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THE RADIATION CHEMISTRY OF AQUEOUS SOLUTIONS OF INORGANIC NITROGEN COMPOUNDS

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The radiolysis of solutions of inorganic nitrogen compounds is an extremely complex and important problem in radiochemistry owing to the multiplicity of the valency states of nitrogen and the comparative ease of their mutual interconversion. Although a great deal of work has been done on the mechanism of the radiolytic reactions of nitrogen compounds in solution, much remains obscure.

1. NITROGEN FIXATION INDUCED BY IONISING RADIATION IN THE PRESENCE OF WATER

Orekhov et al.[1-3] found that on irradiating a KOH solution with Co^{60} γ-rays in the presence of oxygen, the nitrite formed and the equivalent quantity of nitrate increased linearly with the dose. The G value* for the nitrogen entering into combination was about 0.2 atoms. Increasing the air pressure on the solution (up to 25 atm) had no appreciable effect on G. They considered that this reaction depends on the reaction of free OH radicals, formed by the radiolysis of water, with free molecules of nitrogen, simultaneously with atomic hydrogen or the radical HO_2:

$$OH + N - N + HO_2 \rightarrow NOH + HNO_2. \quad (1)$$

This reaction of nitrogen was not observed in acid solutions.

Primak and Fuchs irradiated a mixture of nitrogen and oxygen with a nuclear reactor in the presence of nickel or other metals in a quartz ampoule. No products were formed with dry gases. A significant quantity of $Ni(NO_3)_2 \cdot 6H_2O$ was produced when air at 1 atm was saturated with water at 28°. The yield of bound nitrogen, G, was about 3 atoms, but the accuracy of the determinations was not high.

Wright et al.[5] studied the formation of HNO_3 from air and nitrogen irradiated over water in a nuclear reactor. G (HNO_3) was about 1 molecule (calculated from the energy absorbed by the gases).

Dmitriev and Pshezhetskii[6,7] found that G was 0.2 atoms for the oxidation of nitrogen at atmospheric pressure over water by 200 keV electrons. The reaction proceeded essentially at the expense of the energy absorbed in the gaseous phase.

Jones[8] found that nitric acid and nitrous oxide were formed by a beam of fast electrons (1 MeV) acting on a nitrogen–oxygen–water system. With high integral doses (using up all the water vapour present in the mixture) the HNO_3

* In this and all subsequent cases, G is the amount of radiolytic reaction (in molecules, atoms, ions, etc.,) per 100 eV of energy absorbed.

formed decomposed, giving a corresponding quantity of NO_2. Jones showed that the yield depended on the oxygen concentration reaching a maximum with 15.4 mole % of oxygen, in contrast to the conclusion of Wright et al.[5].

2. RADIOLYSIS OF AMMONIA, HYDRAZINE, AND HYDROXYLAMINE SOLUTIONS

Rigg et al.[9] found that nitrites were formed by the radiolysis of ammonia solutions in the presence of oxygen. The yield depended largely on the mean pH and free-ammonia concentration, which was determined by the equilibrium

$$NH_3 + H^+ \rightleftharpoons NH_4^+. \quad (2)$$

The maximum value of G for NO_2^- was ~1.3 ions. There was no difference between the behaviour of $(NH_4)_2SO_4$ solutions saturated with air or oxygen, but in degassed solutions ammonia was not oxidised. The following mechanism was suggested:

$$NH_3 + OH \rightarrow NH_2 + H_2O, \quad (3)$$

$$NH_2 + O_2 \rightarrow NH_2O_2, \quad (4)$$

$$NH_2O_2 + OH \rightarrow HNO_2 + H_2O. \quad (5)$$

The radical NH_2 can undergo disproportionation:

$$2NH_2 \rightarrow NH_3 + NH. \quad (6)$$

The radical NH is unstable and breaks up into NH_3, N_2, and possibly H_2. This explains the absence of oxidation products on irradiating ammonia solutions in vacuo. The reaction in the presence of oxygen is

$$NH + O_2 \rightarrow HNO_2, \quad (7)$$

with the direct formation of nitrous acid.

According to Sharpatyi et al.[10] irradiation of an ammonia solution (0.15 M; pH 14), saturated with nitrogen, in the presence of 1 M $NaNO_3$ by Co^{60} γ-rays produced nitrite with $G(NO_2^-) = 6$ ions. In the absence of $NaNO_3$ but with oxygen present, $G(NO_2^-) = 1.5$ ions, as Rigg et al. found[9]. Proskurnin et al.[10,11] explained the increase in $G(NO_2^-)$ in solutions containing $NaNO_3$ by the occurrence of the following reactions:

$$9OH + 1.5NH_3 + 1.5OH^- \rightarrow 1.5NO_2^- + 7.5H_2O, \quad (8)$$

$$9H + 4.5NO_3^- \rightarrow 4.5NO_2^- + 4.5H_2O. \quad (9)$$

$1.5NO_2^-$ ions are formed in reaction (8) while reaction (9) forms $4.5NO_2^-$ ions; thus the total yield amounts to 6 ions/100 eV. Reaction (8) takes place in the absence of $NaNO_3$, but with oxygen present, giving $G(NO_2^-) = 1.5$ ions. Proskurnin et al. consider that the role of oxygen is merely to render the H atoms inactive. Thus neither the HO_2 radical, nor other radicals, nor hydrogen peroxide (in alkaline solutions) take part in the oxidation of ammonia. According to Eqn. (9), nine molecules of water, dissociated by radiolysis, must be used in the oxidation of ammonia, which is evidence for the participation of ionised and excited water molecules in the reaction.

Dewhurst and Burton[12] studied the conversion of hydrazine solutions by Co^{60} γ-rays. They found that the yields of products in air-free solutions were independent of the hydrazine concentration greater than 2×10^{-2} M, and were $G(-N_2H_4) = G(NH_3) \cong 5.2$ and $G(N_2) = G(H_2) = 2.5$. However, the yields fall appreciably in more dilute solutions. Saturation with hydrogen and the addition of $(NH_4)_2SO_4$ (0.02 M) or KBr (10^{-4} to 10^{-3} M) does not alter the value of G to any extent. $G(H_2) = G(N_2)$ when pH lies between 0.3 and 12.3, and $G(NH_3) = 2G(N_2) \cong G(-N_2H_4)$ in this range. The yields are practically constant up to pH 8 but fall appreciably at higher values. The H and OH radicals formed during the radiolysis of water are assumed to react with acidified hydrazine as follows:

$$N_2H_4 + H^+ \rightarrow N_2H_5^+, \quad (10)$$

$$N_2H_5^+ + H \rightarrow H_2 + N_2H_4^+, \quad (11)$$

$$N_2H_5^+ + OH \rightarrow H_2O + N_2H_4^+, \quad (12)$$

$$N_2H_4^+ + \text{water} \rightarrow N_2H_3 + H^+(aq), \quad (13)$$

$$2N_2H_3 \rightarrow N_4H_6, \quad (14)$$

$$N_4H_6 \rightarrow N_2 + 2NH_3. \quad (15)$$

The diminution in yield at low hydrazine concentrations is explained by competition between reactions (11) and (12) and the recombination reaction of H and OH. In more concentrated solutions (above 2×10^{-2} M) the H and OH radicals are largely consumed by the decomposition of hydrazine.

Cottin and Lefort[13] found that in the radiolysis of hydrazine sulphate solutions by Po^{210} α-particles $G(H_2)$ was independent of hydrazine concentration between 10^{-4} and 10^{-2} M, and was equal to 1.6 molecules. Lefort and Haissinsky[14] treated hydrazine solutions with Co^{60} γ-rays and Po^{210} α-particles. As Dewhurst and Burton found[12], the yield with γ-rays depended on concentration and pH and the radiolysis was believed to occur at the expense of H and OH radicals. The yield with α-particles was significantly lower, giving, for a 2×10^{-3} M solution in 0.1N H_2SO_4, $G(-N_2H_4) = 1.0$, $G(N_2) = 0.55$, and $G(NH_3) = 0.9$, while γ-rays, acting on a 10^{-3} M solution, gave $G(-N_2H_4) = 2$ and $G(N_2) = 2.2$. The action of α-particles on acid solutions produced also hydrogen peroxide and oxygen, which were not found after γ-irradiation. This is explained by the following reactions:

$$N_2H_4 + OH \rightarrow N_2H_3 + H_2O \rightarrow \tfrac{1}{2}N_2 + NH_3 + H_2O, \quad (16)$$

$$OH + OH \rightarrow H_2O_2, \quad (17)$$

$$2H_2O_2 + N_2H_4 \rightarrow N_2 + 4H_2O, \quad (18)$$

$$H_2O_2 + OH \rightarrow HO_2 + H_2O, \quad (19)$$

$$HO_2 + OH \rightarrow H_2O + O_2. \quad (20)$$

Lefort and Tarrago[15] found that ammonium ions, nitrogen, hyponitrous acid ($H_2N_2O_2$), and hydrogen were produced by Co^{60} γ-rays acting on a hydroxylamine sulphate solution (concentration 5×10^{-3} M) in the absence of air. The yield was $G(-NH_2OH) = 6.8 \pm 0.2$, $G(NH_4^+) = 2.25 \pm 0.1$, $G(N_2) = 2.0 \pm 0.05$, $G(H_2N_2O_2) = 0.33 \pm 0.05$, and $G(H_2) = 0.45 \pm 0.2$. The following mechanism was suggested*:

$$NH_3OH^+ + H \rightarrow H_2O + NH_3^+ \text{ (or } NH_2), \quad (21)$$

$$NH_2 + NH_3OH^+ \rightarrow NH_4^+ + ONH_2, \quad (22)$$

$$NH_3OH^+ + OH \rightarrow H_2O + ONH_3^+ \text{ (or } ONH_2), \quad (23)$$

$$2ONH_2 \rightarrow N_2 + 2H_2O, \quad (24)$$

$$H_2O_2 + ONH_2 \rightarrow NO + 2H_2O, \quad (25)$$

$$NO + ONH_2 \rightarrow H_2N_2O_2, \quad (26)$$

$$NO + NH_2 \rightarrow N_2 + H_2O. \quad (27)$$

In the presence of oxygen nitrate ions are formed.

* The pH of solution was about 4.0; in these conditions hydroxylamine exists as NH_3OH^+.

TABLE 1. Yield of hydrogen and nitric oxide on irradiation of aqueous KNO_2 with Co^{60} γ-rays (from Schwarz [20]).

Concentration of KNO_2, M	$G(H_2)$, molecules/100 eV	$G(NO)$, molecules/100 eV
$4 \cdot 10^{-5}$	0.440	—
$1.2 \cdot 10^{-3}$	0.408	—
$1.6 \cdot 10^{-2}$	0.356	—
$5.8 \cdot 10^{-2}$	0.320	—
0.165	0.298	0.026
0.394	0.226	0.081

3. RADIOCHEMICAL OXIDATION OF NITRITE TO NITRATE

In 1935 Fricke and Hart [16] were the first to observe that nitrite in a deaerated solution was oxidised to nitrate by X-rays, with the simultaneous evolution of the equivalent quantity of hydrogen. $G(NO_3^-)$ was ~0.7 ion and was independent of the initial nitrite concentration between 5×10^{-5} and 10^{-1} M, and of pH between 2 and 11.

Haissinsky and Lefort [17] showed that sodium nitrite was oxidised to nitrate by X-rays and Po^{210} α-particles. Lefort [18] found that, in the absence of oxygen, the initial yield for the oxidation in 10^{-3} M KNO_2 at pH 6 was 1.75 molecules for X-rays and 0.4 molecule for α-particles.

In a more detailed investigation, Schwarz and Allen [19] found that irradiation of an air-free solution of KNO_2 by X-rays or γ-rays resulted initially mainly in the formation of molecular hydrogen and hydrogen peroxide. The subsequent reaction between the nitrite and the peroxide formed nitrate. The main peculiarity is the competition between reactions (29) and (30)*:

$$H_2O \rightarrow H_2,\ H_2O_2,\ H,\ OH,$$

$$OH + NO_2^- \rightarrow NO_2 + OH^-, \quad (28)$$

$$H + NO_2^- \rightarrow NO + OH^-, \quad (29)$$

$$H + H_2O_2 \rightarrow OH + H_2O, \quad (30)$$

$$NO + NO_2 + H_2O \rightarrow 2HNO_2, \quad (31)$$

$$2NO + H_2O \rightarrow HNO_2 + H^+ + NO_3^-. \quad (32)$$

$G(H_2O_2)$ falls rapidly as the nitrite concentration increases to 2×10^{-3} M and becomes almost constant for concentrations between 10^{-3} and 10^{-2} M. In nitrite solutions containing air or oxygen, the increase of $G(-NO_2^-)$ with increase of the ratio of nitrite concentration to oxygen concentration follows the empirical equation

$$-1/G(-NO_2^-) = (0.87 \pm 0.08) + (1.09 \pm 0.06)[O_2]/[NO_2^-]. \quad (33)$$

Schwarz [20] found that $G(H_2)$ decreased with increase of KNO_2 concentration (see Table 1). Nitric oxide was formed in concentrated solutions of KNO_2; $G(NO) \cong 0.01$ to 0.1 molecule.

According to Orekhov et al. [1-3] the oxidation of KNO_2 in aqueous solution with Co^{60} γ-rays may be expressed by the following equation

$$C_E = C_0 e^{-kE},$$

where C_0 is the initial nitrite concentration and C_E is its concentration after the absorption of energy E. The constant k decreases with increase of pH. They consider that the oxidation is a result of the reaction between NO_2^- ions and OH and HO_2 radicals formed during the radiolysis of water.

Schwarz and Salzman [21], who studied the formation of H_2O_2 during radiolysis of KNO_2 solutions up to 10^{-1} M, found that $G(H_2O_2)$ decreased with increase of concentration, giving 0.62 molecule with 2.3×10^{-4} M and 0.42 with $9.6 \times \times 10^{-2}$ M. They suggest that the mechanism described above [19] should be supplemented by the following reaction:

$$H + NO_3^- \rightarrow NO_2 + OH^-. \quad (34)$$

4. RADIOLYTIC REACTIONS IN AQUEOUS NITRATE AND NITRIC-ACID SOLUTIONS

Many foreign and Soviet workers have studied the radiochemistry of nitrates in aqueous solution. Nitrite ions, hydrogen, oxygen, hydrogen peroxide, nitrogen, and nitrous and nitric oxides are formed on radiolysis.

Yield of Nitrite

Published data about the yield of nitrite (the main product of radiolysis of aqueous nitrates) is given in Table 2. It is seen that $G(NO_2^-)$ increases with increase of nitrate concentration and decrease of acidity, and with rise of temperature and addition of glycerine or glucose to the solution.

According to Kabakchi et al. [28], the nature of the cation as a rule has no significant effect on $G(NO_2^-)$. $G(NO_2^-)$ reaches a definite limit with increase of solute concentration only in solutions of nitrates with the strongly hydrated lithium and beryllium cations. If the concentration is increased further, $G(NO_2^-)$ decreases noticeably and tends to the value for the solid salt, as very strong solutions of $LiNO_3$ and $Be(NO_3)_2$ have structures similar to the solids.

Ryabchikova et al. [33] found that $G(NO_2^-)$ was negligible in silver nitrate solutions. The main product was metallic silver. The yield depended on concentration and was 0.55,

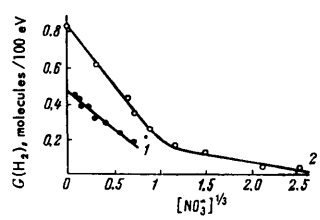


Fig. 1. Dependence of $G(H_2)$ on the concentration of NO_3^- ions in the solution: 1) irradiation of $NaNO_3$ solutions [37] by Co^{60} γ-rays; 2) irradiation of $Ca(NO_3)_2$ solutions with a mixed beam of neutrons and γ-rays [38].

* It was found that in the $KNO_2 - H_2O_2$ system, the ratio of the velocity constants of reactions (29) and (30) is 0.47 ± 0.03.

TABLE 2. Yield of nitrite ions (ions /100 eV) on radiolysis of nitrate solutions.

Salt irradiated	Salt concentration, M	Type of radiation	Dose rate, eV ml^{-1} sec^{-1}	Conditions of irradiation	$G(NO_2)$, ions/100eV	Reference
KNO_3	10^{-2}	X-rays (105 kV)	—	in the presence or absence of air	0.6—0.9	22
KNO_3	10^{-3} 10^{-3}	X-rays Po^{210} α-particles	—	in the absence of air	0.8 0.18	18
KNO_3	0.01 0.1 1.0	Co^{60} γ-rays	$\sim 1.5 \cdot 10^{15}$	in the presence of air in neutral solutions	$\sim$2.0 (initial yield)	1—3
KNO_3	1.0		$\sim 1.5 \cdot 10^{15}$	solution contained 1 M KOH and 10^{-2} M glucose	$\sim$6.0	1—3
$NaNO_3$	0.012 0.1 1.0 3.0	X-rays (90 kV)	up to $\sim 10^{16}$	pH = 6.5; solutions saturated with oxygen	1.0 1.3 2.0 3.3	23
$NaNO_3$	1.0		up to $\sim 10^{16}$	solutions saturated with oxygen, pH = 0.5 pH = 1.5 pH = 2.2 pH = 6.5 pH = 8.4—13	0 0.9 1.6 2.0 2.4	23
$NaNO_3$	1.0	(50 kV)	$1 \cdot 10^{15}$	neutral solution saturated with nitrogen	2.2	24
$NaNO_3$	1.0	Co^{60} γ-rays	$1.1 \cdot 10^{15}$ $1.1 \cdot 10^{15}$	in alkaline solution in the presence of air between 20 and 25° 40° 80°—90° solutions contained 1 M KOH and 10^{-3} to 10^{-1} M glycerine; in the presence of air	1.5—1.8 $\sim$3.3 $\sim$4.0 $\sim$5.8	25, 26
$NaNO_3$	1.0	Co^{60} γ-rays		less than 2.5×10^{-4} M glycerine solution contained air, 1 M KOH, 10^{-3} M glycerine; at 35° 80°—90° solution contained 1 M KOH saturated with nitrogen solution contained 1 M KOH and 2.3×10^{-3} M glycerine; saturated with nitrogen	$\sim$1.6 $\sim$0.4—0.5 $\sim$4.5—4.8 $\sim$4.5—4.8 $\sim$5.3—5.8	25. 26
$Ca(NO_3)_2$	0.1—10.0	U^{235} fission products	—	solution at ~ 80°	very small	27
KNO_3	0.01	Co^{60} γ-rays	$\sim 1.4 \cdot 10^{10}$— $-3 \cdot 10^{14}$	neutral solutions saturated with air (Griess reagent present)	0.53	28, 29
KNO_3	0.1 1.0 2.0		$\sim 1.4 \cdot 10^{10}$— $-3 \cdot 10^{14}$	neutral solutions saturated with air or nitrogen (Griess reagent present)	2.42 4.09 4.5	28. 29
	0.01 0.1 1.0	P^{32} β-rays	—	neutral solutions saturated with air (Griess reagent present) neutral solutions saturated with air or nitrogen (Griess reagent present)	0.56 2.28 4.02	
	0.1 2.0	Pu^{239} α-particles	—		1.2 3.4	
$NaNO_3$	2.0—6.0	Co^{60} γ-rays	—	neutral solutions, saturated with air (Griess reagent present)	4.5	28
KNO_3	2.0—6.0				4.5	
NH_4NO_3	2.0—6.0				4,5	28
$Sr(NO_3)_2$	1.0—3.0				4.5	
$Ba(NO_3)_2$	1.0—3.0				4.5	
$Pb(NO_3)_2$	1.0—3.0		—		4.5	
NiO_3	2.0 $\sim$4.0 $\sim$5.0 $\sim$6.0				4.8 5.1—5.2 5.2—5.3 3.6—3.7	
$Be(NO_3)_2$	$\sim$0.5 $\sim$1.0 2.5 0.1			cooled to temperature of liquid nitrogen	4.6 5.1 3.3 0.2	
$NaNO_3$	1.0 3.0 and 5.0				0,8 1.4	30
$Th(NO_3)_4$	$\sim$0.2—2.7	U^{235} fission products mixed beam of neutrons and γ-rays		between 20° and 300°	insignificant	31
$Ca(NO_3)_2 \cdot 4H_2O$	$\sim$10 for NO_3^-	Co^{60} γ-rays		fused crystalline hydrate	0.5—0.75	32

3.7, and 5.95 atoms/100 eV for 0.1, 0.5, and 1 M solutions respectively. The almost total absence of nitrite ions can be explained either by reaction of Ag^+ with OH radicals, forming Ag^{2+} ions which subsequently oxidise the nitrite ions, or by the direct action of the OH radical on the nitrite. The possibility that Ag^{2+} ions are formed in $AgNO_3$ solutions

was pointed out by Sworski[34]. Thus the nature of the cation has no appreciable effect on $G(NO_2^-)$ only when it cannot undergo oxidation or reduction by the products of radiolysis of water.

The data published about the effect of the nature of the saturating gas on $G(NO_2^-)$ are conflicting. According to Proskurnin et al.[25,35] $G(NO_2^-)$ for 1 M $NaNO_3$ saturated with nitrogen is about $2\frac{1}{2}$ times greater than when saturated with air. Furthermore, the radiolytic reduction of nitrate does not depend on temperature between -10° and 90° if the irradiation is carried out in an inert gas[36]. If the solution is saturated with air, then $G(NO_2^-)$ is strongly temperature-dependent in this range. On the other hand, Kabakchi et al.[28,29] found that the nature of the saturating gas had no effect on $G(NO_2^-)$ at nitrate concentrations above 0.1 M, though in dilute solutions saturated with air or oxygen $G(NO_2^-)$ was somewhat lower than when saturated with nitrogen. According to Bakh[24], this is due to competing reactions of NO_3^- and the molecular oxygen present with atomic hydrogen.

With high-energy radiation (α-particles, recoil protons, and U^{235} fission products*), $G(NO_2^-)$ is appreciably lower than with low-energy radiation.

Yield of Hydrogen

Hydrogen is another product of the reduction of nitrate solutions. Bakh et al.[24] found that $G(H_2)$ decreased with increase of nitrate concentration, giving 0.5, 0.18, and 0.05 molecules respectively for 0.1, 1.0, and 5 M solutions of $NaNO_3$ irradiated with X-rays (dose 10^{15} eV $ml^{-1}sec^{-1}$), and saturated with nitrogen.

Mahlman and Boyle[37] treated nitrate solutions with Co^{60} γ-rays and found that $G(H_2)$ was a function of the cube root of the molar nitrate-ion concentration (Fig. 1, curve *1*). The empirical equation to the curve is

$$G(H_2) = 0.46 - 0.40[NO_3^-]^{1/3}. \quad (35)$$

Sowden[38] treated aqueous $Ca(NO_3)_2$ solutions, between 0.037 M and 15.9 M, with mixed radiation from a reactor and noticed a similar dependence on nitrate concentration. From curve *2* (Fig. 1) it is seen that the relationship between $G(H_2)$ and $[NO_3^-]^{1/3}$ is linear until the nitrate-ion concentration is approximately unimolar, and can be expressed by an equation of the type

$$G(H_2) = A - k[NO_3^-]^{1/3}. \quad (36)$$

The parameter k = 0.65 represents the probability of reaction between the solute and H or OH radicals. The constant A = 0.84 is the hypothetical hydrogen yield at zero concentration.

Decrease of $G(H_2)$ with increase of nitrate concentration was also observed with $UO_2(NO_3)_2$ [39,40] and $Th(NO_3)_4$.[31] Sowden and Lynde[27] found that the relationship between $G(H_2)$ and $Ca(NO_3)_2$ concentration after exposure to U^{235} fission products can be expressed by an equation similar to (36), as was also found for γ-rays and a mixed stream of neutrons and γ-rays. The values of the parameters A and k are 2.0 and 0.8 respectively.

$G(H_2)$ for U^{235} fission products and neutrons is appreciably higher than for γ-rays and X-rays. The high concentration of H atoms in the path of the recoil nuclei from

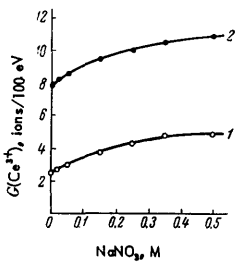


Fig. 2. Influence of $NaNO_3$ in the reduction of Ce^{4+} in 0.8 N H_2SO_4; initial concentration of $Ce^{4+} = 4 \times 10^{-4}$ M (from Sworski[45]): 1) in absence of Te^+; 2) in presence of 2×10^{-3} M Tl^+.

TABLE 3. Dependence of $G(H_2O_2)$ and $G(O_2)$ on concentration of $NaNO_3$ solution (dose rate 10^{15} eV ml^{-1} sec^{-1}; from Bakh et al.[24]).

$NaNO_3$, M	$G(H_2O_2)$	$G(O_2)$	G(Σ oxidation equiv.)
0.1	1.60	0.07	3.48
1.0	1.77	0.47	5.42
5.0	1.66	1.45	9.12

U^{235} fission products and of the recoil protons, caused by the passage of fast neutrons through water, increases the probability of recombination processes and the formation of molecular products.

According to Sharpatyi et al.[41], $G(H_2)$ for a 1.0 M solution of $NaNO_3$ is 0.06 molecule (Co^{60} γ-rays) and falls to 0.04 molecule in the presence of 10^{-3} M glycerine.

Thus the decrease in $G(H_2)$ with increase of nitrate concentration is typical for all forms of radiation, and is explained by reaction (34).[23]

Formation of Nitrogen and its Oxides

The formation of nitrogen and its oxides is observed when nitrate solutions are subjected to radiation with high density of ionisation. Bidwell et al.[39] treated uranyl nitrate solutions with U^{235} fission products and found that $G(N_2)$ decreased with increase of $UO_2(NO_3)_2$ concentration; $G(N_2)$ was 0.004 molecule for a solution 1 M in nitrate.

Boyle and Mahlman[31] treated thorium nitrate solution with U^{235} fission products and a mixed beam of neutrons and γ-rays and found that $G(N_2)$ was independent of temperature between 20° and 300°, but depended on the type of radiation and increased with increase of concentration. $G(N_2)$ for a 2.73 M solution was 0.06 molecule for U^{235} fission products, 0.006 for mixed fast neutrons and γ-rays, and 0.001 for γ-rays alone. They consider that the formation of nitrogen results from the direct action of the radiation on the nitrate. This is supported by the fact that $G(N_2)$ is independent of pH and tends to zero at a concentration of about 0.2 M. Oxides of nitrogen, mainly N_2O, were also found.

* U^{235} fission products are streams of recoil nuclei which cause a very high density of ionisation in their path.

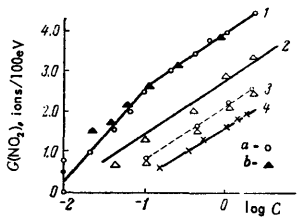


Fig. 3. Dependence of $G(NO_2^-)$ on KNO_3 concentration: 1) with Co^{60} γ-rays (*a* solutions saturated with air; *b* solutions saturated with nitrogen)[28,29]; 2) with Pu^{239} α-particles[28,29]; 3) calculated curve[28,29]; 4) direct action of Co^{60} γ-rays[47].

TABLE 4. Yields for radiolytic reduction of AmO_2^{2+} in acid solutions (from Zaitsev et al.[44]).

H_2SO_4, M	$G(-AmO_2^{2+})$	$HClO_4$, M	$G(-AmO_2^{2+})$	HNO_3, M	$G(-AmO_2^{2+})$
0.1	4.04	0.2	4.04	0.5	7.1
1.0	2.85	2.0	3.20	3.0	8.9
2.0	2.50	4.0	3.20	6.0	9.0
4.0	2.02	6.0	3.40	9.0	10.6
6.0	1.80	4M $HClO_4$+			
10.0	2.20	+ 2M $NaClO_4$	3.55	14.3	6.0

According to Sowden[38] $G(N_2)$ was $(3.2 \pm 0.6) \times 10^{-3}$ molecules on irradiating 9.4 M $Ca(NO_3)_2$ with mixed fast neutrons and γ-rays from a reactor.

Molecular nitrogen[27] is also formed by the action of U^{235} fission products on $Ca(NO_3)_2$ solutions between 0.2 and 10 M. In the 10 M solution $G(N_2)$ is ~0.09 molecule/100 eV. Below 4 M the relationship between $G(N_2)$ and concentration may be expressed by the empirical equation

$$G(N_2) = 0.004[NO_3^-]^{1/4}. \quad (37)$$

Nitrous oxide was found among the products formed from concentrated $Ca(NO_3)_2$.

Oxidation Products

Oxygen and hydrogen peroxide are among the oxidation products of nitrate solutions. The formation of oxygen has been observed by several authors[24,41]. According to Bakh et al.[23,24], hydrogen peroxide is formed by treating $NaNO_3$ solutions with X-rays, but Sowden and Lynde[27] did not find peroxide in $Ca(NO_3)_2$ solutions treated with U^{235} fission products.

Increase of pH to about 8 caused an increase of $G(H_2O_2)$ but G remained constant when the pH was raised further[23]; a similar relationship was observed for NO_2^- (see Table 2). In Bakh's view the decrease in $G(NO_2^-)$ and $G(H_2O_2)$ is explained by the non-radiolytic reaction

$$HNO_2 + H_2O_2 \rightarrow HNO_3 + H_2O, \quad (38)$$

and also by the radiochemical reaction between NO_2^- and H_2O_2, described by Allen and Schwarz[19]. The nature of the saturating gas had an effect on $G(H_2O_2)$ only in dilute solutions. The yields of H_2O_2 were practically identical in 1 M $NaNO_3$ saturated with hydrogen, nitrogen, or oxygen.

According to Bakh et al.[24], $G(O_2)$ increases with increase of $NaNO_3$ concentration while the change in $G(H_2O_2)$ is insignificant (Table 3).

In the radiolytic decomposition of 1 M $NaNO_3$ with Co^{60} γ-rays, Sharpatyi et al.[41] found that $G(O_2)$ was 0.4 molecule and fell to zero in the presence of 10^{-3} M glycerine.

Radiolysis of Nitric Acid

There are only a few published references to the radiolysis of aqueous nitric acid. Medvedovskii et al.[42] found that the integral dose corresponding to the setting up of a stationary potential in the Fe^{3+}/Fe^{2+} system was significantly smaller in nitric acid than in other acids at the same concentration. They think that this is related to the fact that NO_3^- is reduced by the action of radiation, and that HNO_2 is formed, which can easily oxidise Fe^{2+}.

Challenger and Masters[43] found that radiolytic reduction of Ce^{4+} in nitric acid gave a larger $G(Ce^{3+})$ than reduction in 0.8 *N* H_2SO_4; in 1 *N* HNO_3 $G(Ce^{3+})$ was 8.3 ions. According to their explanation, the increase is due to the formation of an additional quantity of reducing agent (HNO_2) by the reaction of OH radicals with HNO_3.

Zaitsev et al.[44] studied the reduction of Am^{6+} and Am^{5+} by their own α-particles in H_2SO_4, HNO_3, and $HClO_4$ (see Table 4).

It can be seen from Table 4 that the yield of AmO_2^{2+} in nitric acid is 1.5–2 times as large as the maximum yield from 0.2 M $HClO_4$ and 0.1 M H_2SO_4. They consider that reduction in nitric acid solutions occurs at the expense of the secondary products of the reaction between radicals and HNO_3.

Mechanism of Reduction of NO_3^- Ions

The available experimental data on the effect of ionising radiation on aqueous nitrate solutions is interpreted in different ways by various authors.. This is particularly true of concentrated solutions where the solute is subjected to the combined direct and indirect effects of the radiation.

It is generally accepted[23–25,28,29,45] that reduction takes place at the expense of H atoms formed during the radiolysis of water. In Bakh's opinion[23] the first stage in the reduction of nitrate to nitrite is reaction (34). The subsequent transition from NO_2 to NO_2^- can occur either by a second reaction with an H atom

$$NO_2 + H \rightarrow NO_2^- + H^+ \quad (39)$$

or, more probably, by disproportionation:

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3. \quad (40)$$

In both cases two H atoms are used up in forming a single NO_2^- ion.

Sharpatyi et al.[26,35] suggest that the reduction of nitrate by H atoms takes place by a somewhat different mechanism. Atomic hydrogen reacting with NO_3^- gives HNO_3^- or NO_3^{2-} ions (depending on pH), where the nitrogen is quadrivalent:

$$NO_3^- + H \rightarrow HNO_3^- \quad (41)$$

or

$$NO_3^- + H + OH^- \rightarrow NO_3^{2-} + H_2O. \quad (42)$$

Further, these ions can disproportionate or be oxidised to nitrate, thus:

$$2HNO_3^- \rightarrow NO_3^- + NO_2^- + H_2O, \quad (43)$$

$$HNO_3^- + O_2 \rightarrow NO_3^- + HO_2 \quad (44)$$

or

$$NO_3^{2-} + O_2 \rightarrow NO_3^- + O_2^-. \quad (45)$$

The authors believe that the decrease in $G(NO_2^-)$ in a nitrate solution saturated with air, compared with a solution saturated with nitrogen, confirms this mechanism.

It is also confirmed indirectly by the dependence of $G(NO_2^-)$ in 1 M alkaline $NaNO_3$ on the dose rate[36]. In solutions saturated with air, $G(NO_2^-)$ remains constant with change of dose rate between 2×10^{12} and 5×10^{16} eV $ml^{-1}sec^{-1}$. In the absence of oxygen (solution saturated with nitrogen) $G(NO_2^-)$ is independent of the dose rate between $\sim 2.5 \times 10^{13}$ and 5×10^{16} eV $ml^{-1}sec^{-1}$, but with a mixture of 2.5% oxygen and nitrogen $G(NO_2^-)$ is directly proportional to the logarithm of the dose rate. This is explained[36] by the simultaneous occurrence of disproportionation of the HNO_3^- ion and its oxidation to NO_3^- by oxygen.

Sharpatyi and Molin's[46] investigation of electron-paramagnetic-resonance (e.p.r.) spectra and kinetics of the build-up of radicals during radiolysis of a frozen aqueous sodium nitrate solution showed that NO_2 was the main product of the conversion of NO_3^- to NO_2^- and NO_2^- to NO_3^-. During the reduction of nitrate to nitrite a radical containing quadrivalent nitrogen (HNO_3^-) was also observed. These radicals only disappear at temperatures between -70° and -90°. The e.p.r. spectra showed that the yield of radicals from the reduction of nitrate ions depends on solution concentration and not on the nature of the gas saturating it, and increases with the addition of alkali or glycerine.

Thus the reduction of NO_3^- ions proceeds mainly by the action of atomic hydrogen formed by radiolysis of water. But $G(NO_2^-)$ in nitrate solution, with a concentration as low as 0.1 M, was found to exceed the value estimated on the assumption that all the H atoms are used up in reducing NO_3^- ions (1.8 to 1.9 ions for light-particle radiation and ~ 0.6 ion for α-particles). Some authors[28,29,45,47] explain the increase in $G(NO_2^-)$ in concentrated nitrate solutions as a direct effect of radiation on the solute. Sworski[45] found that the presence of nitrate in a solution of Ce^{4+} in 0.8 N H_2SO_4 treated with Co^{60} γ-rays increased $G(Ce^{3+})$; the increase was the same in the presence and absence of Tl^+ ions (Fig. 2). Since Tl^+ is an effective acceptor of OH radicals, the observed increase in $G(Ce^{3+})$ in the presence of NO_3^- cannot be ascribed to the reaction between Ce^{4+} and these radicals. Sworski explains these results by the direct action of the radiation on the nitrate, consisting in excitation of NO_3^- ions on collision with low-energy electrons* or with excited water molecules.

Mahlman and Schweitzer[47] studied the action of Co^{60} γ-rays on solutions of a series of nitrates at concentrations from 0.001 M to 5.0 M and containing 2×10^{-4} M Ce^{4+} in 0.4 M H_2SO_4 (Table 5). The increase in $G(Ce^{3+})$ in sufficiently concentrated solutions (above 0.04 M) is connected with the formation of NO_2^- ions, which react with Ce^{4+}:

$$NO_2^- + 2Ce^{4+} + H_2O \rightarrow 2Ce^{3+} + 2H^+ + NO_3^-. \quad (46)$$

Since the increase does not occur in strongly acid dilute nitrate solutions, the effect observed in concentrated solutions is thought to result from the direct action of γ-rays on NO_3^- ions:

$$NO_3^- \sim\sim\rightarrow NO_2^- + \tfrac{1}{2}O_2. \quad (47)$$

It may be seen from Table 5 that the nitrite yield due to direct action, $G(NO_2^-)_{dir}$, does not depend on the nature of the cation. The dependence of $G(NO_2^-)_{dir}$ on NO_3^- concentration is expressed by the equation

$$G(NO_2^-)_{dir} = 1.22 \log [NO_3^-] + 1.70. \quad (48)$$

Kabakchi et al.[28,29] treated nitrate solutions between 0.1 M and near saturation with Co^{60} γ-rays, Pu^{239} α-particles, and P^{32} β-rays. Griess' reagent was added to the solutions to react with the nitrite ions at the moment of formation and to protect them against the radiolysis products of

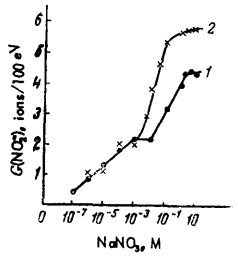


Fig. 4. Dependence of $G(NO_2^-)$ on the concentration of $NaNO_3$ (pH 14)[41]: 1) in absence of glycerine; 2) in presence of 10^{-3} M glycerine.

TABLE 5. Nitrite yield (ions /100 eV) through the direct action of Co^{60} γ-rays (from Mahlman and Schweitzer[47]).

NO_3^-, M	Cation									
	Li	Na	K	Rb	Cs	NH_4	Zn	Mg	Al	Th
0.1	0.54	0.50	—	0.48	0.52	0.55	0.49	0.53	—	0.50
0.14	—	—	0.68	—	—	—	—	—	—	—
0.15	—	—	—	—	—	—	—	0.69	—	—
0.20	0.82	0.88	—	—	—	0.83	0.86	0.78	—	0.78
0.30	1.07	1.02	—	0.89	1.14	1.04	—	—	0.90	1.19
0.34	—	—	1.12	—	—	—	—	—	—	—
0.40	—	—	—	1.22	—	—	1.17	1.19	—	—
0.50	1.36	1.33	1.39	1.37	1.38	1.37	—	—	—	1.38
0.60	—	—	—	—	—	—	1.27	1.27	1.21	—
0.90	—	—	—	—	—	—	—	—	1.39	—
1.0	1.86	1.62	1.73	—	1.76	1.72	1.63	1.54	—	1.74
1.36	—	—	1.94	—	—	—	—	—	—	—
1.50	—	—	—	—	—	—	—	—	1.75	—
1.75	—	—	2.02	—	—	—	—	—	—	—
2.0	2.10	—	—	—	—	2.11	—	1.79	—	2.19
3.0	—	2.24	—	—	—	2.53	—	—	2.03	2.54
4.0	—	—	—	—	—	—	—	2.42	—	—
5.0	—	2.59	—	—	—	2.71	—	—	—	—

* Low energy-electrons are produced in the ionisation of water[48,49]; they lose their energy by inelastic collisions. If this energy falls below the lowest excitation energy of water, these electrons can have a greater cross-section for reaction with solutes than with water. The part played by low-energy electrons in radiation chemistry is obscure.

water. Fig. 3 shows the relationship between $G(NO_2^-)$ and KNO_3 concentration for Co^{60} γ-rays and Pu^{239} α-particles (curves *1* and *2*); curve *3* was calculated from

$$G'(NO_2^-) = G(NO_2^-) - G(H)/2, \qquad (49)$$

where $G(NO_2^-)$ is the total nitrite yield and $G(H)/2$ is the NO_2^- yield due to reduction of NO_3^- by H atoms. The independence of $G'(NO_2^-)$ of the type of radiation and the considerable influence of NO_3^- concentration is ascribed to direct action of the radiation. For comparison, curve *4* shows Mahlman and Schweitzer's[47] data for the direct effect of Co^{60} γ-rays on aqueous KNO_3.

Other explanations of the increase of $G(NO_2^-)$ in concentrated nitrate solutions are offered by a number of authors[1-3,23,24,32,50]. They consider that the excitation of water molecules, as well as their ionisation, plays a part. It may be seen from Table 2 that on adding glucose or glycerine to an alkaline nitrate solution $G(NO_2^-)$ increases by a factor of 3 (5 to 6 ions; i.e. the radiolysis products of water are completely used up). According to Proskurnin et al.[1-3,32,50] this increase in $G(NO_2^-)$ is due to some of the water molecules acquiring sufficient energy for ionisation, but being in one "cell", the H atoms and OH radicals recombine, not having time to diffuse into the bulk of the solution and react with the solute. The presence of two acceptor radicals, capable of reacting with the two parts of the dissociating water molecule (in this case the NO_3^- ion is the acceptor of the H atom and the glucose or glycerine is the acceptor of the OH radical), and the simultaneous occurrence of two coupled oxidation-reduction reactions, enable greater use to be made of the absorbed energy by drawing on the energy of excitation of water.

Work by Sharpatyi et al.[41] on the effect of $NaNO_3$ concentration in alkaline solutions (between 10^{-7} M and 6 M) on radiolytic transformations (Fig. 4) is of interest in this connection.

With increase of concentration from 10^{-7} M to 5×10^{-4} M $G(NO_2^-)$ increases and remains constant at ~4.3 equiv. between 5×10^{-4} M and 10^{-2} M. In more concentrated solutions, $G(NO_2^-)$ increases linearly into log [$NaNO_3$]. Between 1 M and 6 M $G(NO_2^-)$ again remains constant (~g equiv.). The addition of 10^{-3} M glycerine does not change the shape of the curve (Fig. 4, curve *2*), although it diminishes its sloping portion. The sloping portion of curve *1* is explained by the practically complete reaction of H atoms with nitrate ions.

At present the experimental material available is still insufficient to decide between one or another mechanism of the radiolytic transformations of nitrate solutions. For example, if we accept the hypothesis of Proskurnin et al., it is difficult to explain the considerable increase in $G(NO_2^-)$ observed by Sworski at large nitrate concentrations, even in the presence of such effective acceptors of H atoms and OH radicals as Ce^{4+} and Tl^+ ions. On the other hand, if we take into account the contribution of the solute to the electron density, which is 0.05 for 1 M $NaNO_3$ and 0.11 for 2 M, we find that the effect of the direct action of radiation, even on very concentrated solutions, is only a few percent. Additional factual material is therefore necessary for the final solution of the question of radiochemical processes in concentrated nitrate solutions; for example, reliable data about the initial yield of molecular oxygen; the effect of dose rate over a wide range on the yield at different NO_3^- concentrations; the determination by electron paramagnetic resonance of the concentration and nature of the free radicals appearing immediately on irradiation; etc.

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PROGRESS IN THE ANALYTICAL CHEMISTRY OF URANIUM, THORIUM, AND PLUTONIUM

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INTRODUCTION

Extensive use of atomic energy had led to the rapid development of the analytical chemistry of uranium, thorium, and plutonium, and several thousand papers on this subject have been published.

Numerous data on the chemistry of uranium, thorium, and plutonium are collected in the monograph by Seaborg and Katz (Russian translation edited by Nikolaev[1]) and in a recent monograph by Seaborg[2]. The most complete review of the literature on the analytical chemistry of thorium is given in a monograph by Ryabchikov and Gol'braikh[3]. The analytical chemistry of uranium is dealt with in monographs and review articles by Rodden[4-6], Palei[7], and others[8-23]; interesting data on the chemistry of thorium are given in reviews by Rodden[4,24], Schoeller[25], Moeller[26], Bonardi[27], and others[8,11,31,28,29], and on the chemistry of plutonium in reviews by Metz and Harvey[30-34].

This article reviews modern chemical methods for determining uranium, thorium, and plutonium, and discusses the analytical reactions of these elements. Physical, physicochemical, and other instrumental methods, which