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Kinetics of the Oxidative Addition of Iodine to β-Diketonatobis(triphenylphosphite)rhodium(I) Complexes

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Abstract

The oxidative addition reactions of a number of Rh(I) complexes of the type [Rh(β-diketone)(P(OPh)$_3$)$_2$] with I$_2$ were studied in petroleum ether (80–100 °C). The reactions proceed via two consecutive first-order reactions to give the final product [Rh(β-diketone)(P(OPh)$_3$)$_2$(I)$_2$] with the iodide ligands in the axial positions. Various electronegative substituents of the β-diketone ligand have only a small influence on the reaction rates.

Introduction

The oxidative addition of the halogens to coordinatively unsaturated rhodium(I) complexes has received considerable attention in recent years. The majority of these studies dealt with the isolation and identification of these products [1–6]. A kinetic study by Kuwae *et al.* [7] dealt with the following oxidative addition reaction:

$$[\mathrm{Rh(EE)(L)_2}] + \mathrm{I_2} \longrightarrow [\mathrm{Rh(EE)(L)_2(I)_2}] \qquad (1)$$

where EE = dimethyldithiocarbamate (dtc) or acetylacetone (acac) and L = 2,4,6-trimethylphenylisocyanide. The results indicate that the reaction proceeds via a charge transfer complex, [Rh(EE)(L)$_2$]·I$_2$, which is rearranged in two consecutive zero-order reactions, with respect to the I$_2$ concentration, to give the *cis*-diiodo and finally the *trans*-diiodo complex. The structure of the final product was proposed on the basis of ^{1}H NMR and IR spectra, which indicate an octahedral geometry in which the EE-ligand and the two isocyanide ligands are in an equatorial plane and the two iodide ligands in the axial positions. The latter isomerization process was followed by a much slower reaction of *trans*-[Rh(EE)(L)$_2$(I)$_2$] with the excess iodine to give [Rh(EE)(L)$_2$(I$_3$)(I)].

We have recently reported [8–10] on the oxidative addition of iodomethane to [Rh(LL)(CO)(PX$_3$)] complexes (LL = β-diketones or cupferron, X = Ph, *p*-PhCl or *p*-PhOMe) for which the results were strongly in favour of an ionic S$_\mathrm{N}$2 two-step mechanism. This paper reports the kinetic study of the oxidative addition of iodine to various [Rh(β-diketone)(P(OPh)$_3$)$_2$] complexes in petroleum ether. The crystal structure determination [11] of the final reaction product, [Rh(TFAA)(P(OPh)$_3$)$_2$(I)$_2$], confirmed the *trans* addition of the iodide ligands.

Experimental

The [Rh(β-diketone)(P(OPh)$_3$)$_2$] complexes (β-diketone = acetylacetone (acac), benzoylacetone (BA), dibenzoylmethane (DBM), trifluoroacetylacetone (TFAA), trifluorobenzoylacetone (TFBA) and hexafluoroacetylacetone (HFAA)) were synthesized by methods described previously [11, 12]. Triple sublimed iodine was used throughout. Analytical grade petroleum ether (80–100 °C) was used as solvent, except in the case of [Rh(HFAA)(P(OPh)$_3$)$_2$] where CCl$_4$ was used as solvent due to the insolubility of the latter complex in petroleum ether. To, therefore, enable the comparison of the reaction rates of the different β-diketone complexes, the reaction rate of [Rh(TFBA)(P(OPh)$_3$)$_2$] was determined in both solvents.

The reaction rate constants were obtained by following the reactions at the given wavelengths (see Table II), using a Durrum, model D-110, stopped-flow spectrophotometer. An excess of iodine was used in order to achieve pseudo-first-order reaction conditions. The change in absorbance with time revealed that the overall reactions proceed via two consecutive reactions. The reaction rates of the two processes differ sufficiently to allow the graphical determination of the rate constants. Plots of $\ln(A_t - A_\infty)$ *versus* time for each process, were linear and the pseudo-first-order rate constants, k^1_obs and k^2_obs, are tabulated in Tables I and II.

The value of the equilibrium constant for reaction (2) was determined

$$[\mathrm{Rh(TFAA)(P(OPh)_3)_2(I)_2}] + \mathrm{I_2} \overset{K}{\rightleftharpoons} [\mathrm{Rh(TFAA)(P(OPh)_3)_2(I_3)(I)}] \qquad (2)$$

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TABLE I. Observed Rate Constants for the Two Consecutive Processes in the Reaction of [Rh(TFAA)(P(OPh)$_3$)$_2$] (1.46 × 10^{-4} mol dm^{-3}) with Excess I_2 at Various Temperatures (λ_{exp} = 415 nm)

Temperature (°C)	$[I_2] \times 10^3$ (mol dm^{-3})	$k^1_{obs} \times 10^{-1}$ (s^{-1})	$k^2_{obs} \times 10^2$ (s^{-1})
17	4.97	2.10	4.05
	3.97	1.75	3.58
	2.98	1.69	3.52
	1.99	1.56	4.76
24.9	4.97	4.80	5.08
	3.97	4.74	6.27
	2.98	4.84	6.08
	1.99	3.91	5.75
30.5	4.97	5.82	9.75
	3.97	7.70	8.85
	2.98	7.03	8.78
	1.99	7.39	8.11

TABLE II. Average[a] Observed Rate Constants for the Two Consecutive Processes in the Reaction of [Rh(β-diketone)(P(OPh)$_3$)$_2$] with Excess I_2[b] at 25.0 °C

β-diketone	λ_{exp}	k^1_{obs} (s^{-1})	k^2_{obs} (s$^{-1} \times 10^3$)
acac	415	31(8)	7.9(20)
BA	370	60(10)	9.7(10)
DBM	370	150(30)	14(2)
TFAA	415	46(4)	57(5)
TFBA	415	74(13)	60(2)
TFBA[c,d]	380	92(14)	
TFBA[d]	380	140(26)	40(7)
HFAA[d]	380	39(7)	4.4(10)

[a] Mean value of 3 to 5 kinetic runs. [b] $[I_2]$ were 10–60 fold excess with respect to the [Rh(I)]. [c] [Rh(I)]:$[I_2]$ = 1:1. [d] In CCl_4 medium.

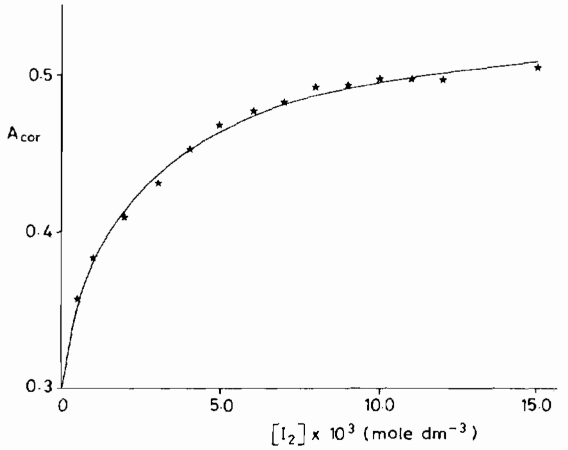


Fig. 1. Plot of A_{cor} (corrected absorbance) *vs.* $[I_2]$ at 25 °C in CCl_4. λ = 400 nm, [Rh(III)] = 7.5 × 10^{-5} mol dm^{-3}, $A_{cor} = A - [I_2]\epsilon_{I_2}$.

spectrophotometrically on a Hitachi 150-20 spectrophotometer. The $[I_2]$ was varied from 5 × 10^{-4} to 1.5 × 10^{-2} mol dm^{-3}. From the definition of *K*, the mass balance and Beer's Law, eqn. (3), can be derived

$$A = \frac{A_r + A_p K[I]_2}{1 + K[I]_2} \tag{3}$$

A is the absorbance at a given concentration of I_2, A_r and A_p are the absorbances of the reactant and product, respectively. The results are represented in Fig. 1. The value of *K* was determined as 3.5(5) × 10^2 dm^3 mol^{-1} by fitting the absorbance *versus* $[I_2]$ data to eqn. (3) by using a non-linear least-squares program [13]. The solid line in Fig. 1 is the computer fit of the data.

Results and Discussion

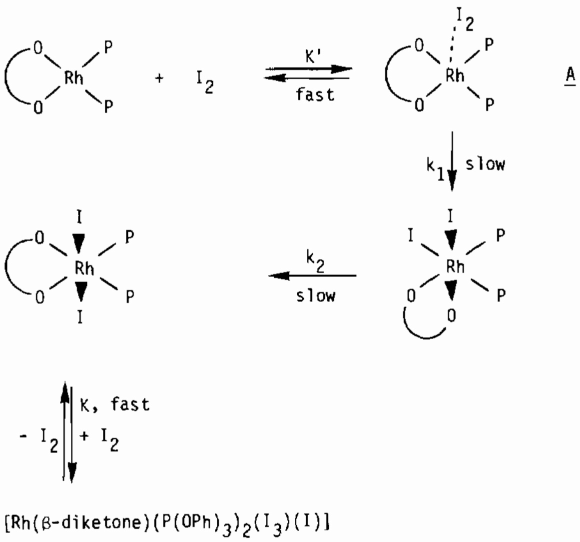
Immediately after mixing the Rh(I) and iodine solutions, an absorption maximum appeared at about 400 nm. The values of k^1_{obs} and k^2_{obs} were obtained by following the change in the absorbance of this absorption maximum. The decrease in the absorbance was very small (only about 0.03) and this may explain the relative large error in the values of k^1_{obs} and k^2_{obs}.

The kinetic results (shown for the reaction of [Rh(TFAA)(P(OPh)$_3$)$_2$] in Table I as an example) indicate that k^1_{obs} and k^2_{obs} are both essentially independent of the concentration of I_2. The rate constants for all the complexes are summarized in Table II. The zero-order dependence of the reaction rate on the $[I_2]$ is also proved by the fact that the value of k^1_{obs} for the reaction of [Rh(TFBA)(P(OPh)$_3$)$_2$] under second-order and pseudo-first-order conditions (excess I_2) are approximately the same, see Table II.

A concerted three-centre *cis*-addition is a well known mechanism for the oxidative addition of homonuclear molecules like H_2 and I_2 to metal complexes [14, 15]. The crystal structure determination of the product of the reaction between [Rh(TFAA)(P(OPh)$_3$)$_2$] and I_2, however, showed that the two iodide ligands are in the axial positions [11]. With this in mind, as well as the immediate appearance of an absorption maximum at about 400 nm, the observed two consecutive first-order reactions and the formation of the triiodide species, Scheme 1, is proposed.

The first step in the proposed mechanism, is the formation of the *cis*-diiodo complex via the charged transfer complex, A. According to this reaction scheme, k^1_{obs} is given by

$$k^1_{obs} = \frac{k_1 K'[I_2]}{1 + K'[I_2]} \tag{4}$$



Scheme 1.

When $K'[I_2] \gg 1$, eqn. (4) simplifies to $k^1_{obs} = k_1$. This is consistent with the kinetic results, since k^1_{obs} is independent of the concentration of I_2. Since the *cis–trans* isomerization proceeds intramolecularly, the scheme also predicts $k^2_{obs} = k_2$; thus independent of the I_2 concentration in agreement with the kinetic results. The final equilibrium was too fast to observe kinetically.

The k^2_{obs} step is characterized by a decrease in $(A_0 - A_\infty)$ when the concentration of I_2 is decreased and is spectrophotometrically unobserved when the reaction is done under second-order conditions. The occurrence of the second step under such conditions is, however, confirmed by the fact that the *trans*-diiodo complex ($[Rh(TFAA)(P(OPh)_3)_2(I)_2]$) was isolated from a reaction mixture in which $[Rh(TFAA)(P(OPh_3)_2]:I_2 = 1:1$ [11]. A small difference in the absorbances of the *cis*- and *trans*-diiodo complex is probably the reason why the k^2_{obs} step is spectrophotometrically undetectable at low $[I_2]$.

The determination of the stability constant of $[Rh(TFAA)(P(OPh)_3)_2(I_3)(I)]$, see Fig. 1, confirmed the formation of the triiodide species in a very fast (in contrast to a slow reaction proposed by Kuwae *et al.* [7]) reaction. The formation of the triiodide species (with a stability constant of about 350 dm^3 mol^{-1} for the TFAA complex) explains why the k_2 step is observed only at a relative high $[I_2]$. In this regard the coordination of I_3^- to metal ions has been proposed in a number of cases [7, 16, 17].

It is well known that the rate of the oxidative addition of CH_3I to metal complexes is influenced by electronic effects [8, 10, 18]. The reactivity of the complexes $[Rh(\beta\text{-diketone})(CO(PPh_3)]$ towards the oxidative addition of CH_3I increased for example 50 fold from β-diketone = hexafluoroacetylacetone to acetylacetone [8]. This order reveals the effect of electronegative substituents of the β-diketone (the electronegativity of CH_3 and CF_3 are 2.3 and 3.35 respectively [19]) on the nucleophilicity of these complexes and thus their reactivity towards oxidative addition reactions.

It is, however, apparent from the results in Table II that the substituents of the β-diketone have little effect on the rate of oxidative addition of iodine to these complexes. This may be explained by considering the proposed reaction scheme and the rate law, eqn. (4). The first rate determining step (k_1) is the rearrangement of the charge transfer complex and not only an oxidative addition reaction, while the second rate determining step (k_2) is an isomerization reaction.

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