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Abstract

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ON THE RADIOLYSIS OF CERTAIN Co(III) COMPLEXES

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In a previous work it was shown that the hexamines of Co(III): $[Co(NH_3)_6]Cl$ and $[Co\,en_3]Cl_3$, under the action of γ- and ultraviolet radiation, undergo changes of a hydrolytic character, very weakly expressed under ordinary conditions (^{1}). For a more detailed study of the mechanism of radiolysis in the complexes mentioned and as a continuation of work (^{1}), the radiation-chemical behavior of the following complex salts of Co(III) was studied: $[Co(NH_3)_5H_2O]Cl_3$ and $[Co(NH_3)_4(H_2O)_2]Cl_3$. At the same time, investigations were undertaken with a hexaacidocomplex of composition $K_3[Co(C_2O_4)_3] \cdot 3H_2O$, and also with aqueous solutions of cobalt compounds of the acidopentammine series, the photolysis of which had been well studied by Adamson (^{2}).

The changes occurring upon irradiation of aqueous solutions of $[Co(NH_3)_5H_2O]Cl_3$ and $[Co(NH_3)_4(H_2O)_2]Cl_3$ ($C = 0.001$; 0.005 and $0.01\,M$) were recorded by taking absorption spectra on an SF-4, and by measuring electrical conductivity and pH. At high doses ($5.5 \cdot 10^{13}$ MeV) the solutions strongly change color from pink and pink-violet to yellow-brown and brown, often with precipitation of hydroxides.

With dilution of solutions of the corresponding complexes, the effect of γ-radiation increases strongly (Figs. 1 and 2). Aftereffects of radiation exposure, expressed in a subsequent very large increase in light absorption of the solution, are especially characteristic of the diaquotetrammine complex; the result is practically complete irreversibility of the radiolysis process. By contrast, in $[Co(NH_3)_5H_2O]Cl_3$, at the same doses of γ-radiation, the aftereffects are not so noticeable, and reverse processes, accompanied by a return of the spectra to the spectra of unirradiated solutions, occur rather readily upon acidification. These reverse processes are connected, in all probability, with partial or complete conversion of the hydroxo complexes formed in the course of radiolysis into aquo complexes.

Table 1

Change in the extinction coefficient as a function of irradiation dose for $0.005\,M$ $[Co(NH_3)_5H_2O]Cl_3$, $[Co(NH_3)_4(H_2O)_2]Cl_3$.
$\varepsilon_{init}\,[Co(NH_3)_5H_2O]Cl_3 = 44$,
$\varepsilon_{init}\,[Co(NH_3)_4(H_2O)_2]Cl_3 = 40$

Initial substance	Dose, 10^{13} MeV	Wavelength λ, mμ	Extinction coefficient ε
$[Co(NH_3)_5H_2O]Cl_3$	0.55	355	44
$[Co(NH_3)_5H_2O]Cl_3$	1.65	355	48
$[Co(NH_3)_5H_2O]Cl_3$	2.2	355	186
$[Co(NH_3)_5H_2O]Cl_3$	5.5	360	260
$[Co(NH_3)_5H_2O]Cl_3$	4 h PRK-4	355	60
$[Co(NH_3)_5H_2O]Cl_3$	12 h PRK-4	360	94
$[Co(NH_3)_4(H_2O)_2]Cl_3$	0.55	355	90
$[Co(NH_3)_4(H_2O)_2]Cl_3$	1.65	355	100
$[Co(NH_3)_4(H_2O)_2]Cl_3$	5.5	355	360
$[Co(NH_3)_4(H_2O)_2]Cl_3$	5 h PRK-4	355	80
$[Co(NH_3)_4(H_2O)_2]Cl_3$	12 h PRK-4	355	200

It should be said that dark processes are characteristic of the Co(III) ammine compounds considered here. Judging from the absorption spectra, electrical conductivity, pH, and the change in color of solutions kept for 30 days in the dark (no substantial difference was found when the experiments were carried out in glass, quartz, and paraffined vessels), solutions that had stood exhibit, in qualitative terms, the same processes ⋯

processes that were observed in irradiated solutions of the complexes. Consequently, one may speak in this case of an acceleration of dark reactions under the action of γ-radiation.

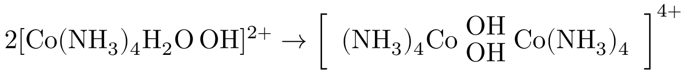
This applies especially to the diaquo complex. Irradiated solutions of the latter, as well as solutions of the monoaquo complex, exhibit catalytic activity, as can be judged from the decomposition reaction of hydrogen peroxide. It was found that $0.005\,M$ solutions of $[Co(NH_3)_4 \cdot (H_2O)_2]Cl_3$ irradiated with a dose of $5.5 \cdot 10^{13}$ MeV (3 hours elapsed from preparation of the solutions to the experiments for determining catalytic activity) possess an activity of 67.5 moles of H_2O_2 per mole of complex (in 15 min at $1.5\,N$ H_2O_2); at a dose of $4.12 \cdot 10^{13}$ MeV and under otherwise equal conditions, the activity is 28.5 moles of H_2O_2 per mole of complex. Nonirradiated solutions, after standing for 6 hours, have no catalytic activity. We regard this interesting fact as direct confirmation of our conclusions on the hydrolytic character of the radiation-chemical decomposition of the complex. Schematically, the first act of this decomposition may be represented by the following reactions:

Fig. 1. Changes occurring upon irradiation with a dose of $1.65 \cdot 10^{13}$ MeV in the absorption spectra of solutions of $[Co(NH_3)_5H_2O]Cl_3$ as a function of concentration. *a*—initial solutions; *b*—irradiated solutions. 1—$0.001\,M$; 2—$0.005\,M$; 3—$0.01\,M$.

$$[Co(NH_3)_4(H_2O)_2]^{3+} \xrightarrow[H_2O]{\gamma} [Co(NH_3)_4H_2O\,OH]^{2+} + H^+ \qquad \text{(rapid)}, \qquad \text{(I)}$$

Fig. 1. Changes occurring upon irradiation with a dose of $1.65 \cdot 10^{13}$ MeV in the absorption spectra of solutions of $[Co(NH_3)_5H_2O]Cl_3$ as a function of concentration. *a*—initial solutions; *b*—irradiated solutions. 1—0.001 M; 2—0.005 M; 3—0.01 M.

Figure 1: Fig. 1. Changes occurring upon irradiation with a dose of $1.65 \cdot 10^{13}$ MeV in the absorption spectra of solutions of $[Co(NH_3)_5H_2O]Cl_3$ as a function of concentration. *a*—initial solutions; *b*—irradiated solutions. 1—0.001 M; 2—0.005 M; 3—0.01 M.



$$2[Co(NH_3)_4H_2O\,OH]^{2+} \rightarrow \left[\ (NH_3)_4Co \begin{matrix} OH \\ OH \end{matrix} Co(NH_3)_4\ \right]^{4+} \qquad \text{(slow)}. \qquad \text{(II)}$$

If one considers the kinetic aspect of the influence of γ-radiation, it should be assumed that the radiation promotes the second stage of the process—the enlargement of molecules with the initial formation of a dinuclear complex.

To confirm our conclusions regarding the formation of a diol complex in the process of radiation action, we specially synthesized

$$\left[(NH_3)_4Co \begin{matrix} OH \\ OH \end{matrix} Co(NH_3)_4\right] Cl_4$$

(3) and showed that freshly prepared nonirradiated solutions of the latter also strongly catalyze the decomposition of hydrogen peroxide. Knowing the catalytic activity of the diol complex of known concentration and determining the catalytic activity of an irradiated solution of $[Co(NH_3)_4(H_2O)_2]Cl_3$ of the same molar concentration, one can calculate the yield of this radiation-chemical reaction on the assumption that the catalytic activity of the irradiated diaquo complex is due chiefly to the presence of the diol complex: it is equal to 67 mol/100 eV.

Figure 3 gives the absorption spectra of a freshly prepared 0.05 M solution of the diol complex and a 0.005 M solution of $[Co(NH_3)_4(H_2O)_2]Cl_3$,

irradiated with a dose of $5.5 \cdot 10^{13}$ MeV. It is easy to note the similarity of the spectral characteristics of these two solutions. From the plots, from the magnitude of the rise of the light-absorption curve (assuming that the rise is due to the stage of formation of the diol complex), one can calculate the yield of the radiation-chemical reaction. This method of calculation gives a yield close to 77 mol/100 eV. Thus, the results of calculating the reaction yield by the two indicated methods are sufficiently close.

Fig. 2. Changes occurring upon irradiation with a dose of $1.65 \cdot 10^{13}$ MeV in the absorption spectra of solutions of $[Co(NH_3)_4(H_2O)_2]Cl_3$ as a function of concentration. The designations of the curves are the same as in Fig. 1.

Fig. 2

Figure 2: Fig. 2

Fig. 3

Figure 3: Fig. 3

It should be especially noted that there is a far-reaching analogy between all the transformations described here, which aqueous solutions of complex aquopentaamminecobaltates Co(III) undergo under the action of γ-radiation, and the processes that occur in the same systems under the action of ultraviolet radiation. The great similarity in the character of the changes in the absorption spectra, pH, electrical conductivity, etc., under the action of both types of radiation (we do not present here all the experimental material on the photolysis of these systems) should be regarded as an argument in favor of a hydrolytic mechanism, and not an oxidation-reduction one involving water radicals.

Of interest in this respect proved to be the trioxalato complex of Co(III): $K_3[Co(C_2O_4)_3] \cdot 3H_2O$, where the mechanism of radiolysis, as our experiments showed, repeats in all details the mechanism of the photochemical decomposition of the complex ([4],[5]). In this case, with increasing irradiation dose, the light-absorbing capacity of the solution decreases, which is associated with a decrease in the concentration of the initial trioxalate due to the oxidation-reduction process

$$2K_3[Co(C_2O_4)_3] \rightarrow 2CoC_2O_4 + CO_2 + 3K_2C_2O_4.$$

Radiolysis is accompanied by acidification of the solution, an increase in electrical conductivity, and precipitation of a pink precipitate of Co(II) oxalate. Analysis of the reaction products and of the changes in the spectrophotometric curve made it possible to calculate the yield of the radiation-chemical reaction under consideration—OH is 42 mol/100 eV. The process of reduction of Co(III) to Co(II) in this case, in view of the complete simi-

Fig. 3. Absorption spectra of solutions of $[(NH_3)_4Co(\mu\text{-}OH)_2Co(NH_3)_4]Cl_4$: 1 –0.0005 M; 2 –0.001 M; 3 –0.005 M; 4 –0.001 M at pH 8.15; 5 –0.001 M at pH 8.15, 3.5 h after preparation; 6 –0.005 M solution of $[Co(NH_3)_4(H_2O)_2]Cl_3$, irradiated with a dose of $5.5 \cdot 10^{13}$ MeV.

···with the analogous photochemical reaction can hardly be explained by the participation of water radicals.

As is known, the primary act of an oxidation-reduction photochemical reaction in solutions of complex salts is an electron transfer ligand—central atom or central atom—ligand, leading subsequently to decomposition of the complex ([6]). At the same time, as Adamson ([2]) believes, an oxidation-reduction photochemical

Fig. 4

Figure 4: Fig. 4

reaction can occur only in the case when the complex ion contains a ligand capable of being oxidized, as in the case of $[Co(NH_3)_5J]Cl_2$; in this system one can also find traces of Co(II) and J_2 molecules in the course of exposure to UV radiation. From this point of view, if the analogy between photo- and radiation-chemical reactions is extended to the case of hexaammine-type complexes studied by us (^{1}), then under the action of these two kinds of radiation a reduction mechanism due to electron transfer ligand—central atom fundamentally cannot occur.

Fig. 4. Changes occurring in the absorption spectra of a $0.005\,M$ solution of $K_3[Co(C_2O_4)_3] \cdot 3H_2O$ as a function of irradiation dose: 1 —initial solution; 2 —irradiated with a dose of $0.55 \cdot 10^{13}$ MeV; 3 —irradiated with a dose of $1.65 \cdot 10^{13}$ MeV; 4 —irradiated with a dose of $5.5 \cdot 10^{13}$ MeV

Thus, the decrease in electrical conductivity with increasing pH due to the cleavage of ammonia, the enhancement of the effects of radiation upon dilution of the solutions, the reversibility of the observed changes upon acidification of the irradiated solutions, and, finally, the detection of catalytic activity in irradiated solutions of $[Co(NH_3)_5H_2O]^{3+}$ and $[Co(NH_3)_4(H_2O)_2]^{3+}$, as well as direct proof of the presence of the diaquo complex in the irradiated solution $[Co(NH_3)_4(H_2O)_2]^{3+}$—all this, taken together, confirms the hydrolytic mechanism of the radiation-chemical decomposition of the Co(III) ammines studied.

By contrast, the hexacido ion Co(III) $[Co(C_2O_4)_3]^{3-}$, which contains in its composition an oxalate ligand capable of being reduced, in complete agreement with the data on photochemical behavior, decomposes under the action of γ-radiation by an oxidation-reduction mechanism.

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