A. V. EGUNOV and P. I. DOLIN

1962

SovietRxiv

Abstract

Full Text

PHYSICAL CHEMISTRY

A. V. EGUNOV and P. I. DOLIN

RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS OF AMMINE COMPLEXES OF COBALT (III) AND NICKEL (II)

(Presented by Academician A. N. Frumkin, 11 VII 1961)

This paper presents certain experimental data on the question of the radiation-chemical stability of aqueous solutions of ammine complexes of Co (III) and Ni (II). The investigation was carried out in an atmosphere of atmospheric oxygen and in an atmosphere of nitrogen. The experiment is discussed and certain arguments are given in favor of substantiating the proposed scheme for the decomposition of the Co (III) ammine complex.

At the present time there are few data in the literature on the action of ionizing radiation on aqueous solutions of complex compounds. As regards the radiolysis of aqueous solutions of complex compounds of Co (III) and Ni (II), there are no data at all for these compounds. The question itself of the influence of substituents and of the role of complex formation on the radiation-chemical stability of the central ion is of great interest. It makes it possible to approach more closely the consideration of the mechanism of the primary act of the action of ionizing radiation on a substance. This is all the more so because the usual state of ions in solution is a complex-like state. For example, in water the dissolved substance is usually present in the form of an aquo complex. Fricke and Hart (^{1}) were the first to study the action of X-radiation on aqueous solutions of potassium ferrocyanide, $K_4(Fe(CN)_6)$, in the concentration range 10^{-4}–10^{-1} mole/l. The experiments were carried out at pH 2–11, in the absence of atmospheric oxygen. Under these conditions the radiolysis of $K_4(Fe(CN)_6)$ was accompanied by oxidation of ferrocyanide to ferricyanide. The process was accompanied by an increase in pH and the evolution of H_2.

In work (^{2}) the action of γ-radiation from Co^{60} was also studied on aqueous solutions of ferrocyanide under several different conditions. In the presence of atmospheric oxygen, the oxidation yield depended on pH, concentration, and the "age" of the solution. The maximum value of the oxidation yield was found to be 7.5. Moreover, at pH $<$ 11 ferrocyanide was oxidized to ferricyanide, while at pH $>$ 11 the reverse process was observed—the reduction of ferri- to ferrocyanide. In the absence of atmospheric oxygen, the oxidation yield depended strongly on pH and was considerably smaller than in the presence of the latter. A. A. Balandin, V. I. Spitsyn, and others (^{3}) studied the behavior of aqueous solutions

Fig. 1. Irradiation cells

Figure 1: Fig. 1. Irradiation cells

of complex compounds of platinum and palladium under the action of electrons with an energy of about 6 MeV. It was found that $Na_2(Pt(OH)_5Cl)$ had the least stability toward the action of radiation. The authors attribute this effect to the trans influence of Cl on the Pt–OH bonds. The stability of $PdCl_2$ and $PdCl_4$ proved to be lower than the stability of analogous Pt compounds. There are data (4) on the decomposition of the thiosulfate complex of silver, $Na_3(Ag(S_2O_3)_2)$, under the action of electrons. The decomposition was accompanied by the liberation of metallic silver and Ag_2S.

From the material cited it is evident that the radiation-chemical stability of complex compounds in aqueous solutions is influenced to a significant extent by such factors as the nature of the central ion, the nature of the substituents, the acidity of the medium, the atmosphere, and others. From the available experimental data it is still impossible to present with complete

mechanisms occurring in aqueous solutions of complex compounds under the action of radiation. This area requires further study.

Experimental Part

Nickel ammine $(\mathrm{Ni(NH_3)_6})\mathrm{Cl_2}$ was obtained by treating $\mathrm{NiCl_2}$ with concentrated ammonia according to (5). Cobalt ammine $(\mathrm{Co(NH_3)_6})\mathrm{Cl_3}$, according to Biltz (6), was prepared from saturated solutions of $\mathrm{CoCl \cdot 6H_2O}$ and $\mathrm{NH_4Cl}$ in a 20% ammonia solution. Aqueous solutions of $(\mathrm{Ni(NH_3)_6})\mathrm{Cl_2}$ and $(\mathrm{Co(NH_3)_6})\mathrm{Cl_3}$ were prepared immediately before the experiment. The concentration of the solutions in all experiments was $5 \cdot 10^{-3}$ mol/l. At such a concentration of dissolved substance it was possible to neglect completely the effect of direct action and to assume that the radiation is absorbed by the water.

Fig. 1. Irradiation cells

Irradiation was carried out with a source of γ-radiation, Cs^{137}, with an activity of 600 g-eq Ra. The source had the form of a cylinder 300 mm in diameter and 100 mm high. The experiments were conducted at a dose rate of $5 \cdot 10^{15}$ eV/ml • sec in the case of a quartz-glass cell (Fig. 1, 1) and $7.2 \cdot 10^{15}$ eV/ml • sec in the case of a glass cell with a thin membrane bottom (Fig. 1, 2). The dose rate was determined with a ferrosulfate dosimeter. The quartz cell was used to record the absorption spectra of the solutions under study before and after irradiation. The glass cell with a thin membrane bottom was used to determine the yield of gaseous radiolysis products by the method described in (7). Spectrophotometric studies were carried out on an SF-4 spectrophotometer. The change in pH was recorded with a glass electrode on an LP-5 potentiometer. Saturation of the solutions with nitrogen was carried out by the method described in (8).

Fig. 2. Absorption spectrum of (Ni(NH3)6)Cl2 in 5% solution before (a) and after (b) 48 h irradiation

Figure 2: Fig. 2. Absorption spectrum of (Ni(NH3)6)Cl2 in 5% solution before (a) and after (b) 48 h irradiation

Fig. 3 and Fig. 4

Figure 3: Fig. 3 and Fig. 4

It is known that dilute neutral aqueous solutions of nickel ammine are decomposed by water with formation of $Ni(OH)_2$. To avoid such an effect, we studied the radiation-chemical stability of Ni(II) ammine in a 5% ammonia solution. In such a solution $(Ni(NH_3)_6)Cl_2$ can remain for a long time. Under the action of γ-radiation the external appearance of the nickel ammine solution does not change. Figure 2 shows the absorption spectrum of nickel ammine before and after 48 hours of irradiation at a dose rate of $5 \cdot 10^{15}$ eV/ml • sec.

Fig. 2. Absorption spectrum of $(Ni(NH_3)_6)Cl_2$ **in 5% solution before (a) and after (b) 48 h irradiation**

It may be said that no visible changes are present in the absorption spectrum after 48 hours of irradiation. From Fig. 3 it is evident that the yield of gaseous radiolysis products, both in the case of a 5% solution of NH_4OH and in the case of nickel ammine in this solution, does not depend on the dose. In addition, the presence of nickel ammine does not affect (within the experimental error) the value of the yield, equal to 0.310 ± 0.01. Taking all the above into account, it may be said that, in aqueous solution, in the presence of 5% NH_4OH, nickel ammine is stable toward the action of γ-radiation.

Upon irradiation of a neutral aqueous solution of $(Co(NH_3)_6)Cl_3$, a brown precipitate is formed. This precipitate is in a highly dispersed state. Upon standing for 24 hours the precipitate settles completely and after

separated from the solution and dried, is obtained in the form of a fine black powder. By means of electronographic and qualitative chemical analysis it was possible to show that the precipitate is $Co(OH)_2$.

Fig. 4 presents the change in the pH of the solution during irradiation. At the initial moment the pH rapidly increases from the initial value of 5.9 to 8.8$±$0.2; upon further irradiation the pH remains practically constant. It is important to note here that a pH value of about 8-9 corresponds to the precipitation of $Co(OH)_2$ from simple cobalt salts. The constancy of the pH upon further irradiation may be ascribed to the formation of a buffer mixture

Fig. 3. Dependence of the yield of gaseous radiolysis products (a—$(Ni(NH_3)_6)Cl_2$ in 5% solution, b—NH_4OH in the same solution) on dose

Fig. 4. Dependence of the change in pH on dose during radiolysis of

$(Co(NH_3)_6)Cl_3$

$NH_4OH{-}NH_4Cl$ from the decomposed cobalt ammine ion. The buffer mixture $NH_4OH{-}NH_4Cl$ produces a pH of about 8-9.

The facts set forth can evidently be explained as follows: the Co^{3+} ion in the complex ion $(Co(NH_3)_6)^{3+}$ is reduced by a hydrogen atom to Co^{2+}, and decomposition of the complex ion $(Co(NH_3)_6)^{2+}$ into Co^{2+} and $6NH_3$ occurs. The six ammonia molecules liberated give:

$$3NH_3 + 3H_2O \to 3NH_4OH,$$

$$3NH_3 + 3Cl^- + 3H^+ \to 3NH_4Cl.$$

In total, the process of radiation-chemical decomposition of the Co^{3+} ammine can be written in the following form:

$$(Co(NH_3)_6)^{3+} + H + 3Cl^- + 5H_2O \to Co(OH)_2 + 3NH_4Cl + 3NH_4OH.$$

Thus, the radiation-chemical stability of nickel and cobalt ammines has been studied. It has been established that nickel ammine is stable to the action of γ-radiation, whereas cobalt ammine decomposes with the formation of $Co(OH)_2$.

Institute of Electrochemistry
Academy of Sciences of the USSR

Received
5 VII 1961

CITED LITERATURE

1. H. Fricke, E. J. Hart, *J. Chem. Phys.*, **3**, 596 (1935).
2. X. Tarrago, E. Marsi, M. Lefort, *C. R.*, **244**, 343 14/1 (1957).
3. A. A. Balandin, V. I. Spitsyn, V. I. Duzhenkov, L. I. Barsova, Abstracts of reports at the Tashkent Conference on the Peaceful Uses of Atomic Energy, 1959, p. 61.
4. G. G. Ryabchikova, V. I. Duzhenkov, P. Ya. Glazunov, ibid., 1959, p. 73.
5. L. K. Lepin, *Inorganic Synthesis*, Moscow, 1932, p. 169.
6. Biltz, *Zs. anorg. Chem.*, **83**, 177 (1914).

7. P. I. Dolin, *Collection of Works on Radiation Chemistry*, Publishing House of the Academy of Sciences of the USSR, 1955, p. 7.

8. S. A. Brusentseva, Candidate’ s dissertation, 1960, p. 44.

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.