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Author(s)	Komura, Kazuhisa; Mitsugashira, Toshiaki; Mito Asae; Otozai, Kiyoteru
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Target Chemistry of Ruthenium

Kazuhisa KOMURA*, Toshiaki MITSUGASHIRA**,
Asae MITO* and Kiyoteru OTOZAI*

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The target chemistry of ruthenium concerning the measurement of the Ru(d, p) reaction cross sections was discussed. The uniform and firm metallic ruthenium was obtained by the electrodeposition from RuNOCl₃ solution. The bombarded target was dissolved in NaOH-Cl₂ solution. The solvent extraction by CCl₄ was successfully applied to separate ruthenium from rhodium and technetium. The back-extraction of ruthenium from the CCl₄ solution was carried out by 2*N*-NH₄OH. Ruthenium was precipitated as sulfide, and used for counting source. It was found that the losses of ruthenium occurred in the procedures of the synthesis of RuNOCl₃, the electrodeposition of ruthenium, the dissolution of the target, and the preservation of the CCl₄ solution of ruthenium. Several devices were suggested to suppress the loss of ruthenium within the error of the cross section measured.

I. INTRODUCTION

Previously, the authors measured radiochemically the excitation functions for the (d, p) reactions on ⁹⁶Ru, ¹⁰²Ru and ¹⁰⁴Ru, and explained the results successfully by using a simple semiclassical theory.¹⁾ As ruthenium is one of the elements whose chemical properties are poorly known, it is significant to report the chemical knowledges which were obtained in the course of treating the ruthenium target.

II. TARGET PREPARATION

II-1 Synthesis of Ruthenium Nitrochloride

For the cross section measurement it is important to prepare an uniform and firm target with the definite thickness and the known chemical form. The metallic ruthenium was successfully electrodeposited on the copper foil from dilute sulfuric acid media containing ruthenium nitrochloride RuNOCl₃.

The ruthenium nitrochloride was synthesized as follows.²⁾ One gram of JIS guaranteed RuCl₃·H₂O (Ru > 99.9%) was taken in a 100 ml beaker and dissolved in 20 ml of distilled water by heating under an infrared lamp. After drying up the solution, the residue was dissolved in 10 ml of conc. HCl, and then the N₂O₄ gas, which was generated from fuming HNO₃, was blown into the solution cooled on ice. The color of the solution changed gradually from deep brown

* 小村 和久, 三藤 安佐江, 音在 清輝: Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka, Japan.

** 三頭 聰明: The Research Institute for Iron, Steel and Other Metals, Tohoku University, Sendai, Japan.

(RuCl_3) to deep wine red (RuNOCl_3). After passing the N_2O_4 gas for 10 minutes, the gas blowing was once stopped and the solution was left alone for a while. This procedure was repeated three times for the completion of the synthetic reaction between RuCl_3 and N_2O_4 gas. Excessive N_2O_4 and HCl were evaporated under an infrared lamp, and the ruthenium nitrocylchloride thus prepared was dissolved in 150 ml of distilled water. Some part of ruthenium also vaporized as volatile tetroxide RuO_4 , but the loss of ruthenium was not so large due to the existence of HCl .

II-2 Electrodeposition of Ruthenium

The electrolytic solution was prepared just before the electrodeposition by mixing 15 ml of 2N- H_2SO_4 and 35 ml of RuNOCl_3 solution containing 80~100 mg of ruthenium.³⁾ The solution was transferred into the electrolytic glass cell with a platinum anode and a copper cathode of 10 μm thick. Ruthenium was deposited on the copper cathode having 20 cm^2 of effective area at constant current of 0.5~0.6 A. The greater part of ruthenium was deposited within first two hours and the solution changed to faint green in color. About 0.5~1 hour was still more required to deposit ruthenium completely. When the solution became colorless, it was sucked out by a syringe without cutting off the electric current, and the cathode was carefully taken apart from the cell. The metallic ruthenium on the copper foil was washed sufficiently with the distilled water, and dried.

The ruthenium electrodeposited on the copper foil had a smooth silvery surface and the thickness of 3~4 mg/cm^2 . It was failed to prepare the self-supported ruthenium target by dissolving the copper backing with conc. HNO_3 .

The blackening of the electrolytic cell, the stirring rod *etc.* indicated that a significant amount of ruthenium was anodically oxidized to Ru(VIII) state to form the volatile RuO_4 , and then deposited on the surface of the glass ware in a lower oxidation state such as RuO_2 .

The overall chemical yield of ruthenium through these procedures was only 30~40% because of the losses of ruthenium during the concentration and the electrodeposition of the RuNOCl_3 solution.

II-3 Deuteron Bombardment

The ruthenium target thus prepared was bombarded for 20 minutes by 0.5 μA deuteron beams from the cyclotrons of Osaka University ($E_d=11.2$ and 12.0 MeV) and of Kyoto University ($E_d=14.6$ MeV). When the current of deuteron beam exceeded 1 μA , the ruthenium happened to fall off from the copper backing.

III. PREPARATION OF COUNTING SOURCE

III-1 Dissolution of Ruthenium Target

Putting the irradiated target in a glass filter (No. 3) with a cock, the copper backing was dissolved in 5 ml of conc. HNO_3 , and the resultant copper solution containing the copper and zinc activities was discarded, whereas the metallic ruthenium remained on the glass filter. About 30 ml of boiling water was poured into the glass filter for washing and heating of the ruthenium and the glass

filter. Then, ruthenium was dissolved in 5 ml of hot 6*N*-NaOH solution containing sufficient amount of Cl₂, stirring with a glass rod. This procedure was repeated three times. The metallic ruthenium was completely dissolved within 5 minutes. The ruthenium solution obtained was transferred into a 100 ml beaker.

It must be cared that the Cl₂ content in NaOH solution affects the dissolving rate of ruthenium seriously. Namely, the dissolving rate was very slow in both cases that the amount of Cl₂ was deficient and excessive. Furthermore, in the case of excessive Cl₂, the excess oxidation to Ru(VIII) caused the great loss of ruthenium. It was found that the most effective NaOH-Cl₂ solution could be prepared as follows. When the NaOH solution showed the color in golden yellow and small bubbles happened to arise by stirring the solution with a glass rod, the Cl₂ gas blowing was stopped and 10 ml of fresh 6*N*-NaOH was added to each 100 ml of NaOH-Cl₂ solution. The alkaline solution thus prepared dissolved the metallic ruthenium most swiftly without the noticeable loss.

III-2 Solvent Extraction of Ruthenium by Carbontetrachloride

In order to measure radiochemically the (d, p) reaction cross sections of ruthenium, it was necessary to isolate pure ruthenium from rhodium and technetium activities produced in the ruthenium target by the reactions (d, xn) and (d, α), respectively. The solvent extraction by CCl₄³⁾ was used to separate ruthenium from many interfering rhodium and technetium activities.

The ruthenium existed in the alkaline NaOH-Cl₂ solution, mentioned above, as sodium ruthenate Na₂RuO₄ and sodium perruthenate NaRuO₄, which were inextractable in CCl₄. The alkaline solution was acidified by an addition of 2*N*-H₂SO₄ to convert the ruthenium to extractable RuO₄, and transferred into a 200 ml separating funnel. After an addition of 10 mg rhodium carrier, the ruthenium solution was shaken vigorously with 30 ml of CCl₄ for one minute. Ruthenium was extracted in the organic phase, while rhodium and technetium remained in the aqueous phase. As the distribution of ruthenium between organic and aqueous phases was only about 30 in this condition, the extraction was repeated three times to collect the ruthenium quantitatively. The organic phase containing ruthenium was transferred to another separating funnel, washed with 10 ml of distilled water twice, and preserved in a 100 ml Erlenmyer flask. The ruthenium distributed to the washing solution was recovered by shaking with 10 ml of CCl₄, and added to the original CCl₄ solution. The ruthenium fraction thus purified contained no detectable impurities of rhodium and technetium isotopes.

When it was necessary to preserve the ruthenium fraction for one day more, the fraction was covered with 10 ml of distilled water in an Erlenmyer flask wrapped tightly with thin polyethylene sheet, and kept at 0°C to suppress the volatilization of ruthenium.

III-3 Precipitation of Ruthenium Sulfide

The ruthenium in CCl₄ was back-extracted into the aqueous phase by shaking with 20 ml of 2*N*-NH₄OH three times, and transferred into a 100 ml beaker. Because ruthenium forms a stable ammonia complex with NH₄OH, the ammo-

niacal solution was concentrated to 20 ml on a hot plate, and the ruthenium was precipitated as sulfide by passing H_2S gas into the solution. It was found that the addition of 2~3 mg of rhodium improved the coagulation of ruthenium sulfide and made possible to recover ruthenium quantitatively. The precipitate was collected on a filter paper (No. 5C, Toyo Roshi Co.) using a chimney of 25 mm inner diameter, and used as the counting source.

The chemical yield of the ruthenium in each step after the dissolution of the target was examined by using radioactive tracer. It was ascertained that the loss of ruthenium was satisfactorily small compared with the accuracy of the cross section measurement.

IV. CONCLUSION

In the target chemistry of ruthenium it is of importance to diminish the volatilization of ruthenium as small as possible. This was attained by (1) controlling the quantity of Cl_2 gas blown into NaOH solution, (2) preserving the CCl_4 solution of ruthenium covered with distilled water at $0^\circ C$, and (3) using the coprecipitation with rhodium carrier.

The solvent extraction of ruthenium by CCl_4 was successfully applied from the view points of shortening the time required for the isolation of ruthenium, and determining accurately the time of the separation of ruthenium from rhodium. The latter was particularly important in order to estimate the amount of the short-lived ^{97}Rh ($T_{1/2}=32$ min), which decays into ^{97}Ru , the product of ^{96}Ru (d, p) reaction.

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