

THE STUDY OF RHODIUM(III) COMPLEXES BY PAPER ELECTROPHORESIS AND ION-EXCHANGE CHROMATOGRAPHY

III. RHODIUM(III) IN PERCHLORIC ACID

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INTRODUCTION

Work has been in progress in this laboratory^{1,2}, which involved a study of the action of different mineral acids on rhodium(III) hydroxide with the aim of finding a method for the analytical separation of this element. In the acids HCl, HBr, HNO₃ and H₂SO₄ a single species of rhodium(III) could not be found. It was concluded that only partition chromatography might yield a reliable separation of the metal from other platinum metals, and that ion exchange and paper electrophoresis are unreliable.

In this paper an attempt has been made to investigate the possibility of obtaining rhodium as a single species in perchloric acid, taking into consideration its remarkable stability, complete dissociation and extreme reluctance to form co-ordination complexes.

EXPERIMENTAL

(i) Preparation of rhodium perchlorate

Rhodium hydroxide was prepared as a yellow precipitate by carefully adding a solution of 2 *N* NaOH to an aqueous solution of Na₂RhCl₆ (Johnson, Matthey and Co., London). The precipitate was washed with distilled water by centrifugation until the wash water was neutral to indicator. The washed precipitate of rhodium hydroxide was dissolved in *N* perchloric acid, whereby a yellow solution was obtained, which did not change colour on standing for several weeks.

The solution was subjected to paper electrophoresis according to the method of LEDERER AND WARD³, using 3 × 40 cm paper strips (Papeterie d'Arches No. 302) and *N* perchloric acid as electrolyte. After applying a potential of 250 V for 45 min the current was switched off. Rhodium was detected by spraying the paper with a solution of stannous chloride and potassium iodide in 5*N* HCl. Three cationic bands were obtained as shown in Fig. 1a. The slowest band was the weakest in intensity, the second band had a higher intensity, while the most rapid band was the most prominent.

(ii) Effect of aging

The solution of rhodium hydroxide in perchloric acid was allowed to stand at room temperature in a stoppered tube. Electrophoresis of the solution after it had stood for

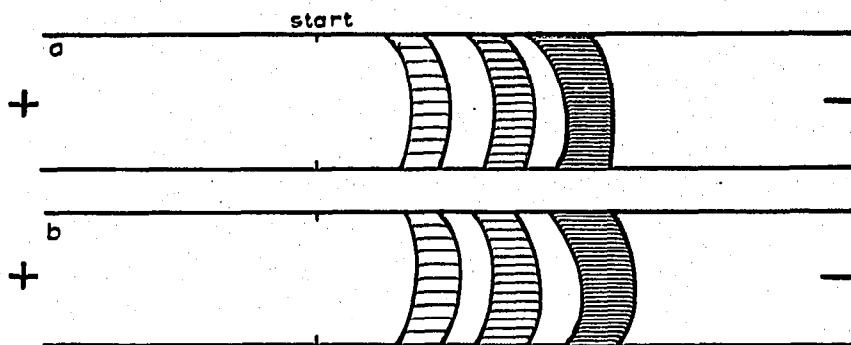


Fig. 1a. Paper electropherogram of a fresh solution of $\text{Rh}(\text{OH})_3$ in 1.0 N HClO_4 (250 V for 45 min, electrolyte 1 N HClO_4). Fig. 1b. Paper electropherogram of the same solution as in Fig. 1a aged for 1 month in a stoppered tube at room temperature. Conditions as in Fig. 1a.

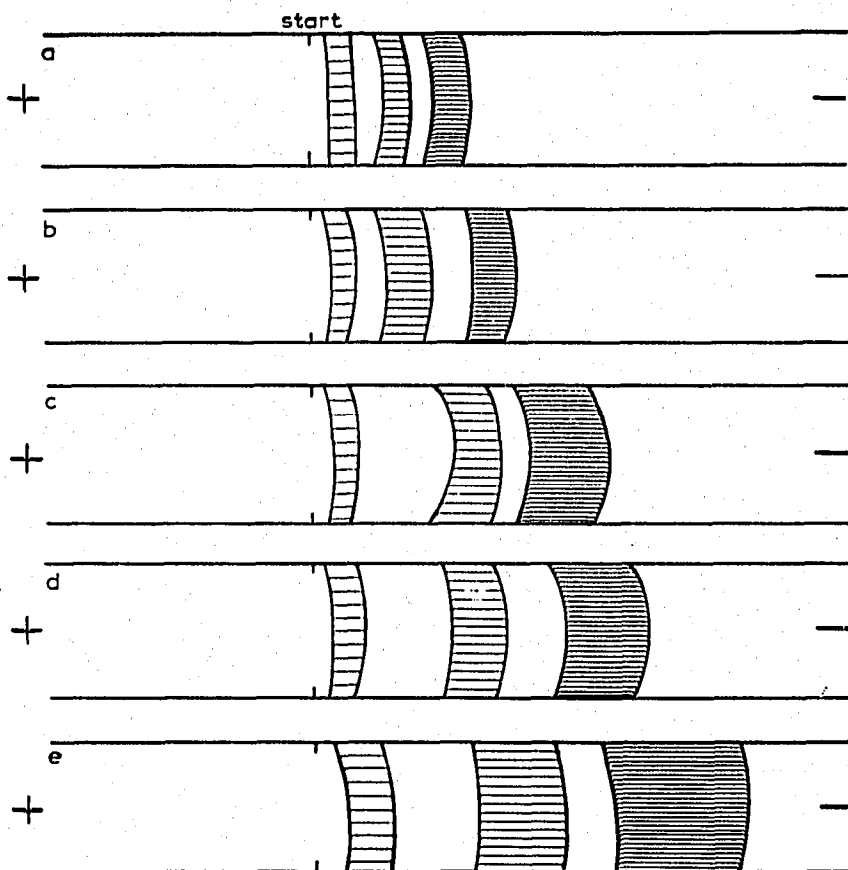


Fig. 2. Paper electropherogram of a fresh solution of $\text{Rh}(\text{OH})_3$ in N HClO_4 (250 V for 45 min), using as electrolyte: (a) 1.5 N HClO_4 , (b) 1 N HClO_4 , (c) 0.75 N HClO_4 , (d) 0.1 N HClO_4 and (e) 0.05 N HClO_4 .

different lengths of time always gave the same electropherogram as shown in Fig. 1b. This indicates that no appreciable change occurs on aging the solution; this is also indicated by the colour of the solution.

(iii) *Effect of the electrolyte concentration*

Electropherograms obtained by varying the concentration of the electrolyte used are shown in Fig. 2. The number, the intensity and the relative positions of the three

bands remained unaltered by dilution of the electrolyte. But with solutions below 1 *N* the bands moved more rapidly. With 0.05 *N* HClO₄, the bands became very diffuse so more dilute solutions were not tried.

(iv) Effect of heating the solution

A portion of the rhodium hydroxide solution in HClO₄ was heated on a water-bath for 45 min and also over a naked flame for about 5 min and then electrophorized. The three bands were still observed, which indicates the stability of these compounds.

(v) Action of AgNO₃

We considered the possibility that the bands observed might contain some co-ordinated chloro-groups, which had been carried with the precipitate to the perchloric solution. A portion of the solution was mixed with AgNO₃ in the cold. The mixture still gave three bands on electrophoresis. But, when the mixture was heated on a water-bath for about 45 min and again electrophorized, only a single rhodium band, faster than the second but slightly slower than the third band of the original solution, was repeatedly found. We presume that this band corresponds to the most prominent band, but is somewhat slowed down owing to its high concentration and also to the presence of Ag⁺ ions which travel still faster. The first two bands probably contained Cl⁻ covalently linked to Rh which was removed by heating with AgNO₃.

(vi) Ion exchange studies

The nature of the three cationic bands produced by the original solution, and their charges were further studied by ascending chromatography on Whatman paper No. 1 impregnated with Dowex-50 (for details see ref. 1).

The rhodium perchlorate solution was developed with various concentrations of HClO₄. Three spots with intensities similar to those obtained in paper electrophoresis were found in this case also. The major portion, which is the fastest in electrophoresis, is held strongly at the point of application and does not move at all. The other two bands move with different speeds in different concentrations of HClO₄. Comparison of the *R_F* values with those of other ions shows that bands 1 and 2 carry one and two positive charges, respectively, and have presumably two and one chloro-groups co-ordinated to the Rh(III). The third band which appears to carry three positive charges is most likely Rh(H₂O)₆⁺⁺⁺.

(vii) Removal of Cl by repeated precipitation as Rh(OH)₃ and dissolution in HClO₄

It appeared to us from the above results that it might be possible to remove the co-ordinated Cl by repeated precipitation of Rh(OH)₃ and redissolution in HClO₄.

One sample was therefore reprecipitated six times and submitted to paper electrophoresis. Only one band of rhodium could be detected and this had the same speed as the fastest band of the original solution.

(viii) *Comparison of the speed of Rh(III) with other trivalent ions*

The rhodium(III) perchlorate solution obtained according to (vii), and Fe⁺⁺⁺ perchlorate were electrophorized side by side on the same paper strip. Both were found to have moved about the same distance, the Rh(III) lagging a little behind the Fe⁺⁺⁺.

(ix) *Ion exchange studies with Rh(III) perchlorate prepared according to (vii)*

On Dowex-50 paper the Rh(III) solution prepared according to (vii) gave only one strongly adsorbed band at the point of application, confirming the conclusion of (vi).

(x) *Electrophoretic behaviour of Rh(III), prepared according to (vii), with varying electrolyte concentration*

The solution obtained according to (vii) gave only one band with all concentrations of HClO₄ in the range 0.25–1.5 N. With lower concentrations the band was much diffused.

CONCLUSION

Our results indicate that "rhodium hydroxide" when precipitated from RhCl₅[−] solutions contains appreciable amounts of co-ordinated chloro-groups. The complexity of the products obtained when Rh(OH)₃ is treated with H₂SO₄ or HNO₃ may be partly due to the formation of mixed chloro-sulphato or chloro-nitrato complexes. Although heating with AgNO₃ or reprecipitation may remove the chloro-groups, only the first of the two methods shows any promise of an analytical application since with each precipitation considerable losses are incurred.

We have also shown how a solution of Rh(H₂O)₆(ClO₄)₃ may be prepared.

SUMMARY

The action of HClO₄ on rhodium hydroxide was studied with paper electrophoresis and ion exchange chromatography. The existence of chloro-complexes due to precipitation of co-ordinated Cl in the preparation of Rh(OH)₃ was demonstrated. These can be decomposed by repeated precipitation or heating with AgNO₃.

REFERENCES

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