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Table 1

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Abstract

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THE ACTION OF HIGH-ENERGY ELECTRONS ON COMPLEX COMPOUNDS OF PLATINUM

Earlier, with the participation of one of us ([1]), metallic platinum with enhanced catalytic activity was obtained by the action of a beam of accelerated electrons on aqueous solutions of platinum salts. In the present work the influence of ionizing radiation on solid platinum complexes of various composition and structure has been studied. On this question only the investigation of Holder ([2]) is known, who studied the chemical transformations of platinum complexes upon their irradiation with thermal neutrons.

Table 1

Methods of synthesis and composition of the platinum salts studied

Compound	Method of synthesis	Platinum content, % found	Platinum content, % calculated
Potassium chloroplatinate $K_2[PtCl_6]$	Interaction of $H_2[PtCl_6]$ with KCl	40.02	40.16
Ammonium chloroplatinate $(NH_4)_2[PtCl_6]$	Interaction of $H_2[PtCl_6]$ with NH_4Cl	44.07	43.97
Potassium chloroplatinite $K_2[PtCl_4]$	According to ([3])	46.81	47.04
Ammonium chloroplatinite $(NH_4)_2[PtCl_4]$	According to ([4])	52.01	52.32
Tetraammineplatodichloride $[Pt(NH_3)_4]Cl_2 \cdot H_2O$	According to ([5])	55.28	55.42
Cis-dichlorodiammineplatinum $[Pt(NH_3)_2Cl_2]$	According to ([6])	64.50	65.03

Compound	Method of synthesis	Platinum content, % found	Platinum content, % calculated
Trans-dichlorodiammineplatinum $[Pt(NH_3)_2Cl_2]$	According to (5)	64.86	65.03

* The preparation was irradiated in the anhydrous state.

Table 1 gives data on the composition and methods of synthesis of the compounds we investigated. The salts obtained were dried in a drying oven at 120° for several hours, then sieved through sieves with a mesh diameter of 0.15 mm, after which all preparations were again dried in a Fischer pistol under vacuum (4 mm Hg) at a temperature of 56°.

The radiation source was a 1.0 MeV electron accelerator tube ([7]). A sample of the preparation (about 0.2 g and with a layer thickness of about 2 mm) was placed in a glass thermostated cell 20 mm in diameter, which had a pocket for a thermocouple and two outlets for passing gas through. From above the cell was closed with a mica window 8-10 μ thick (Fig. 1).

The electron beam with an energy of 0.8 MeV was completely absorbed in the salts being irradiated. The magnitude of the intensity of the electron current in the reaction cell was measured by a Faraday collector with an entrance aperture equal to,

cell window. The integral dose was varied in the range 10^{22}–10^{24} eV/g. The dose rate was $5 \cdot 10^{19}$–10^{20} eV/g $\cdot$ sec.

The experiments were carried out in a stream of dry argon at constant temperature. In the case of potassium and ammonium chloroplatinates the irradiation temperature was 90–95°, and for the remaining salts 145–150°. Heating of the irradiated preparations occurred at the expense of the energy of the absorbed electrons. Preliminary experiments showed that at the indicated temperatures the salts under investigation do not decompose in the absence of radiation.

After irradiation the preparations were dissolved in water. In the case of poorly soluble salts, treatment with water was carried out with heating. The metallic platinum that separated was filtered off and determined by the gravimetric method. The results of the experiments are presented in Figs. 2 and 3. The initial yields are given in Table 2.

Under the action of fast electrons the platinum salts studied are reduced to metallic platinum. The exception is potassium chloroplatinate, in which no visible changes occur under the doses used. Ammonium chloroplatinate is reduced to an insignificant extent. Salts of divalent platinum decompose more readily than salts of tetravalent platinum. In the dose interval 10^{22}–$5 \cdot 10^{23}$ eV/g the degree of decomposition of the Pt^{2+} complexes increases with increasing dose. With a further increase in the integral dose, the degree of decomposition of

Fig. 1. Diagram of the reaction cell: 1—glass cell, 2—mica window, 3—pocket for the thermocouple, 4—tube for gas inlet, 5—tube for gas outlet, 6—refrigerator

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the salts remains unchanged. As is seen from the curves in Figs. 2 and 3, the degree of reduction depends on the composition of the salt. Ammonium salts decompose more readily than potassium salts. Complex compounds containing different addends in the inner sphere decompose faster than salts with identical addends. Decomposition of cis-$[Pt(NH_3)_2Cl_2]$ occurred under the conditions of our experiments by 5%, trans-$[Pt(NH_3)_2Cl_2]$ by 7%, whereas $[Pt(NH_3)_4]Cl_2$ decomposes by only 3%. Thus, spatial isomerism also affects the radiation stability of the complexes.

Fig. 1. Diagram of the reaction cell: 1—glass cell, 2—mica window, 3—pocket for the thermocouple, 4—tube for gas inlet, 5—tube for gas outlet, 6—refrigerator

Table 2

Initial yields of metallic platinum upon irradiation of complex compounds

Compound	Initial yield of platinum, atoms/100 eV
$(NH_4)_2[PtCl_6]$	0.090
$(NH_4)_2[PtCl_4]$	0.143
$K_2[PtCl_4]$	0.018
$[Pt(NH_3)_4]Cl_2$	0.047
cis-$[Pt(NH_3)_2Cl_2]$	0.036
trans-$[Pt(NH_3)_2Cl_2]$	0.338

The practically complete cessation of further decomposition of the studied salts after absorption of a definite integral irradiation dose is noteworthy. In one series of experiments the irradiated preparations $K_2[PtCl_4]$ and $(NH_4)_2[PtCl_4]$ were carefully ground and again subjected to irradiation. However, the degree of reduction of the salts did not increase in this case.

It may be assumed that at high integral irradiation doses the process of reverse oxidation of the free platinum formed by atomic chlorine, arising as a result of the radiation decomposition of the compounds studied, begins to play a noticeable role. Confirmation of this supposition is the fact that the decomposition of complexes containing reducing agents—NH_3 in the inner sphere or NH_4^+ as the cation—proceeds to a greater extent than that of complexes containing only chlorine in the inner—

···sphere. The presence of NH_4Cl and free chlorine in the gas that had passed through the cell with the irradiated preparations was established qualitatively.

The reduction of aqueous solutions of platinum complex compounds takes place at much lower doses than that of the solid salts. A solution of $[Pt(NH_3)_4]Cl_2$ decomposes by 8.7% at a dose of $1.5 \cdot 10^{21}$ eV/ml and by 17.4% at a dose of $3 \cdot 10^{21}$ eV/ml. The decomposition of salts dried only at room temperature also occurs to a much greater extent than that of salts dried by heating in vacuum. Thus, K_2PtCl_4, dried at room temperature, at a dose of $7 \cdot 10^{23}$ eV/g is reduced by 17%. Probably, in moist preparations the decomposition proceeds under the action of products of the radiolysis of the water contained in the salt.

Fig. 2. Decomposition of salts under the action of a high-energy electron beam as a function of the integral dose: 1–$(NH_4)_2[PtCl_6]$, 2–$[Pt(NH_3)_4]Cl_2$, 3–cis-$[Pt(NH_3)_2Cl_2]$, 4–trans-$[Pt(NH_3)_2Cl_2]$. Experimental temperature 145-150°.

Fig. 3. Decomposition of potassium (1) and ammonium (2) chloroplatinates under the action of a high-energy electron beam. Experimental temperature 90-95°.

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