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STUDIES OF REACTION MECHANISM OF *CIS* AND *TRANS* DICHLOROBIS(*o*-PHENYLENEBISDIMETHYLARSINE)COBALT(III) IONS

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A large amount of data on substitution reactions of octahedral complexes are available in which the single variable is the ligand not replaced in the reaction or the nature of the entering group. These data are particularly abundant for chelate complexes of Co^{III} of general formula $[Co(AA)_2Cl_2]^+$ where AA represents a nitrogen–nitrogen chelating agent such as ethylenediamine.

Insufficient attention has been paid to the study of the part played by the central metal ion in determining the rate and mechanism of the reaction. Taube[1] and Basolo and Pearson[2] have discussed the rate of the electronic configuration of the central metal but up till now it has not been possible to carry out any very extensive experimental study of this problem because of the limited availability of series of complexes, having as single variable the central metal ion.

Chelate complexes[3] of the type $MD_2Cl_2^{n+}$ where D = *o*-phenylenebis(dimethylarsine), "diarsine", exist for many of the transition metals. A systematic study of the kinetic behaviour of these complexes should provide accurate information about the effect of the nature, the electronic configuration and the oxidation state of the metal upon the kinetic rate and possibly upon the mechanism of these reactions.

We report here the kinetic results of a study of the isomerisation and SCN^- substitution of *cis*$[CoD_2Cl_2]^+$ in methanol at 54.9 °C. We include also the kinetic results of isotopic exchange with ^{36}Cl and the SCN^- substitution of *trans*-$[CoD_2Cl_2]^+$ in the same solvent.

We began our study with these complexes because they may also furnish useful information for a comparison of the behaviour of complexes of Co^{III} containing four donor arsenic atoms with the complexes containing four donor nitrogen atoms. This study ought to throw more light on the part played by the ligands in determining the rates and mechanism of substitution reactions.

The studies of *cis*$[CoD_2Cl_2]^+$ have been carried out in methanol at 54.9 °C. Fig. 1 shows the curves log ε *versus* the wavelength of the spectra of *cis*$[CoD_2Cl_2]^+$ and *trans*$[CoD_2Cl_2]^+$. At four different wavelengths the extinction coefficients of the two species are identical, which indicates that we ought to observe four isos-

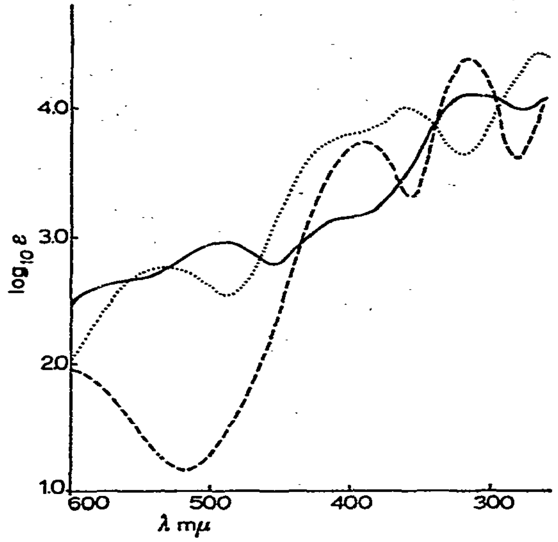


Fig. 1. Visible and ultra-violet absorption spectra of: ——— *cis*$[CoD_2Cl_2]^+$; - - - - *trans*-$[CoD_2Cl_2]^+$; …… $[CoD_2(SCN)_2]^+$.

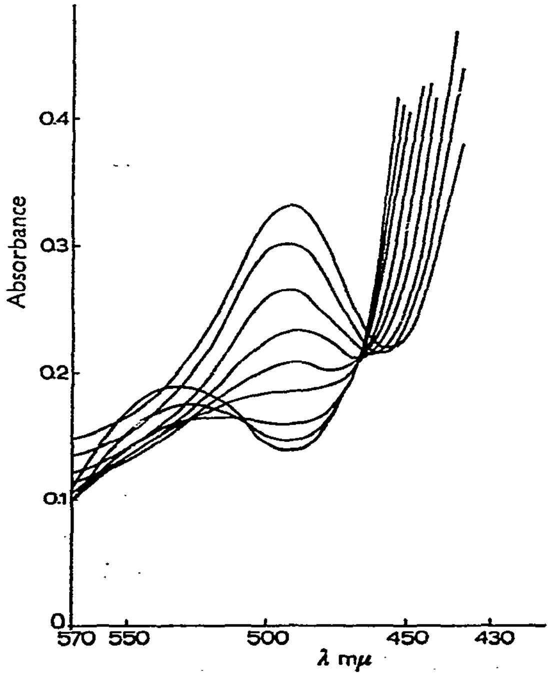


Fig. 2. Spectrum of a solution originally containing *cis*$[CoD_2Cl_2]^+$ ($9.2 \cdot 10^{-3}$ *M*) and potassium thiocyanate ($2.54 \cdot 10^{-2}$ *M*) in methanol at 54.9 °C (for its change with time see Fig. 3).

bestic points for a *cis–trans* isomerisation reaction, provided that no intermediate is formed in detectable quantity during the reaction. Experimentally the existence of these isosbestic points has been demonstrated and the reaction rate has been found to be of first order in complex and independent of the Cl^- concentration, that is:

$$\frac{d(cis)}{dt} = -k_I(cis) = -\frac{d(trans)}{dt}$$

where $k_I = 1.67 \cdot 10^{-6} sec^{-1}$.

It is very interesting to observe that a rate constant of the same order of magnitude has been found for the SCN^- substitution of this complex under the same experimental conditions.

This process of SCN^- substitution is of special interest. The spectrum of $[CoD_2(SCN)_2]^+$, which is the final product of the reaction, is given in Fig. 1, where it is possible to see that isosbestic points ought to be experimentally detectable at 560 mμ, 528 mμ, 466 mμ, 342 mμ, 292 mμ, provided that no intermediate is formed during the reaction. In Fig. 2 the experimental spectrophotometric results for the visible range are reported for a typical kinetic run.

The curves clearly show that the expected isosbestic points do not exist and that the reaction must go through at least one intermediate. It has not yet been possible to isolate and examine this intermediate but, owing to a fortunate relationship between the spectra, we have been able to analyze the reaction mixture spectrophotometrically, assuming that there is only one intermediate. It was also possible, by subtracting the contributions from the *cis* dichlorocomplex and the final di-isothiocyanato product, to obtain the spectrum of the intermediate. This is very similar in shape to that of the *trans* dichloro complex but there are significant differences in extinction coefficient in the 350–430 mμ region.

There are three possible forms of the intermediate, depending on the number of SCN^- groups present:

case I) *trans*$[CoD_2Cl_2]^+$, *i.e.*, no SCN^-

case II) one SCN^-, *e.g.*, $[CoD_2SCNCl]^+$.

case III) two SCN^-, *i.e.*, an unstable isomer of the final product.

It was therefore important to decide which of the above possibilities was most likely.

Fig. 3 shows the curves for one of these kinetic runs, while Table I shows the experimental results for a set of these kinetic runs. These results indicate that both the successive reactions have a rate independent of SCN^- concentration, with the value of:

$$k_1 = 1.9 \cdot 10^{-6}\ sec^{-1} \text{ and } k_2 = 4.6 \cdot 10^{-6}\ sec^{-1}$$

For case I we would expect to find that the specific rate constant, k, for SCN^- substitution in *trans*$[CoD_2Cl_2]^+$ equal to $k_2 = 4.6 \cdot 10^{-6} sec^{-1}$.

TABLE I

FIRST-ORDER RATE CONSTANTS FOR THE REACTION $cis[CoD_2Cl_2]^+ + SCN^- \xrightarrow{k_1}$ INTERMEDIATE $\xrightarrow[+SCN^-]{k_2}$ $[CoD_2(NCS)_2]^+ + 2Cl^-$ IN METHANOL AT 54.9 °C.

Initial complex (10^{-4} *M*)	*Initial* [SCN^-] (10^{-4} *M*)	$k_1 \cdot 10^6$, (sec^{-1})	$k_2 \cdot 10^6$, (sec^{-1})
0.773	23.0	2.0	5.0
0.820	43.4	1.8	4.3
0.845	51.4	2.0	4.5
0.925	156.5	1.8	4.9
0.920	257.0	1.9	4.3
0.920	320.0	2.0	4.8

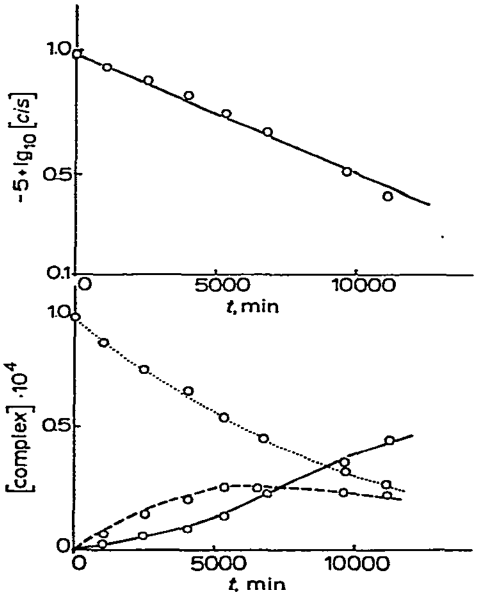


Fig. 3. Composition of the reaction mixture as a function of time of the kinetic run reported in Fig. 2: ...... $cis[CoD_2Cl_2]^+$; – – – – intermediate; ——— $[CoD_2(SCN)_2]^+$.

We carried out a series of kinetic studies of SCN^- substitution of *trans*-$[CoD_2Cl_2]^+$ in methanol at 55 °C and observed a first order rate law with respect to the complex and independent of the SCN^- concentration. Furthermore, the reaction proceeds without formation of any detectable intermediate, in contrast to the analogous reaction of $cis[CoD_2Cl_2]^+$. The first order rate constant, k, was found to be $k = 1.2 \cdot 10^{-6}$ sec^{-1}, while the expected k for case I ought to be $k = 4.6 \cdot 10^{-6}$ sec^{-1}.

In addition, if the intermediate was $trans[CoD_2Cl_2]^+$, then its addition to a solution of $cis[CoD_2Cl_2]^+$ at the beginning of the reaction with SCN^- should not alter the scheme of two successive first-order reactions:

$$cis[CoD_2Cl_2]^+ \xrightarrow{k_1} trans[CoD_2Cl_2]^+ \xrightarrow[-Cl+SCN^-]{k_2} [CoD_2(NCS)_2]^+$$

It follows that $\dfrac{d(trans)}{dt} = k_1(cis) - k_2(trans)$

and when (*trans*) is maximum, we have:

$$\frac{d(trans)}{dt} = 0 \text{ so that } k_1(cis)_{t_{max.}} = k_2(trans)_{t_{max.}} \text{ or } \left(\frac{cis}{trans}\right)_{t_{max.}} = \frac{k_2}{k_1}$$

The ratio $\left(\dfrac{cis}{trans}\right)_{t_{max.}}$ should be independent of the amount of *trans* complex added at the beginning of the reaction.

If the intermediate is not *trans*$[CoD_2Cl_2]^+$ then we are studying two independent reactions:

1) $cis[CoD_2Cl_2]^+ \xrightarrow[+SCN^-]{k_1} \text{intermediate} \xrightarrow[+SCN^-]{k_2} [CoD_2(NCS)_2]^+ + 2Cl^-$

2) $trans[CoD_2Cl_2]^+ \xrightarrow[+2SCN^-]{k} [CoD_2(NCS)_2]^+ + 2Cl^-$

With $k = 1.2 \cdot 10^{-6}$ sec^{-1} as already reported.

Table II reports the values obtained for a set of kinetic runs assuming that the intermediate is *trans*$[CoD_2Cl_2]^+$ and the values obtained assuming that the intermediate is not *trans*$[CoD_2Cl_2]^+$.

TABLE II

THE REACTION BETWEEN *cis*$[CoD_2Cl_2]^+$ AND SCN^- IN THE PRESENCE OF VARYING AMOUNTS OF *trans*$[CoD_2Cl_2]^+$ IN METHANOL AT 54.9 °C

$[cis\text{-}Cl_2]_0$ $\times 10^4$ *M*	$[trans\text{-}Cl_2]_0$ $\times 10^4$ *M*	$[SCN^-]_0$ $\times 10^4$ *M*	k_2/k_1 *(case 1)**	k_2/k_1 *(case 2)***
0.82	0	43.4	2.1	2.2
0.71	0.169	100.0	1.42	1.8
0.56	0.235	31.0	1.04	1.9

* Case 1 assumes that the intermediate is the *trans*-dichloro complex.
** Case 2 assumes that they are different species.

It is possible to see that the k_2/k_1 values do not agree with the assumption that *trans*$[CoD_2Cl_2]^+$ is the intermediate. All these data therefore seem to exclude that the intermediate is *trans*$[CoD_2Cl_2]^+$ (case I).

It is now necessary to decide whether the intermediate is a chlorothiocyanato complex or whether it is an unstable dithiocyanato isomer which subsequently isomerises. To do this we studied the reaction under conditions where there was insufficient thiocyanate to displace all the coordinate chlorine.

Table III reports the results for a set of these kinetic runs. It is apparent

TABLE III

RATE CONSTANTS FOR THE DISAPPEARANCE OF *cis*$[CoD_2Cl_2]^+$ IN THE PRESENCE OF SMALL QUANTITIES OF SCN^-, AND THE COMPOSITION OF THE PRODUCT

$[cis\text{-}Cl_2]_{init.}$ $(10^{-4}\ M)$	$[SCN^-]_{init.}$ $(10^{-4}\ M)$	k_1 $\times 10^6\ sec^{-1}$	$[CoD_2(SCN)_2]_{final}$ $(10^{-4}\ M)$	$[CoD_2(SCN)_2]_{final}/$ $\frac{1}{2}\ [SCN^-]_{initial}$
0.880	0.123	1.8	0.00	0.0
0.880	0.210	2.1	0.050	0.48
0.825	0.245	2.1	0.080	0.65
0.875	0.305	2.1	0.088	0.58
0.778	0.415	2.1	0.135	0.65
0.861	0.610	2.1	0.190	0.62

that the amount of dithiocyanato complex is insufficient to account for all the thiocyanate that has been added and it must be concluded that another thiocyanate-containing complex is present.

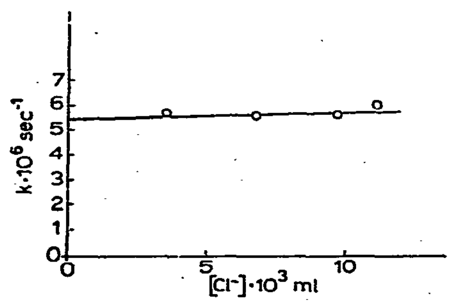
Of course, competition studies are required to throw more light on this problem. Nevertheless, the reported data are, in our opinion, reasonable evidence for concluding that the intermediate is a $[CoD_2(NCS)Cl]^+$ isomer.

Work is now in progress using labelled material to study the rate of uptake of SCN^-, and loss of chloride and to clarify definitely this reaction.

All the reactions studied up till now proceed at a rate that is independent of the nature and concentration of the entering reagent. We had extended our study to other reactions in order to see if there is any generalization of this behaviour.

One of the most interesting kinetic studies is that of isotopic exchange because of the similarity of the nature of the entering and the leaving groups.

We have carried out a set of kinetic runs on the isotopic exchange of ^{36}Cl in *trans*$[CoD_2Cl_2]^+$. The reactions were studied in methanol at 75 °C. The rate law



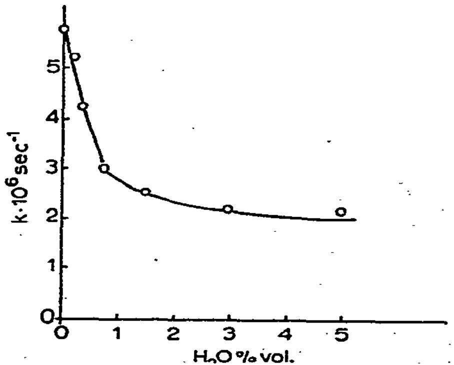


Fig. 4. Rate of isotopic exchange of *trans*$[CoD_2Cl_2]^+$ with ^{36}Cl at 75 °C as function of $[Cl^-]$ concentration.

Fig. 5. Rate of isotopic exchange of *trans*$[CoD_2Cl_2]^+$ with ^{36}Cl at 75 °C as function of % of water in methanol.

was found to be first order in complex and independent of the Cl^- concentration. Fig. 4 shows the values of k_{obs} *versus* $[Cl^-]$ for a set of these kinetic runs. The reactions were notably inhibited by small quantities of water. Fig. 5 shows the values of k_{obs} *versus* % of water for a set of kinetic runs carried out in methanol–water solutions. It will be interesting in the future to determine the importance of the entropy factor and the enthalpy factor in determining the change in k_{obs}. However, if we confine our attention to the data concerning the dependence of the rate of reaction on the concentration of entering groups, we can conclude that the reactions of *cis* and *trans*$[CoD_2Cl_2]^+$ go through a similar scheme in which the slow step is a dissociative process, possibly via solvolysis, with fast entry of the species X, into the reactive intermediate.

$$\mathrm{A}\begin{cases} \mathit{cis}[\mathrm{CoD_2Cl_2}]^+ & \xrightarrow[\text{slow}]{k_1} [\mathrm{CoD_2Cl}]^{2+}+\mathrm{Cl}^- \\ [\mathrm{CoD_2Cl}]^{2+}+\mathrm{Cl}^- & \xrightarrow[\text{fast}]{} \mathit{trans}[\mathrm{CoD_2Cl_2}]^+ \\ [\mathrm{CoD_2Cl}]^{2+}+\mathrm{SCN}^- & \xrightarrow[\text{fast}]{} \text{product} \end{cases}$$

$$\mathrm{B}\begin{cases} \mathit{trans}[\mathrm{CoD_2Cl_2}]^+ & \xrightarrow[\text{slow}]{k} [\mathrm{CoD_2Cl}]^{2+}+\mathrm{Cl}^- \\ [\mathrm{CoD_2Cl}]^{2+}+{}^{36}\mathrm{Cl}^- & \xrightarrow[\text{fast}]{} [\mathrm{CoD_2Cl}{}^{36}\mathrm{Cl}]^+ \\ [\mathrm{CoD_2Cl}]^{2+}+2\mathrm{SCN}^- & \xrightarrow[\text{fast}]{} [\mathrm{CoD_2(NCS)_2}]^+\mathrm{Cl}^- \end{cases}$$

where the five-coordinate activate complex in scheme A and B may be or may be not the same.

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