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Figure 1

Figure 1: Figure 1

Abstract

Full Text

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THE ACTION OF γ- AND ULTRAVIOLET RADIATION ON AQUEOUS SOLUTIONS OF THE TRIETHYLENEDIAMINE COMPLEX OF COBALT (III)

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Relatively few works have so far been devoted to the study of the behavior of complex compounds under the action of radiation. This is understandable if one takes into account the difficulties that arise in interpreting the results, for example, of the radiolysis of even the simplest systems.

Nevertheless, in recent years a number of interesting works have been published in Soviet and foreign journals ([3,4]). The work of Hausman and Davis ([1]) is devoted to the study of the products of radiolysis under the action of γ-radiation on the complex mercury salt $Me_2[Hg_2Cl_2C_2O_4]$. The authors discuss in detail possible variants of the mechanism of decomposition of the oxalate salt, and also attempt quantitatively to characterize the rate of the radiolytic process. A. A. Balandin, V. I. Spitsyn, V. N. Duzhenkov, and L. I. Barsova ([2]) irradiated a number of complex compounds of Pt and Pd with electrons. The greater or lesser resistance to radiation of individual complexes is associated by the authors with I. I. Chernyaev' s law of trans-influence.

Fig. 1. Absorption spectra of solutions of [Co en_3]Cl_3, irradiated with a γ-source to a total dose of 285,000 r, at concentrations of the initial solution 0.01 *M (1)*, 0.002 *M (2)*, and 0.001 *M (3)*. 1′, 2′, 3′—the same as 1, 2, 3, with the solution aged 20 days.

Recently there appeared a paper by A. V. Evgunov and P. I. Dolin ([5]), in which it was shown that upon γ-irradiation of dilute aqueous solutions of $[Co(NH_3)_6]Cl_3$ with large doses, decomposition of the hexammine occurs with formation, as the authors believe, of the hydroxide of divalent cobalt. A reduction mechanism is proposed, i.e., through the intermediate formation of the $[Co(NH_3)_6]^{2+}$ ion. By the time the work of Evgunov and Dolin appeared in print, we had also completed experiments on irradiation of cobalt(III) hexammine nitrate.* In contrast to the authors mentioned, we studied the behavior of this complex also under irradiation with such doses at which

formation of the hydroxide still does not occur. Our results speak in favor of a hydrolytic mechanism of decomposition of $[Co(NH_3)_6](NO_3)_3$ through intermediate formation of hydroxocomplexes, and possibly also of compounds with ol bridges.

In the present communication some experimental data are set forth that were obtained upon γ-irradiation (Co^{60}) of another Co(III) compound of the hexammine type, of composition [Co en_3]Cl_3. At the same time we subjected the ethylenediamine complex to the action of ultraviolet radiation (PRK-4 and PRK-7 lamps), believing that such a comparative study would facilitate the clarification of certain questions connected with the mechanism of radiation-chemical–

* The work is in press in the journal *Radiokhimiya*.

chemical behavior of the complex salt. In the literature there is a whole series of works on the properties and behavior of complex ions under conditions of ultraviolet irradiation ([6–8]).

In these works the conclusion is drawn, in particular, that the oxidation-reduction mechanism is manifested reliably only when the addends in the irradiated complex are oxidants or reducing agents, as, for example, the ions J^- in $[Co(NH_3)_5J]^{2+}$. [Co en_3]$^{3+}$ is a complex ion with a chelate-forming addend, which explains its special stability under ordinary conditions. The overall instability constant, as follows from the work of Bjerrum ([10]), is expressed by the value $10^{-48.69}$, i.e., it is considerably stronger than the ion $[Co(NH_3)_6]^{3+}$, for which $K = 10^{-35.21}$. From the work of Bjerrum ([10]) it is also known that, in order to determine the stepwise instability constants of such strong complexes as the hexamines considered here, it is necessary to use activated carbon as a catalyst promoting the cleavage of amino groups.

In our experiments this catalytic role is apparently performed by γ- and ultraviolet radiation.

The irradiation experiments were carried out in aqueous solutions with complex concentrations of 0.01, 0.002, and 0.001 mole/liter in special test tubes with hermetically sealed stoppers. The solutions were irradiated with Co^{60} at a total dose from 2500 to 300,000 r. The experiments were carried out in neutral, acidic, and alkaline solutions, and also under conditions of saturation with oxygen and hydrogen. Special experiments showed that the age of the solution affects the irradiation results. In solutions that had stood for 20 days (upon irradiation with 285,000 r), decomposition proceeded somewhat more deeply than in freshly prepared solutions under otherwise equal conditions (Fig. 1).

Fig. 2. Absorption spectra of a 0.01 M solution of [Co en_3]Cl_3, irradiated with a γ-source at a total dose of 30,000 r. 1 –initial solution, 2 –irradiated solution, 3 –irradiated solution, age of the solution 26 days, 4 –spectrum of the solution acidified with 0.1 N $HClO_4$ after irradiation.

The depth of the changes upon irradiation was followed by recording absorption

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Figure 2: Fig. 2. Absorption spectra of a 0.01 M solution of [Co en_3]Cl_3, irradiated with a γ-source at a total dose of 30,000 r. 1 —initial solution, 2 —irradiated solution, 3 —irradiated solution, age of the solution 26 days, 4 — spectrum of a solution acidified with 0.1 N $HClO_4$ after irradiation

spectra in the ultraviolet and visible regions of the spectrum and by measuring the pH and electrical conductivity of the solutions (see Table 1). As is seen from Fig. 1, irradiation with large doses (285,000 r) produces a strong change in the absorption spectra. Changes in the spectra were practically absent in the case of irradiation with a dose of 2500 r. Subsequently the behavior of [Co en_3]$^{3+}$ under irradiation with medium doses, 20,000–30,000 r, was studied.

The external behavior of [Co en_3]$^{3+}$ in γ-radiation and photoradiation experiments differs sharply from the behavior of $[Co(NH_3)_6]^{3+}$; in solutions of the former no precipitation of hydroxide is observed, although here too a considerable alkalinization of the solution is observed. The color of the solution of [Co en_3]Cl_3, as well as of [Co en_3]$(NO_3)_3$, very quickly becomes red during irradiation. The reddening occurs especially rapidly in the case of irradiation with large doses of γ-radiation, and also when a PRK-7 lamp is used as the source of ultraviolet radiation. Such a change in color is apparently connected first with aquation, and then with the formation of deeper hydrolysis products. It is known, for example, that the binuclear tetraethylenediamine complex has a ruby-red color.

The aftereffect of radiation, for example ultraviolet radiation, is manifested in the fact that the absorption spectra of the solutions continue to change over the course of one or two days. At the same time, a noticeable reversibility of the photolysis process is observed, expressed in a partial return of the absorption spectra.

The radiolysis process is especially readily reversible upon weak acidification (0.1 N $HClO_4$) of solutions of the complex irradiated with moderate doses (20 000 r), as can be seen in Fig. 2. The light-absorption curve of the irradiated solution (0.01 mol/l) with time approaches the initial one (the initial curve is the absorption spectrum of a freshly prepared unirradiated solution). This return is evidently connected with the formation of a diaquotetrammine complex, whose spectrum differs little from the spectrum of [Co en_3]Cl_3. Similar results were obtained in the study of solutions of the triethylenediamine complex of Co(III) subjected to ultraviolet radiation. Fig. 3 shows the rapid increase of optical density (λ = 285 mμ) with time upon irradiation of a 10^{-2} mol/l solution of [Co en_3]Cl_3 with a PRK-4 lamp, possibly indicating the chain character of photolysis.

Fig. 3

Figure 3: Fig. 3

Fig. 4

Figure 4: Fig. 4

Fig. 3. Change in light absorption of irradiated solutions with time (PRK-4 lamp) at solution concentrations:
1 –0.01 M [Co en_3]Cl_3, $\lambda = 285$ mμ;
2 –0.01 M solution of [Co en_3]$(NO_3)_3$, $\lambda = 285$ mμ;
3 –0.01 M solution of $[Co(NH_3)_6](NO_3)_3$, $\lambda = 275$ mμ.

Two characteristic features are observed in the changes of the absorption spectra of irradiated solutions in comparison with freshly prepared ones. First, an elevation of the spectrophotometric curve is observed. In this connection it should be noted that A. A. Grinberg [11] and one of us showed, using complex compounds of Pt(II) as an example, that the increase of optical density in standing solutions is connected with reversible hydrolysis. Probably an analogous phenomenon occurs upon irradiation of the complex compound of Co(III), except that here the question is not spontaneous hydrolysis, but hydrolysis under the action of radiation. Second, upon irradiation of [Co en_3]Cl_3, and also in the case of $[Co(NH_3)_6](NO_3)_3$, it was observed that the absorption spectra change most rapidly and to the greatest extent in the ultraviolet region. Upon careful examination of the literature data [12] on the absorption spectra of Co(III) complexes containing, in the inner sphere, hydroxogroups along with amino groups, as well as ol groups, one can see a strong elevation of the light-absorption curves in the ultraviolet region in comparison with the corresponding curves for hexammine ions.

These two points may be regarded as arguments in favor of a hydrolytic mechanism for the partial decomposition of the ethylenediamine complex of Co(III). In this case, radiation promotes the detachment of the ethylenediamine group.

Fig. 4. Absorption spectra of 0.01 M solutions of [Co en_3]Cl_3, saturated with oxygen and hydrogen before irradiation (PRK-4):
1 –initial solution;
2 –irradiated solution;
3 –irradiated solution saturated with hydrogen;
4 –irradiated solution saturated with oxygen.

As shown in Fig. 4, the influence of hydrogen and oxygen does not decisively affect the behavior of solutions under irradiation conditions; moreover, in a stream of hydrogen the complex undergoes still smaller changes than in

in the presence of oxygen, so that preference can hardly be given to an oxidation-reduction mechanism.

From the work of Bjerrum and Rasmussen ([3]) it is known that the instability constants corresponding to the processes (catalyst: activated carbon)

$$[\mathrm{Co\ en_3}]^{3+} \xrightarrow{\mathrm{H_2O}} \text{cis-}[\mathrm{Co\ en_2(H_2O)_2}]^{3+} + \mathrm{en}, \qquad \text{(I)}$$

$$[\mathrm{Co\ en_3}]^{3+} \xrightarrow{\mathrm{H_2O}} \text{trans-}[\mathrm{Co\ en_2(H_2O)_2}]^{3+} + \mathrm{en}, \qquad \text{(II)}$$

are respectively $K_{\mathrm{cis}} = 10^{-13.28}$, $K_{\mathrm{trans}} = 10^{-15.24}$.

The violet color of the product isolated after alcohol treatment of the irradiated (γ-ultraviolet radiation, PRK-7) solution also seems to indicate preferential formation of cis-complexes.

The diaquo ions obtained according to equations (I) and (II) should have acidified the solution; this does not occur, probably because of the interaction of protons with the liberated ethylenediamine, owing to which the equilibrium is shifted toward formation of hydroxo complexes

$$[\mathrm{Co\ en_2(H_2O)_2}]^{3+} \rightleftarrows [\mathrm{Co\ en_2H_2OOH}]^{2+} + \mathrm{H_3O^+}$$

$$[\mathrm{Co\ en_2H_2OOH}]^{2+} \rightleftarrows [\mathrm{Co\ en_2(OH)_2}]^{+} + \mathrm{H_3O^+}.$$

Hydroxide ions can form more complex polymeric hydrolysis products.

Table 1

Change in pH of solutions of $[\mathrm{Co\ en_3}]\mathrm{Cl_3}$ and $[\mathrm{Co\ en_3}](\mathrm{NO_3})_3$ as a result of irradiation

Composition of the complex compound	Concentration of complex, mol/l	Dose, r	pH, initial	pH, irradiated	Note
$[\mathrm{Co\ en_3}]\mathrm{Cl_3}$	0.001	285 000	6.8	7.43	
$[\mathrm{Co\ en_3}]\mathrm{Cl_3}$	0.002	285 000	6.93	7.48	
$[\mathrm{Co\ en_3}]\mathrm{Cl_3}$	0.01	285 000	7.28	7.52	
$[\mathrm{Co\ en_3}]\mathrm{Cl_3}$	0.001	285 000	6.44	7.3	Age of solutions 22 days
$[\mathrm{Co\ en_3}]\mathrm{Cl_3}$	0.002	285 000	6.7	7.3	Age of solutions 22 days

Composition of the complex compound	Concentration of complex, mol/l	Dose, r	pH, initial	pH, irradiated	Note
$[Co\ en_3]Cl_3$	0.01	285 000	6.91	7.32	Age of solutions 22 days
$[Co\ en_3]Cl_3$	0.01	30 000	6.62	7.77	
$[Co\ en_3](NO_3)_3$	0.001	285 000	7.0	7.53	
$[Co\ en_3](NO_3)_3$	0.002	285 000	7.16	7.64	
$[Co\ en_3](NO_3)_3$	0.01	285 000	7.32	7.74	
$[Co\ en_3](NO_3)_3$	0.001	285 000	6.85	7.48	Age of solutions 20 days
$[Co\ en_3](NO_3)_3$	0.002	285 000	6.96	7.48	Age of solutions 20 days
$[Co\ en_3](NO_3)_3$	0.01	285 000	7.44	7.54	Age of solutions 20 days
$[Co\ en_3]Cl_3$	0.01	PRK-7 lamp, 10 h	7.2	8.73	
$[Co\ en_3]Cl_3$	0.01	PRK-4 lamp, 10 h	6.4	8.05	

Thus, it may be considered that under the action of ultraviolet light and γ-radiation on $[Co\ en_3]Cl_3$, a strong acceleration occurs of processes associated with the cleavage of the ethylenediamine group, which under ordinary conditions proceed with great difficulty and extremely slowly. In the present case a certain analogy may be drawn between the catalytic action of radiation and the catalytic action of activated carbon, taking into account the possible role of water radiolysis products (in particular, $OH^{\cdot}$ radicals).

In full agreement with the values of the thermodynamic instability constant, the ethylenediamine complex proves to be more resistant to the action of γ- and ultraviolet radiation than the $[Co(NH_3)]^{3+}$ ion.

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