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Abstract

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ON THE RADIOLYSIS OF AQUO COMPLEXES OF Co(III)

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The action of γ-radiation (Co^{60}, intensity 100 rad/sec) on dilute aqueous solutions of Co(III) salts was investigated: cis-, trans-$[Co\,en_2(H_2O)_2]Cl_3 \cdot H_2O$ and $[Co(NH_3)_3(H_2O)_3](NO_3)_3$. The syntheses were carried out according to ([1]) and ([2]). Solutions of 0.005 mol/l and 0.001 mol/l were irradiated. The changes in pH and in the molecular electrical conductivity of the complex solutions as a result of irradiation are given in Table 1. Changes in the light absorption of the solutions are shown in Figs. 1 and 2.

Table 1

Change in pH and molecular electrical conductivity of solutions of $[Co(NH_3)_3(H_2O)_3](NO_3)_3$ and $[Co\,en_2(H_2O)_2]Cl_3$ under the action of γ- and ultraviolet radiation

Initial substance	Conc., mol/l	Dose, million rad	Additives	pH, initial	pH, irradiated	η, ohm$^{-1}\cdot$cm^{-1}, initial	η, ohm$^{-1}\cdot$cm^{-1}, irradiated
$[Co(NH_3)_3(H_2O)_3](NO_3)_3$	0.005	1	–	4.03	8.12	302	284
$[Co(NH_3)_3(H_2O)_3](NO_3)_3$	0.005	1	$HClO_4$	2.09	2.32	903	880
$[Co(NH_3)_3(H_2O)_3](NO_3)_3$	0.005	1	NH_4OH	9.5	9.72	244	369
$[Co(NH_3)_3(H_2O)_3](NO_3)_3$	0.005	0.5	–	4.03	4.22	302	279
$[Co(NH_3)_3(H_2O)_3](NO_3)_3$	0.005	0.3	–	4.03	5.26	302	280
cis-$[Co\,en_2(H_2O)_2]Cl_3$	0.005	2.4	–	4.03	7.82	–	–
cis-$[Co\,en_2(H_2O)_2]Cl_3$	0.005	6	–	3.75	7.41	370	326
Same	0.005	2	–	3.75	6.98	370	339
Same	0.005	1	–	3.75	6.38	–	–
Same	0.005	0.5	–	3.75	6.04	–	–
Same	0.005	0.3	–	3.75	5.28	370	336
Same	0.005	1	$HClO_4$	2.33	6.44	8.24	486
Same	0.005	1	en	9.61	10.39	388	333

Fig. 1 and Fig. 2 spectra plots

Figure 1: Fig. 1 and Fig. 2 spectra plots

Initial substance	Conc., mol/l	Dose, million rad	Additives	pH, initial	pH, irradiated	η, ohm^{-1} · cm^{-1}, initial	η, ohm^{-1} · cm^{-1}, irradiated
trans-$[Co\,en_2(H_2O)_2]Cl_3$	0.001	2	–	4.15	7.99	412	347
trans-$[Co\,en_2(H_2O)_2]Cl_3$	0.001	2.5	–	4.88	7.62	193	270

By analogy with ([3]), irradiated solutions of $[Co(NH_3)(H_2O)_3](NO_3)_3$ exhibit the phenomenon of catalytic activity: a 0.005 mol/l solution irradiated with a dose of $2 \cdot 10^6$ rad decomposes 37.3 moles of H_2O_2 per mole of complex, and at a dose of $1 \cdot 10^6$ rad, 47.8 moles of H_2O_2 per mole of complex.

In special experiments, the presence of Co(II) was detected in solutions of cobalt triaquoammine irradiated with a dose of $3 \cdot 10^5$ rad. The latter was determined quantitatively by the method described in ([4]). Upon irradiation with a dose of $7.5 \cdot 10^5$, Co(II) was detected in acidified ($HClO_4$) aqueous solutions down to pH 4. Under analogous conditions Co(II) was also found upon irradiation of two other aquo complexes of the hexammine type: $[Co(NH_3)_5H_2O]Cl_3$ and $[Co(NH_3)_4(H_2O)_2]Cl_3$.

A negative reaction for divalent cobalt was shown by aqueous solutions, irradiated with the maximum dose of $4 \cdot 10^4$ rad, of the following complexes: $[Co(NH_3)_6]X_3$, where $X = Cl^-$, Br^-, J^-, SO_4^{2-}, $C_2O_4^{2-}$, NO_3^-, as well as $[Co(NH_3)_5X]Cl_2$, where $X = Cl^-$, Br^-, OH^-, and $[Co\,en_3]X_3$, where $X = Cl^-$, NO_3^-.

For aquoammine complexes of Co(III) at a concentration of 0.005 mol/l and at a dose of $3 \cdot 10^5$ rad, the radiation-chemical yields were calculated by quantitative determination of Co(II): $[Co(NH_3)_5H_2O]Cl_3$–1.2 mol per 100 eV; $[Co(NH_3)_4(H_2O)_2]Cl_3$–1.9 mol/100 eV; $[Co(NH_3)_3(H_2O)_3] \cdot (NO_3)_3$–2.3 mol/100 eV. According to these data, the aquoammine complexes are arranged in the following series with respect to stability toward oxidation-reduction transformations with formation of Co(II): $[Co(NH_3)_6]^{3+} > [Co(NH_3)_5H_2O]^{3+} > [Co(NH_3)_4(H_2O)_2]^{3+} > [Co(NH_3)_3(H_2O)_3]^{3+}$. However–

Fig. 1. Change in the absorption spectra of a 0.005 mol/l aqueous solution of $[Co(NH_3)_3(H_2O)_3](NO_3)_3$ as a function of the dose of γ-radiation. 1–initial solution, 2–solution irradiated with a dose of 0.1 million rad, 3–solution irradiated with a dose of 0.3 million rad, 4–solution irradiated with a dose of 2

million rad, 5–solution irradiated with a dose of 1 million rad

Fig. 2. Change in the absorption spectra of a 0.005 mol/l aqueous solution of cis-$[Co\,en_2 \cdot (H_2O)_2]Cl_5 \cdot H_2O$ as a function of the dose of γ-radiation. 1–initial solution, 2–solution irradiated with a dose of 0.5 million rad, 3–solution irradiated with a dose of 6 million rad, 4–solution irradiated with a dose of 2.5 million rad

the series with respect to stability against the precipitation of brown precipitates of cobalt hydroxide during radiolysis turns out to be the reverse of that described above. It is clear, apparently, that the hydrolytic mechanism previously accepted by us for some Co(III) complexes (3, 5) is not always predominant; in certain cases it is combined with an oxidation–reduction one.

Divalent cobalt was also detected in irradiated aqueous solutions (0.005 mol/l) of cis-, trans-$[Co\,en_2(H_2O)_2]Cl_3$. Depending on the dose, the following values were obtained for the yields of the radiation-chemical transformation of the cis salt:

Dose, rad	$3 \cdot 10^5$	$7.5 \cdot 10^5$	$1 \cdot 10^6$
Yield, mol/100 eV	1.31	0.87	0.85

The initially observed conditions of the medium in the aquocomplexes (pH 4-5) are due to their characteristic acid–base equilibria, which, in turn, ensure the transition Co(III) $\rightarrow$ Co(II). The decrease in the yield of Co(II) as the dose increases is probably connected with an increase in pH due to destruction of the complex with cleavage of an amino group.

In the complex compounds of Co(III) studied by us earlier it was shown that, in the main, the action of γ-radiation (as well as ultraviolet radiation) is accompanied by a deepening of the hydrolytic processes that proceed slowly under ordinary conditions. In a number of cases the greater stability of the complex toward the action of ionizing radiation was found

in direct connection with the thermodynamic strength of complex cations, as, for example, in the case of $[Co(NH_3)_6]Cl_3$ and $[Co\,en_3]Cl_3$ ([5]).

The circumstance that the appearance of Co(II) is observed in aquocomplexes of the hexammine type and is not observed in the hexaammine, triethylenediamine, or pentaammineaquocomplexes gives grounds for considering the role of inner-sphere water in the reduction process. We have no direct data on the radiolysis of inner-sphere water. Such radiolysis could be of interest for explaining the reduction of the central complex-forming atom, since radicals are formed in its immediate vicinity, some of which possess reducing properties.

It is noteworthy, in particular, that with an increase in the number of coordinated water molecules, i.e., on going from

$$[Co(NH_3)_5H_2O]^{3+} \rightarrow [Co(NH_3)_3(H_2O)_3]^{3+},$$

the yield of Co(II) increases, as shown in Fig. 1. Taking into account the initial acid–base interactions, which lead to an increase in the acidity of the solutions, it must be assumed that the pH will be lower in the case of the triaquocomplex; and a decrease in pH, as a rule, promotes the transition Co(III) → Co(II).

Table 2

Catalytic activity of irradiated aqueous solutions of $[Co(NH_3)_3(H_2O)_3](NO_3)_3$ **and** $[Co\,en_2(H_2O)_2]Cl_3$

Starting substance	Conc., mol/l	Dose, min. rad	Catalytic activity, mol H_2O_2/mol complex
cis-$[Co\,en_2(H_2O)_2]Cl_3$	0.005	2	1.37
cis-$[Co\,en_2(H_2O)_2]Cl_3$	0.001	1	13.17
trans-$[Co\,en_2(H_2O)_2]Cl_3$	0.001	1	2.56
$[Co(NH_3)_3(H_2O)_3](NO_3)_3$	0.005	0.3	2.4
$[Co(NH_3)_3(H_2O)_3](NO_3)_3$	0.005	1	47.8
$[Co(NH_3)_3(H_2O)_3](NO_3)_3$	0.005	2	37.3

It seems, however, that the oxidation–reduction mechanism accompanies the hydrolytic one, since the characteristic change in the absorption spectra and the decrease in electrical conductivity confirm the idea of enlargement of the molecules due, apparently, to the formation of polynuclear complex particles, probably with ol bridges. An additional argument is the circumstance that irradiated solutions of aquocomplexes begin to possess catalytic activity (decomposition of H_2O_2). The data are given in Table 2. In this respect the triaquocomplex is the most active of those considered above. The catalytic activity is not due to Co(II), since special experiments showed that a solution of $[Co(NH_3)_4(H_2O)_2]Cl_3$, irradiated with a dose of $3 \cdot 10^5$ rad, has no catalytic activity, although Co(II) is readily detected in it. The same may be said of cis-$[Co\,en_2(H_2O)_2]Cl_3 \cdot H_2O$.

In conclusion, it may be noted that the geometric isomers cis- and trans-$[Co\,en_2(H_2O)_2]Cl_3$ behave differently under the action of equal doses of γ-radiation and with all other conditions being equal. In particular, the catalytic activity in terms of decomposition of H_2O_2 is higher for the cis isomer. The radiation-chemical yield of the reaction (calculated as Co(II)) is equal to: for cis-$[Co\,en_2(H_2O)_2]Cl_3 \cdot H_2O$—1.4 mol/100 eV, for trans-$[Co\,en_2(H_2O)_2]Cl_3$—

2.0 mol/100 eV, at an initial-substance concentration of 0.001 mol/l and at a dose of $1 \cdot 10^6$ rad.

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