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Academician of the Academy of Sciences of the MSSR A. V. Ablov and D. M. Palade

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Abstract

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Academician of the Academy of Sciences of the MSSR A. V. Ablov and D. M. Palade

KINETICS OF AQUATION OF TRANS-HALOGENONITRO-BIS-DIMETHYLGLYOXIMATOCOBALTIAT IONS

It is known that, in cobaltammines, substitution reactions in the inner coordination sphere are very often accompanied by a change in the spatial configuration. We have shown (^1) that, upon substitution in the inner sphere of complex compounds of trivalent cobalt with dimethylglyoxime of the type $[Co(DH)_2AB]$, the spatial arrangement of the ligands remains unchanged: the two dimethylglyoxime residues lie in one plane, and groups A and B are in the trans position relative to one another. To explain the mechanism of substitution reactions in octahedral complexes, a hypothesis was proposed according to which substitution in them proceeds with "edge displacement" (^2). However, in cobalt dioximes the substitution reaction cannot proceed by this mechanism. In consequence, a study was undertaken of the kinetics of aquation reactions in halogenoaquo-bis-dimethylglyoximatocobalt ([3,]4) and in dihalogeno-bis-dimethylglyoximatocobaltiate ions (^5).

Of particular interest was the study of the kinetics of aquation of trans-halogenonitro-bis-dimethylglyoximatocobaltiate ions, since it is known ([1,]6) that, in cobalt dioximes, the trans influence of groups increases in the order

$$NO_2 > Br > Cl.$$

Chloronitro- and bromonitro-bis-dimethylglyoximatocobaltic acids $H[Co(DH)_2(NO_2)Cl] \cdot H_2O$ and $H[Co(DH)_2(NO_2)Br] \cdot 2H_2O$ were prepared

Table 1

Acids	Calculated, % Co	Calculated, % Cl(Br)	Found, % Co	Found, % Cl(Br)
$H[Co(DH)_2(NO_2)Cl]\cdot H_2O$	14.53	9.10	14.41; 14.42	9.06
$H[Co(DH)_2(NO_2)Br]\cdot 2H_2O$ *	12.98	17.60	13.01	17.59; 17.65

* Bromonitro-bis-dimethylglyoximatocobaltic acid had previously (^1) been described with one molecule of water of crystallization.

according to (^1). The substances were purified by reprecipitating them from warm aqueous solutions with concentrated acids (hydrochloric acid and, respectively, hydrobromic acid). Table 1 gives the analytical results.

The rate of replacement of halogen by water was measured by determining, at a given moment in time, the concentration of free halogen ions in the solution of the complex by measuring the e.m.f. of the concentration cell:

$$\mathrm{Ag}\,\Big|\,\mathrm{AgHal}\,\Big|\,\begin{matrix}0.01\,M\ \mathrm{KHal}\\ \text{in } 0.1\,N\ \mathrm{HNO_3}\\ \text{(standard solution)}\end{matrix}\,\Big|\,\begin{matrix}\text{saturated}\\ \text{solution}\\ \mathrm{KNO_3}\text{ in } N\\ \mathrm{HNO_3}\end{matrix}\,\Big|\,\begin{matrix}0.0025\,M\\ \mathrm{H[Co(DH)_2(NO_2)Hal]}\\ \text{in } 0.1\,N\ \mathrm{HNO_3}\end{matrix}\,\Big|\,\mathrm{HalAg}\,\Big|\,\mathrm{Ag}$$

The cell for measuring the e.m.f. of the concentration cell consisted of two cylindrical vessels with platinum electrodes sealed into them and coated with silver halide. Contact between the vessels was effected by means of a bridge filled with saturated potassium nitrate solution.

Halogen-silver electrodes were prepared according to (5). To measure the emf of the concentration cell, a high-resistance dc potentiometer of the PPTV-1 type was used; as the null instrument, a mirror galvanometer of the M-21 type was employed, with a sensitivity of $5 \cdot 10^{-10}$ A/mm. The temperature was kept constant within ±0.02° by means of an E-149 ultrathermostat.

Results of the measurements and their discussion

The measured potential of the concentration cell is related to the concentration of free halogen ions by the known equation:

$$E = 2.303\frac{RT}{nF}\lg\frac{a}{x}, \qquad (1)$$

where a is the standard concentration of the halide ion in the half-cell containing the KHal solution (in g-ion/l), and x is the concentration of free halogen ions in the solution of the complex at the given moment in time.

Fig. 1. Dependence of $\lg(C-x)$ on temperature. A–for $[\mathrm{Co(DH)_2(NO_2)Cl^-}]$, B–for $[\mathrm{Co(DH)_2(NO_2)Br^-}]$. 1—40°, 2—30°, 3—25°, 4—18°.

Figure 1: Fig. 1. Dependence of $\lg(C-x)$ on temperature. A–for $[\mathrm{Co(DH)_2(NO_2)Cl^-}]$, B–for $[\mathrm{Co(DH)_2(NO_2)Br^-}]$. 1—40°, 2—30°, 3—25°, 4—18°.

Fig. 1. Dependence of $\lg(C-x)$ on temperature. *A*–for $[\mathrm{Co(DH)_2(NO_2)Cl^-}]$, *B*–for $[\mathrm{Co(DH)_2(NO_2)Br^-}]$. 1—40°, 2—30°, 3—25°, 4—18°.

Halogenonitro-bis-dimethylglyoximatocobaltiate ions in aqueous solution undergo aquation according to the equation:

$$[\mathrm{Co(DH)_2(NO_2)Hal}]^- + \mathrm{H_2O} \rightarrow [\mathrm{Co(H_2O)(DH)_2NO_2}] + \mathrm{Hal}^-. \qquad (2)$$

According to the equation for a first-order reaction, the aquation rate constant k is equal to:

$$k = \frac{2.303}{t} \lg \frac{C}{C-x}, \qquad (3)$$

where C is the initial concentration of the halogenonitro complex and x is the concentration of free halogen ions in the solution of the complex. From equation (1), x is found from the measured emf values.

Figure 1 gives the dependence of the logarithm of the concentration of halogenonitrocobaltiate ions, $\lg(C-x)$, on time at 18, 25, 30, and 40°. From this, the rate constants of aquation of chloronitro- and bromonitro-bis-dimethylglyoximatocobaltiate ions were determined graphically; they are given in Table 2 together with the activation energy and the logarithms of the pre-exponential factors Z. For comparison, data are also given on the aquation rate of dihalogeno-bis-dimethylglyoximatocobaltiate ions (5). Figure 2 gives the dependence of $\lg k$ on $1/T$, from which the activation energy was determined graphically. The rate of hydration of the bromonitro compound is somewhat greater than that of the chloronitro-bis-dimethylglyoximatocobaltiate ions.

Table 2

Kinetic characteristics of the aquation reactions of $[\mathrm{Co(DH)_2XY}]^-$ ions

Complex ion	Medium	$k \cdot 10^6$, sec^{-1}, at 18°	$k \cdot 10^6$, sec^{-1}, at 25°	$k \cdot 10^6$, sec^{-1}, at 30°	$k \cdot 10^6$, sec^{-1}, at 40°	Activation energy E, kcal/mol	Logarithm of the pre-exponential factor, lg Z
$[Co(DH)_2(NO_2)Cl]^-$	0.1 N HNO_3	38.4	103	197	659	23.5	14.9
$[Co(DH)_2(NO_2)Cl]^-$	0.1 N KNO_3*	–	101	–	–	–	–
$[Co(DH)_2(NO_2)Br]^-$	0.1 N HNO_3	46.0	115	230	817	23.7	15.1
$[Co(DH)_2Cl_2]^-$	0.1 N HNO_3	106	270	–	–	23.9	14.0
$[Co(DH)_2Br_2]^-$	0.1 N HNO_3	144	–	–	–	24.5	–

* Initial value pH ≈ 2.80.

The aquation of the dichloro complex proceeds approximately three times faster than the aquation of the chloronitro complex. Even if it is assumed that the probability of chlorine leaving the dichloro ion is twice as great as the probability of chlorine leaving the chloronitro ion, since in the first ion there are two chlorines in the inner sphere and in the second one there is one, then even in this case the aquation rate of the dichloro ion could be only twice as great as the hydration rate of the chloronitro ion. If our data are compared with the data on the kinetics of aquation of the trans-dichloro- and trans-chloronitrodiethylenediaminecobalt(III) ions $[Co\,en_2Cl_2]^+$ and $[Co\,en_2(NO_2)Cl]^+$ (7-9), it turns out that in the ethylenediamine complexes the aquation rate of trans-chloronitro is much greater than the aquation rate of the trans-dichloro complexes ($k = 66 \cdot 10^{-3}$ min^{-1} and $1.9 \cdot 10^{-3}$ min^{-1}). It is also interesting to note the fact that, whereas the aquation rate of the dichloro-bis-dimethylglyoximatocobaltate ion depends strongly on the pH of the medium, the hydration rate of the chloronitro ion in the pH interval 1-3 does not depend on the acidity of the medium.

Fig. 2. Dependence of lg k on $1/T$.
1 –for $[Co(DH)_2(NO_2)Cl]^-$, 2 –for $[Co(DH)_2(NO_2)Br]^-$

The data obtained are difficult to reconcile with the assumption that, in the dioximes of trivalent cobalt, the reaction proceeds by an S_N1 mechanism, since in that case, taking into account the greater trans-activity of the nitro group than of chlorine and bromine, the aquation rate should be greater for halogenonitro ions than for dihalogeno ions.

Most likely, the reaction proceeds by an S_N2 mechanism with the formation of an intermediate complex with coordination number seven. In that case, the decrease in the aquation rate in the series dihalogeno > halogenonitro ions can be explained by additional steric hindrances to the access of water molecules to the reaction center, which are created by the nitro group in the complex ion.

Institute of Chemistry
Academy of Sciences of the Moldavian SSR

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