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KINETICS OF ISOTOPIC EXCHANGE OF SULFATE IONS IN AQUEOUS SOLUTIONS OF AMMINE AND AQUOAMMINE COMPLEXES OF TRIVALENT COBALT

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The present communication is a continuation of our work (^{1}) on the study of the kinetics of isotopic exchange of SO_4^{2-} ions in aqueous solutions of ammine and aquoammine complexes of trivalent cobalt containing SO_4^{2-} in the inner coordination sphere. Recently, much attention has been given to the kinetics of isotopic exchange of anionic addends in complex cobalt salts ($^{2-5}$).

In the present work we studied the kinetics of isotopic exchange of SO_4^{2-} ions in aqueous solutions of the following complex compounds: $[Co(NH_3)_4(H_2O)SO_4]_2SO_4 \cdot 2H_2O$ and $[Co(NH_3)_5SO_4]_2 \cdot SO_4 \cdot H_2O$. Preparations of this composition were obtained by recrystallization of the corresponding acid sulfates (with the HSO_4^- ion in the outer sphere) from alcoholic solutions (^{6,7}). The amount of impurities did not exceed 1%. Outer- and inner-sphere SO_4^{2-} ions were separated with benzidine hydrochloride. The separation error did not exceed ±1%. Sulfur-35 in the form of sodium sulfate was used in the work.

Fig. 1. Temperature dependence of the rate of isotopic exchange of SO_4^{2-} *ions. 1, 2, and 4—aqueous 0.1 N solution of* $[Co(NH_3)_5SO_4]_2SO_4 \cdot H_2O$*; 3, 5, and 6—aqueous 0.1 N solution of* $[Co(NH_3)_4(H_2O)SO_4]_2SO_4 \cdot 2H_2O$*; 1—50°, 2—60°, 3—30°, 4—70°, 5—40°, 6—50°.*

Aqueous solutions of sulfatoaquotetramminecobalt sulfate and sulfatopentamminecobalt sulfate differ from the systems studied by us earlier only in the concentration of hydrogen ions.

The results of measuring the pH of aqueous 0.1 *N* solutions of normal and acid sulfates are as follows:

Complex salt	pH
$[Co(NH_3)_5SO_4]HSO_4 \cdot 2H_2O$	2.2
$[Co(NH_3)_4(H_2O)SO_4]HSO_4 \cdot 1.5H_2O$	2.2

Fig. 2

Figure 1: Fig. 2

Fig. 3

Figure 2: Fig. 3

Complex salt	pH
$[Co(NH_3)_5SO_4]_2SO_4 \cdot H_2O$	5.2
$[Co(NH_3)_4(H_2O)SO_4]_2SO_4 \cdot 2H_2O$	4.4

The difference in the concentrations of H ions leads to a significant change in the physicochemical properties of aqueous solutions of complex salts and is sharply reflected in the mobility of the complex bond $Co^{3+} \ldots SO_4^{2-}$.

Kinetics of isotopic exchange of SO_4^{2-} ions in aqueous solutions of $[Co(NH_3)_4(H_2O)SO_4]_2SO_4 \cdot 2H_2O$.

Temperature dependence of the rate of isotopic exchange. These experiments were carried out with solutions of $0.1\,N$ concentration (with respect to Co^{3+}), at 30, 40, and $50^\circ \pm 0.01^\circ$ (Fig. 1, curves 3, 5, 6). In the temperature interval studied, the rate of isotopic exchange of SO_4^{2-} ions between the outer and inner coordination spheres is well characterized by the first-order kinetic equation $-kt = \ln(1-F)$, where F is the fraction exchanged. The temperature coefficient of the reaction is equal to 5. The change in the rate constant of isotopic exchange with temperature is well described by the Arrhenius equation (Fig. 2, curve 1). The activation energy of the process is 32 ± 1 kcal/mole.

Comparison with the results obtained in studying the temperature dependence of the rate of isotopic exchange of SO_4^{2-} ions in solutions of $[Co(NH_3)_4(H_2O)SO_4]HSO_4 \cdot 1.5H_2O$ shows that, under identical temperature and concentration conditions, isotopic exchange

Fig. 2. Temperature dependence of the reaction rate constant.
1 –$0.1\,N$ solution of $[Co(NH_3)_4(H_2O)SO_4]_2SO_4 \cdot 2H_2O$,
2 –$0.1\,N$ solution of $[Co(NH_3)_5SO_4]_2SO_4 \cdot H_2O$.

Fig. 3. Dependence of the rate of isotopic exchange of SO_4^{2-} ions on the concentration of the complex salt.
1–3 –solutions of $[Co(NH_3)_4(H_2O)SO_4]_2SO_4 \cdot 2H_2O$ (at 40°),
4–6 –solutions of $[Co(NH_3)_5SO_4]_2SO_4 \cdot H_2O$ (at 60°);
1—$0.5\,N$, 2—$0.1\,N$, 3—$0.2\,N$, 4—$1\,N$, 5—$0.5\,N$, 6—$0.1\,N$.

of SO_4^{2-} in aqueous solutions of the acid sulfate proceeds at a lower rate (the temperature coefficient of the reaction is equal to 4).

Fig. 4. Dependence of the rate of isotopic exchange of SO_4^{2-} ions on their concentration; 1—3—solutions of $[Co(NH_3)_4(H_2O)SO_4]_2SO_4 \cdot 2H_2O$ (at 40°); 4—6—solutions of $[Co(NH_3)_5 \cdot SO_4]_2SO_4 \cdot H_2O$ (at 60°); 1 and 4—solution without addition of Na_2SO_4 (0.1 *N*); 2 and 5—10 mol. of Na_2SO_4 added, 3 and 6—20 mol. of Na_2SO_4 added.

Figure 3: Fig. 4. Dependence of the rate of isotopic exchange of SO_4^{2-} ions on their concentration; 1—3—solutions of $[Co(NH_3)_4(H_2O)SO_4]_2SO_4 \cdot 2H_2O$ (at 40°); 4—6—solutions of $[Co(NH_3)_5 \cdot SO_4]_2SO_4 \cdot H_2O$ (at 60°); 1 and 4—solution without addition of Na_2SO_4 (0.1 *N*); 2 and 5—10 mol. of Na_2SO_4 added, 3 and 6—20 mol. of Na_2SO_4 added.

Concentration dependence of the rate of isotopic exchange (at 40°). Changing the concentration of $[Co(NH_3)_4(H_2O)SO_4]_2SO_4 \cdot 2H_2O$ (Fig. 3; curves 1—3) from 0.05 *N* to 0.2 *N* does not lead* to a noticeable change in the mobility of the complex bond $Co^{+3} \ldots SO_4^{2-}$. There is even a certain tendency toward a slowing of the rate of exchange of SO_4^{2-} ions with increasing concentration of the complex salt. In the concentration interval studied, re-

The isotopic-exchange reaction is of zero order with respect to the concentration of $[Co(NH_3)_4(H_2O)SO_4]^+$.

In studying the dependence of the rate of isotopic exchange on the concentration of SO_4^{2-}, 10 and 20 mol. of sodium sulfate were added to a solution containing 1 mol of $[Co(NH_3)_4(H_2O)SO_4]_2SO_4 \cdot 2H_2O$. It turned out that the rate of isotopic exchange of SO_4^{2-} ions increases with increasing concentration of sulfate groups in the solution (Fig. 4, curves 1—3). In solutions of the acid sulfate $[Co(NH_3)_4(H_2O)SO_4]HSO_4 \cdot 1.5H_2SO$, however, an increase in the concentration of the complex salt accelerates the isotopic exchange of SO_4^{2-}, while an increase in the concentration of sulfate groups in the solution has practically no effect on the rate of the exchange reaction (1).

The results of studying the temperature and concentration dependences of the rate of isotopic exchange of SO_4^{2-} in aqueous solutions of $[Co(NH_3)_4 \cdot (H_2O)SO_4]_2SO_4 \cdot 2H_2O$ made it possible to advance a number of considerations concerning the mechanism of the isotopic distribution of sulfate ions between the outer and inner

Fig. 4. Dependence of the rate of isotopic exchange of SO_4^{2-} ions on their concentration; 1—3—solutions of $[Co(NH_3)_4(H_2O)SO_4]_2SO_4 \cdot 2H_2O$ (at 40°); 4—6—solutions of $[Co(NH_3)_5 \cdot SO_4]_2SO_4 \cdot H_2O$ (at 60°); 1 and 4—solution without addition of Na_2SO_4 (0.1 *N*); 2 and 5—10 mol. of Na_2SO_4 added, 3 and 6—20 mol. of Na_2SO_4 added.

* The limited solubility of this complex salt did not permit the investigation of solutions of higher concentrations.

coordination spheres. In aqueous solutions containing the complex ion $[Co(NH_3)_4(H_2O)SO_4]^+$, there occurs a process of protolytic dissociation of the inner-sphere water molecule

$$[Co(NH_3)_4(H_2O)SO_4]^+ \rightleftharpoons [Co(NH_3)_4(OH)SO_4] + H^+.$$

A decrease in the concentration of H^+ ions shifts the equilibrium to the right. The hydroxogroup formed in the inner sphere apparently increases the mobility of the complex-bound sulfate groups*. Isotopic distribu-

* A similar influence of hydroxo groups on the mobility of inner-sphere sulfate groups was observed by Fialkov and Nazarenko (^{8}) in studying the kinetics of isotopic exchange of SO_4^{2-} ions in aqueous solutions of green chromium sulfate complexes.

the distribution of SO_4^{2-} ions between the outer and inner coordination spheres is a secondary process, and its rate at a given temperature and concentration of H^+ ions is determined by the state of the above-mentioned acid–base equilibrium.*

Kinetics of isotopic exchange of SO_4^{2-} ions in aqueous solutions of $[Co(NH_3)_5SO_4]_2 \cdot SO_4 \cdot H_2O$

The exchange of SO_4^{2-} ions at 50, 60, and 70° is well described by a first-order kinetic equation (Fig. 1, curves 1, 2, 4). The temperature coefficient of the reaction is close to 3.5. The change in the rate constant of isotopic exchange with temperature obeys the Arrhenius equation (Fig. 2, curve 2). The activation energy of the process is 27 ± 1 kcal/mole.

The change in the rate of isotopic exchange with temperature is approximately the same as in aqueous solutions of $[Co(NH_3)_5SO_4]HSO_4 \cdot 2H_2O$. However, under identical temperature and concentration conditions, the exchange of SO_4^{2-} in solutions of the normal sulfate $[Co(NH_3)_5SO_4]_2SO_4 \cdot H_2O$ proceeds more slowly. Apparently this is explained by the different ratio of the concentrations of SO_4^{2-} ions in the outer sphere and of the complex cation.

Concentration dependences of the rate of isotopic exchange

(at 60°). Increasing the concentration of $[Co(NH_3)_5SO_4]_2SO_4 \cdot H_2O$ accelerates the isotopic exchange of SO_4^{2-} (Fig. 3, curves 4–6). The process proceeds in the same direction when the concentration of SO_4^{2-} ions in the solution is increased (upon addition of 10 and 20 mol of Na_2SO_4 per 1 mol of complex salt) (Fig. 4, curves 4–6), in contrast to what was observed in an analogous experiment in the study of the acid sulfate $[Co(NH_3)_5SO_4]HSO_4 \cdot 2H_2O$ (1).

These experimental data give grounds to assume that, in the mechanism of isotopic exchange of SO_4^{2-} ions in aqueous solutions of the normal sulfate

$[Co(NH_3)_5SO_4]_2SO_4 \cdot H_2O$, an important role is played by the aquation reaction of the complex ion:

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

with the subsequent associative process (1).

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* The results of studying the influence of the concentration of H^+ ions over a wider range will be presented in another communication.

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

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