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The Cation-exchange Separation of Nitrosylruthenium(III) from Ruthenium(III and IV) and Its Radiochemical Applications

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The cation-exchange separation was made on a 0.1 M perchloric acid solution of the evaporated residue of a hydrochloric acid solution which contained nitrosylruthenium(III) of 10 mg—100 μg Ru and ruthenium(III and IV) of 100—10 μg Ru; the nitrosylruthenium species were eluted by the use of 80—90 m*l* of 0.1 M perchloric acid, and the ruthenium species, by the use of 100 m*l* of 3 M hydrochloric acid containing 50 vol% ethyl alcohol for the columns (3—8 m*l*) of the HR type. It was found by means of the separation that a ^{106}Ru-nitrosylruthenium tracer can be quantitatively prepared by passing nitric oxide into a hydrochloric acid solution of ^{106}Ru-ruthenium(III and IV). The separation on dipotassium pentachloronitrosylruthenate(III) irradiated by thermal neutrons indicated that the specific activities caused by ^{103}Ru in the ruthenium fractions are a few hundred times as high as those in the nitrosylruthenium fractions.

In acid aqueous solutions, both ruthenium(III and IV) and nitrosylruthenium(III) species are present as stable species. However, the chemical behavior of nitrosylruthenium(III) is different from that of ruthenium(III) and (IV). The separation of the nitrosylruthenium(III) species from the ruthenium(III or IV) species is necessary in order to study the chemistry of ruthenium. Kepak and Kanka have reported that an efficient separation was achieved by adsorption on iron(II) hydroxide.[1] We attempted to separate small amounts of ruthenium(III and IV) and nitrosylruthenium(III) species in hydrochloric acid solutions by the use of the cation-exchange technique.

The separation can be carried out on a perchloric acid solution of the evaporated residue of a hydrochloric acid solution of 10 mg—100 μg nitrosylruthenium(III) and 100—10 μg ruthenium(III and IV). This paper will also report on such applications of the separation to the radiochemistry of ruthenium as preparing the labeled nitrosylruthenium(III) species and the separation of ^{103}Ru with high specific activities from dipotassium penta-

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[1] *Chem. Abstr.*, **67**, 95533w (1967); F. Kepak and J. Kanka, *Int. J. Appl. Radiat. Isotopes*, **18**, 673 (1967).

chloronitrosylruthenate(III) irradiated by thermal neutrons.

Experimental

Ru(III and IV)[*1] in a hydrochloric acid solution was prepared by distilling ruthenium tetroxide into an alcoholic hydrochloric acid solution, evaporating the distillate, and dissolving the evaporated residue with a hydrochloric acid solution, or by dissolving the commercial $RuCl_3 \cdot 3H_2O$ with a hydrochloric acid solution. Ru(III)NO in a hydrochloric acid solution was prepared by bringing nitric oxide into contact with Ru(III and IV) in a hydrochloric acid solution.[2]

The sample solutions for the cation-exchange separation were prepared by evaporating hydrochloric acid solutions of Ru(III and IV) or/and Ru(III)NO, dissolving the evaporated residue in 10 m*l* of a 0.1 M perchloric acid solution, and allowing the solution to digest for thirty minutes in a boiling-water bath.

Dipotassium pentachloronitrosylruthenate(III) was prepared by adding an excess of potassium chloride in a hydrochloric acid solution of Ru(III)NO and was recrystallized from a 0.1 M hydrochloric acid solution.[3]

The ^{106}Ru was purchased from the Radiochemical Centre, Amersham, England, and was purified by the distillation of the tetroxide. The radiochemical purity of the ^{106}Ru was examined by means of its γ-ray spectrum; no impurity was found with respect to γ-emitters. The tracer solutions of the ^{106}Ru were prepared by the same procedures as the solutions containing the ordinary amount of Ru(III and IV) or Ru(III)NO.

The cation exchanger used was Dowex 50, X-4, with a hydrogen-ion form. The chromatographic procedures were carried out with columns 1 cm in diameter and 3—8 m*l* in volume at the flow rate of 1 m*l*/min.

The ruthenium was determined spectrophotometrically by the phenanthroline method[4] and the thiourea method.[4] The latter could not, however, be applied to the samples containing Ru(III)NO species. The radioactivities of ^{106}Ru or ^{103}Ru in solutions were measured as gross γ-activities with a well-type NaI(Tl) scintillator.

Results and Discussion

Sorption of Ruthenium and Nitrosylruthenium Species in Perchloric Acid Solutions on Cation-exchange Resins. The study of the species of ruthenium(IV) in perchloric acid solutions has indicated that the average charge on the aqueous species is +2, and extensive polymerization was observed in these solutions.[5] In the perchloric acid solution of the ruthenium(III and IV) chloride[*2] prepared as has been described above, almost all the ruthenium species were found by iodometric titration to be in the Ru(IV) state and were expected to be cationic from their strong sorption on the cation exchanger. The species in the solution of the nitrosylruthenium(III) chloride[*2] will be discussed later.

The distribution coefficients (K_d) of ruthenium and nitrosylruthenium species between the cation exchanger and perchloric acid-hydrochloric acid solutions were determined with ^{106}Ru tracers of the ruthenium and nitrosylruthenium species. A part of the perchloric acid in the solutions was replaced by hydrochloric acid in order to observe the effect of chloride ions on the distribution coefficients. As will later be decribed in more detail, we found a certain abnormal behavior of the radioactive tracer of the ruthenium species on the cation exchanger, and the values of the distribution coefficients obtained were not considered to give a strict measure of the sorption of ruthenium species on the cation exchanger. The values of K_d for the ruthenium species were great over the range of chloride concentration less than 0.04 M at the 0.15 M hydrogen-ion concentration (log K_d:

Table 1. Separation of the Ru(III and IV) and the Ru(III)NO chlorides

Ru added (mg)		Ru found (mg)	
Ru(III)-NO	Ru-(III and IV)	RuNO-fraction	Ru-fraction
10.9	10.0	10.7 (90)*	6.94 (100)*
10.9	1.00	10.9 (80)	0.642 (270)
10.9	0.400	10.6 (80)	0.362 (100)
10.9	0.200	11.0 (80)	0.176 (30)
0.100	0.104	0.098(90)	0.104 (30)
0.109	0.100	0.109(80)	0.097 (—)
10.9	0.100	10.5 (80)	0.098 (30)
0.130	0.100	0.130(80)	0.094 (30)
2.61	0.100	—	0.098 (30)
10.9	0.050	11.0 (80)	0.053 (20)
10.9	0.025	10.7 (80)	0.026 (20)
10.9	0.010	10.7 (80)	0.011 (20)

* Volume (m*l*) required for the elution.

[*1] The Ru(IV) was estimated by iodometric titration to be 20—40%.

2) J. M. Fletcher, I. L. Jenkins, F. M. Lever, F. S. Martin, A. R. Powell and R. Todd, *J. Inorg. Nucl. Chem.*, **1**, 378 (1955).

3) "Gmelins Handbuch der Anorganischen Chemie," Ruthenium (1938), S. 93.

4) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd Ed., Interscience Publishers, New York (1959), p. 784, 781.

5) F. P. Gortsema and Cobble, *J. Amer. Chem. Soc.*, **83**, 4317 (1961).

[*2] In this paper, the ruthenium(III and IV) and the nitrosylruthenium(III) chlorides are the evaporated residues of a hydrochloric acid solution of Ru(III and IV) and of Ru(III)NO respectively. The ruthenium chloride has been thought to be $Ru(OH)Cl_3$ (N. V. Sidgwick, "Chemical Elements and Their Compounds," Vol. II, Oxford, (1950), p. 1476). The nitrosylruthenium(III) chloride is considered to be $H_2[RuCl_4OHNO] \cdot 2H_2O$ and $RuCl_3NO \cdot nH_2O$.[3]

Table 2. Behavior of ^{106}Ru-tracer in the separation

Sample	Found in RuNO-fraction			Found in Ru-fraction		
	Activity %	μg	vol (ml)	Activity %	μg	vol (ml)
*Ru[1]	38.2	—	150	61.0	—	200
*Ru, Ru 100 μg[2]	10.8	0	90	89.0	97	100
*Ru, Ru 100 μg[3]	10.2	0	90	89.5	99	100
*Ru, Ru 100 μg, RuNO 100 μg[4]	11.3	91	80	88.4	103	90
**Ru (4 μg)	3.4	—	90	94.6	—	120
**Ru (4 μg), Ru 100 μg[4]	0.3	0	90	98.9	103	30
**Ru (4 μg), Ru 100 μg, RuNO 100 μg[4]	0.9	98	90	98.2	104	20
Ru 100 μg, radioactive RuNO (120 μg)	98.4	130	90	1.6	94	30

*Ru: The ^{106}Ru-tracer stored in 0.2M HCl.

**Ru: The ^{106}Ru-tracer eluted in the ruthenium fraction with a carrier in the separation. This was stored in 3M HCl and used within several days after the preparation.

1) To *Ru solution, an equal volume of 6M HCl was added and then the solution was evaporated.

2) The *Ru was digested as 3M HCl solution and evaporated. Then, the carrier was added and the mixture was evaporated.

3) The *Ru and the carrier were mixed and the mixture was digested as 6M HCl solution after addition of Br_2(aq) and evaporated.

4) The mixture was evaporated.

about 3.0 for $[Ru_{aq}]$ = the order of 7×10^{-8}M) and decreased upon the addition of hydrochloric acid to the solution phase ($\log K_d$: 2.9 for $[Cl^-]=0.16$, $[H^+]=0.31$; 1.8 for $[Cl^-]=0.5$, $[H^+]=0.65$, $[Ru_{aq}]=7\times10^{-8}$M). The K_d values for the nitrosylruthenium species were less than 10(ml/g) over the chloride-concentration range of 10^{-3} to 0.1M and the hydrogen-ion concentration range of 0.02 to 0.4M.

Mutual Separation of the Ruthenium(III and IV) and the Nitrosylruthenium(III) Chlorides by Cation-exchange Technique. The separation method was examined using sample solutions of the 0.1M perchloric acid solution of the ruthenium or/and the nitrosylruthenium chlorides and a cation-exchanger column 1 cm in diameter and 8 ml in volume. For ruthenium species less than 100 μg Ru and nitrosylruthenium species less than 10 mg Ru, the separation was satisfactorily done by the following procedure: the sample solution (10 ml) was passed through the column, and then 80—90 ml of 0.1M perchloric acid was passed to elute the nitrosylruthenium species. The ruthenium species absorbed were eluted by 100 ml of 3M hydrochloric acid containing 50 vol% ethyl alcohol. The results of the separation are given in Table 1. The use of a perchloric acid solution in the cation-exchange separation of this type has been reported on the separation of platinum from palladium, rhodium, and iridium.[6]

The recoveries of ruthenium and nitrosylruthenium species were often less than 100%; the average deviation(%) on the recovery was −2.3% for 11 samples of ruthenium species containing 100 μg of Ru and −1.4% for 11 samples of nitrosylruthenium species containing 10.9 mg Ru. When ruthenium species more than 100 μg Ru were present in the sample solutions, the ruthenium species were not eluted quantitatively with an ethanolic hydrochloric acid solution. Incomplete recoveries in the ion-exchange separations have also been described in connection with the separation of platinum metal species.[7] The nitrosylruthenium species eluted were thought to be anionic, neutral, and univalent cationic chloro complexes; the anionic and neutral species were eluted, and then the univalent cationic complex was eluted as a single band. This cationic species was identified as $[RuCl_2(H_2O)_3NO]^{1+}$ by comparing the visible spectrum of its solution with the data provided by Mercer and Campbell.[8] The bivalent and tervalent cationic species of nitrosylruthenium were not present in the perchloric acid solution of the nitrosylruthenium chloride.

It was observed that the behavior of the radioactive ruthenium species was in part different from that of the carrier of ruthenium species in the cation-exchange separation (Table 2). The separations were carried out using columns 1 cm in diameter and 3 ml in volume. The ^{106}Ru-tracer of ruthenium (III and IV) had been stored in 0.2M hydrochloric acid, and its concentration was estimated to be 10^{-7}M. About 40% of the activity was eluted with 0.1M perchloric acid in the nitrosylruthenium fraction. Similar phenomena were observed even when 100 μg ruthenium species was added to the radioactive ruthenium species as a carrier and the mixture was evaporated after the addition of hydrochloric acid. When the radioactive species and the

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[6] P. Stevenson, A. Frank, R. Berg and W. Nervik, *J. Amer. Chem. Soc.*, **75**, 4876 (1953).

[7] O. Samuelson, "Ion-exchange Separations in Analytical Chemistry," John Wiley & Sons, New York (1963), p. 399.

[8] E. E. Mercer, W. A. Campbell, Jr., and R. M. Wallace, *Inorg. Chem.*, **3**, 1018 (1964).

carrier eluted in the ruthenium fraction were treated again by the same separation procedure, almost all the activities were found in the ruthenium fraction.

There have been studies[9-12] of a variety of ruthenium(III) and (IV) species in hydrochloric acid solutions, and the equilibria among the species have been considered to be complicated. It can be suggested that part of the radioactive tracers of ruthenium species may form neutral and/or anionic species, or polymers, and that they can not be converted to the species of the carrier even by evaporating them with the carrier in a hydrochloric acid solution.

The data in Table 2 indicate that no appreciable exchange of ruthenium atoms between ruthenium and nitrosylruthenium species occurred under the experimental conditions used.

Preparation of the Radioactive Nitrosylruthenium Tracer. It has been reported that the nitrosylruthenium tracer can be prepared in a good yield by treating the evaporated residue of a hydrochloric acid solution of ^{106}Ru with fuming nitric acid.[13] Nitrosylruthenium(III) in ordinary amounts has been prepared by passing nitric oxide into a dilute hydrochloric acid solution of ruthenium(III and IV).[2] We determined the yield when the nitrosylruthenium tracer was prepared with fuming nitric acid or with nitric oxide. The method of preparing with fuming nitric acid was as follows; 1 m*l* of a dilute hydrochloric acid solution of ^{106}Ru was evaporated to dryness, and then a few drops of fuming nitric acid were added and the mixture was evaporated on a boiling-water bath. The evaporation with fuming nitric acid was then repeated. The residue was dissolved in 1 m*l* of concentrated hydrochloric acid and evaporated; a 0.1 M hydrochloric acid solution of radioactive nitrosylruthenium(III) was thus prepared. The method of preparing with nitric oxide was as follows; nitric oxide was passed into a dilute hydrochloric acid solution of the ^{106}Ru tracer for about twenty hours; the solution was then evaporated and again evaporated after the addition of hydrochloric acid. A 0.1 M hydrochloric acid solution of radioactive nitrosylruthenium(III) was thus prepared.

The carriers of ruthenium(III and IV) and nitrosylruthenium(III), each containing 100 μg Ru, were added to the radioactive nitrosylruthenium(III), and a cation-exchange separation was carried out on the mixture in order to determine the yield in the preparation of radioactive nitrosylruthenium(III). The results are shown in Table 3. It was found that the radioactive nitrosylruthenium tracer was prepared in a much better yield with nitric oxide than with fuming nitric acid. It was also observed that a part of the activity escaped in air in the preparation with fuming nitric acid if the reaction mixture was heated at a considerable temperature by means of a boiling-water bath or an infrared lamp.

TABLE 3. EXAMINATION OF THE YIELD IN THE PREPARATION OF RADIOACTIVE NITROSYLRUTHENIUM TRACER

Method	Activity found in RuNO-fraction %	Activity found in Ru-fraction %
Fuming nitric acid	64.6	32.9
	67.4	32.0
	60.9	36.6
	63.8	35.6
Nitric oxide	98.8	1.0
	98.1	1.6
	98.7	1.1
	97.9	1.8

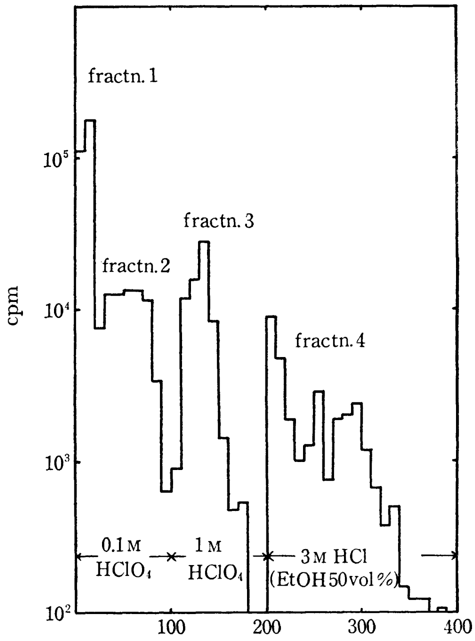

Fig. 1. The cation-exchange separation of the irradiated $K_2[RuCl_5NO]$.
Activities(%), Ru(mg) and specific activities (cpm/mg Ru) found in fractions 1, 2, 3 and 4 were: 58.0, 2.16, 1.06×10^5; 19.4, 0.386, 2.56×10^5; 15.2, 0.001,* 6.02×10^7; and 7.4, 0.001,* 2.89×10^7; respectively. *: less than the detection limit.

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[9] H. H. Cady and R. E. Connick, *J. Amer. Chem. Soc.*, **79**, 4242 (1957); **80**, 2646 (1958).

[10] R. E. Connick, "Advances in the Chemistry of the Coordination Compounds," ed. by S. Kirschner, MacMillan, New York (1961), p. 17.

[11] S. K. Shukla, *J. Chromatogr.*, **8**, 96 (1962).

[12] A. Ohyoshi, E. Ohyoshi, M. Senoo and M. Shinagawa, *J. Nucl. Sci. Technol.*, **3**, 237 (1966).

[13] J. Griess, *J. Electrochem. Soc.*, **100**, 429 (1953); M. H. Lietzke and J. Griess, *ibid.*, **100**, 434 (1953).

The Separation on Dipotassium Pentachloronitrosylruthenate(III) Irradiated by Thermal Neutrons. Dipotassium pentachloronitrosylruthenate(III) was irradiated by thermal neutrons to prepare a ^{103}Ru-tracer with a high specific activity by the use of the hot-atom reactions. The irradiation was carried out on a rotatory specimen rack (about $3.5 \times 10^{11} n_{th}$ cm^{-2} sec^{-1}) in a nuclear reactor of the TRIGA MARK II type at Rikkyo University.

In a typical example, $K_2[RuCl_5NO]$ (10 mg) was irradiated for 15 hr over 4 days and then cooled at room temperature for several days. The irradiated sample was thereafter dissolved in an ethanolic hydrochloric acid solution and evaporated. The residue was dissolved in a 0.1M perchloric acid solution to prepare the solution for the cation-exchange separation. The separation was carried out with a column 1 cm in diameter and 3 m*l* in volume. The results of the separation are shown in Fig. 1. The γ-activities could be measured excluding the β-activity of ^{35}S produced by ^{35}Cl(n, p)^{35}S. The γ-activities caused by ^{97}Ru and ^{105}Ru, the daughter of ^{105}Ru, were estimated to be very small parts of the total γ-activity. A small contribution by ^{42}K was possible in the activity of fraction 1 in Fig. 1. The γ-activities of fractions 1, 2, 3 and 4 were identified as those of ^{103}Ru by measuring their γ-spectra and their half-lives. The specific activities (cpm/mg Ru) of the ruthenium fractions (fractions 3 and 4) were a few hundred times as large as those of the nitrosylruthenium fractions (fractions 1 and 2). The activity in the ruthenium fraction was 23% of the total activity. The separation included elution with 1M perchloric acid (fraction 3 in Fig. 1); the species eluted was a ruthenium species with a high specific activity.

It was shown that the cation-exchange separation is useful in the preparation from the irradiated nitrosylruthenium complex of a ^{103}Ru-tracer with a high specific activity.

We have prepared ^{15}*N*-nitrosylruthenium(III) complexes in a semimicro scale.[14,15] The separation method has then been usefully used to examine the formation of nitrosylruthenium(III) by the use of limited amounts of nitric oxide.

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[14] E. Miki, T. Ishimori, H. Yamatera and H. Okuno, *Nippon Kagaku Zasshi*, **87**, 703 (1966).

[15] E. Miki, This Bulletin, **41**, 1835 (1968).