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Note

Solution chemistry of rhodium(III) in hydrobromic acid solutions

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It has now become common practice to investigate a large number of metal ions when studying a new ion-exchange resin or new eluent in ion-exchange chromatography and to represent the results in the form of a "periodic table" as was first published by Kraus and Nelson¹ for anion exchangers and hydrochloric acid solutions.

In most of these studies rhodium(III) is included, which is surprising as it usually does not form a single species in any of the media used and the results will vary with the age of the solution and its method of preparation. This was illustrated for hydrochloric acid solutions in the quantitative studies of Blasius and Preetz².

Few data are available for hydrogen bromide solutions, apart from a kinetic study on the formation of cationic species³ and some preliminary work⁴ mainly at a hydrogen bromide concentration of *ca.* 1 *N.* Recently we have seen several studies that deal with hydrobromic acid solutions of rhodium and felt that some additional data would be of interest to other workers.

In our previous work on the solution chemistry of rhodium(III) we used paper electrophoresis extensively, together with some column and ion-exchange paper chromatography. As the last technique has now been superseded by the use of thin layers of ion-exchange resins, we used these in the present study, because paper electrophoresis does not give good results at higher concentrations of hydrobromic acid.

EXPERIMENTAL

We studied rhodium solutions in hydrobromic acid by paper electrophoresis, partition chromatography with *n*-butanol-hydrobromic acid and ion-exchange resin thin-layer chromatography. In this paper we discuss only the results obtained with the last technique, which gave the best results.

For the separation of cationic species we employed Polygram Ionex-25 SA-Na thin layers (Macherey, Nagel & Co., Düren, G.F.R.). These layers contain silica gel but none of the rhodium species are adsorbed on silica from solutions of hydrobromic acid, which was used as the eluent. We were first concerned about whether the neutral thin layer hydrolysed the species when the solution is spotted on the layer but the same chromatograms are obtained whether the spots are placed behind the liquid front or simply on the dry layer. A relatively low concentration of hydrobromi

acid has to be used because a number of species are not separated well at higher concentrations, as we have shown previously with other eluents and media⁵.

Anionic species were separated on Polygram Ionex-25 SB-Ac (Macherey, Nagel & Co.), 2.2 *N* hydrobromic acid being used for development. After development for a distance of about 10 cm, which took 60 min, the chromatograms were sprayed lightly with tin(II) chloride-potassium iodide reagent, which yielded dark red to purple spots with all rhodium species on heating in an air oven at about 100°.

RESULTS

Rhodium hydroxide free of chloride was prepared from commercial rhodium chloride by re-precipitating twice with sodium hydroxide and re-dissolving in perchloric acid⁶. The hydroxide was then dissolved in various concentrations of hydrobromic acid and also in perchloric acid-hydrobromic acid and perchloric acid in the cold.

The chromatograms of these fresh solutions are shown in Fig. 1. After 1 week at room temperature, further chromatograms were prepared and these are shown in Fig. 2.

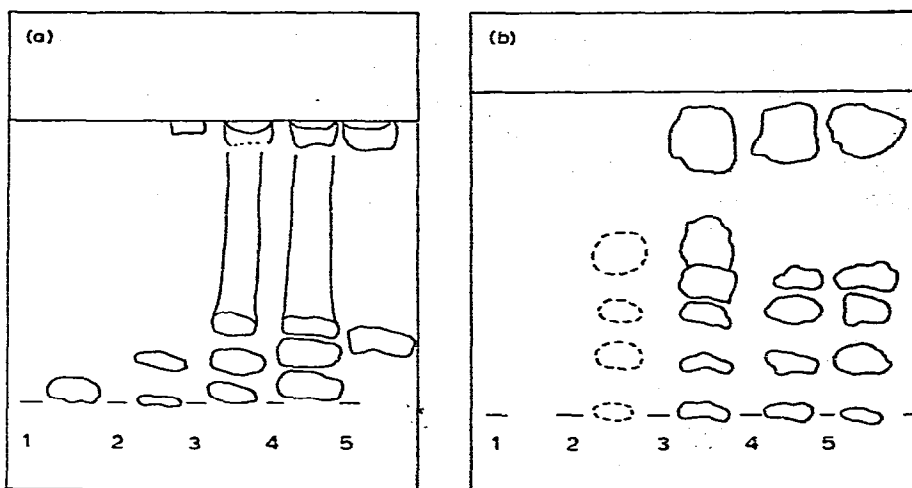


Fig. 1. (a) Chromatogram on Ionex 25 SA-Na layers developed with 0.3 *N* HBr. (b) Chromatogram on Ionex 25 SB-Ac layer developed with 2.2 *N* HBr. Samples: fresh cold solutions of (1) $\text{Rh}(\text{OH})_3$ dissolved in 1 *N* HClO_4 ; (2) $\text{Rh}(\text{OH})_3$ dissolved in 1 *N* HClO_4 containing 0.05 *N* HBr; (3) $\text{Rh}(\text{OH})_3$ in 1 *N* HBr; (4) $\text{Rh}(\text{OH})_3$ in 4.4 *N* HBr; (5) $\text{Rh}(\text{OH})_3$ in 8.8 *N* HBr.

Another series of solutions was prepared from rhodium hydroxide in different ways as follows: (a) dissolved in cold concentrated hydrobromic acid; (b) dissolved in concentrated hydrobromic acid and heated on a naked flame; (c) dissolved in concentrated hydrobromic acid and heated for 30 min on a steam-bath. The chromatograms of the fresh solutions are shown in Fig. 3 and of the solutions aged for 1 week at room temperature in Fig. 4.

A third series of solutions was prepared: (a) commercial rhodium chloride was dissolved in concentrated hydrobromic acid; (b) this solution was heated for 1 h

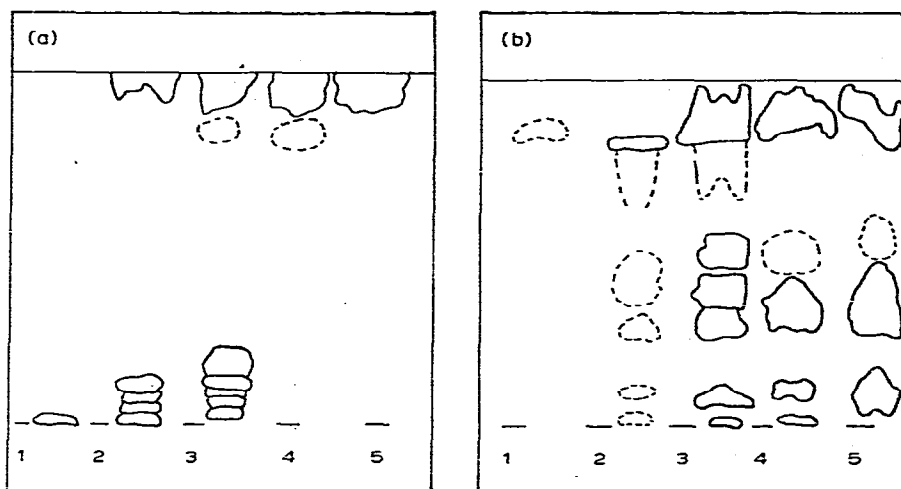


Fig. 2. Chromatograms of the same solutions as in Fig. 1 on the same thin layers after ageing the solutions for 1 week at room temperature.

on a water-bath; (c) ammonium chlororhodate (Fluka, Buchs, Switzerland) was dissolved in concentrated hydrobromic acid; (d) this solution was heated on a water-bath. The chromatograms of these solutions are shown in Fig. 5.

It is evident from these chromatograms that in none of these solutions is there only a single rhodium species. The most complex solutions are obtained with dilute hydrobromic acid at room temperature, but heating various rhodium compounds in concentrated hydrobromic acid will always produce a solution containing more than one species.

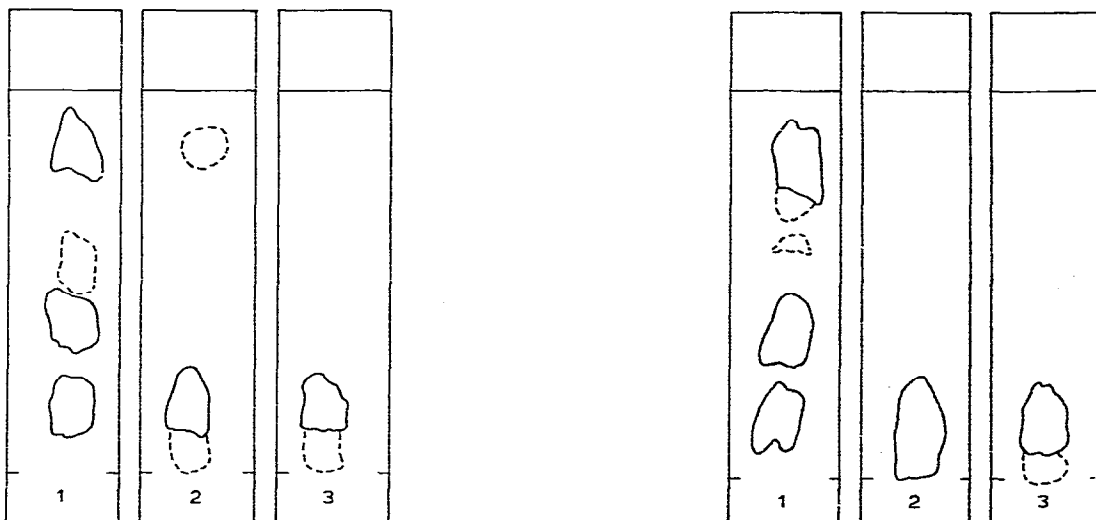


Fig. 3. Chromatograms on Ionex 25 SB-Ac layers developed with 2.2 *N* HBr for 1 h. Samples: (1) $\text{Rh}(\text{OH})_3$ dissolved in concentrated HBr; (2) solution 1 heated for 5 min on a naked flame; (3) solution 1 heated for 30 min on a steam-bath.

Fig. 4. Chromatograms of the same solutions as in Fig. 3 aged for one week.

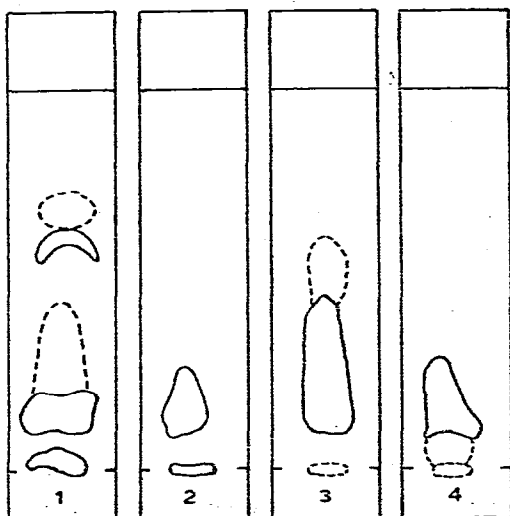


Fig. 5. Chromatograms on Ionex 25 SB-Ac layers developed with 2.2 *N* HBr. Samples: (1) Commercial RhCl_3 dissolved in concentrated HBr; (2) solution 1 heated for 1 h on a water-bath; (3) a sample of ammonium chlororhodate dissolved in concentrated HBr; (4) solution 3 heated for 30 min on a water-bath.

Hence the solution of rhodium(III) in hydrobromic acid is very similar to that in hydrochloric acid, and it seems evident that equilibrium adsorption or batch extraction studies of rhodium(III) in hydrobromic acid are meaningless unless the solution of rhodium that is studied is specified in terms of its method of preparation and its age, and even then only results for complex mixtures can be recorded, which have little analytical utility.

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