

THE STUDY OF RUTHENIUM (III) COMPLEXES BY
PAPER ELECTROPHORESIS AND SPECTROPHOTOMETRY
SOLUTION CHEMISTRY OF POTASSIUM
AQUOPENTACHLORORUTHENITE. EFFECT OF AGEING

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Although over the last hundred years extensive chemical investigation has been carried out¹ leading to the description of more than 500 solid compounds of ruthenium^{2, 3}, very little is as yet known about the actual ionic species of the element present in such common media as hydrochloric acid, nitric acid, sulphuric acid, perchloric acid, etc.^{1, 3-6}. This gap in the knowledge of the solution chemistry of ruthenium has offered considerable difficulties not only to the advancement of the knowledge of the chemistry of this element but also to the establishment of fundamental processes for its qualitative and quantitative analysis³. In his recent critical review of methods of isolating and separating the six platinum metals, BEAMISH⁷ remarks: "One cannot over-emphasise the fact that even today too few authors have recognised the potential complexity of equilibria in platinum metal solutions, the character of which may well affect all methods of separation as well as methods of determination. In some instances these deficiencies may have resulted in unmerited criticisms. . ."

Studies on the solution chemistry of rhodium in this laboratory have led us to the conclusion that the great variety of relatively stable complexes formed in solution are responsible for the poor yield often found during the quantitative determination⁸⁻¹⁴. In the case of ruthenium the difficulties are still more accentuated by its wide range of stable valency states and also by its marked tendency to complex formation and polymerisation. On account of its importance among the fission products and particularly because of the trouble it causes during the separation of fission products, the study of the solution chemistry of ruthenium has recently become imperative^{3, 15}. FLETCHER and coworkers have studied the chemical behaviour of ruthenium in nitric acid¹⁶⁻²². Complexes of lower oxidation states of ruthenium in perchloric acid have been investigated by WEHNER AND HINDMAN¹ and NIEDRACH AND TEVEBAUGH⁴. Ru³⁺, RuCl²⁺, and RuCl₂⁺ species were identified by CONNICK and coworkers^{5, 23}. The solution behaviour of K₂RuCl₆ in aqueous medium has been studied by FORCHERI and coworkers⁶.

Because of the great variety of the complexes of ruthenium formed in solution and also because of the slowness with which the equilibria between them are established, the use of equilibrium measurements to determine the formula of the species in solution is impracticable^{5, 13, 14}. This has obliged several workers to use ion-exchange^{3, 23}

and chromatography¹⁷ for the separation and identification of such species. Paper electrophoresis has recently been exploited by some workers^{6, 8-14, 24-29} and has been shown to offer several outstanding advantages over other separation methods. It permits (1) the examination of the purity of a compound, (2) the identification of the number and nature of the ionic species in a solution, (3) the verification of the completion of a reaction, (4) the observation of the nature of a product when it is subjected to any process such as dissolution, crystallisation, etc., (5) the clarification of the mechanism of a reaction, and finally (6) the study of the solution chemistry of an element.

The primary purpose of the work reported here has been to apply paper electrophoresis to the study of the changes introduced in the nature of ruthenium species when a solution of $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ in $N/10$ HCl is allowed to age at room temperature. Simultaneous spectrophotometric observations were also made to note the modifications in the absorption spectra of the species caused by such changes. A comparative study of the informatory value of the two techniques in the study of the solution chemistry of an element was thus also possible.

EXPERIMENTAL

The solution of $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ was obtained by dissolving 0.0278 g of potassium chlororuthenite, K_2RuCl_5 , (Johnson, Matthey & Co., Ltd., London) in 5 ml of 0.1 N hydrochloric acid³⁰. The solution was stored at room temperature in a glass stoppered tube to study the effect of ageing.

Paper electrophoretic studies were carried out by the glass plate technique as described by LEDERER AND WARD³¹. Filter paper strips 2.7×40 cm (Papeterie d'Arches No. 302) were wetted with the electrolyte and the excess of liquid removed from the paper by pressing it between the folds of another filter paper. After given intervals of ageing, aliquots of the ruthenium solutions were applied by means of a micropipette along the starting line at the centre of the paper. The paper was then clamped between two glass plates of 7×32 cm and placed on two similar electrode vessels each containing the same volume of the electrolyte. The two ends of the paper dipped well into the electrolyte. A platinum wire formed the anode while a thin carbon rod served as the cathode. 0.1 N hydrochloric acid was used as the electrolyte and 250 V were applied across the two electrodes. Good separations with sharp electrophoretic bands were observed within 25 min. Prolongation of the electrophoresis caused fading away of the electrophoretic bands. The electrophoresis was therefore generally discontinued once good separation with well-defined bands had been obtained. Only in the case of the raspberry-red band (see later), could the electrophoresis be continued as long as desired and as far as the length of the paper permitted, without appreciable change in colour or intensity occurring.

The absorption spectra were recorded with a Unicam SP 500 spectrophotometer using 10 mm quartz cells. For the observation of the spectra the stock solution had to be diluted to one hundredth of its concentration.

Spectral and electrophoretic observations were made simultaneously after the same period of ageing of the solution in order to compare the results of the two methods.

RESULTS AND DISCUSSION

When the solution of $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ is allowed to stand, its pale amber colour changes slowly through brown to dark raspberry-red.

In Figs. 1 A and B are shown side by side the absorption curves and the corresponding electrophoregrams of the ruthenium species after a given time of ageing of the solution.

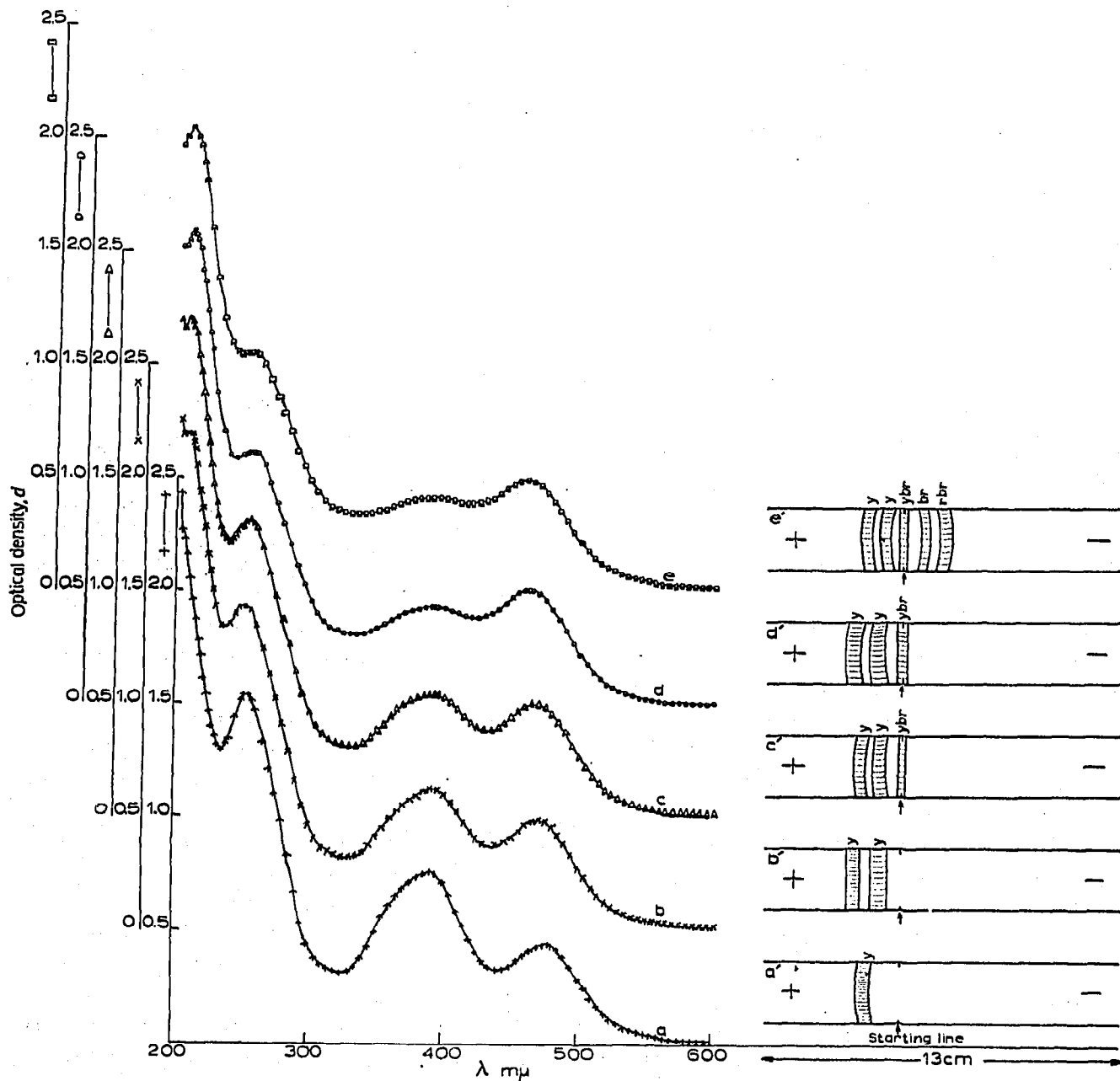


Fig. 1 A. Effect of ageing, at room temperature, on the absorption curve (a-e) and on the electrophoregram (a'-e'), of a solution of $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ in 0.1 N hydrochloric acid. Abbreviations used for denoting the colour of the bands: y = yellow; ybr = yellowish brown; br = brown; rbr = raspberry-red. a, a': fresh solution; b, b': solution aged for 24 h; c, c': solution aged for 3 days; d, d': solution aged for 6 days; e, e': solution aged for 10 days. (Continued on p. 99.)

The single, yellow and fast anionic band of the fresh solution (Fig. 1 A, a') shows that at the start the solution contains exclusively $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ and therefore the absorption curve traced in Fig. 1 A, a, should represent the characteristic spectrum of the complex $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$. Leaving the solution at room temperature for 24 h seems to cause hydration of $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$, sufficient to produce slower anionic

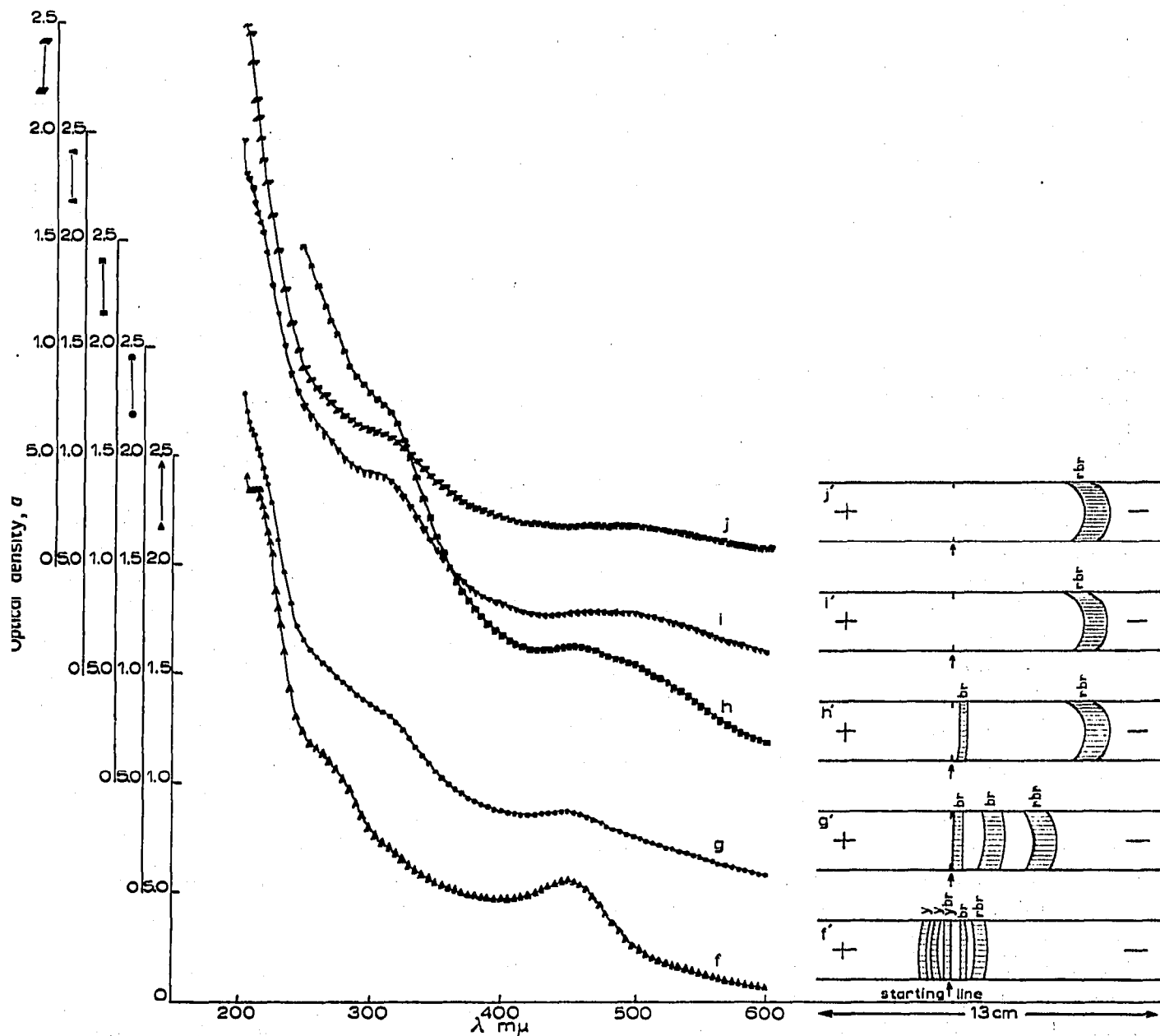


Fig. 1 B. Effect of ageing, at room temperature, on the absorption curve (f-j) and on the electrophoretogram (f'-j') of a solution of $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ in 0.1 N hydrochloric acid. Abbreviations used for denoting the colour of the bands: y = yellow; ybr = yellowish brown; br = brown; rbr = raspberry-red. f, f': solution aged for 20 days; g, g': solution aged for 45 days; h, h': solution aged for 88 days; i, i': solution aged for 105 days; j, j': raspberry-red solution obtained either by elution of the 105 days aged solution through Dowex-2 resin column or by elution of the raspberry-red electrophoretic band with 0.1 N HCl.

species $[\text{Ru}(\text{H}_2\text{O})_2\text{Cl}_4]^-$ (Fig. 1 A, b'). The electrophoregram c' after 3 days of ageing shows the production of a third yellowish brown ruthenium complex which is neutral and may be $[\text{Ru}(\text{H}_2\text{O})_3\text{Cl}_3]^0$. Thus the effect of ageing of the $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ solution manifests itself as a progressive replacement of the negatively charged chloro-group of the complex by a neutral aquo-group. Ruthenium species of more and more positive character are therefore formed in the solution at the expense of the more negative ones, resulting in the gradual disappearance first of the anions, then of the neutral species, which are replaced by cationic ruthenium complexes. The electrophoregrams e' (Fig. 1 A) and f' (Fig. 1 B), taken after 10 and 20 days respectively, give a typical picture of these changes where five ionic species, two anionic, one neutral, and two cationic ones, are found to be present in the solution. More prolonged ageing is accompanied by a gradual disappearance of the anions, which is complete after 45 days (Fig. 1 B, g') when three cations only, two brown and one raspberry-red, are observed on the electrophoregram. The two slower cationic species of ruthenium, in their turn, are also transformed by ageing into the fast raspberry-red complex. This transformation was found to be complete after 105 days when the electrophoresis of the aged solution showed only one raspberry-red cationic band (Fig. 1 B, i'). No further change in the mobility of the raspberry-red ruthenium complex was observed on further ageing of the solution, or on passing it through a column of Dowex-2 resin or on eluting it from an electrophoregram and re-electrophorising the solution thus obtained (Fig. 1 B, j'). When some crystals of potassium iodide were added to the raspberry-red solution, iodine was liberated. This indicated that the raspberry-red species contained ruthenium(IV) formed through oxidation of ruthenium(III) by air during ageing.

Although the absorption curves have also undergone considerable modifications on ageing of the solution, as is shown by the curves in Figs. 1 A and B, it is not possible from these changes alone to state definitely the cause of these variations. The spectral data give no clue as to the number and nature of the species formed during ageing. Since the purity of the fresh solution and of the raspberry-red solution is shown by electrophoresis, one only can conclude in these cases that the spectra represented in curves a, i, and j correspond to the single species whose nature has been shown by electrophoresis. Curve a shows that the complex $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ gives three absorption maxima at 254, 390, and 478 $m\mu$. The absorption at these maxima varies in the order: absorption at 254 $m\mu \gg$ absorption at 390 $m\mu >$ absorption at 478 $m\mu$. On ageing, *i.e.*, on the hydration of the complex $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$, the maximum at 254 $m\mu$ gradually degenerates into a shoulder with progressive shift towards the longer wavelengths. Thus for the curves i and j the shoulder extends between 290 and 310 $m\mu$. In the curves c, d, e, and less so in f, generation of a fourth maximum on the higher frequency side of the maximum at 254 $m\mu$, at about 210 $m\mu$, is observed. The most remarkable effect that ageing has on the spectrum is the introduction of the maxima at 390 and 478 $m\mu$. The absorption of the maximum at 478 $m\mu$ increases with a gradual shift of the maximum towards the shorter wavelengths, while the maximum at 390 $m\mu$ is progressively suppressed. This change is so pronounced that even after 20 days (Fig. 1 B, f'), when traces of the anionic species are still present in the solution, the maximum at 390 $m\mu$ has already disappeared and that at 478 $m\mu$ has shifted to 450 $m\mu$.

The absorption curves i and j, which correspond to the fast cationic, raspberry-red complex on the electrophoregrams, are similar and represent in all probability

the spectrum of the complex $[\text{Ru}(\text{H}_2\text{O})_6]^{4+}$ (the presence of Ru(IV) in the raspberry-red complex had already been shown by the iodine liberation test). The spectrum of the electrophoretically pure $[\text{Ru}(\text{H}_2\text{O})_6]^{4+}$ complex thus contains a shoulder in the region 290–310 $m\mu$ and a less prominent maximum at $\sim 490 m\mu$. A similar absorption curve has been reported by WEHNER AND HINDMAN¹ for Ru(IV) solution in perchloric acid.

CONCLUSION

As in the case of rhodium, paper electrophoresis promises to be a very effective tool in the study of the solution chemistry of ruthenium. The well-defined electrophoretic bands obtained suggest the possibility of isolating even the intermediate species of ruthenium in a pure state. Paper electrophoresis may hence be used to solve the problem of the obtention of pure ruthenium species for colligative determinations⁶. Its advantages as a simple and rapid technique for the interpretation of the absorption spectra are evident.

SUMMARY

The effect of ageing on a solution of $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ in 0.1 *N* HCl was studied by paper electrophoresis and spectrophotometry. It was shown that during ageing the complex $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ undergoes gradual hydration involving progressive replacement of the Cl^- group of the complex by an aquo-group. Absorption spectra of electrophoretically pure $[\text{Ru}(\text{H}_2\text{O})\text{Cl}_5]^{2-}$ and $[\text{Ru}(\text{H}_2\text{O})_6]^{4+}$ are reported.

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