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SUBSTITUTION REACTIONS OF Pt^{IV} BIS(DITERTIARYARSINE) COMPLEXES

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This work is part of a series of systematic studies on the reaction mechanisms of octahedral complexes of the type $[\mathrm{M\ diars_2Cl_2}]^{n+}$, where diars = *o*-phenylenebis(dimethylarsine). In previous papers[1,2] we examined and discussed the isomerisation and thiocyanate substitution reactions of the complex *cis*-$[\mathrm{Co\ diars_2Cl_2}]^+$.

In the present work some aspects of the kinetic behaviour of the cationic complex $[\mathrm{Pt\ diars_2Cl_2}]^{2+}$ are examined.

A great deal of work was carried out with the complex[3] *trans*-$[\mathrm{Pt\,en_2Cl_2}]^{2+}$, so that a comparison between the kinetic behaviour of the two named complexes (of which $[\mathrm{Pt\ diars_2Cl_2}]^{2+}$ is assumed to have a *trans* configuration on the basis of the preparative method used) ought to be of great help to understand the kinetic effect of the variation of the groups bonded to the central atom. In fact[2] we have here two similar complexes containing four nitrogen or four arsenic groups, respectively, with the remaining two ligands being replaceable.

The first experiment studied regards the reaction between $[\mathrm{Pt\ diars_2Cl_2}]^{2+}$ and thiocyanate ions in dry methanol[4]. The process turned out to involve oxidation–reduction with the formation of the reduced species $[\mathrm{Pt\ diars_2}]^{2+}$ in equilibrium with the five co-ordinated complex $[\mathrm{Pt\ diars_2SCN}]^+$.

On the basis of all the data obtained, the following atom-transfer process has been proposed.

$$[\mathrm{ClPt\ diars_2Cl}]^{2+} + \mathrm{SCN^-} \xrightarrow{k_2} [\mathrm{Cl\ldots Pt\ diars_2..Cl\ldots SCN}]^{3+} \xrightarrow{\text{fast}}$$

$$\xrightarrow{\text{fast}} [\mathrm{Pt\ diars_2}]^{2+} + \mathrm{Cl^-} + \mathrm{ClSCN} \qquad (1)$$

$$[\mathrm{Pt\ diars_2}]^{2+} + \mathrm{SCN^-} \xrightleftharpoons{k_1} [\mathrm{Pt\ diars_2SCN}]^+ \qquad (2)$$

The possibility that the reaction goes through an intermediate of the type $[\mathrm{Pt\ diars_2ClSCN}]^{2+}$, with a mechanism of the type operating[5] on *trans*-$[\mathrm{Pt\,en_2Cl_2}]^{2+}$ has been ruled out because it would imply that the reaction is autocatalytic and would also be catalyzed by $[\mathrm{Pt\ diars_2}]^{2+}$ if added to the reaction mixture. While this reaction is a simple pseudo-first order reaction it does not appear to be catalyzed either by $[\mathrm{Pt\ diars_2}]^{2+}$ or by $[\mathrm{Pt\ diars_2SCN}]^+$.

To examine whether species such as [Pt diars$_2$]$^{2+}$ or [Pt diars$_2$X]$^+$ may provide any catalytic effect in X$^-$ substitutions, the bromide substitution reaction of [Pt diars$_2$Cl$_2$]$^{2+}$ in methanol at 30 °C has been studied. The only variables investigated were the [Pt diars$_2$]$^{2+}$ and the [Br$^-$] concentrations. The ionic strength has been kept constant, $\mu = 5.7 \cdot 10^{-2}$ g.eq./l, by the addition of the correct amount of NaNO$_3$. Platinous and platinic complexes have been used in the chloride or nitrate forms. Bromide has been employed as sodium salt. Spectrophotometric techniques have been used to follow the reactions.

Reactions carried out without addition of [Pt diars$_2$]$^{2+}$ were very slow and scarcely reproducible. The reaction rate, however, was strongly increased when [Pt diars$_2$]$^{2+}$ was added to the reaction mixture. The spectrophotometric behaviour of the reactions studied verified the existence of four isosbestic points in the U.V. range, at wavelengths of 359 mμ, 310 mμ, 275 mμ and 248 mμ, suggesting that the reaction progressed without the formation of any intermediate in experimentally observable amount. Moreover Fig. 1 shows that [Pt diars$_2$Cl$_2$]$^{2+}$ and [Pt diars$_2$Br$_2$]$^{2+}$ have the same extinction coefficients at the same wavelengths at which isosbestic points were observed in the reaction under investigation. This fact and the spectrum of the final product, suggested that the reaction product was the species [Pt diars$_2$Br$_2$]$^{2+}$. This compound has also been isolated in the solid state from the reaction mixture.

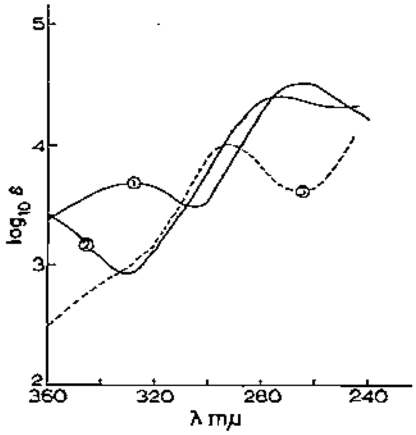


Fig. 1. Ultra-violet absorption spectra of: 1) [Pt diars$_2$Cl$_2$]$^{2+}$; 2) [Pt diars$_2$Br$_2$]$^{2+}$; 3) [Pt diars$_2$Br]$^+$ in methanol.

The catalytic reaction rates were not of pseudo first-order type, and it has been possible to demonstrate that this was due to the fact that the reaction product slows down the reaction rate. The observed rate constants, k_{obs}, were then calculated from pseudo first-order rate laws, and the values of k_{obs} were extrapolated to time zero.

To attempt to clarify the reaction mechanism we studied the role played by

$[Br^-]$ and $[Pt\ diars_2]^{2+}$ in determining the reaction rate. A set of kinetic runs has been carried out using constant bromide concentration and changing the $[Pt\ diars_2]^{2+}$ concentration within the range:

$$[Pt\ diars_2{}^{2+}]_{min} \ll [Pt\ diars_2Cl_2{}^{2+}]_{initial} \ll [Pt\ diars_2{}^{2+}]_{max}$$

Fig. 2 reports the observed specific rate constants as function of $[Pt\ diars_2]^{2+}$ concentration. A linear dependence of k_{obs} *versus* $[Pt\ diars_2]^{2+}$ concentration is observed.

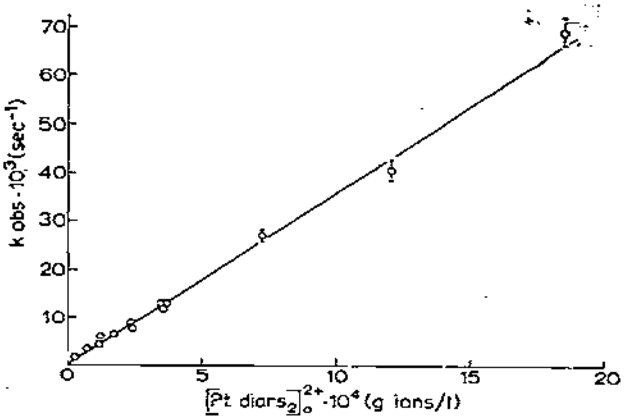


Fig. 2. Pseudo first-order rate constants for the catalytic reactions between $[Pt\ diars_2Cl_2]^{2+}$ and excess of bromide ($NaBr = 5.7 \cdot 10^{-2}\ M$) plotted as a function of $[Pt\ diars_2](NO_3)_2$ concentration in methanol at 30 °C at ionic strength $= 0.057\ M$.

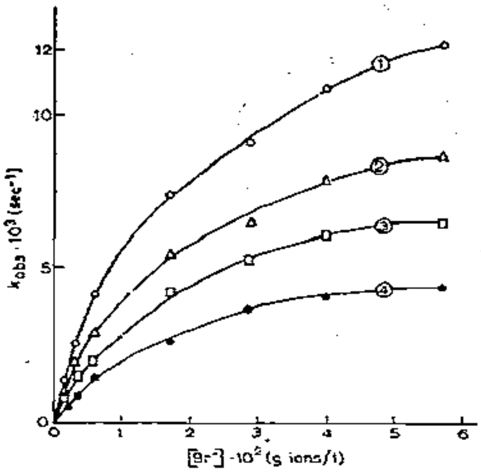
In order to study the role played by Br^-, a number of kinetic runs have been carried out keeping constant the concentration of $[Pt\ diars_2]^{2+}$ in each set, and changing the $[Br^-]$ concentration.

Fig. 3 reports the results of four sets of kinetic runs. A dependence of k_{obs} from bromide concentration is observed. As shown in the figure the dependence is not linear. On the other hand we must notice that the complex $[Pt\ diars_2]^{2+}$ exists in solution in equilibrium with the previously reported[6] five co-ordinated species $[Pt\ diars_2Br]^+$. If we now assume that the five co-ordinated complex is the catalyst, as it probably is, we must take into account the fact that its concentration in solution is a function of its stability constant. Then one can write a reaction scheme of this kind:

$$[Pt\ diars_2]^{2+} + Br^- \overset{K}{\rightleftharpoons} [Pt\ diars_2Br]^+ \tag{3}$$

$$[Pt\ diars_2Cl_2]^{2+} + [Pt\ diars_2Br]^+ \xrightarrow[+Br]{k_2} [Pt\ diars]_2{}^{2+} + 2Cl^-$$

$$+ [Pt\ diars_2Br_2]^{2+} \tag{4}$$



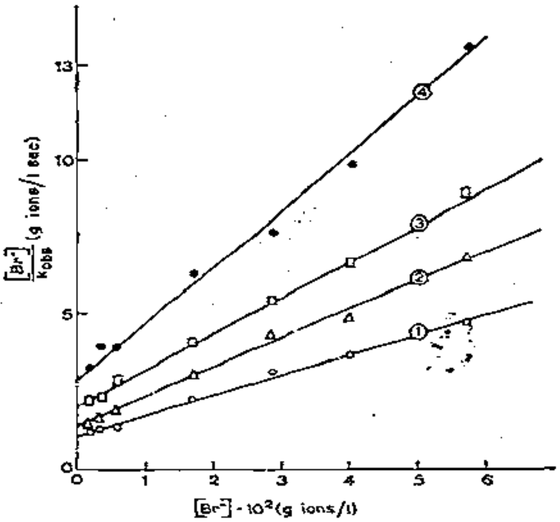


Fig. 3. Pseudo first-order rate constants for the catalytic reactions between $[Pt\ diars_2Cl_2]^{2+}$ and excess of bromide in presence of $[Pt\ diars_2](NO_3)_2$ plotted as a function of sodium bromide concentration in methanol at 30 °C at the following $[Pt\ diars_2](NO_3)_2$ concentrations: 1) $3.5 \cdot 10^{-4}$ *M*; 2) $2.34 \cdot 10^{-4}$ *M*; 3) $1.72 \cdot 10^{-4}$ *M*; 4) $1.14 \cdot 10^{-4}$ *M*.

Fig. 4. Data of Fig. 3 worked out assuming the following expression of the observed pseudo first-order rate constant:

$$k_{Obs} = \frac{k_2K[(Pt\ diars_2)^{2+}]\,[Br^-]}{K[Br^-]+1},$$

so that

$$\text{rate} = k_2[(Pt\ diars_2Cl_2)^{2+}]\,[(Pt\ diars_2Br)^+] \tag{5}$$

From (3) we have

$$[(Pt\ diars_2Br)^+] = \frac{K[(Pt\ diars_2)^{2+}]_0[Br^-]}{K[Br^-]+1} \tag{6}$$

where $[(Pt\ diars_2)^{2+}]_0$ is the total amount (mole/l) of Pt^{II} added and $[Br^-] \gg [(Pt\ diars_2)^{2+}]_0$.

From (5) and (6) it follows:

$$\text{rate} = \frac{k_2K[Pt\ diars_2Cl_2{}^{2+}]\,[Pt\ diars_2{}^{2+}]_0[Br^-]}{K[Br^-]+1} \tag{7}$$

with (for pseudo first-order rate laws)

$$k_{obs} = \frac{k_2K[(Pt\ diars_2)^{2+}]_0[Br^-]}{K[Br^-]+1} \tag{8}$$

Expression (8) may be rearranged in the form:

$$\frac{[Br^-]}{k_{obs}} = \frac{[Br^-]}{k_2[(Pt\ diars_2)^{2+}]_0} + \frac{1}{k_2K[(Pt\ diars_2)^{2+}]_0} \tag{9}$$

It follows that plotting the ratio $[Br^-]/k_{obs}$ *versus* bromide concentration, a straight line ought to be found, provided that $[(Pt\ diars_2)^{2+}]_0$ is kept constant.

In Fig. 4 the values of $[Br^-]/k_{obs}$ *versus* $[Br^-]$ are reported for the four sets of kinetic runs given in Fig. 3. The good straight lines observed have slopes and intercepts that are functions only of the $[(Pt\ diars_2)^{2+}]_0$ concentration, as expected from expression (9).

$$\text{intercept} = \frac{1}{k_2K[(Pt\ diars_2)^{2+}]_0}$$

$$\text{slope} = \frac{1}{k_2[(Pt\ diars_2)^{2+}]_0} \tag{10}$$

The data of the intercepts and of the slopes must be linear functions of

$$\frac{1}{[(Pt\ diars_2)^{2+}]_0}$$

and the observed straight lines must cross the origin of the axis.

Fig. 5 reports the values of the intercepts and slopes obtained from Fig. 4 as functions of

$$\frac{1}{[(Pt\ diars_2)^{2+}]_0}$$

Two straight lines crossing the origin are observed, as expected. The values of k_2 and K were calculated from relation (10); they are $k_2 = 50.5$ l.moles^{-1}sec^{-1}; $K = 60$ l.moles^{-1}.

From the agreement between the experimental data and the reported scheme, we propose the following reaction mechanism:

$$[Pt\ diars_2]^{2+} + Br^- \overset{K}{\rightleftharpoons} [Pt\ diars_2Br]^+ \tag{11}$$

$$[ClPt\ diars_2Cl]^{2+} + [Pt\ diars_2Br]^+$$

$$\xrightarrow{k_2} [Cl..Pt\ diars_2..Cl..Pt\ diars_2Br]^{3+}$$

$$\xrightarrow{fast} [Pt\ diars_2]^{2+} + Cl^- + [Pt\ diars_2ClBr]^{2+} \tag{12}$$

$$[Pt\ diars_2ClBr]^{2+} \xrightarrow[+Br^-]{fast} [Pt\ diars_2Br_2]^{2+} + Cl^- \tag{13}$$

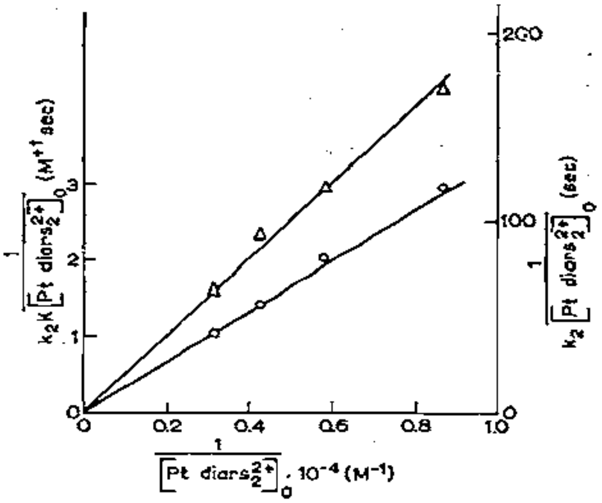


Fig. 5. Values of the intercepts (○) and of the slopes(△) of the curves of Fig. 4 reported as a function of $\frac{1}{[(\text{Pt diars}_2)^{2+}]_0}$.

where reaction (13) may be or may be not a reaction catalyzed by $[\text{Pt diars}_2]^{2+}$.

From this scheme it appears that the name "substitution reaction", in this case, is improper, as the mechanism is a oxidation–reduction atom-transfer process analogous to that operating in the reaction with thiocyanate[4]. The peculiar difference is that the species undergoing oxidation in the reaction described here gives rise to the product $[\text{Pt diars}_2\text{Br}_2]^{2+}$ which would also be expected in a true substitution reaction.

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