Exchange of Sulfate Ions in Aqueous Solutions of Acidoammine Complexes of Trivalent Cobalt

`![Fig. 1](figure)`

1957

SovietRxiv

Fig. 1

Figure 1: Fig. 1

Abstract

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Chemistry

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Exchange of Sulfate Ions in Aqueous Solutions of Acidoammine Complexes of Trivalent Cobalt

(Presented by Academician I. I. Chernyaev, 30 XI 1956)

The study of the kinetics of isotopic exchange has been of great help in investigating the properties, structure, and transformations of complex compounds ([1,2]). Of great interest in this respect are the systematic studies by A. A. Grinberg and co-workers ([1]) on the mechanism and kinetics of isotopic exchange of halide addends in a series of complex compounds of the platinum metals. Similar studies have also been carried out for a number of complex compounds of trivalent cobalt. In particular, mention should be made of the work of Etel and Johnson ([3]), who studied chlorine exchange in trans-$[CoEn_2Cl_2]^+$, and of Long's work ([4]) on the exchange of $C_2O_4^{2-}$ in cobalt and chromium trioxalates. Among later studies in this area one should cite the work of Adamson ([5]), who studied the exchange of SCN^- ions in complex ammines of cobalt and chromium.

Fig. 1. Temperature dependence of the rate of isotopic exchange of SO_4^{2-} ions in a 0.1 *n* aqueous solution of $[Co(NH_3)_5SO_4] \cdot HSO_4 \cdot 2H_2O$: 1—30°, 2—40°, 3—50°, 4—60°, 5—70°.

The purpose of the present work was to study the isotopic exchange of SO_4^{2-} ions in a series of acido- and acidoaquoammine salts of trivalent cobalt containing these ions in the inner and outer coordination spheres. Isotopic exchange of sulfate ions was first studied by one of us jointly with Yu. P. Nazarenko ([6]) as applied to green modifications of chromium sulfate complexes. We have studied the exchange of sulfate ions in aqueous solutions of the following cobalt acidoammines: $[Co(NH_3)_5SO_4]HSO_4 \cdot 2H_2O$ and $[Co(NH_3)_4H_2OSO_4]HSO_4 \cdot 1.5H_2O$.

In this investigation it is of interest to study the mobility of the bond $Co^{3+} \dots SO_4^{2-}$ in the inner sphere, as well as the influence of inner-sphere ammonia and water molecules on the rate of isotopic exchange of SO_4^{2-} in aqueous solutions of these complexes.

The preparations were obtained sufficiently pure. The content of inner-sphere sulfato groups (the determination was carried out with hydrochloric-acid benzi-

Fig. 2

Figure 2: Fig. 2

dine) in both preparations was equal to $50 \pm 1\%$.

Exchange of SO_4^{2-} ions in aqueous solutions of sulfato-pentaammine-cobalt bisulfate. In studying the kinetics of isotopic exchange of SO_4^{2-} ions, we used S^{35} in the form of sodium sulfate as the radioactive indicator. Separation of inner- and outer-

of sulfate ions SO_4^{2-} was followed with time, using a solution of benzidine hydrochloride. The separation error did not exceed 1%.

In the course of the work, the rate of ion exchange between the outer and inner coordination spheres was studied at 30, 40, 50, 60, and 70° (Fig. 1). Further, in order to establish the mechanism of isotopic exchange of SO_4^{2-} ions in aqueous solutions of sulfato-pentammine-cobalt bisulfate, the dependence of the exchange rate on the concentration of the complex salt (Fig. 2) and of sulfate ions present in the outer sphere (Fig. 3) was studied. Experiments to study the concentration dependences of the rate of isotopic exchange were carried out at 60°.

Fig. 2. Dependence of the rate of exchange of SO_4^{2-} ions on the concentration of the complex salt in solution.
I –solutions of $[Co(NH_3)_4H_2OSO_4]HSO_4 \cdot 1.5H_2O$ (40°), **II** –solutions of $[Co(NH_3)_5SO_4]HSO_4 \cdot 2H_2O$ (60°), 1–0.05 N, 2–0.1 N, 3–0.2 N, 4–0.1 N, 5–0.3 N, 6–1 N.

The data obtained indicate that exchange of SO_4^{2-} ions in aqueous solutions of $[Co(NH_3)_5SO_4]HSO_4 \cdot 2H_2O$ proceeds at a measurable rate and is well described by a first-order kinetic equation:

$$-kt = \ln(1 - F).$$

The rate of exchange of SO_4^{2-} ions in aqueous solutions of sulfato-pentammine-cobalt bisulfate changes rather rapidly with temperature. The temperature coefficient of the reaction is approximately equal to 3; the activation energy of the isotopic exchange process is 25 kcal/mol. The values of the half-exchange times and of the exchange-rate constants for SO_4^{2-} ions at various temperatures are as follows:

Temperature, °C	$\tau_{1/2}$, min	k, min^{-1}
30	8100	$8.56 \cdot 10^{-5}$
40	2000	$3.47 \cdot 10^{-4}$
50	420	$1.65 \cdot 10^{-3}$
60	132	$5.25 \cdot 10^{-3}$

Fig. 3

Figure 3: Fig. 3

Temperature, °C	$\tau_{1/2}$, min	k, min^{-1}
70	44	$1.58 \cdot 10^{-2}$

The process of isotopic exchange of SO_4^{2-} ions in aqueous solutions of $[Co(NH_3)_5SO_4]HSO_4$ proceeds simultaneously with the aquation process of the complex ion; an increase in temperature increases the rate of exchange of SO_4^{2-} ions between the outer and inner coordination spheres. In the same direction there is an increase in the rate of release of SO_4^{2-} ions from the inner coordination sphere, with subsequent formation of the aquo ion according to the scheme:

$$[\text{complex } SO_4]^+ + H_2O \rightleftarrows [\text{complex } H_2O]^{3+} + SO_4^{2-}$$

The rate of exchange of sulfate ions also increases with increasing concentration of the complex ion:

Concentration, equiv/l	$\tau_{1/2}$, min	k, min^{-1}
0.1	122	$5.25 \cdot 10^{-3}$
0.3	108	$6.42 \cdot 10^{-3}$
1.0	76	$9.12 \cdot 10^{-3}$

A tenfold increase in the concentration of the complex increases the rate of exchange of SO_4^{2-} ions approximately twofold (see also Fig. 2). These data permit the conclusion that there is a bimolecular mechanism for the isotopic exchange of SO_4^{2-} ions in aqueous solutions of $[Co(NH_3)_5SO_4]HSO_4 \cdot 2H_2O$.

In studying the influence of the concentration of outer-sphere sulfate io-

additions on the rate of isotopic exchange, 5 and 10 moles of Na_2SO_4 were added per 1 mole of $[Co(NH_3)_5SO_4]HSO_4 \cdot 2H_2O$. The results obtained (Fig. 3) indicate that the rate of isotopic exchange does not depend on the concentration of outer-sphere sulfate ions. These results make it possible to conclude that an associative mechanism is absent in the process of isotopic exchange of SO_4^{2-} ions in aqueous solutions of sulfato-pentaamminecobalt(III) bisulfate.

Fig. 3. Effect of sodium sulfate on the rate of isotopic exchange of SO_4^{2-} ions in aqueous solutions: 1-3 –$[Co(NH_3)_4H_2OSO_4]HSO_4 \cdot 1.5H_2O$ (40°), 1 – without addition of Na_2SO_4; 2 –5 Na_2SO_4 added; 3 –10 Na_2SO_4 added; 4 – aqueous solutions of $[Co(NH_3)_5SO_4]HSO_4 \cdot 2H_2O$ (60°): a –without addition of Na_2SO_4, b –5 Na_2SO_4 added, c –10 Na_2SO_4 added.

Summarizing the experimental data obtained on the dependence of the rate of isotopic exchange of SO_4^{2-} ions in aqueous solutions of sulfatopentaamminecobalt(III) bisulfate on temperature, time, and concentration, one may draw tentative conclusions about the mechanism of the exchange process. The most probable assumption is that the process of exchange of SO_4^{2-} ions between the outer and inner coordination spheres of sulfatopentaamminecobalt(III) bisulfate proceeds through the intermediate formation of an aquopentaamminecobalt ion, i.e., the primary process is replacement of the sulfato group by water in the inner coordination sphere:

$$[Co(NH_3)_5SO_4]^+ + H_2O \rightleftarrows [Co(NH_3)_5H_2O]^{3+} \cdot SO_4^{2-} \quad (1)$$

$$[Co(NH_3)_5H_2O]^{3+} \cdot SO_4^{2-} \rightleftarrows [Co(NH_3)_5H_2O]^{3+} + SO_4^{2-} \quad (2)$$

$$[Co(NH_3)_5H_2O]^{3+} + {}^{\times}SO_4^{2-} \rightleftarrows [Co(NH_3)_5H_2O]^{3+} \cdot {}^{\times}SO_4^{2-} \quad (3)$$

$$[Co(NH_3)_5H_2O]^{3+} \cdot {}^{\times}SO_4^{2-} \rightleftarrows [Co(NH_3)_5{}^{\times}SO_4]^+ + H_2O \quad (4)$$

If one proceeds from this mechanism of the process of isotopic exchange of SO_4^{2-} ions, then the rate of exchange should be governed by the rate of formation of the intermediate aquo ion (2), i.e., at higher temperatures the exchange should proceed faster. This proposition is in good agreement with the experimental data obtained on the temperature dependence of the exchange rate.

Exchange of SO_4^{2-} ions in aqueous solutions of sulfato-aquotetraamminecobalt(III) bisulfate. In the course of the work, the dependence of the rate of isotopic exchange of SO_4^{2-} ions on such factors as time, temperature, and the concentration of complex and sulfate ions in solution was established. The rate of exchange of SO_4^{2-} ions in aqueous solutions of $[Co(NH_3)_4H_2OSO_4]HSO_4 \cdot 1.5H_2O$ increases sharply with temperature (Fig. 4). The temperature coefficient of the reaction is close to 4. The activation energy of the process of isotopic exchange is 29 kcal/mole. We give the values of the half-exchange times and exchange rate constants for different temperatures:

Temperature, °C	$\tau_{1/2}$, min	k, min^{-1}
30	1260	$5.5 \cdot 10^{-4}$
40	262	$2.65 \cdot 10^{-3}$
50	68	$1.02 \cdot 10^{-2}$
60	17	$4.08 \cdot 10^{-2}$

If these indices, obtained in studying the exchange of SO_4^{2-} ions in aqueous solutions of $[Co(NH_3)_5SO_4]HSO_4 \cdot 2H_2O$ and $[Co(NH_3)_4H_2OSO_4] \cdot HSO_4 \cdot 1.5H_2O$,

Fig. 4. Temperature dependence of the rate of isotopic exchange of SO_4^{2-} ions in a 0.1 N aqueous solution of $[Co(NH_3)_4H_2OSO_4]HSO_4 \cdot 1.5H_2O$. 1—30°, 2—40°, 3—50°, 4—60°.

Figure 4: Fig. 4. Temperature dependence of the rate of isotopic exchange of SO_4^{2-} ions in a 0.1 N aqueous solution of $[Co(NH_3)_4H_2OSO_4]HSO_4 \cdot 1.5H_2O$. 1—30°, 2—40°, 3—50°, 4—60°.

are compared, it is seen that exchange in solutions of the latter, other conditions being equal, proceeds considerably faster. The rate of isotopic exchange in aqueous solutions of aquo-tetrammine-cobalt bisulfate changes more sharply with temperature. Consequently, replacement of an ammonia molecule by water in the inner coordination sphere of the complex ion promotes an increase in the lability of the complex-bound sulfate groups.

The study of the rate of exchange of SO_4^{2-} ions at different concentrations of the complex salt in solution gave, in general, the same dependence as in the preceding system* (see Fig. 2):

Concentration, equiv/l	$\tau_{1/2}$, min	k, min^{-1}
0.05	296	$2.34 \cdot 10^{-3}$
0.1	262	$2.65 \cdot 10^{-3}$
0.2	236	$2.94 \cdot 10^{-3}$

Fig. 4. Temperature dependence of the rate of isotopic exchange of SO_4^{2-} ions in a 0.1 *n* aqueous solution of $[Co(NH_3)_4H_2OSO_4]HSO_4 \cdot 1.5H_2O$. 1—30°, 2—40°, 3—50°, 4—60°.

Experiments on concentration dependences were carried out at 40°. Fig. 3 gives the results obtained in studying the dependence of the rate of exchange on the concentration of outer-sphere sulfate ions; for this purpose 5 and 10 mol of Na_2SO_4 were added per 1 mol of $[Co(NH_3)_4H_2OSO_4] \cdot HSO_4 \cdot 1.5H_2O$. In aqueous solutions of this complex a certain increase in the rate of isotopic exchange is observed with increasing concentration of SO_4^{2-} ions.

However, this insignificant change in the rate of isotopic exchange does not justify speaking of different mechanisms of the exchange process in aqueous solutions of $[Co(NH_3)_5SO_4]HSO_4 \cdot 2H_2O$ and $[Co(NH_3)_4H_2OSO_4]HSO_4 \cdot 1.5H_2O$.

The experimental results obtained give grounds to suppose that the first stage of the process of isotopic exchange of SO_4^{2-} ions in aqueous solutions of sulfato-aquo-tetrammine-cobalt bisulfate is aquation of the complex ion with formation of the diaquo form according to the scheme:

$$[Co(NH_3)_4H_2OSO_4]^+ + H_2O \rightleftarrows [Co(NH_3)_4(H_2O)_2]^{3+} \cdot SO_4^{2-}$$

$$[Co(NH_3)_4(H_2O)_2]^{3+} \cdot SO_4^{2-} \rightleftarrows [Co(NH_3)_4(H_2O)_2]^{3+} + SO_4^{2-}$$

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Received
19 XI 1956

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* The low solubility of the complex salt made it impossible to study exchange of SO_4^{2-} at concentrations > 0.2 *n*.

Note: Figure translations are in progress. See original paper for figures.