

PHYSICAL METHODS  
OF INVESTIGATION

## The State of Ruthenium in Nitrite–Nitrate Nitric Acid Solutions as Probed by NMR

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**Abstract**—The state of ruthenium in nitric acid solutions treated with sodium nitrite has been studied by <sup>14</sup>N, <sup>15</sup>N, <sup>17</sup>O, and <sup>99</sup>Ru NMR. In the acidity range 2.7–0.12 mol/L, the dominating ruthenium species are the [RuNO(NO<sub>2</sub>)<sub>2</sub>(NO<sub>3</sub>)(H<sub>2</sub>O)<sub>2</sub>]<sup>0</sup> and [RuNO(NO<sub>2</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>+</sup> complexes. When the acidity is decreased to 0.06 mol/L, trinitro- and tetranitronitrosoruthenium(II) complexes predominate in solution. In an acidic medium, the trinitro- and tetranitronitrosoruthenium(II) complexes exhibit catalytic activity toward oxidation with air of nitrite to nitrate.

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Ruthenium is one of the macrocomponents of waste from processing spent nuclear fuel (SNF). Depending on the type of reactor, the conditions of burning nuclear fuel, and the time of its storage, ruthenium concentrations from 0.7 to 29.4 g per liter of liquid waste have been found, the content of nonradioactive ruthenium in nitric acid solutions of SNF being many times higher than the content of its radioactive isotopes. The necessity of searching for methods to isolate ruthenium from such solutions led to the emergence of interest in studying the state and chemical behavior of ruthenium in nitric acid solutions in the mid-twentieth century (about 100 works in the 1950s–1970s). The results of these studies were surveyed and summarized in the review by Forsterling (1983) [1]. The overwhelming part of ruthenium in nitric acid solutions of waste from processing SNF is the form of nitroso complexes containing a stable (RuNO)<sup>3+</sup> moiety. The other ligands that complete the coordination of ruthenium to octahedral are nitrate, nitrite, and hydroxide ions and water molecules. The existence of coordinated nitrite ions is due to the presence of a stationary concentration of nitrous acid in the system (up to 10<sup>-2</sup> mol/L) generated on radiolysis of HNO<sub>3</sub> [2, 3]. The quantitative proportions of different nitrosoruthenium complexes in actual and model nitric acid solutions of SNF depend strongly on many factors, such as acidity, the contents of nitrate ion and nitrous acid, temperature, solution prehistory, etc.

The available data on the time it takes for nitric acid solutions to reach equilibrium are contradictory. For solutions of nitroso nitrate complexes, these data vary from several hours to many months. For solutions of nitroso nitrite complexes, this range is from 20–24 h to one year. We may only unambiguously state that the

composition of equilibrium solutions depends on aging conditions and that the equilibration rate increases sharply with increasing temperature. In addition, the fact that mononuclear nitrosoruthenium nitrate complexes are noticeably more labile than nitrosoruthenium nitrite complexes may be considered as proven.

Up to the end of the twentieth century, the composition of ruthenium complexes in solutions was determined by indirect methods (chromatography, extraction). Modern physical methods offer new possibilities for studying the compositions of solutions. One of the most informative methods for studying the state of equilibrium and predominant complex species in solution is NMR with the use of the nuclei of a central atom, ligands, and a solvent (<sup>99</sup>Ru, <sup>14</sup>N, <sup>15</sup>N, <sup>17</sup>O). NMR allows one to observe a system in situ, without separation and isolation of its components. Among the above isotopes, the most concentration-sensitive is <sup>14</sup>N. It was found that coordinated and free nitrate ions give rise to separate <sup>14</sup>N NMR signals and that the coordinated nitrate is observable down to a concentration of 0.002 mol/L [4, 5]. Other N-containing ligands (both coordinated and free NO, NO<sub>2</sub><sup>-</sup>, NH<sub>3</sub>) [5–9] that can appear in this system as a result of different reactions can also be observed by NMR. Coordinated aqua and hydroxo ligands are detected by natural abundance <sup>17</sup>O NMR at a complex concentration of 0.2–0.3 mol/L. As a rule, the coordinated water signal is shifted upfield by 70–100 ppm from the signal of the solvent (see, e.g., [10]). The possibilities of the NMR method in determining the structures of platinum metal complexes in solutions were considered in detail in [11].

The present work deals with the study of the ruthenium state in nitric acid solutions treated with sodium nitrite (so-called nitration).

### EXPERIMENTAL

The complex  $\text{Na}_2[\text{RuNO}(\text{NO}_2)_4\text{OH}] \cdot 2\text{H}_2\text{O}$  was synthesized from pure grade (Russian State Standard) ruthenium trichloride by a routine procedure [12]. The X-ray powder diffraction pattern of the synthesized compound coincided with the pattern calculated from X-ray crystallography data [13], and the IR spectrum was consistent with the spectrum described in [14]. The other reactants were no worse than chemically pure.

An initial solution for nitration was prepared by dissolving 3 mmol of  $\text{Na}_2[\text{RuNO}(\text{NO}_2)_4\text{OH}] \cdot 2\text{H}_2\text{O}$  in a 1 : 1  $\text{HNO}_3(\text{conc}) + \text{H}_2\text{O}$  mixture. The solution was heated in a water bath for 16 h and then evaporated to a minimum volume (wet salts). Then, 10 mL of water was added, and the solution was evaporated once more. The residue was dissolved in 5 mL of 3 M  $\text{HNO}_3$  on heating and kept in a water bath for 1 h. After that, the solution was transferred to a 10-mL volumetric flask, and the volume was completed to the mark with 3 M  $\text{HNO}_3$ . The resulting 0.3 M ruthenium solution in  $\sim 3$  M  $\text{HNO}_3$  (solution I) was used in experiments.

Nitrated nitric acid solutions of ruthenium for NMR were prepared as follows. To solution I (3 mL), water enriched in  $^{17}\text{O}$  (0.2 mL) was added, and nitration was carried out by adding solid  $\text{Na}^{15}\text{NO}_2$  at room temperature and heating the resulting solutions for 30 min at  $80^\circ\text{C}$  in a sealed system. Solution II was obtained by the interaction of solution I with 0.216 g of  $\text{Na}^{15}\text{NO}_2$ ; solution III, by the interaction of II with 1.118 g of  $\text{Na}^{15}\text{NO}_2$ ; solution IV, by the interaction of III with 0.418 g of  $\text{Na}^{15}\text{NO}_2$ ; solution V, by keeping solution IV for 25 days at room temperature; and solution VI, by the interaction of solution V kept for nine months with 0.034 g of  $\text{Na}^{15}\text{NO}_2$ . After cooling the solutions, NMR spectra were recorded. A total of five series of spectra were recorded for solutions with concentrations of  $\text{H}^+$  2.7 (solution II), 1.5 (III), 0.06 (IV), 0.2 (V), and 0.12 mol/L (VI). To estimate the acidity of solutions, 0.1 mL was sampled and diluted 100-fold, and the pH was measured on an Anion 4100 ionometer.

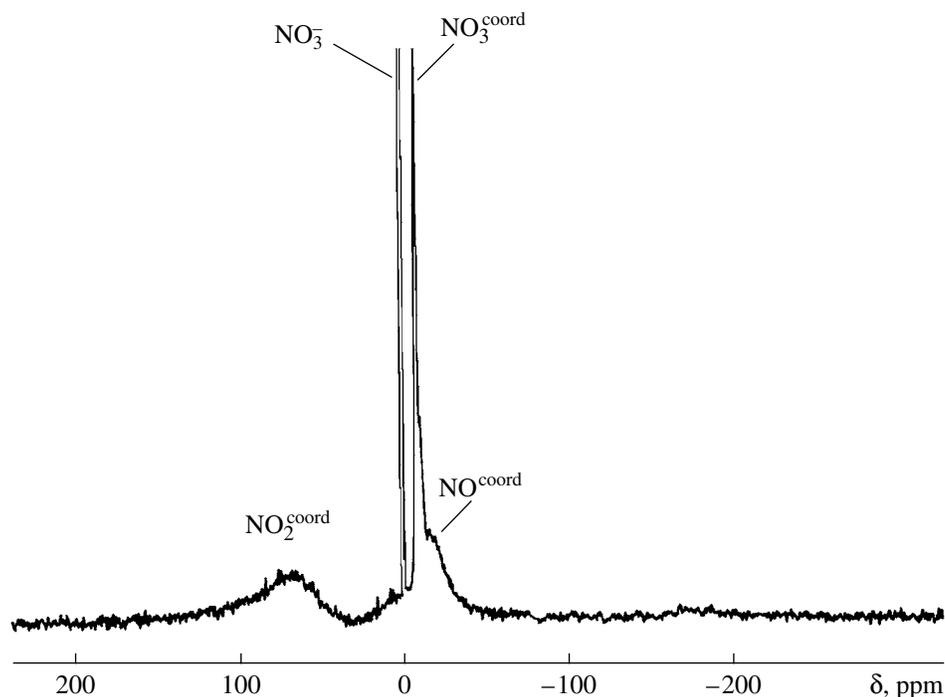
The  $^{99}\text{Ru}$ ,  $^{14}\text{N}$ ,  $^{15}\text{N}$ , and  $^{17}\text{O}$  NMR spectra of aqueous solutions were recorded on a Bruker MSL-400 spectrometer operating at the frequencies 18.42, 28.9, 40.56, and 54.2 MHz, respectively. Chemical shifts ( $\delta$  scale, ppm) were measured with respect to the signals of external references: 1 M  $\text{NaNO}_3$  ( $^{14}\text{N}$ ) or  $\text{K}^{15}\text{NO}_3$  ( $^{15}\text{N}$ ), water ( $^{17}\text{O}$ ), and 0.5 M  $\text{K}_4[\text{Ru}(\text{CN})_6]$  solution ( $^{99}\text{Ru}$ ). The error of determination of  $\delta$  depended on the line width and was no more than 0.1 ppm for  $^{15}\text{N}$ , no more than 2 ppm for  $^{14}\text{N}$  and  $^{17}\text{O}$ , and no more than 20 ppm for  $^{99}\text{Ru}$ .

The interaction of sodium nitrite with 2–3 M  $\text{HNO}_3$  solutions, including ruthenium- and zinc-containing solutions, was carried out by the following procedure: 5-mL portions of 2–3 M  $\text{HNO}_3$  were placed in 25-mL volumetric flasks, 0–0.2 mL of solution I was added, and a zinc nitrate sample (0–6.25 mmol) was dissolved. To the resulting solution, a required volume of 8.33 M  $\text{NaNO}_2$  solution was added portionwise at room temperature, and the resulting solution was heated for 30–40 min at  $80^\circ\text{C}$ . The residual acidity of the solution was determined by titration of a 0.1-mL sample diluted 100-fold with a standard alkali solution in the presence of Methyl Orange. The final solutions contained  $(0 - 1.2) \times 10^{-2}$  mol/L of ruthenium and 0–1.25 mol/L of zinc nitrate.

### RESULTS AND DISCUSSION

The  $^{14}\text{N}$  NMR spectrum of solution I shows the strong signal due to the free nitrate ion ( $\delta = -1.5$  ppm), the signal due to the coordinated nitrate ion ( $\delta = -10.5$  ppm), initially described in [4], and the broad signal due to the coordinated nitroso group ( $\delta \sim -18$  ppm) [5–9]. No signal of coordinated  $\text{NO}_2^-$  is observed. The  $^{99}\text{Ru}$  NMR spectrum of this solution is almost featureless. This can be caused by the presence of several complex species in this solution, the concentration of each of them being below the detection limit of the spectrometer, as well as by polymerization of complex particles, which strongly broadens spectral lines. Thus, ruthenium in this solution can be in the form of several nitroso nitrate aqua complexes, which are, most likely, not only monomeric.

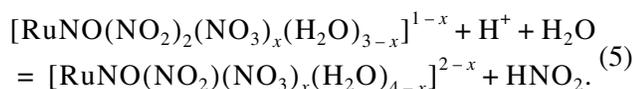
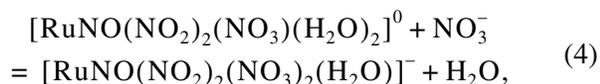
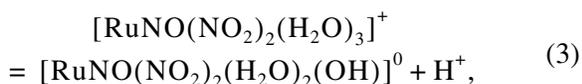
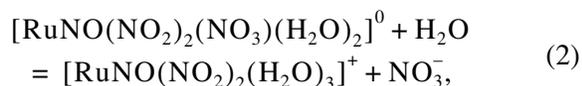
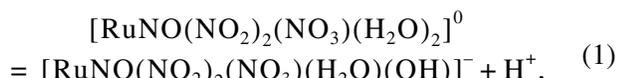
Figure 1 shows the  $^{14}\text{N}$  NMR spectrum of a 0.33 M  $\text{Na}_2[\text{RuNO}(\text{NO}_2)_4\text{OH}] \cdot 2\text{H}_2\text{O}$  solution in 3 M  $\text{HNO}_3$  kept for one day at room temperature. In addition to the line of the free nitrate ion ( $\delta = -1.3$  ppm), the spectrum shows the lines of coordinated nitrite ions ( $\delta \sim 70$  ppm, the range of the  $\text{H}_2\text{O}-\text{Ru}-\text{NO}_2$  trans coordinates), nitrate ions ( $\delta = -9.8$  ppm), and nitroso group ( $\delta \sim -18$  ppm, the  $\text{H}_2\text{O}-\text{Ru}-\text{NO}$  coordinate) with an intensity ratio close to 2 : 1 : 1 if the weakening of the lines of coordinated nitrite ions ( $\text{NO}_2^{\text{coord}}$ ) is taken into account [5]. This means that, in 3 M  $\text{HNO}_3$ , two of the four coordinated nitro groups of the initial complex  $[\text{RuNO}(\text{NO}_2)_4\text{OH}]^{2-}$  are destroyed within one day, which is consistent with the conclusions [15–19] that  $\text{NO}_2^{\text{coord}}$  in this complex exhibits a strong trans influence and that *cis*-dinitronitrosoruthenium compounds are stable. The  $^{99}\text{Ru}$  NMR spectrum of this solution ( $T = 323$  K) is represented by one strong line ( $\delta = 3993$  ppm, the width  $W_{1/2} \sim 1600$  Hz), which retains its characteristics in the spectrum recorded 40 days later ( $\delta = 3987$  ppm,  $W_{1/2} \sim 1600$  Hz). Taking into account the presence of the signal due to the coordinated nitrate ion, we may assume that the predominant ruthenium form is the complex



**Fig. 1.**  $^{14}\text{N}$  NMR spectrum of a  $0.33 \text{ M Na}_2[\text{RuNO}(\text{NO}_2)_4\text{OH}] \cdot 2\text{H}_2\text{O}$  solution in  $3 \text{ M HNO}_3$  recorded within one day after its preparation.

*cis*- $[\text{RuNO}(\text{NO}_2)_2(\text{NO}_3)(\text{H}_2\text{O})_2]^0$  (**A**). To remove the remaining two nitro groups, the complex should be heated for a long time in concentrated nitric acid. Even sulfamic acid, which is one of the best denitrating agents [20, 21], destroys only three nitro groups in the initial tetranitrohydroxynitrosoruthenium complex at room temperature over a period of two months [5].

Depending on the equilibrium concentration of  $\text{H}^+$  and  $\text{NO}_3^-$ , the aging time of solutions, and the degree of openness of the system, complex **A** in a nitric acid solution can undergo several types of transformations:



Processes (1) and (3) of proton elimination are the fastest and it takes virtually no time for them to reach equilibrium [15, 16]. Processes (2) and (4)—substitu-

tion of water for the coordinated nitrate ion and the reverse process—are noticeably slower and it takes several tens of hours for them to reach equilibrium. The reaction half-times for these reactions at  $0^\circ\text{C}$  are 1 and 3.8 days, respectively. Removal of one of the two remaining coordinated nitro groups is possible only if equilibrium (5) is shifted due to removal of nitrous acid from the solution (caused by oxidation or evaporation of nitrogen oxides from the open system) [22]. At room temperature, this process is extremely slow and is able to have a noticeable effect on the ruthenium distribution over complex species only weeks and months after the preparation of solutions.

The NMR data on ruthenium in nitric acid solutions nitrated with isotope-labeled  $\text{Na}^{15}\text{NO}_2$  are summarized in the table. All solutions contain the coordinated nitro and nitroso groups; for solutions II–IV, the signals of nitroso groups are recorded only in  $^{14}\text{N}$  NMR spectra, since these groups are almost not involved in isotope exchange under the experimental conditions used. The  $^{14}\text{N}$ – $^{15}\text{N}$  exchange in the coordinated nitroso group requires the rupture of the strong Ru–NO bond and is an extremely slow process. In particular,  $^{15}\text{NO}^{\text{coord}}$  signals comparable in intensity with the  $^{15}\text{NO}_3^{\text{coord}}$  and  $^{15}\text{NO}_2^{\text{coord}}$  signals appeared in the spectrum only after keeping the solution in  $0.12 \text{ M HNO}_3$  for 11 months. It is worth noting that, in alkaline solutions where reversible nitroso–nitro transformations take place, nitrogen

Chemical shifts ( $\delta$ , ppm) and assignment of signals in the NMR spectra of nitrated ruthenium solutions in nitric acid

Solution ( $c_{\text{H}^+}$ , mol/L)	II (2.7)	III (1.5)	IV (0.06)	V (0.2)	VI (0.12)	Assignment
$^{15}\text{N}$ , $T = 300\text{ K}$	200.8 ( $^{14}\text{N}$ )	202.4, <b>200.6</b> , <b>198.4</b> , 196.5	<b>206.5</b> , 203.4, 203.0	203.1, <b>197.2</b>		$\text{HNO}_2$
	64.1(1)*, 63.4(1), 60.0(1.4)	64.0(1), 63.5(1), 60.3(1)	93.3(8), 90.7(4), 84.7(1), 84.4(1)	65.3(1*2), 62.9(1.4)	64.1(1), 63.6(1), 61.3(1.8)	$\text{NO}_2^{\text{coord}}$
		<b>87.2, 84.5, 83.1, 79.9, 66.9, 65.9, 61.4**</b>	<b>86.5</b>	<i>Group of narrow and broad signals in the range 87–66</i>		$\text{NO}_2^{\text{coord}}$
	0.9	0.8	1.4	1.5	0	$\text{NO}_3^-$
	-9.8(1.2)	-9.9(0.8)		-9.4(1)	-10.9(1.1)	$\text{NO}_3^{\text{coord}}$
				<b>-19.8, -23.1</b>	-21.3, -24.7	$\text{NO}^{\text{coord}}$
$^{14}\text{N}$	$\sim -20$	-17	-16, -31	-19, -23	-20	$\text{NO}^{\text{coord}}$
$^{17}\text{O}$ , $T = 323\text{ K}$	684.3	683.6	683, <b>641</b>	681	682	$\text{NO}_2^{\text{coord}}$
	410.6	409.3	408	409	409.6	$\text{NO}_3^-$
			376			$\text{NO}^{\text{coord}}$
			98, 33			$\text{OH}^{\text{coord}}$
	18.8	18.9				?
	-0.9	-5.3	-7.6	-4.5	-5.6	$\text{H}_2\text{O}$
	-71	-72		-71	-71	$\text{H}_2\text{O}^{\text{coord}}$
$^{99}\text{Ru}/W_{1/2}$ , Hz, ( $T = 323\text{ K}$ )	3950/1600	3953/2000		3937/1800		<b>A, B</b> <b>C</b> <b>D</b>
			3425/650, 3580/1000			

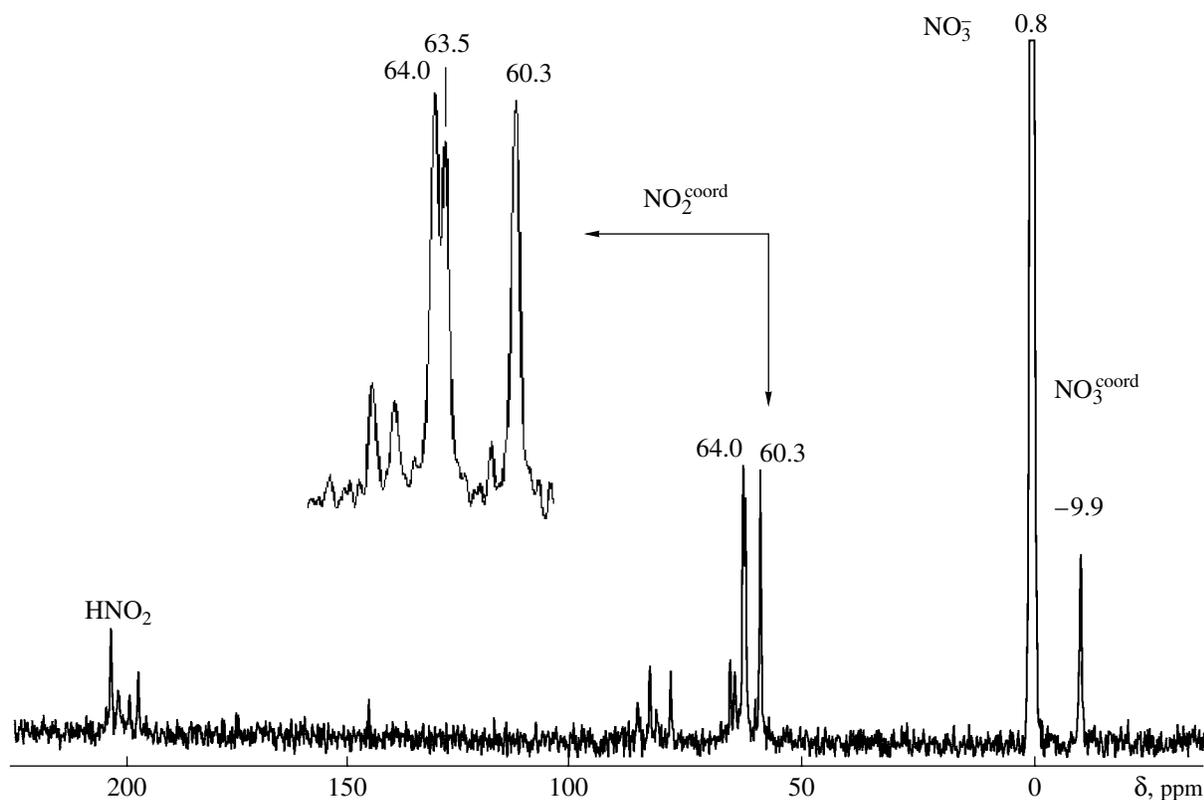
\*The relative intensities of signals are parenthesized.

\*\*Weak signals are shown boldface.

isotope exchange between the nitroso group and nitrite ion is noticeably faster [7].

The presence of strong lines of free and coordinated nitrate ions in the  $^{15}\text{N}$  NMR spectra is evidence that nitrogen isotope exchange between nitrite and nitrate ions in an acid medium is rather fast. It is obvious that nitrous acid and nitrogen oxides are directly involved in the exchange mechanism. Nevertheless, the  $\text{NO}_2^{\text{coord}} : \text{NO}_3^- : \text{NO}_3^{\text{coord}}$  intensity ratios in the  $^{14}\text{N}$  and  $^{15}\text{N}$  NMR spectra of the same solutions are noticeably different. As might be expected, in the  $^{15}\text{N}$  NMR spectra, the  $\text{NO}_2^{\text{coord}} : \text{NO}_3^-$  intensity ratio is higher while the  $\text{NO}_3^{\text{coord}} : \text{NO}_3^-$  intensity ratio is lower than those in the  $^{14}\text{N}$  NMR spectra. This indicates that complete isotope equilibrium between nitrite and nitrate ions under the experimental conditions is not achieved.

Figure 2 shows the full  $^{15}\text{N}$  NMR spectrum of solution **III**. The strongest line at  $\delta \sim 200$  ppm (202.4) is due to free  $\text{HNO}_2$  [23]. Despite the fact that nitrous acid in solution exists in two tautomeric forms, fast exchange between them always leads to the observation of a single, slightly broadened signal for  $\text{HNO}_2$ . For the same reason, no separate signals are observed for  $\text{HNO}_2$  and free  $\text{NO}_2^-$ . A decrease in acidity leads to an increase in the content of the deprotonated form of nitrous acid (nitrite ion) and to a downfield shift of the corresponding signal, i.e., toward the signal of free  $\text{NO}_2^-$  ( $\delta = 233$  ppm) [6, 7, 24]. The other lines in the spectrum at  $\delta \sim 200$  ppm may be assigned to coordinated  $\text{HNO}_2$  or to the nitrite ion coordinated through its oxygen atom. These signals are observed in the spectra of virtually all solutions.



**Fig. 2.**  $^{15}\text{N}$  NMR spectrum of a 0.3 M ruthenium solution in nitric acid nitrated to  $c_{\text{H}^+} = 1.5$  mol/L (solution III, chemical shifts of the strongest signals are given).

The NMR spectra of solutions with  $c_{\text{H}^+} \geq 0.12$  mol/L (II, III, V, VI) are quite similar. The strongest signals in these spectra correspond to the trans coordinates  $\text{H}_2\text{O}-\text{Ru}-\text{NO}_2$  ( $\sim 60\text{--}65$  ppm in the nitrogen NMR spectra and  $-71$  to  $-72$  ppm on the oxygen NMR spectrum) and  $\text{H}_2\text{O}-\text{Ru}-\text{NO}$  ( $\sim -20$  ppm in the  $^{14}\text{N}$  NMR spectrum and  $\sim 410$  ppm in the  $^{17}\text{O}$  NMR spectrum, the latter coinciding with the much stronger signal of  $\text{NO}_3^-$ ). The spectra of these solution also show a signal of coordinated nitrate ion ( $-9.4$  to  $-10.9$  ppm in the nitrogen NMR spectrum). We assigned NMR signals based on the data in [5–9]. In  $^{17}\text{O}$  NMR spectra, signals are rather broad and are not resolved for the same trans coordinates in different complexes. The  $^{99}\text{Ru}$  NMR spectra of solutions II, III, and V are represented by a rather broad single line at  $3945 \pm 8$  ppm, which was preliminarily assigned to *cis*- $[\text{RuNO}(\text{NO}_2)_2(\text{NO}_3)(\text{H}_2\text{O})_2]^0$  (A). In the  $^{15}\text{N}$  NMR spectra that show sets of narrow lines, this species should give rise to four signals:  $\text{NO}^{\text{coord}}$ ,  $\text{NO}_3^{\text{coord}}$ , and two lines of  $\text{NO}_2^{\text{coord}}$  (*trans* to  $\text{H}_2\text{O}^{\text{coord}}$  and  $\text{NO}_3^{\text{coord}}$ ). Under the isotope equilibrium condition, all these lines should have equal intensities in the same spectrum. For the coordinated nitrite ion, this

condition is met by the  $^{15}\text{N}$  NMR lines at  $(64.1 \pm 0.1)$  and  $(63.5 \pm 0.1)$  ppm. Inasmuch as the trans influence of  $\text{NO}_3^{\text{coord}}$  is somewhat higher than that of  $\text{H}_2\text{O}^{\text{coord}}$ , we assign the former signal to  $\text{NO}_2^{\text{coord}}$  at the trans coordinate  $\text{NO}_3-\text{Ru}-\text{NO}_2$  and the latter signal to  $\text{NO}_2^{\text{coord}}$  at the  $\text{H}_2\text{O}-\text{Ru}-\text{NO}_2$  trans coordinate. The intensity of the signal of coordinated nitrate ion coincides (within 20%) with the intensities of the above lines. The discrepancy is due to both the errors of determination and the lack of nitrogen isotope equilibrium in the ligand. The chemical shift of this line relative to the internal reference is  $(-10.8 \pm 0.1)$  ppm. With respect to the external reference, this chemical shift changes within 1.5 ppm, together with the line of free nitrate ion, whose chemical shift depends on acidity and ionic strength of a solution. An increase in pH leads to partial deprotonation of complex A by reaction (1).

The  $^{15}\text{N}$  NMR spectrum of solution VI shows signals due to coordinated nitroso groups (Fig. 3). Inasmuch as there are two such signals, the solution should contain, in addition to complex A, another nitrosoruthenium complex. Taking into account the moderate stabilities of nitrosoruthenium nitrate complexes (for example, the stability constant of  $[\text{RuNO}(\text{NH}_3)_4(\text{NO}_3)]^{2+}$

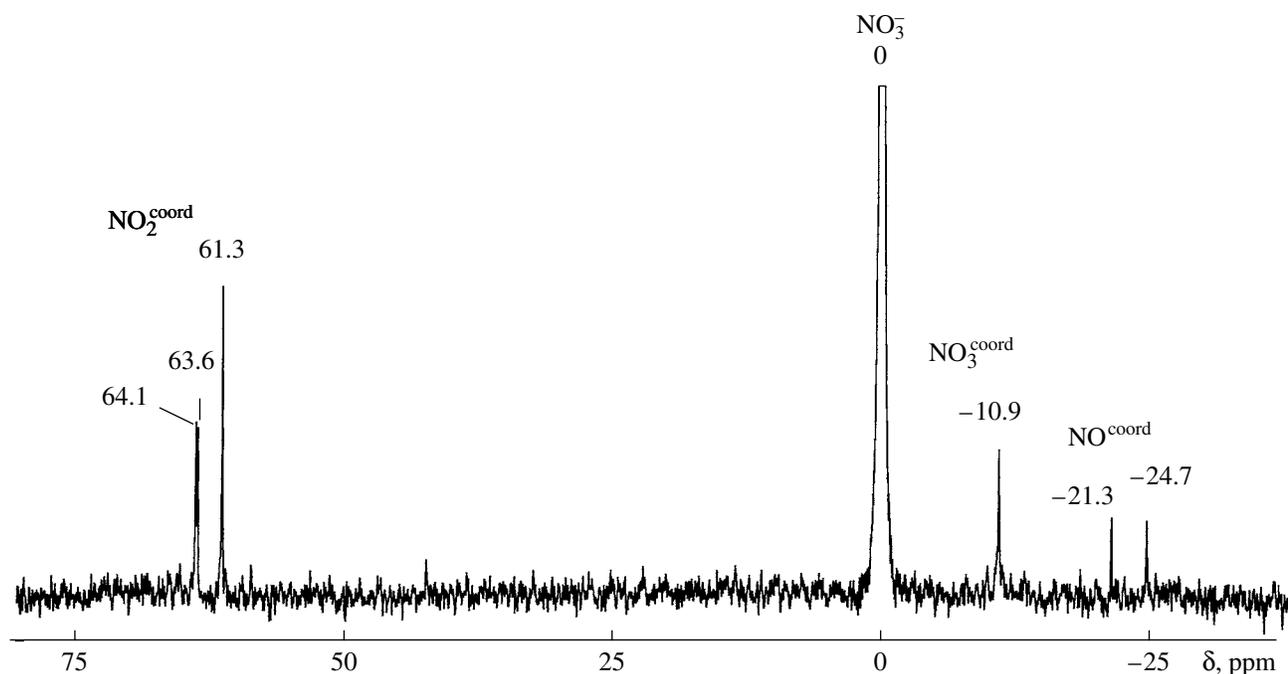


Fig. 3.  $^{15}\text{N}$  NMR spectrum of solution IV kept for 10 months and then nitrated to  $c_{\text{H}^+} = 0.12$  mol/L (solution VI).

with respect to nitrate ion is 3 [25]), we may state that, according to Eq. (2), complex **A** in an aqueous solution is in equilibrium with its aquated form *fac*- $[\text{RuNO}(\text{NO}_2)_2(\text{H}_2\text{O})_3]^+$  (**B**). The coordinated nitro groups in this complex have an identical environment and give rise to one  $^{15}\text{N}$  NMR signal. This signal is also observed in the spectra of solutions II and III, and its position (60.0–61.3 ppm) depends of solution acidity: the signal is shifted downfield with an increase in pH (reaction (3)). The intensity of this line for complex **B** is proportional to twice the concentration of **B** and, therefore, the content of **B** in the solutions under consideration is somewhat lower than the content of complex **A**. The observation of only one signal in the  $^{99}\text{Ru}$  NMR spectrum can be due to the fact that the chemical shifts of **A** and **B** are close to each other and their signals are not resolved. This assumption is indirectly confirmed by a large and variable width of the single line in the  $^{99}\text{Ru}$  NMR spectra of the solutions under consideration.

Despite the fact that the acidity of solution V has an intermediate value, the spectra of this solution differ from the spectra of solutions III and VI: the signals for V are noticeably broader and are shifted downfield. The signals at 64.1 and 63.5 ppm are not resolved; rather, one line at 65.3 ppm is observed. The signal at 60.0–61.3 ppm is also shifted downfield and is observed at 62.9 ppm. Similar changes in spectral characteristics are usually induced by the introduction of paramagnetic particles into a system (for example, NO).

Indeed, keeping solution IV for 25 days at room temperature (solution V was prepared in such a way) should lead to the accumulation of NO in the solution due to disproportionation of nitrous acid:  $3\text{HNO}_2 = \text{HNO}_3 + 2\text{NO} + \text{H}_2\text{O}$ . Heating this sample in the course of preparation of solution VI led to a considerable decrease in the solubility of NO and its removal from the solution. As a result, the positions and widths of lines in the spectra of solution VI are in good agreement with those for solutions II and III.

Thus, the dominating complex species in solutions II–VI are the same: *cis*-diaquanitratodinitro- (**A**) and *fac*-triaquadinitronitrosoruthenium (**B**) complexes. Nitration of solutions from  $c_{\text{H}^+} = 2.7$  to 0.12 mol/L does not lead to a noticeable change in the compositions of these species. It is evident that these solutions also contain some amounts of other ruthenium complexes, which is indicated by the presence of weak signals with chemical shifts typical of coordinated nitro groups and nitrous acid. It cannot be ruled out that these species, as well as the dominating complexes, are oligomers with low nuclearity.

The positions of the major lines in the NMR spectra of solution IV nitrated to  $c_{\text{H}^+} = 0.06$  mol/L radically differ from those described above. Solution IV does not contain ruthenium species with the coordinated nitrate ion and coordinated water molecules on the trans coordinate  $\text{H}_2\text{O}-\text{Ru}-\text{NO}_2$ . The  $^{15}\text{N}$  NMR spectrum of this solution is shown in Fig. 4. It displays the signals of coordinated nitro groups in the range of

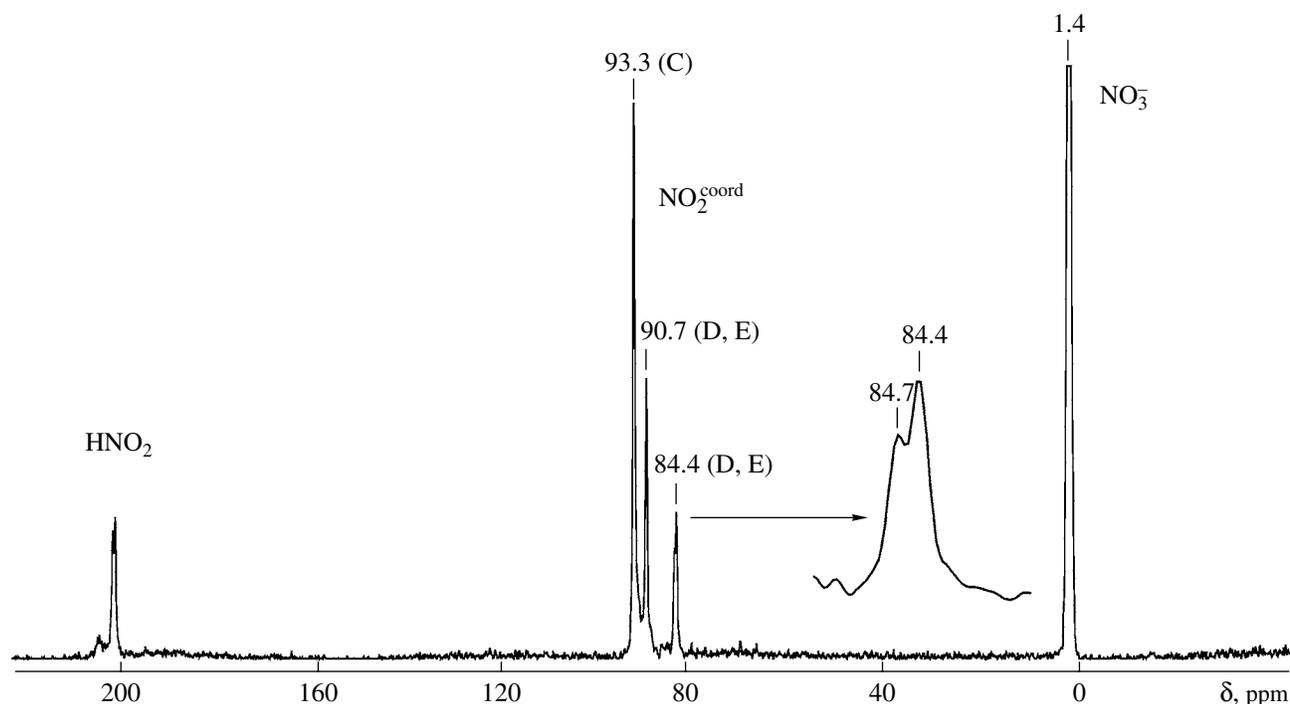
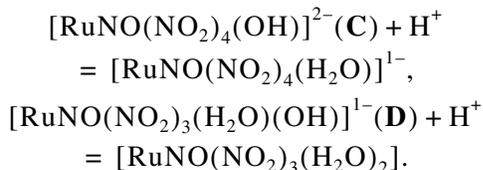
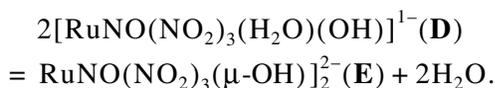


Fig. 4.  $^{15}\text{N}$  NMR spectrum of 0.3 M ruthenium solution in nitric acid nitrated to  $c_{\text{H}^+} = 0.06$  mol/L (solution IV).

chemical shifts typical of  $\text{HO-Ru-NO}_2$  (84.4 and 84.7 ppm) and  $\text{O}_2\text{N-Ru-NO}_2$  (90.7 and 93.3 ppm) [6, 7]; the signal of the coordinated nitrate ion is absent. The  $^{14}\text{N}$  NMR spectrum of solution IV shows two signals of coordinated nitroso groups (–16 and –31 ppm). The  $^{17}\text{O}$  NMR spectrum shows two signals of  $\text{OH}^{\text{coord}}$  (98 and 33 ppm). The  $^{99}\text{Ru}$  NMR spectrum shows two lines of ruthenium complexes (3580 and 3425 ppm). Taking into account a higher degree of nitration in this solution, we can state that the predominant ruthenium species in it are tetranitro- (C) and trinitronitrosoruthenium (D) complexes in an approximately 1 : 1 ratio. The other coordinates in these complexes are occupied by hydroxide ions partially protonated according to the equilibria



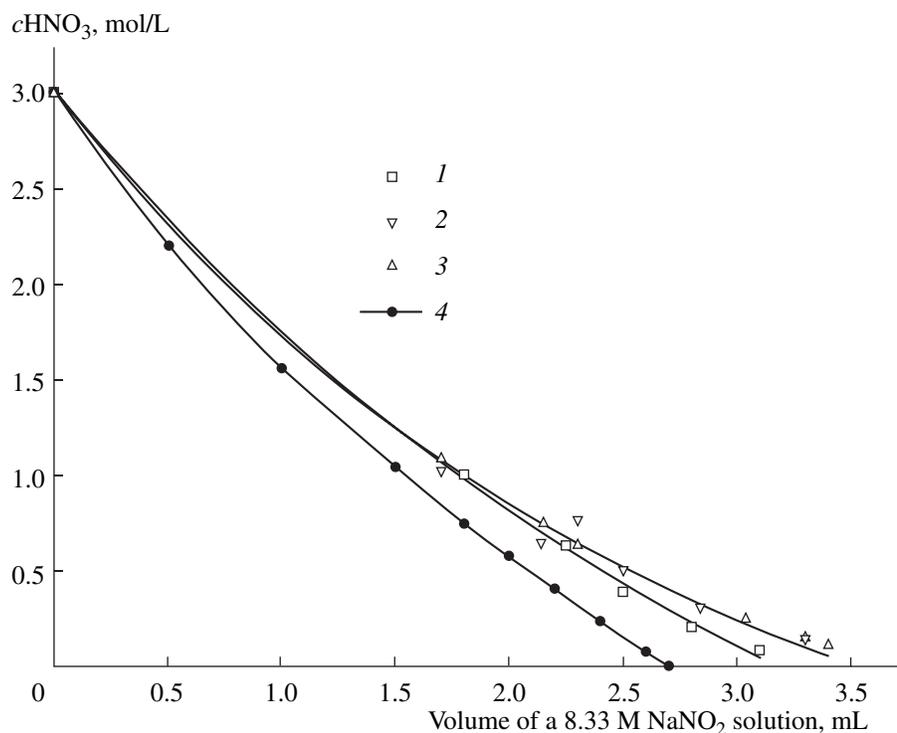
Due to these dynamic equilibria, the signals of these complexes are somewhat broadened and shifted upfield with respect to the signals for alkaline and neutral solutions [6, 7]. The most broadened line is the  $^{99}\text{Ru}$  NMR signal of the trinitronitrosoruthenium complex, which can exist as monomer (D) and as dimer (E):



The molecular and crystal structure of the potassium salt of this dimer was studied in [26]. The above equilibrium requires elimination (or addition) of the coordination water molecule and is achieved noticeably more slowly than in the protonation–deprotonation processes. As a result, the  $^{15}\text{N}$  NMR spectrum shows two closely spaced signals corresponding to the  $\text{HO-Ru-NO}_2$  coordinate. One of these signals should be assigned to the monomer (D) and the other to the dimer (E) of the trinitronitrosoruthenium complex. The environments of the coordinated *trans* nitro groups in complexes D and E are virtually the same; therefore, these groups give rise to one signal for the  $\text{O}_2\text{N-Ru-NO}_2$  coordinate (90.7 ppm), with the intensity being twice as large as the overall intensity of the signals at 84.4 and 84.7 ppm. The line at 93.3 ppm in the  $^{15}\text{N}$  NMR spectrum, which we assign to the tetranitro complex C, is 1 ppm shifted upfield from the values reported in [6, 7] due to protonation.

When solution IV was kept for 25 days at room temperature, it was noticeably acidified, which led to radical differences in the compositions of predominant complexes (the return to the dinitro complexes stable in an acid medium). This can be explained by the transformation of the free and coordinated nitrous acid to considerably stronger nitric acid due to oxidation with air and disproportionation.

Upon nitration of nitric acid solutions, we found that the residual acidity of solutions, as a rule, exceeds the acidity calculated assuming that the nitrite is con-



**Fig. 5.** Residual concentration of nitric acid ( $V_0 = 5$  mL) vs. the volume of the added 8.33 M sodium nitrite solution (treatment time, 30–40 min at 80°C). (1)  $\text{HNO}_3 + \text{NaNO}_2$ , (2)  $\text{HNO}_3 + \text{NaNO}_2 + \text{Ru}$ , (3)  $\text{HNO}_3 + \text{NaNO}_2 + \text{Ru} + \text{Zn}(\text{NO}_3)_2$ , and (4) calculated data points.

sumed only by equation  $2\text{HNO}_3 + 3\text{NaNO}_2 = 3\text{NaNO}_3 + 2\text{NO} \uparrow + \text{H}_2\text{O}$ . To elucidate the influence of ruthenium complexes on the residual acidity, we carried out a series of nitrations of nitric acid solution in the presence of ruthenium and without ruthenium. The plots of the residual acid concentration versus the volume of the added 8.33 M sodium nitrite solution are shown in Fig. 5.

The figure also shows the calculated residual acidities for comparison. As can be seen, the actual consumption of sodium nitrite is noticeably larger than the calculated one even in the blank experiments, which is associated with partial return of nitrogen oxides in the system after oxidation by air oxygen:  $4\text{NO} + 3\text{O}_2 + 2\text{H}_2\text{O} = 4\text{HNO}_3$  (total).

In the presence of ruthenium ( $1.2 \times 10^{-2}$  mol/L), the slope of the curve in the range of low residual concentrations of the acid is even gentler: the residual acidity is higher than in the blank solutions. This can be due to the catalytic activity of ruthenium complexes for oxidation of nitrite to nitrate in an acid medium. Inasmuch as the deviation from the blank runs is especially pronounced in the range of low acidity, nitrite complexes containing more than two nitro groups seem to be the catalysts. A similar effect, especially pronounced for heterometallic ruthenium–copper nitro complexes, was previously observed in [8]. The most stable heterometallic complexes are formed by ruthenium nitroso compounds and zinc [27–29]. To verify their catalytic activ-

ity in oxidation of nitrite to nitrate in an acid medium, we added zinc to some of the runs. The presence of zinc ions in the solution has no noticeable effect on the residual acidity (Fig. 5).

Thus, in nitrite–nitrate nitric acid solutions with the acidity 2.7–0.12 mol/L, the predominant ruthenium species are  $[\text{RuNO}(\text{NO}_2)_2(\text{NO}_3)(\text{H}_2\text{O})_2]^0$  and  $[\text{RuNO}(\text{NO}_2)_2(\text{H}_2\text{O})_3]^+$ . When solutions are nitrated up to  $c_{\text{H}^+} = 0.06$  mol/L, trinitro- and tetranitronitrosoruthenium(II) complexes become predominant. These complexes act as catalysts in oxidation with air of nitrite to nitrate.

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