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Mechanism of Octahedral Substitution in non Aqueous Media.
III*. Isotopic Exchange Reaction in *trans*-Cyanosulphitebis(ethylenediamine)-cobalt(III) with $^{14}CN^-$ in Ethylene Glycol: a Comparison with the same Reaction in Water

GAETANO SCHIAVON and CARMEN PARADISI

Istituto Chimico 'G. Ciamician', Università di Bologna, Italy

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We have studied the isotopic exchange reaction between trans-*[Coen$_2$SO$_3$CN] and KCN, alternatively labelled with ^{14}C in ethylene glycol, over the temperature range 40–60 °C. The activation parameters are: $\Delta H^{\ddagger} = 18.3$ Kcal mol^{-1}; $\Delta S^{\ddagger} = -23.9$ cal K^{-1} mol^{-1}.*

An examination of the reaction at 60 °C over the range of KCN concentration 5×10^{-2}–5×10^{-1} M, *at constant complex concentration, has shown that the isotopic exchange reaction rate is independent of KCN concentration. This result allows us to formulate a possible reaction mechanism of the D type, in agreement both with present views on octahedral substitution reactions and with the fact that the sulphite group labilizes by way of a dissociative mechanism when it is placed in* trans *with respect to the labile ligand. This result however is at variance with the one obtained in a study carried out previously on the same reaction in water, where a first-order dependence of the isotopic exchange rate on KCN concentration was found.*

Introduction

The considerable amount of kinetic data available in the literature regarding the lability of octahedral cobalt(III) complexes have led to the conclusion that the only mechanism viable for nucleophilic substitution of labile ligands are of type I_d or D. Reactions have been observed in which the rate of substitution depends on the concentration of the entering ligand, but this does not imply that they are associative in nature, rather the effect is attributed to an ionic association pre-equilibrium or to a proton tranfer, as in the case of basic catalysis.

Complexes of the type *trans*-[Coen$_2$SO$_3$X] appear to react *via* a D mechanism, generating the identifiable pentacoordinate intermediate [Coen$_2$SO$_3$]$^+$ [1].

When the ligand X is fairly labile, these complexes are very reactive in acid and basic hydrolysis reactions and in nucleophilic substitution reactions involving the ligand X in *trans* position with respect to the sulphite group [2].

We have studied isotopic exchange reactions in the systems: *trans*-[Coen$_2$SO$_3$Cl]–Li^{36}Cl; *trans*-[Coen$_2$SO$_3$NCS]–KS^{14}CN; *trans*-[Coen$_2$SO$_3$NCSe]–KSe^{14}CN in ethylene glycol at 4 °C. In every case exchange was quantitative within the time necessary for reagents separation (1min) [3].

trans-[Coen$_2$SO$_3$CN] is much less labile than the analogues above. Its absorption spectrum in the visible range in aqueous solution remains unaltered at room temperature for several days, and also in ethylene glycol at 60 °C and with an excess of KCN thus demonstrating that substitution of the sulphite group by a cyanide group does not occur.

Earlier we published a study [4] dealing with reactions of complex *trans*-[Coen$_2$SO$_3$CN] in aqueous solution and we reported that the isotopic exchange rate of labelled cyanide increases with increasing free cyanide ion concentration in solution. Two possible mechanisms can be envisaged for the cyanide-dependent pathway of the exchange reaction in water: bimolecular, or S$_N$1cb *via* proton exchange between the base CN$^-$ and one molecule of ethylenediamine coordinated to the metal. We believed a bimolecular mechanism to be most likely.

In order to confirm the hypothesis put forward in ref. [4], we have investigated the isotopic exchange reaction in the system *trans*-[Coen$_2$SO$_3$-

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CN]–KCN labelled with $^{14}CN^-$ in ethylene glycol. In this system we have a neutral complex, for which complications due to the ionic association pre-equilibrium with the anionic base can be excluded, and a dipolar solvent which supplies its conjugate base $HOCH_2CH_2O^-$ in the presence of the base CN^-. If the isotopic exchange reaction in water proceeds *via* a base catalyzed mechanism, also in this medium a reaction catalyzed by added base CN^- can be anticipated.

We have therefore studied isotopic exchange reactions in ethylene glycol over the temperature range 40–60 °C between *trans*-[$Coen_2SO_3CN$] and KCN alternatively labelled with ^{14}C over the concentration range of KCN 5×10^{-2}–5×10^{-1} *M*.

We report furthermore the experimental procedures followed and the results obtained in the study of the kinetics of the isotopic exchange reaction between *trans*-[$Coen_2SO_3CN$] and KCN in water from which activation parameters were obtained.

Experimental

trans-cyanosulphitebis(ethylenediamine)cobalt(III) was prepared by Tobe's procedure [5].

Kinetic Experiments

For isotopic exchange rate determinations an aqueous solution of KCN, titrated with $AgNO_3$ to which a little quantity of $K^{14}CN$ of high specific activity was added, was utilized. The initial radioactivity of $K^{14}CN$ was determined adding to this solution a saturated solution of $Zn(NO_3)_2$, so that $Zn(CN)_2$ and $Zn(OH)_2$ precipitated. The precipitate was centrifuged and repeatedly washed with water, re-dissolved in a small volume of diluted NH_3 solution, and re-precipitated with a diluted acetic acid solution. $Zn(CN)_2$ was thus isolated, and washed with water and acetone and finally transferred in a compact homogeneous form to plastic discs for radioactivity measurements. The latter were carried out with a G. M. counter for solid samples. The saturation method was utilized, saturation values corresponding to 12 mg of samples with homogeneous surface and constant area. The reproducibility of radioactive determinations was very satisfactory. With the aqueous solution, prepared as described above, of $K^{14}CN$ the complex *trans*-[$Coen_2SO_3{}^{14}CN$] was prepared by reacting *trans*-[$Coen_2SO_3Cl$] and $K^{14}CN$ as reported in ref. [5].

Kinetic measurements were taken by utilizing the labelled complex and KCN initially inactive, and the reaction progress was monitored by measuring the radioactivity increasing with time from $A_o = 0$ to A_∞, where A_∞ is the radioactivity corresponding to the isotopic equilibrium distribution of the initially inactive CN^-.

TABLE I. First-Order Rate Constants for the Isotopic Exchange Reaction between *trans*-[$Coen_2SO_3CN$] and KCN Labelled with ^{14}C in Ethylene Glycol. Complex concentration was 6.25×10^{-3} *M*.

No.	[KCN] × 10^2	t °C	10^8 R mol l^{-1} s^{-1}	10^5 k s^{-1}
1	5	40	4.0	0.6
2	5	45	6.2	1.0
3	5	50	11.0	1.8
4	5	60	25.8	4.1
5	6	60	28.3	4.5
6	10	60	27.6	4.4
7	15	60	26.9	4.3
8	40	60	25.0	4.0
9	50	60	25.4	4.1

A different series of measurements was carried out with a non-labelled complex and $K^{14}CN$. Using the same procedure as above a series of samples having radioactivity decreasing from A_o to A_∞ over time was obtained.

$Zn(CN)_2$ samples containing $^{14}CN^-$ originally present as ligand and $^{14}CN^-$ originally present as free ion, and corresponding to equal reaction progress, gave invariably as sum the initial radioactivity value, *i.e.* A_o.

Two different approaches were adopted when separating reagents depending on whether the solvent was water or ethylene glycol. In the first case, a saturated solution of $Zn(NO_3)_2$ was added to a portion of reaction mixture, sampled at a given time, and cooled to 0 °C in order to quench the exchange reaction, whereupon the procedure described above for the preparation of $Zn(CN)_2$ samples was followed. In ethylene glycol such a method was not convenient, and the separation of reagents was attained by letting the reaction mixture, cooled at 0 °C, through a refrigerated column of chlorinated anionic resin IRA-400. The column was repeatedly washed with cold water and CN^- was finally eluted by means of 2 *N* $NaNO_3$ solution. From this eluate, $Zn(CN)_2$ was precipitated in the way described above.

Results

As is apparent from the data in Table I that the rate of isotopic exchange reaction (R of McKay's equation) in ethylene glycol is independent of KCN concentration over the range 5×10^{-2}–5×10^{-1} *M*. The activation parameters are: $\Delta H^{\ddagger} = 18.3$ Kcal mol^{-1}; $\Delta S^{\ddagger} = -23.9$ cal K^{-1} mol^{-1}.

TABLE II. Observed Rate of Isotopic Exchange Reaction (R_{obs} McKay's equation) between *trans*-[Coen$_2$SO$_3$CN] and KCN Labelled with ^{14}C in Water. Complex concentration was 0.105 *M*.

No	[KCN]	μ	t °C	10^6 R_{obs} mol l^{-1} s^{-1}
1	0.1	0.1	33	0.1
2	0.1	0.1	43	0.4
3	0.1	0.1	53	1.8
4	0.1	0.1	64	4.6
5	0.1	0.5	64	5.4
6	0.1	0.9	64	6.0
7	0.3	0.9	64	6.8
8	0.5	0.9	64	7.4
9	0.7	0.9	64	8.3
10	0.9	0.9	64	9.0

In Table II are reported the values of the isotopic exchange reaction rate determined for the system *trans*-[Coen$_2$SO$_3$CN]–KCN alternatively labelled with ^{14}C, in water, over the temperature range 33–64 °C (experiments 1–4) with constant concentration of reagents. The temperature dependence of the isotopic exchange reaction rate follows the Arrhenius equation and the activation parameters are: $\Delta H^{\ddagger} = 26.3$ Kcal mol^{-1}; $\Delta S^{\ddagger} = -1.3$ cal K^{-1} mol^{-1}. The Table also contains the values of the isotopic exchange reaction rate measured at 64 °C with constant reagent concentration and with an ionic strength varying between 0.1 and 0.9 *M* made up by means of KCl, (experiments 4–6). A linear μ dependence of the isotopic exchange reaction rate is found. Experiments 6 to 10 gave the values of the isotopic exchange reaction rate at 64 °C and $\mu = 0.9$ *M* and with KCN concentration varying over the 0.1–0.9 *M* range.

Considering that the isotopic exchange reaction in water is a combination of a reversible aquation and a reversible basic hydrolysis reactions, we propose the following kinetic equation for the observed isotopic exchange rate (R_{obs}): $R_{obs} = k_{H_2O}[\text{complex}] + k_{OH}[\text{complex}][OH^-] + k_{exch}[\text{complex}][CN^-]$ where [complex] = 0.105 *M*; [OH$^-$] was calculated with the procedure indicated in ref. 4; $k_{H_2O} = 5.2 \times 10^{-5}$ s^{-1}; $k_{OH} = 9.5 \times 10^{-4}$ l mol^{-1} s^{-1} and $k_{exch} = 3.1 \times 10^{-5}$ l mol^{-1} s^{-1} [4]. Plotting logR' ($R' = R_{obs} - k_{H_2O}[\text{complex}] - k_{OH}[\text{complex}][OH^-]$ *versus* log [KCN] a straight line with slope equal to unity, obtains, demonstrating a first-order dependence on KCN concentration of the rate.

Discussion

The fact that the first-order rate constants for the reaction of isotopic exchange between *trans*-[Coen$_2$SO$_3$CN] and KCN labelled with ^{14}C in ethylene glycol is independent of KCN concentration indicates that the contribution of basic catalysis to this exchange reaction is either absent or negligible in this solvent. This observation seems to imply that in water the linear dependence of the exchange rate on KCN concentration is not ascribable to a basic catalysis mechanism.

On the other hand, the comparison between the activation parameters of isotopic exchange reaction in water and in ethylene glycol which shows the heat of activation of the latter to be much lower (18.3 Kcal mol^{-1}) than that of the former (26.3 Kcal mol^{-1}), and the activation entropy of the latter to be much more negative (–23.9 cal K^{-1} mol^{-1}) than that of the former (–1.3 cal K^{-1} mol^{-1}), leads to the conclusion that in ethylene glycol the mechanism is of the D type, in agreement with the data reported in the literature [1] for reactions involving complexes of type *trans*-[Coen$_2$SO$_3$X].

In summary, the results obtained in the study of the isotopic exchange reaction between *trans*-[Coen$_2$SO$_3$CN] and KCN in ethylene glycol are fully consistent with the present views on octahedral substitution reactions and with the fact that the sulphite group labilizes by way of a dissociative mechanism and it seems unlikely that this complex would react associatively in a bimolecular way in water. It is possible that the cyanide ion exchange reaction in water belongs to an altogether novel type of mechanism.

We are presently looking at this reaction in more detail in order to assess the origin of the first-order dependence of the isotopic exchange rate on KCN concentration in water.

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