Reports of the Academy of Sciences of the USSR

CHEMISTRY

1962

SovietRxiv

Abstract

Full Text

Reports of the Academy of Sciences of the USSR
1962. Vol. 144, No. 2

CHEMISTRY

L. I. BARSOVA, A. K. PIKAEV, Academician Vikt. I. SPITSYN, and
Academician A. A. BALANDIN

RADIOLYSIS OF AQUEOUS SOLUTIONS OF SOME RHODIUM COMPOUNDS

In our works (^{1}-^{3}) we have shown that, upon irradiation with high-energy electrons of aqueous solutions of certain complex compounds of platinum and palladium, platinum black and palladium black, respectively, are formed, the catalytic activity of which differs from the activity of analogous catalysts prepared by ordinary chemical methods. In the present work, the conditions for the formation of rhodium black during the radiolysis of aqueous solutions of a series of rhodium salts under the action of a stream of electrons with an energy of 0.8 MeV were investigated.

The irradiation and dosimetry procedure was described in our previous communication (^{3}). The radiolysis of aqueous solutions of the following rhodium salts was studied: chloride $RhCl_3 \cdot 4H_2O$ (“pure” grade), sulfate $Rh_2(SO_4)_3 \cdot 4H_2O$, prepared according to (^{4}), nitrate $Rh(NO_3)_3 \cdot 2H_2O$, prepared according to (^{5}), perchlorate $Rh(ClO_4)_3$, synthesized according to (^{6}), and monochloropentaamminerhodium chloride $[Rh(NH_3)_5Cl]Cl_2$, prepared according to (^{7}). Air-saturated solutions were subjected to radiolysis. The results of experiments on irradiation with accelerated electrons of aqueous solutions of these salts are given in Table 1.

Table 1

Results of experiments on irradiation of aqueous solutions of rhodium compounds

Compound	Solution concentration, M	Dose, eV/ml	Dose rate, eV/ml · sec	Observed effect
$RhCl_3$	0.001—0.01	$4.2 \cdot 10^{21}$	$1.5 \cdot 10^{18}$	Traces of metal
$Rh(NO_3)_3$	0.01	$3.6 \cdot 10^{21}$	$2.5 \cdot 10^{18}$	Formation of $Rh_2O_3 \cdot xH_2O$

Compound	Solution concentration, M	Dose, eV/ml	Dose rate, eV/ml · sec	Observed effect
$Rh_2(SO_4)_3$	0.01 (in 0.1 N H_2SO_4)	$3.6 \cdot 10^{21}$	$2.5 \cdot 10^{18}$	No visible changes
$Rh(ClO_4)_3$	0.014	$6.0 \cdot 10^{21}$	$2.5 \cdot 10^{18}$	No visible changes
$[Rh(NH_3)_5Cl]Cl_2$	0.026; pH 2	$1.8 \cdot 10^{21}$	$5 \cdot 10^{18}$	No visible changes
$[Rh(NH_3)_5Cl]Cl_2$	0.026; pH 7–12	$2.0 \cdot 10^{21}$	$5 \cdot 10^{18}$	Formation of a rhodium mirror
$[Rh(NH_3)_5Cl]Cl_2$	0.026; pH $\geq$ 12.5	$2.0 \cdot 10^{21}$	$5 \cdot 10^{18}$	Precipitation of rhodium black

As is seen from Table 1, among the compounds investigated only monochloropentaamminerhodium chloride, under certain conditions, is reduced to the metal; moreover, in acidic solutions rhodium is not formed at all. In the case of neutral solutions of $[Rh(NH_3)_5Cl]Cl_2$, irrespective of the concentration of the solution* and the absorbed dose rate, rhodium appears in the form of a metallic mirror on the walls of the cell. Only at pH $\geq$ 12.5 does formation of rhodium black occur.

The kinetics of the radiolytic reduction of $[Rh(NH_3)_5Cl]Cl_2$ was studied by measuring the optical density of irradiated solutions at a wavelength of 360 mμ and, in parallel, by weighing the metal precipitated into the sediment. Curves of the change in optical density as a function of dose are shown in Fig. 1. As in the case of palladium chloride (3), opti- the optical density at first increases sharply and then decreases, its fall being accompanied by the precipitation of metallic rhodium. Apparently, the increase in optical density at low doses is caused by the formation of some intermediate compound or by the formation of the metal in the colloidal state. The maximum on the curve of the change in optical density of a 0.026 *M* solution as a function of dose is very diffuse. This is probably due to the simultaneously occurring processes of formation of an intermediate complex (or metal in the colloidal state) and precipitation of rhodium black. Figure 2 shows the dependence of the amount of metal formed on dose for a 0.026 *M* solution of $[Rh(NH_3)_5Cl]Cl_2$ in 0.5 *N* KOH. On the basis of the curves in Fig. 1, the radiation-chemical yield of decomposition of the complex, $G(-Rh^{3+})$, was determined. From the

---

* Monochloropentaamminerhodium chloride is sparingly soluble; its maximum concentration in aqueous solution is approximately 0.03 M.

slope of the curve in Fig. 2 the radiation-chemical yield of metal, $G(\mathrm{Rh})$, was measured. The following data were obtained (dose rate $5 \cdot 10^{18}$ eV/cm^3 • sec):

Fig. 1. Change in optical density (at wavelength 360 mμ) of solutions of rhodium monochloropentammine chloride in 0.5 N KOH as a function of absorbed dose at a dose rate of $5 \cdot 10^{18}$ eV/ml • sec (D_0 is the optical density of the initial solution, D is the optical density of the irradiated solution): 1 —$5 \cdot 10^{-3}$ M solution, 2 —$2.6 \cdot 10^{-2}$ M solution

	$5 \cdot 10^{-3}$	$2.6 \cdot 10^{-2}$
Soln. conc., M	$5 \cdot 10^{-3}$	$2.6 \cdot 10^{-2}$
$G(-\mathrm{Rh}^{3+})$, ions/100 eV	0.1	0.16
$G(\mathrm{Rh})$, atoms/100 eV	–	0.16

Metal precipitation is accompanied by a decrease in the pH of the solution. For example, a 0.03 M solution of rhodium monochloropentammine chloride in 0.01 N KOH has a pH of about 10. After rhodium has precipitated (at a dose of $1.2 \cdot 10^{21}$ eV/ml), the pH becomes 8.6. This is explained by the following facts. First, when Rh^{3+} interacts with H atoms and hydrogen peroxide, H^+ ions are formed:

$$\mathrm{Rh}^{3+} + 3\mathrm{H} \to \mathrm{Rh} + 3\mathrm{H}^+, \tag{1}$$

$$2\mathrm{Rh}^{3+} + 3\mathrm{H}_2\mathrm{O}_2 \to 2\mathrm{Rh} + 6\mathrm{H}^+ + 3\mathrm{O}_2. \tag{2}$$

Fig. 2. Dependence of the amount of metallic rhodium precipitated during irradiation of a 0.026 M solution of rhodium monochloropentammine chloride in 0.5 N KOH on the absorbed dose (dose rate $9 \cdot 10^{18}$ eV/ml • sec, solution volume 10 ml)

Second, ammonia*, formed as a result of radiation decomposition of the ions $[\mathrm{Rh(NH_3)_5Cl}]^{2+}$, is partially oxidized in an alkaline medium by OH radicals. According to (8), this process proceeds as follows:

$$\mathrm{NH_3} + 6\mathrm{OH} + \mathrm{OH}^- \to \mathrm{NO}_2^- + 5\mathrm{H_2O}. \tag{3}$$

The available experimental material still does not allow definite judgments to be made about the mechanism of formation of metallic rhodium during radiolysis of aqueous solutions of $[\mathrm{Rh(NH_3)_5Cl}]\mathrm{Cl_2}$. It should only be noted that, along with processes of interaction of the products of water radiolysis with

---

* During radiolysis of alkaline solutions of $[Rh(NH_3)_5Cl]Cl_2$, evolution of ammonia is observed.

$[Rh(NH_3)_5Cl]^{2+}$, Rh^{3+}, Cl^-, and NH_3, some other processes apparently play a substantial role in this system: sorption of the products of water radiolysis by the surface of rhodium black, catalytic decomposition of H_2O_2 under the action of Rh, etc.

As in the radiolysis of aqueous solutions of palladium nitrate ([3]), irradiation of solutions of rhodium nitrate produces the hydroxide $Rh_2O_3 \cdot xH_2O$. This is evidently explained by the fact that NO_3^- ions and the products of their reduction protect Rh^{3+} from the action of H atoms and hydrogen peroxide. Radiolytic transformations of nitrate ions are accompanied by a certain increase in the pH of the solution, which leads to precipitation of rhodium hydroxide.

Institute of Physical Chemistry
Academy of Sciences of the USSR

Moscow State University
named after M. V. Lomonosov

Received
27 I 1962

CITED LITERATURE

1. A. A. Balandin, V. I. Spitsyn, L. I. Barsova, V. I. Duzhenkov, *ZhFKh*, **33**, 736 (1959).
2. A. A. Balandin, V. I. Spitsyn, V. I. Duzhenkov, L. I. Barsova, in: *Collection of Papers, Tashkent Conference on the Peaceful Use of Atomic Energy*, 1959, 1, Tashkent, 1961, p. 289.
3. V. I. Spitsyn, A. A. Balandin, L. I. Barsova, A. K. Pikaev, *DAN*, **144**, No. 3 (1962).
4. K. Krauss, H. Umbach, *Zs. anorg. Chem.*, **180**, 42 (1929).
5. *Gmelin' s Handbuch der anorganischen Chemie*, 8th ed., System-Nummer 64, Berlin, 1938, p. 5d.
6. G. Grube, H. Autenrieth, *Zs. Electrochem.*, **44**, 298 (1938).
7. V. V. Lebedinskii, *Izv. Sektora platiny i drugikh blagorodnykh metallov*, issue 13, 9 (1936).
8. V. A. Shartatyi, A. A. Zansokhova, V. D. Orekhov, *ZhFKh*, **32**, 1686 (1958).