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May 1973
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REPORT OF SECOND RUTHENIUM CONFERENCE
ARGONNE NATIONAL LABORATORY
DECEMBER 13 - 14, 1948

This document consists of
Pages No.

COPY 1 OF 1,

SPECIAL RE-REVIEW
FINAL DETERMINATION
DECLASSIFICATION CONFIRMED
BY J. Miles DATE 5-8-81
BY AE Barber DATE 5-13-81

The purpose of the conference was the discussion of recent advances in ruthenium chemistry by representatives of all the project laboratories concerned with that element. The laboratories represented were: Argonne National Laboratory, Chicago; Chalk River, Canada; K-25, Oak Ridge; Hanford Works, Richland; Knolls Laboratory, Schenectady; and Illinois Institute of Technology, Chicago.

Summary of Agenda

- I. Analytical Methods for Ruthenium
- II. Pure Ruthenium Compounds
- III. Identification of Species in Complex Mixtures
- IV. Ruthenium in Solvent Extraction
- V. Special Problems and Techniques

Gravimetric Methods

The Argonne people have checked several analytical methods for ruthenium using ammonium chlororuthenate as a standard. They found the best results (consistently 6% high) with a magnesium precipitation of ruthenium metal from 6 M HCl. The thionamide method gave results 10-13% high (5% due to blank) when used for 8 to 10 mg. samples. The Gilchrist method gave a good precipitate of hydrolysed ruthenium oxide from 0.1 gm. samples. Small samples gave colloid precipitates. Numerical results were not presented.

Colorimetric Methods

At Argonne laboratories ruthenium has been oxidized to the tetroxide with persulfate and silver and the light absorbed at 3850 Å by the oxidized solution was measured with a Carey recording spectrophotometer. Samples ranging over a 500 fold change in concentration checked within 2% when they were reduced with mercury and reoxidized for measurement. A calibration curve is necessary for this method.

K-25 has used a similar method involving an alkaline fusion to Na₂ RuO₄ followed by dilution and measurement of light absorption.

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Valence State Analyses

Hanford laboratories measured the iodine liberated by ruthenium tetroxide formed by the action of bromate ion. This was unsuccessful in defining the oxidation state as was an attempt at Knolls laboratory to distill the tetroxide into iodide and titrate with thiosulfate. They have started to use chromous ion to titrate Ru (IV). Knolls also tried to reduce Ru (IV) by various amalgams with the intention of stepwise reoxidation. Argonne tried to do the same with hydrogen instead of mercury but found that ruthenium catalysed the reduction of perchlorate to chloride.

K-25 has done some work on solid compounds. No methods are yet available for distinguishing Ru(III) from Ru(IV) in nitric acid solutions. Two other methods referred to were the thiourea method and the borohydride method. No evaluation of these methods was made.

Radiochemical Methods

Mention was made of the need for a standard counting procedure. It was suggested that an absorber be used to take out the very weak ruthenium β and count only the strong β from the rhodium daughter. The ruthenium γ is satisfactory for counting.

Preparation of Standards

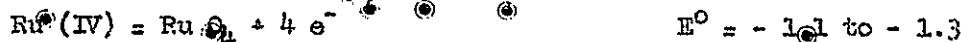
Ruthenium tetroxide distilled from sulfuric acid solutions and trapped in concentrated perchloric acid has been commonly used as a standard. Ammonium chlororuthenate has also been used as a standard. There is a question as to whether this compound contains six chlorides or five chlorides and one hydroxyl. The ruthenium is thought to be in the +4 state.

Pure Compounds

Report K-294 (Nov. 1, 1948) contains thermodynamic data on ruthenium pentafluoride which has been made at K-25 from the metal and fluorine. Work is also being done on the trifluoride. Knolls has made ruthenium nitroso nitrate, $RuNO(NO_3)_3$ following a standard procedure. They were unsuccessful in making a solid perchlorate.

Oxidation potentials

The potentials of the following couples have been bracketed as follows by the use of oxidizing and reducing agents:



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Spectrophotometric Data

Ruthenium which was analyzed to be in the +4 state showed a band at 4600 Å. Various solutions of ruthenium tetroxide which had been reduced showed a peak at 6950 Å. There was some shift in the location of this peak with change of hydrogen ion concentration. Other peaks also appear under various conditions and generally obey Beer's law.

Polarography

Mercury electrodes are attacked by the higher oxidation states of ruthenium. Platinum electrodes have been used successfully and points of inflection in the current voltage curves have been reported for various solutions.

Solvent Extraction

Oak Ridge reported that a great deal of the trouble in extracting ruthenium appears to be due to a stable colloidal form. They have found that ruthenium which has been treated with periodic acid is strongly adsorbed on Tygon tubing. A method for removing ruthenium based on this fact has been devised. Hanford reported on solvent extraction work with tracer ruthenium. A new batch of tracer has given entirely different results from previous experiments and has not yet been explained. Chalk River has found that oxidation of ruthenium by cerium (IV) and extraction into tetrachloroethane gives 96-98% extraction. No other fission products have been detected in the organic phase. Acid deficient systems give very poor extraction yields.

Volatilization

Both Hanford and Argonne reported on oxidizing ruthenium to the tetroxide and volatilizing. Ozone, permanganate and cerium (IV) were good oxidizing agents although the ruthenium stuck to the walls of the apparatus. Cerium was most objectionable in this respect. Only a few percent stuck to the walls when permanganate was used and ozone was reported to give the best recovery.

Summary

Although a large amount of work has been done on ruthenium, there is still a great demand for a good analytical method. Identification of the species in solution and preparation of a pure compound also are high on the list of things to be accomplished.

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