} = k_2 dt \qquad (7)$$

Since

$$\frac{d[C]}{[C](C_0 - [C])} = -\frac{1}{C_0} d\ln\frac{(C_0 - [C])}{[C]} \qquad (8)$$

it follows that

$$d\ln\{(C_0 - [C])/[C]\}/dt = -C_0 k_2 \qquad (9)$$

Setting $\alpha = [C]/C_0$ the rate equation becomes

$$d\ln(1/\alpha - 1)/dt = -C_0 k_2 \qquad (10)$$

By the time the fast reaction is complete and the slow reaction becomes observable half of the rhodium present is converted to product and, hence, at t = 0, $[C] \geqslant C_0/2$ ($\alpha \geqslant ½$). It is important to stress here that a reaction obeying the above rate law, as is observed from $0.5 \leqslant \alpha \leqslant 1$, will almost certainly be mistaken for a first order reaction. This is illustrated in the figure. A hypothetical reaction obeying this rate law will yield the straight line. The curve would be obtained if it were assumed that the reaction is first order ($d\ln(1-\alpha)/dt = -k_{obs}$). For most of the experimental data, the small curvature probably could not be detected, and the plot would be taken as a straight line thus giving rate constants which are 20–25% in error.

Mathematically this can be illustrated as follows:

$$d\ln(1/\alpha - 1)/dt = d\ln\{1/\alpha(1-\alpha)\}/dt = d\{\ln(1-\alpha) - \ln\alpha\}/dt \qquad (11)$$

When $\alpha < 0.5$, $\ln\alpha > \ln(1-\alpha)$ and when $\alpha > 0.5$, $\ln(1-\alpha) > \ln\alpha$. The latter condition is the case here and hence, to a rough approximation,

$$d\{\ln(1-\alpha) - \ln\alpha\}/dt \cong d\{\ln(1-\alpha)\}/dt \qquad (12)$$

and

$$d\{\ln(1-\alpha)\}/dt \cong -C_0k_2 \qquad (13)$$

which occurs with the experimentally observed results.

A possible objection to the proposed mechanism is that it implies that half the rhodium must be converted to the product by the fast reaction, while the experimental results [3] indicated that about 80% had been converted by the time the fast reaction stopped. However, the measurements were spectroscopic and, since the absorption coefficient of A is unknown, there is no way of knowing whether a change of 80% in the optical density, OD, corresponds to 50% product formation. It is readily shown that

$$(OD - OD_\infty)_{fast} = (\epsilon_C + \epsilon_A - \epsilon_0)[C] \qquad (14)$$

and

$$(OD - OD_\infty)_{slow} = (\epsilon_c - \epsilon_A)[C] \qquad (15)$$

where OD_∞ is the optical density at the end of the respective reaction. Therefore, until the value of ϵ_A is known, there is no way to test this possible objection.

References

1 W. Robb and C. G. Nicholson, *Inorg. Chim. Acta, 7,* 645 (1973).
2 C. G. Nicholson and W. Robb, *Inorg. Chim. Acta, 8,* 41 (1974).
3 C. G. Nicholson, "A Mechanistic Study of Some Rhodium(I) Complexes", *Ph.D. Thesis,* University of Natal (1975).
4 J. Chatt and L. M. Venanzi, *J. Chem. Soc.,* 2787 (1955).
5 C. M. Harris, S. E. Livingstone and N. C. Stephenson, *J. Chem. Soc.,* 3697 (1958).
6 R. G. Pearson and M. M. Muir, *J. Am. Chem. Soc., 88,* 2163 (1966).
7 L. M. Vallarino, *Inorg. Chem., 4,* 161 (1965).
8 J. Chatt and L. M. Venanzi, *J. Chem. Soc.,* 4735 (1957).
9 E. Cetinkaya, A. W. Johnson, M. F. Lappert, G. M. McLaughlin and K. W. Muir, *J. Chem. Soc. Dalton,* 1236 (1974).
10 C. K. Thomas and J. A. Stanko, *Inorg. Chem., 10,* 566 (1971).
11 F. W. B. Einstein and C. R. S. M. Hampton, *Canad. J. Chem., 49,* 1901 (1971).