

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

PART II

M. LEDERER

Institut du Radium, Paris (France)

INTRODUCTION

Part I of this paper¹ dealt with the ageing of rhodium chloride solutions and the effect of HCl on freshly precipitated rhodium (III) hydroxide. It was there shown that the yellow solution obtained by adding HCl to rhodium hydroxide according to MACNEVIN AND MCKAY² did not yield a stable product, but a polycation or hydroxylation which, within hours, breaks down into cationic, neutral and anionic rhodium chlorocomplexes.

The methods used in this investigation were paper electrophoresis and ion exchange paper chromatography. Paper partition chromatography provided only information as to the feasibility of a separation with a given solution. It was concluded in this study that only paper partition chromatography may yield reliable separations of Rh-Pd or Rh-Pt, while ion exchange and paper electrophoresis were both unreliable.

In this paper we have examined the action of several mineral acids on rhodium hydroxide to determine whether other acids yield better defined ionic species more suitable for analytical separations.

EXPERIMENTAL

(1) *Preparation of rhodium hydroxide*

As starting product a 10% solution of rhodium chloride in *N* HCl was used, which itself had been prepared by dissolving rhodium hydroxide in HCl and which thus contained an equilibrium mixture of cationic, neutral and anionic species. 0.1 ml of this solution was mixed with 0.2 ml 2 *N* NaOH in a centrifuge tube, slightly warmed to induce precipitation, centrifuged and washed twice with distilled water by centrifugation.

(2) *Reaction of rhodium hydroxide with HBr*

To the rhodium hydroxide (*i.e.* about 5 mg) 0.2 ml of 0.42 *N* HBr was added and the solution warmed for a minute on the water bath to obtain a clear solution. This solution, originally yellow, turns reddish very quickly.

Paper electrophoresis immediately after bringing into solution, produced the

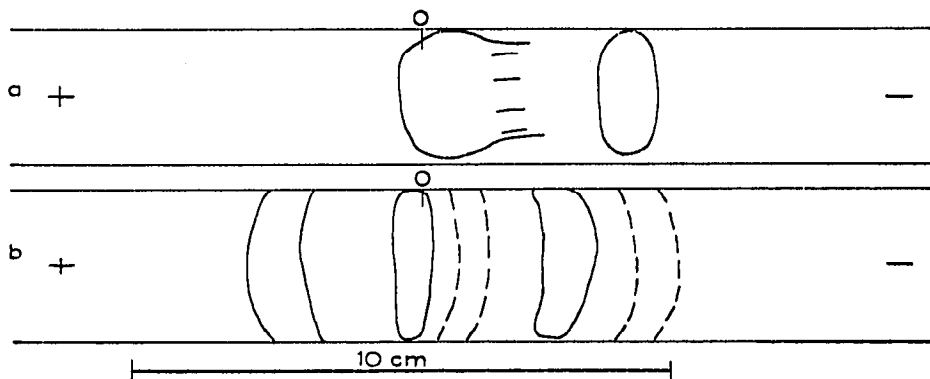


Fig. 1. a. Paper electropherogram of a fresh solution of $\text{Rh}(\text{OH})_3$ in 0.42 N HBr (1 h with 200 V, electrolyte 5% HBr). b. Paper electropherogram of a one-week old solution of $\text{Rh}(\text{OH})_3$ in 0.42 N HBr . Conditions as in Fig. 1a.

pattern shown in Fig. 1a, that is a slow moving cationic band analogous to that formed in HCl , which is preceded by a faint cationic band. Fig. 1b shows the same solution under the same conditions but seven days later. Five differently charged fractions can be identified.

Paper chromatography of the aged solution in butanol-3 N HCl and in butanol-10% HBr produces numerous spots, in the latter solvent also a trail stretching to the liquid front.

The HBr solution of rhodium hydroxide is thus still less suitable for analytical separations than a HCl solution.

(3) Reaction of rhodium hydroxide with HNO_3

To another portion of freshly prepared rhodium hydroxide, 0.2 ml of N HNO_3 were added. On gently heating, this yields a yellow solution which stays yellow for several weeks. Paper electrophoresis of the fresh solution in 0.1 N HNO_3 - 0.9 N NaNO_3 as electrolyte yields a slow moving cationic band and a faint faster cationic band as shown in Fig. 2a. After seven days the solution contains only two rather fast moving

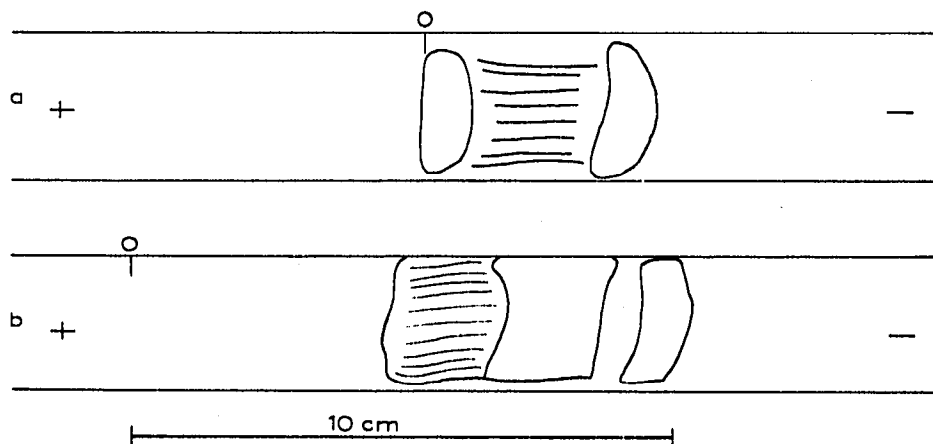


Fig. 2. a. Paper electropherogram of a fresh solution of $\text{Rh}(\text{OH})_3$ in N HNO_3 . (1 h with 200 V, electrolyte 0.9 N NaNO_3 - 0.1 N HNO_3). b. Paper electropherogram of a one-week old solution of $\text{Rh}(\text{OH})_3$ in N HNO_3 (2 h with 200 V, electrolyte as in Fig. 2a).

cationic bands as shown in Fig. 2b. The faster of these is only present in small quantities and reacts very slowly with SnCl_2 -KI in 5 N HCl.

Normal nitric acid thus does not produce anionic rhodium complexes. To study further the nature of the cationic species, the aged solution was chromatographed on Dowex-50 paper with various concentrations of HNO_3 , as shown in Fig. 3. The major

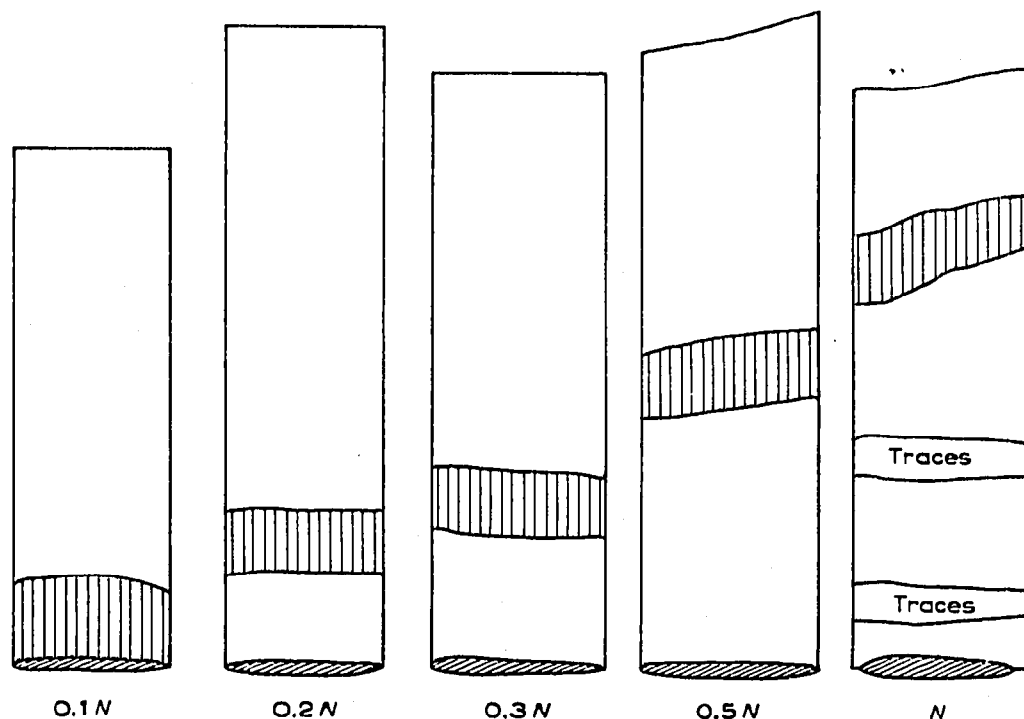


Fig. 3. Movement of Rh(III) nitrate complexes on Dowex-50 paper when developed with 0.1 N, 0.2 N, 0.3 N, 0.5 N and N HNO_3 (left to right). The R_F values of the major band (0.09, 0.19, 0.266, 0.46 and 0.75 resp.) correspond to the movement of a divalent cation. Another band stays at the point of origin.

fraction clearly behaves as a divalent cation (see Part I of this paper) while the small fraction which in electrophoresis moves ahead of the divalent cation is strongly adsorbed on the point of origin and not desorbed in acid concentrations sufficiently high to desorb trivalent cations. We suggest that this may be $\text{Rh}(\text{H}_2\text{O})_6^{+++}$ which on adsorbing on Dowex-50 yields irreversible complexes with the sulphonic groups of the resin. Similar reactions have already been observed with chromium solutions. Partition chromatography in butanol-3 N HCl yields three spots as shown in Fig. 4. in butanol- HNO_3 10% two spots and a long comet.

(4) Reaction of rhodium hydroxide with H_2SO_4

A portion of rhodium hydroxide was mixed with 0.2 ml of N H_2SO_4 and warmed to produce a solution. This solution was yellow and did not visibly change colour on standing. Paper electrophoresis of the fresh solution with 5% Na_2SO_4 -0.1 N H_2SO_4 as electrolyte yielded a weak cationic band and a single anionic band which is the major constituent. The pattern remains constant over 11 days; no changes being

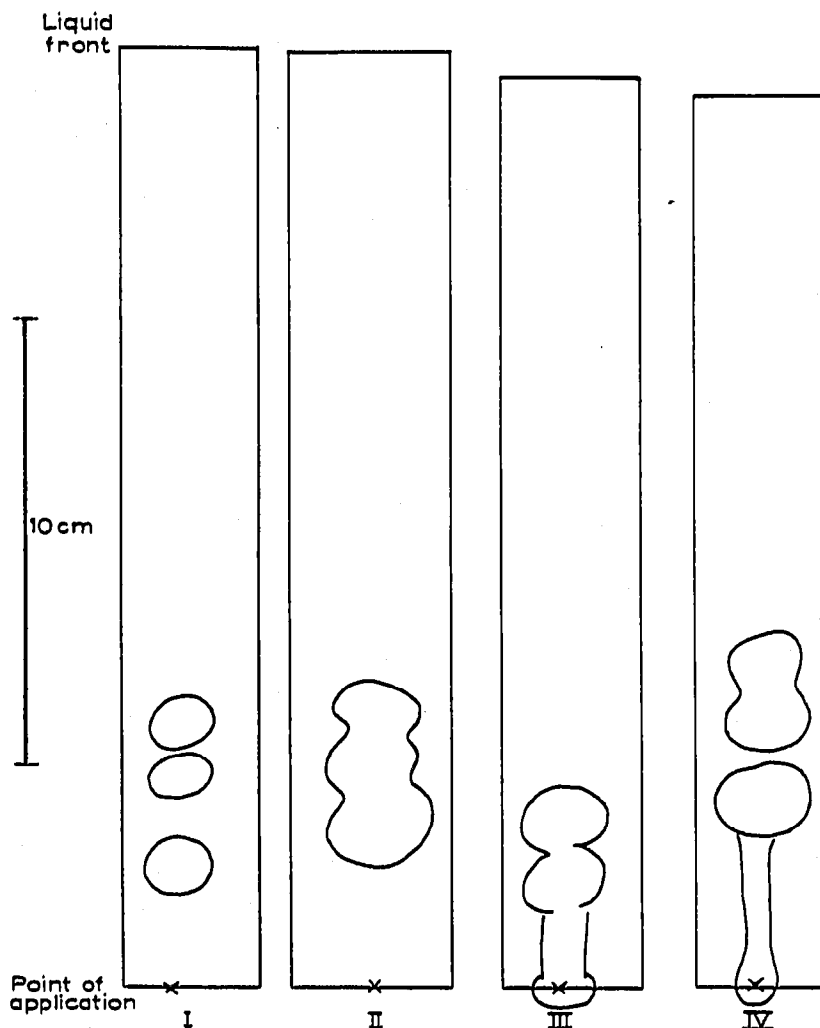


Fig. 4. Position of rhodium (III) after paper chromatographic development with butanol-3 *N* HCl: I. when the week-old solution in *N* HNO₃ is placed on the paper; II. when an aged solution of the chloride is placed on the paper; III. when a week-old solution in *N* H₂SO₄ is placed on the paper; IV. when a week-old solution in 0.42 *N* HBr is placed on the paper.

noted by paper electrophoresis. In butanol-3 *N* HCl three spots are produced as shown in Fig. 4.

To establish whether the anionic band contained sulphato-groups, we reacted another portion of the hydroxide with *N* H₂SO₄ containing radioactive ³⁵S (ca. 0.1 mc/ml). Fig. 5 shows the activity peaks in the solution containing ³⁵S which clearly shows that some sulphate is attached to the anionic band. To investigate the presence of SO₄⁻⁻ groups in the cationic band, much higher activities would have to be used and this did not appear warranted in this case.

CONCLUSION

The reactions of rhodium (III) hydroxide with mineral acids can be represented by the scheme on the next page.

The unstable intermediate cation of low mobility is formed in HCl, HBr and

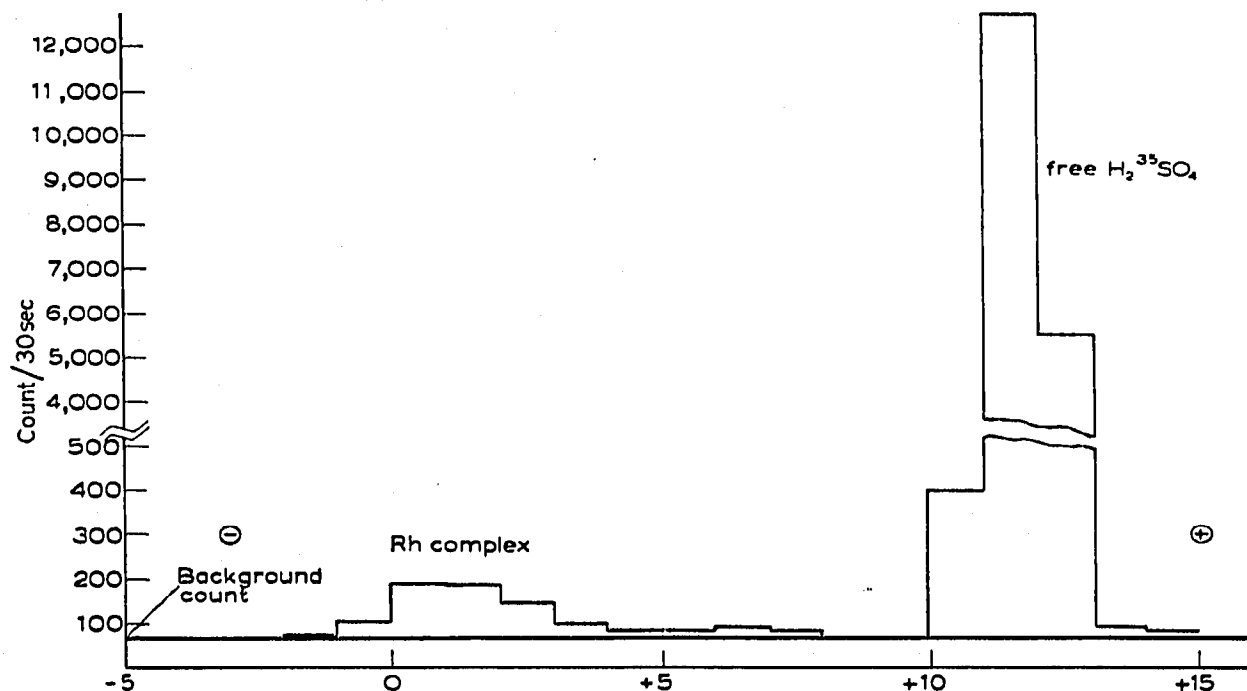
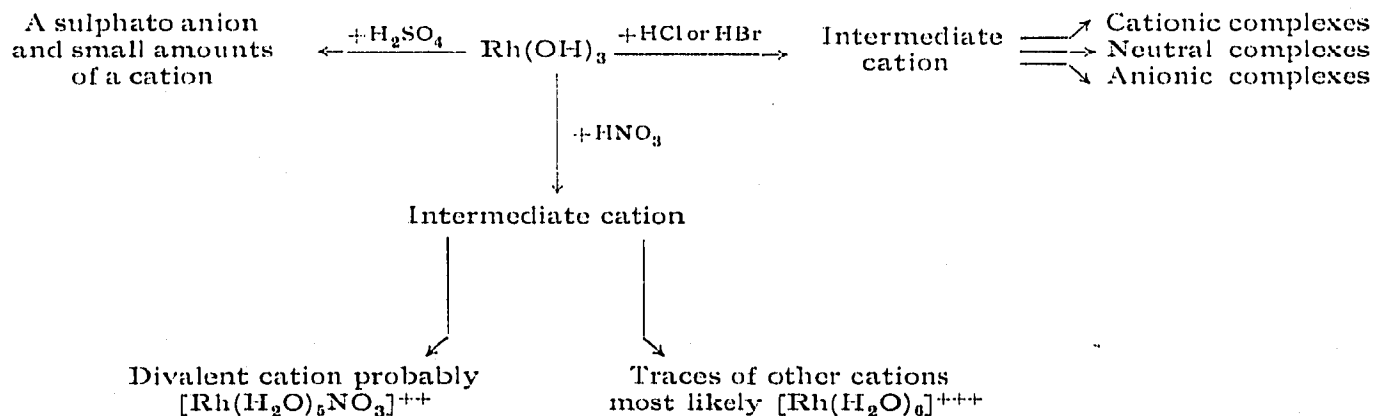


Fig. 5. Paper electropherogram of $\text{Rh}(\text{OH})_3$ dissolved in $N \text{H}_2\text{SO}_4$ containing radioactive ^{35}S as tracer. The distribution of radioactivity along the paper is shown, indicating that some ^{35}S is attached to the anionic Rh band and does not move as free H_2SO_4 . Conditions: 1 h with 200 V, electrolyte: 5% Na_2SO_4 -0.1 $N \text{H}_2\text{SO}_4$.

HNO_3 but not in H_2SO_4 . We would like to recall that Rh metal dissolves only in sulphuric and in none of the other acids. Both phenomena seem to be due to the better complexing ability of SO_4^{--} groups for rhodium.

In none of the acids examined, is there a single species which would promise to be suitable for ion exchange or electrophoretic separations. On the other hand all complexes appear to have a low solvent extractability and group themselves in the low R_F region when developed with butanol-3 $N \text{HCl}$. Paper chromatographic separation from elements such as Pt^{IV} or Pd^{II} is thus possible irrespective of the complexes which Rh(III) may form in mineral acids.



SUMMARY

The action of HBr, HNO₃ and H₂SO₄ on rhodium hydroxide has been studied with paper electrophoresis and ion exchange chromatography. Except in H₂SO₄, an intermediate unstable cation is formed which decomposes into several complexes.

REFERENCES

- ¹ M. LEDERER, *Paper presented to the Congress on Analytical Chemistry*, Moscow, December 1957.
- ² W. M. MACNEVIN AND E. S. MCKAY, *Anal. Chem.*, 29 (1957) 1220.

Received November 27th, 1957