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Mechanism and Kinetics of Rh(IV) Radiation-Chemical Reduction in HNO_3 Solutions

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Abstract—Reduction of Rh(IV) in γ-irradiated and nonirradiated solutions of HNO_3 (0.3–3.0 M) was studied. In both systems, Rh(IV) is completely reduced to Rh(III). The reduction rates in nonirradiated solutions amount to 50–90% of rates in irradiated solutions. Reduction of Rh(IV) with water is postulated. The rates of Rh(IV) reduction in both irradiated and nonirradiated solutions increase with [Rh(IV)] growth and decrease with an increase in [HNO_3] from 0.5–1 to 2–3 M. The dependence of the reduction rates on the dose rate is weak. Mathematical simulation was used to reveal the mechanism and kinetics of radiation-chemical reduction of Rh(IV) in HNO_3 solutions. The rate constant of Rh(IV) reduction with water was calculated by fitting to the experimental data.

Rhodium has several oxidation states, and in nitric acid solutions of the irradiated nuclear fuel it should undergo redox transformations. Published data on the rhodium radiolytic behavior are scarce. In [1, 2] we studied the behavior of Rh(III) and Rh(IV) in HNO_3 and $HClO_4$ and found that Rh(IV) is reduced in both irradiated and radiation-free solutions. In $HClO_4$ solution containing ethanol, isopropanol, or butanol, Rh(III) is reduced to metallic Rh in the form of rhodium black. The Rh(IV) reduction yields obtained in [2] are characterized by a large scattering and do not show clear dependences on the rhodium and HNO_3 concentrations.

In this work, we studied the reduction of Rh(IV) in 0.5–3 M HNO_3 without radiation (blank experiment) and under irradiation with ^{60}Co γ-quanta at widely varied initial parameters. A mathematical model of radiolysis of Rh nitric acid solutions was developed, and the Rh(IV) concentrations were calculated for various experimental conditions. It was shown that this model adequately describes the experimental data. Basing on the calculations, we interpreted the results obtained, found the yield of Rh(IV) reduction, and proposed the mechanism of radiation-chemical processes.

EXPERIMENTAL

The initial solution of Rh(III) nitrate was prepared from a commercial (pure grade) solution of $Rh(NO_3)_3$ by dilution to $(2-4) \times 10^{-2}$ M and addition of HNO_3 to 2–3 M. Solutions of Rh(IV) were prepared by Rh(III) oxidation in HNO_3 solution with solid sodium bismuthate [3]. The Rh(IV) concentration was monitored spectrophotometrically using an absorption band at 550 nm with the extinction coefficient of 4.0×10^2 l mol^{-1} cm^{-1} [4] on a Perkin–Elmer Lambda 40 recording spectrophotometer. The error of determination of the Rh(IV) concentration was ±5%.

The rhodium solutions were irradiated with a ^{60}Co γ-ray source at a dose rate from 0.4 to 1.1–1.4 Gy s^{-1}. The radiation dose was determined by the ferrosulfate method. Two samples were studied simultaneously: one was irradiated and the second (blank) was radiation free.

Reduction of Rh(IV) in blank experiments. The kinetics of Rh(IV) reduction was studied at various concentrations of Rh and HNO_3. Some of the results are listed in Table 1. As seen, the rhodium(IV) con-

Table 1. Variation of Rh(IV) concentration in blank experiments (22–25°C)

Time, min	[HNO_3], M			
	0.5	1.0	2.0	3.0
	[Rh(IV)] × 10^3, M			
0	1.87	1.92	1.95	1.96
5	1.76	1.81	1.83	1.83
10	1.65	1.72	1.73	1.75
15	1.55	1.63	1.65	1.60
75	1.17	1.28	1.31	1.23
135	0.98	1.10	1.10	1.02
1155	0.58	0.60	0.60	0.57

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Table 2. Variation of Rh(IV) concentration in irradiated solutions

Time, min	$[Rh(IV)] \times 10^3$, M, at indicated $[HNO_3]$, M							
	0.5	1.0	2.0	3.0	0.5	1.0	2.0	3.0
	$D = 0.4$ Gy s^{-1}				$D = 1.4$ Gy s^{-1}			
0	2.64	2.72	2.75	2.74	2.64	2.72	2.75	2.74
12	2.26	2.48	2.55	2.41	2.11	2.34	2.44	2.28
24	1.83	2.02	2.18	2.08	1.55	1.94	2.05	1.85
36	1.45	1.75	1.90	1.81	1.21	1.58	1.66	1.60

centration decreases with time and is virtually independent of HNO_3 concentration at a given time of storage. In 2 h, the Rh(IV) concentration decreases by a factor of 2, i.e., the reduction rate is relatively high. We believe that Rh(IV) is reduced with water. Such a reaction is thermodynamically feasible because, in the blank run, the redox potential of the H_2O/O_2 couple ($E = 1.229$ V) is less positive than that of the Rh(IV)/Rh(III) couple ($E = 1.4$ V). It follows from kinetic curves that the reaction order with respect to rhodium is unity, which corresponds to the following formal reaction:

$$Rh(IV) + H_2O \rightarrow Rh(III). \qquad (1)$$

The rate of reaction (1) is

$$-d[Rh(IV)]/dt = K_1[Rh(IV)][H_2O]. \qquad (I)$$

To calculate the rate constant of reaction (1), K_1, we used a model of radiolysis of aqueous solutions described in [5]. At a dose rate equal to zero, for given $[H_2O]$ and [Rh(IV)], we preset various values of K_1, calculated the running Rh(IV) concentrations, and compared with the experiment. For 0.5, 1, 2, and 3 M HNO_3, the water concentration of 54.4, 53.8, 52.1, and 49.8 M, respectively, was used in calculations. Curves calculated for various K_1 are shown in Figs. 1 and 2. As seen, the calculated and experimental values are in good agreement at $K_1 = (3–4) \times 10^{-6}$ l mol^{-1} cm^{-1} for nitric acid concentration of 0.5 M and 3×10^{-6} l mol^{-1} cm^{-1} for 2 M. The K_1 values were refined in experiments with irradiated solutions. The best agreement with the experiment was obtained at K_1 4×10^{-6} and 3×10^{-6} l mol^{-1} cm^{-1} for 0.5–1 and 2–3 M HNO_3, respectively.

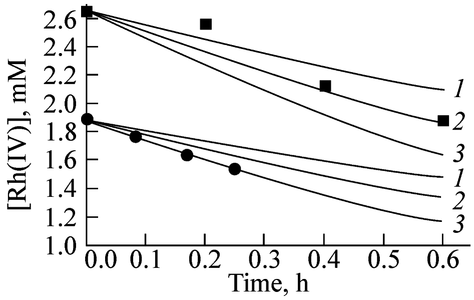

Fig. 1. Kinetics of Rh(IV) reduction in 0.5 M HNO_3 in blank experiments: (*1–3*) calculated at $K_1 = 2 \times 10^{-6}$, 3×10^{-6}, and 4×10^{-6} l mol^{-1} s^{-1}, respectively; (points) experiment.

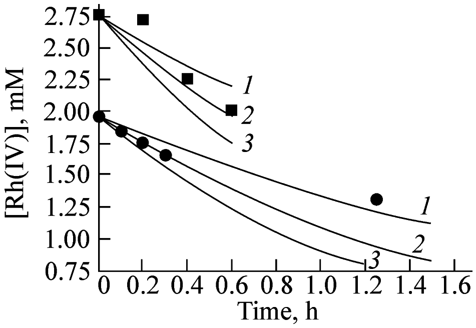

Fig. 2. Kinetics of Rh(IV) reduction in 2.0 M HNO_3 in blank experiments: (*1–3*) calculated at $K_1 = 2 \times 10^{-6}$, 3×10^{-6}, and 4×10^{-6} l mol^{-1} s^{-1}, respectively; (points) experiment.

It follows from the calculation that, at [Rh(IV)] 1×10^{-3}, 2×10^{-3}, and 5×10^{-3} M and $[H_2O]$ 54 M the rates of rhodium(IV) reduction with water ($\tau = 1$ h) are 1.5×10^{-4}, 3.0×10^{-4}, and 7.5×10^{-4} mol l^{-1} h^{-1}, respectively, and 97% reduction in all cases is attained within 20 h.

Rh(IV) reduction in irradiated solutions. Several series of experiments on Rh(IV) reduction kinetics were performed: at a given dose rate (0.4, 1.1–1.4 Gy s^{-1}), constant $[HNO_3]$, and variable rhodium concentration; at a given dose rate, constant [Rh(IV)], and variable $[HNO_3]$; and at given [Rh(IV)], and $[HNO_3]$ and variable dose rate. Some of the data obtained are listed in Table 2.

Table 3. Experimental and calculated rates of Rh(IV) reduction V in irradiated and nonirradiated solutions at t = 12–20 min

$[HNO_3]$	$[Rh(IV)] \times 10^3$	D = 0 Gy^{-1}		D = 0.4 Gy s^{-1}		D = 1.4 Gy s^{-1}	
M		calculated	experimental	calculated	experimental	calculated	experimental
		$V \times 10^5$, mol l^{-1}min^{-1}					
0.5	2.64	3.0	3.5	3.15	3.6	3.4	4.4
1.0	1.92	2.1	2.0	–	–	2.5	2.9
2.0	0.35	0.2	–	–	–	0.42	0.37
2.0	1.86	1.3	–	–	–	2.3	2.0
2.0	2.75	2.3	2.1	2.4	2.4	2.8	2.6
2.0	4.87	3.7	–	–	–	4.5	4.3
3.0	2.74	2.2	2.4	2.5	2.8	3.1	3.8

Table 4. Scheme of radiation-chemical reactions in nitric acid solutions of rhodium

Reaction no.	Reaction	Rate constant, l mol^{-1} s^{-1}
1	$Rh(IV) + H_2O \rightarrow Rh(III)$	See Table 5
2	$e^-_{aq} + H^+ \rightarrow H$	2.4×10^{10} [7]
3	$NO^-_3 + e^-_{aq} \rightarrow NO_2$	2.0×10^{10} [7]
4	$NO^-_3 + H \rightarrow NO_2$	6.0×10^{6} [7]
5	$NO^-_3 + OH \rightarrow NO_3$	5.0×10^{5} [7]
6	$H + O_2 \rightarrow HO_2$	2.0×10^{10} [7]
7	$HO_2 + HO_2 \rightarrow H_2O_2 + O_2$	8.0×10^{5} [7]
8	$NO_2 + NO_2 + H_2O \rightarrow HNO_2 + HNO_3$	1.0×10^{8} [8]
9	$HNO_2 + HNO_3 \rightarrow NO_2 + NO_2$	See Table 5
10	$HNO_2 + NO_3 \rightarrow NO_2$	1.0×10^{7} [9]
11	$HNO_2 + H_2O_2 \rightarrow HNO_3$	See Table 5
12	$HNO_3 + OH \rightarrow NO_3$	1.4×10^{8} [8]
13	$4HNO_2 \rightarrow N_2O_4 + 2NO$	See Table 5
14	$Rh(IV) + e^-_{aq} \rightarrow Rh(III)$	5.0×10^{10} [10]
15	$Rh(IV) + H \rightarrow Rh(III) + H^+$	1.0×10^{8}*
16	$Rh(IV) + HO_2 \rightarrow Rh(III) + O_2 + H^+$	1.0×10^{5}*
17	$Rh(IV) + H_2O_2 \rightarrow Rh(III) + HO_2 + H^+$	2.5×10^{-4} [11]
18	$Rh(IV) + HNO_2 \rightarrow Rh(III) + NO_2 + H^+$	See Table 5
19	$Rh(III) + OH \rightarrow Rh(IV) + OH^-$	1.0×10^{9}*
20	$Rh(III) + NO_3 \rightarrow Rh(IV) + NO^-_3$	1.0×10^{6}*

* Probable values.

As seen, at the chosen irradiation time in 1–3 M HNO_3, the Rh(IV) concentration only slightly depends on the dose rate. The experimental rates of Rh(IV) reduction as functions of the dose rate and HNO_3 and Rh(IV) concentrations are presented in Table 3.

With regard to rhodium(IV) reduction in blank experiments, we calculated the radiation-chemical yields of Rh(IV) reduction for various experimental conditions and found that they vary within almost an order of magnitude. This is caused by a large contribution of Rh(IV) reduction with water and small variation of the rhodium concentration.

To find the kinetic parameters of radiation-chemical reduction of rhodium(IV), we used mathematical simulation.

Mathematical model. We took the model of HNO_3 radiolysis [5, 6] as a basis and added reactions involving Rh(IV) and Rh(III). All the reactions are listed in Table 4.

Table 5. Variable parameters of the model

Parameter	Values at indicated $[HNO_3]$, M				References
	0.5	1.0	2.0	3.0	
Radiation-chemical yields, particles/100 eV (γ-radiolysis)					
$G(e^-_{aq})$	5.2	5.9	6.0	6.2	
$G(H_2)$	0.15	0.1	0.05	0.04	
$G(H_2O_2)$	1.0	1.1	1.2	1.2	
$G(OH)$	3.5	3.3	3.0	2.8	
$G(NO_2)$	0.12	0.3	0.35	0.7	
$G(NO_3)$	0.12	0.3	0.35	0.7	
Rate constants*					
K_1	4.0×10^{-6}	4.0×10^{-6}	3.0×10^{-6}	3.0×10^{-6}	**
K_9	0.007	0.015	0.025	0.04	[12], [13]
K_{11}	1.0×10^3	2.5×10^3	5.0×10^3	7.5×10^3	[12], [14]
K_{13}	25	75	100	125	[12]
K_{18}	82	41	21.3	14.7	***

* Dimension: K_1, K_9, K_{11}, K_{18}, $\mathrm{l\,mol^{-1}\,s^{-1}}$; K_{13}, $\mathrm{l^3\,mol^{-3}\,s^{-1}}$.

** This work.

*** Our calculation from data of [15].

For calculations, the model parameters (radiation-chemical yields of products and rate constants of elementary stages) and external parameters [concentrations of H^+, NO_3^-, HNO_3, and Rh(IV), dose rate, and time of irradiation] should be given.

In HNO_3 radiolysis, e^-_{aq}, H, OH, NO_2, and NO_3 radicals and H_2O_2 and H_2 molecules are formed as primary products. HNO_2 is the secondary product of reaction (8). The radiation-chemical yields of primary products of HNO_3 radiolysis and rate constants of reactions depending on $[HNO_3]$ are listed in Table 5.

The kinetics of reaction (17) was studied in [11]. It was found that the reaction rate is described by the equation

$$-d[\mathrm{Rh(IV)}]/dt = K_{17}[\mathrm{Rh(IV)}][H_2O_2]. \qquad \text{(II)}$$

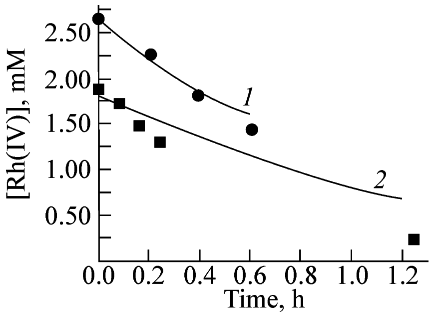

Fig. 3. Kinetics of Rh(IV) reduction in 0.5 M HNO_3 in irradiated solutions: (*1*, *2*) calculated at *D* = 0.4 and 1.08 $\mathrm{Gy\,s^{-1}}$, respectively; (points) experiment.

The rate constant K_{17} is independent of acidity and is equal to $2.5 \times 10^{-4}\ \mathrm{l\,mol^{-1}\,s^{-1}}$ [11].

The kinetics of reaction (18) was studied in [15]. It was found that the reaction rate is described by the equation

$$-d[\mathrm{Rh(IV)}]/dt = K_{18}[\mathrm{Rh(IV)}][HNO_2]/[H^+]. \qquad \text{(III)}$$

$K_{18} = 41\ \mathrm{s^{-1}}$ at 25°C [15].

Using this value of the constant, we calculated K_{18}, $\mathrm{l\,mol^{-1}\,s^{-1}}$, for the given H^+ concentration with regard to the degree of nitric acid dissociation (Table 5).

CALCULATION RESULTS

Using the model parameters, we calculated the Rh(IV) concentrations in irradiated and nonirradiated solutions and the rates of its reduction from the time dependences of the calculated concentrations. The results are presented in Figs. 3–6 and in Table 3. As seen, the calculated values are in satisfactory agreement with the experiment. This correlation indicates that the scheme of reactions in Table 4 adequately describes radiation-chemical processes in nitric acid solutions of rhodium and that the rate constants and radiation-chemical yields of HNO_3 radiolysis products are correct.

Let us analyze data of Table 3. It is seen that, in most cases, the calculated and experimental rates for both irradiated and nonirradiated solutions are fairly close. However, in some cases the disagreement is substantial. This may be connected with the influence of the temperature on the rate of reaction (1) whose contribution at $[Rh(IV)] > 0.35 \times 10^{-3}$ M, as seen from Table 3, amounts to 70–90% of the rates in irradiated solutions (in our experiments, the temperature of solutions was not controlled). However, we may definitely conclude that the rate of rhodium(IV) reduction decreases when $[HNO_3]$ increases from 0.5 to 2–3 M at given [Rh(IV)]; it increases approximately in proportion with the rhodium concentration and weakly depends on the radiation dose rate because of major contribution of the chemical reduction with water.

To reveal the role of particular radiation-chemical reactions in Rh(IV) reduction and Rh(III) oxidation and to find the radiation-chemical yields of Rh(IV) reduction, we calculated the rates of these reactions at varied [Rh(IV)], dose rate, and integral dose of the radiation. The results for [Rh(IV)] 2.6×10^{-3} M, D 0.4 Gy s^{-1}, and dose of 1.5×10^2 Gy are listed in Table 6. The rate of rhodium(IV) reduction with hydrogen peroxide (17) was not given, since it is many times lower than the rates of the other reactions. The low rate of reaction (17) is caused by both small value of K_{17} (2×10^{-4} l mol^{-1} s^{-1}) and low concentration of H_2O_2, which is decomposed, reacting with HNO_2 [reaction (11)]. The equations for the rate of the Rh(IV) radiation-chemical reduction are as follows:

$$-d[Rh(IV)]/dt = d[Rh(III)]/dt = [Rh(IV)](K_{14}[e^-_{aq}] + K_{15}[H] + K_{16}[HO_2] + K_{18}[HNO_2]) - [Rh(III)](K_{19}[OH] + K_{20}[NO_3]), \quad (IV)$$

$$V_{rch} = V_{14} + V_{15} + V_{16} + V_{18} - V_{19} - V_{20}. \quad (V)$$

Then, the radiation-chemical yield of Rh(IV) reduction, G[–Rh(IV)], is

$$G[-Rh(IV)] = V_{rch}/(aD). \quad (VI)$$

When the rate is expressed in mol l^{-1} s^{-1} and the dose rate D in Gy s^{-1}, the coefficient a in (VI) is equal to 1.04×10^{-7}.

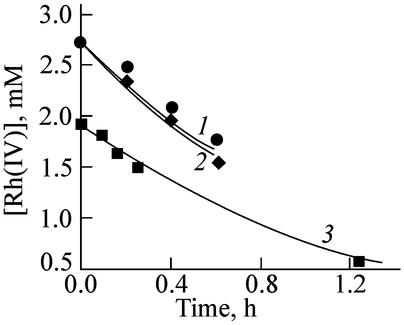

Fig. 4. Kinetics of Rh(IV) reduction in 1.0 M HNO_3 in irradiated solutions: (*1–3*) calculated at D = 0.4, 1.4, and 1.08 Gy s^{-1}, respectively; (points) experiment.

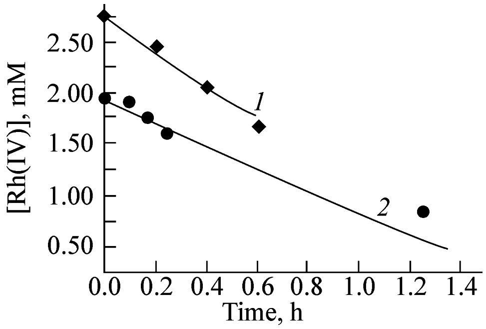

Fig. 5. Kinetics of Rh(IV) reduction in 2.0 M HNO_3 in irradiated solutions: (*1, 2*) calculated at D = 1.4 and 1.08 Gy s^{-1}, respectively; (points) experiment.

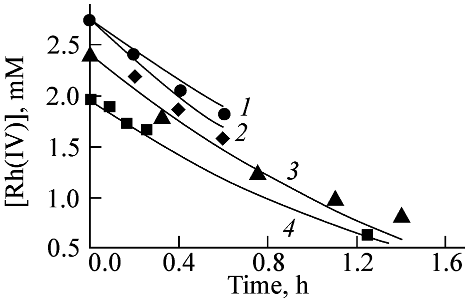

Fig. 6. Kinetics of Rh(IV) reduction in 3.0 M HNO_3 in irradiated solutions: (*1–4*) calculated at D = 0.4, 1.4, 1.4, and 1.08 Gy s^{-1}, respectively; points are experimental.

It follows from Table 6 that reactions with HO_2 radicals and HNO_2 [reactions (16) and (18)] make the main contribution to the overall rate of the radiation-chemical reduction of Rh(IV). The total rate of these reactions and overall rate of Rh(III) oxidation [reactions (19) and (20)] decrease with increasing $[HNO_3]$ from 0.5–1 to 2–3 M. However, these overall rates decrease to a different extent, so that the overall rate and radiation-chemical yield of Rh(IV) reduction decrease in the $[HNO_3]$ range considered. The total rate of reactions (19) and (20) decreases owing to a de-

Table 6. Rates of particular reactions (mol l^{-1} s^{-1}) at a dose rate of 0.4 Gy s^{-1}, dose of 1.5×10^2 Gy, and [Rh(IV)] 2.6×10^{-3} M

$[HNO_3]$, M	Rh(IV) + H_2O, V_1	Rh(IV) + e^-_{aq}, V_{14}	Rh(IV) + H, V_{15}	Rh(IV) + HO_2, V_{16}	Rh(IV) + HNO_2, V_{18}	Rh(III) + OH, V_{19}	Rh(III) + NO_3, V_{20}	Σ,* V_{rch}**	G[–Rh(IV)],** ions/100 eV
0.5	5.3×10^{-7}	1.0×10^{-9}	4.0×10^{-9}	6.2×10^{-8}	1.36×10^{-7}	4.4×10^{-8}	1.07×10^{-7}	5.2×10^{-8}	1.2
1.0	5.2×10^{-7}	7.0×10^{-10}	3.5×10^{-9}	5.0×10^{-8}	1.35×10^{-7}	1.6×10^{-8}	1.29×10^{-7}	5.6×10^{-8}	1.07
2.0	3.9×10^{-7}	4.0×10^{-10}	2.2×10^{-9}	3.3×10^{-8}	1.21×10^{-7}	1.6×10^{-9}	1.23×10^{-7}	3.2×10^{-8}	0.75
3.0	3.7×10^{-7}	2.7×10^{-10}	1.7×10^{-9}	2.6×10^{-8}	1.27×10^{-7}	6.0×10^{-10}	1.20×10^{-7}	3.4×10^{-8}	0.8

* Overall reaction of radiation-chemical reduction.

** V_{rch} and G[–Rh(IV)] were calculated by Eqs. (V) and (VI).

crease in the sum of radiation-chemical yields of radicals OH and NO_3 (Table 5). It follows from Table 6 that the total rate of reactions (16) and (18) decreases mainly at the expense of reaction (16). Calculations showed that the decrease in its rate is caused by increase in the rate of reaction (4) and decrease in the rate of reaction (6) with increase in $[NO_3^-]$. Weak dependence of the rate of Rh(IV) reaction with HNO_2 on $[HNO_3]$ [reaction (18)], despite a substantial decrease in K_{18} in going from 0.5 to 3 M HNO_3 (Table 5), is caused by substantial increase in the radiation-chemical yield of HNO_2 formation. In [16], we showed that, with increase in $[HNO_3]$ from 0.5 to 3 M, $G(HNO_2)$ increases by a factor of approximately ten.

It follows from Table 6 that, under the experimental conditions considered, the contribution of reaction (1) to the overall rate of Rh(IV) reduction amounts to about 90%. Calculations showed that, the lower the rhodium concentration and the higher the dose rate, the smaller the contribution of reaction (1).

To reveal the effect of [Rh(IV)], $[HNO_3]$, and dose rate on the radiation-chemical yield of reduction, we calculated the rates of particular reactions and V_{rch}. From Eq. (VI) we found the values of G[–Rh(IV)], which are listed in Table 7. As seen, the radiation-chemical yields are virtually independent of the dose rate; with doubling of [Rh(IV)] they increase by a factor of 1.2 only. Other conditions being equal, in the range of $[HNO_3]$ 0.5–1.0 M G[–Rh(IV)] is approximately 1.5 times higher than in the range 2–3 M. Calculations showed that the radiation-chemical yields decrease with increase in the radiation dose owing to a decrease in the rate of reaction (18) and an increase in the rate of reaction (20).

We also calculated the radiation-chemical yields when K_1 is equal to zero. They increase by a factor of 1.1.

The expressions for the minimum and maximum possible theoretical yields of rhodium(IV) reduction are as follows:

$$G^{min}[-Rh(IV)] = G(e^-_{aq}) - G(H_2O_2) + G(NO_2) - G(OH) - G(NO_3), \qquad (VII)$$

$$G^{max}[-Rh(IV)] = G(e^-_{aq}) + 2G(H_2O_2) + G(NO_2) - G(OH) - G(NO_3). \qquad (VIII)$$

After substituting the radiation-chemical yields from Table 5 in Eqs. (VII) and (VIII), we obtain G^{min} 0.7, 1.5, 1.8, and 2.2 and G^{max} 3.7, 4.8, 5.4, and 5.8 ions/100 eV in 0.5, 1, 2, and 3 M HNO_3, respectively.

It follows from Table 7 that, at $[HNO_3]$ = 1 and [Rh(IV)] = 5×10^{-3} M, G[–Rh(IV)] is equal to the minimal value (1.5 ions/100 eV). In the other cases, the radiation-chemical yields are lower than G^{min}. This means that the kinetics of radiation-chemical processes does not correspond to the balance of radiation-chemical yields in Eq. (VII).

Earlier, we found that the experimental radiation-chemical yields of Ce(IV) reduction in 1–3 M HNO_3 at γ-radiolysis are equal to the above-indicated maximum possible theoretical radiation-chemical yields (5–6 ions/100 eV) [17]. These high yields are caused by the fact that the rate constant of the reaction between Ce^{4+} and H_2O_2 is equal to 1×10^6 l mol^{-1} s^{-1} [7].

We also calculated the effect of the rate constant of the reaction between Rh(IV) and H_2O_2, K_{17}, on the rates of separate reactions and on the radiation-chemical yields of Rh(IV) reduction and found that these yields become equal to the above maximal values in 0.5, 1, 2, and 3 M HNO_3 at K_{17} ≥5, ≥50, ≥100,

Table 7. Calculated radiation-chemical yields of Rh(IV) reduction at a γ-radiation dose of 1.5×10^2 Gy

$[HNO_3]$, M	$[Rh(IV)] \times 10^3$, M	$G[-Rh(IV)]$, ions/100 eV	
		$D = 0.4$ Gy s^{-1}	$D = 1.4$ Gy s^{-1}
0.5	2.6	1.2	1.29
1.0	2.6	1.07	1.27
2.0	2.6	0.75	0.76
3.0	2.6	0.8	0.7
0.5	5.0	1.4	1.45
1.0	5.0	1.5	1.6
2.0	5.0	1.0	1.05
3.0	5.0	1.0	0.9

and ≥100 l mol^{-1} s^{-1}, respectively. These results confirm the validity of the radiation-chemical yields (Table 7) calculated for $K_{17} = 2.5 \times 10^{-4}$ l mol^{-1} s^{-1}.

Thus, the rates of Rh(IV) reduction in nonirradiated solutions range from 50 to 90% of the rates in irradiated solutions, depending on the initial conditions.

Since reduction with water is significant, it is impossible to obtain the radiation-chemical yields of reduction from the difference in the concentrations in the blank and irradiated solutions.

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