

THE REACTION OF SODIUM OR POTASSIUM NITRITE
WITH RUTHENIUM SALTS

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The paper chromatography and paper electrophoresis of ^{106}Ru tracer has been examined in several publications¹ in relation to the separation of Ru from other fission products. It was observed that Ru tracers separated into several spots owing to the equilibrium mixtures which are formed between the various nitroso-nitrato complexes; the difficulties in identifying these by paper chromatography were shown in the papers by FLETCHER *et al.*²

Usually it is now recommended to distill off the ruthenium as RuO_4 before examining the other fission product elements. We have for some time attempted to find a reaction which would yield a single ionic species with ruthenium, irrespective of its valency and complex state, which could then serve as starting point for a paper chromatographic or paper electrophoretic identification. We shall briefly mention some unsuccessful attempts. Thiourea will react with chloro-complexes, but only incompletely with nitroso-complexes; boiling with HBr or oxidation with bichromate in HCl were found to yield single spots when ruthenium chlorides were reacted, but not with nitroso-nitrato complexes, nor with tracer amounts of ruthenium.

The present study was started at the suggestion of Dr. L. M. VENANZI (Oxford), who mentioned to the authors that recent evidence had shown that the compound described as $\text{K}_2[\text{Ru}(\text{NO}_2)_5]$ is actually $\text{K}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})]$ (see also MURRAY³). Thus its preparation does not involve the removal of the nitrosyl group. We decided therefore to investigate the reaction between nitrite and ruthenium nitrates and chlorides, as the problem of removing the nitrosyl group seems to have been the difficulty in our previous attempts to form a single ionic species with ruthenium.

Dr. VENANZI also kindly supplied us with samples of the sodium and potassium salts prepared in his laboratory according to the syntheses given below:

(1) $\text{K}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})]$ (JOLY AND VÉZES⁴). Potassium nitrite (2 g) was dissolved in water (20 ml) and to the boiling solution, ruthenium trichloride was added in small amounts until a faint precipitate began to appear. A crystal of potassium nitrite was then added to redissolve this and the orange solution evaporated

to about 10 ml. On cooling, the product crystallised out as an orange solid which was purified by recrystallisation from water.

(2) $\text{Na}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})]$ (JOLY AND LEIDIÉ⁵). Ruthenium trichloride was dissolved in water, and solid sodium nitrite was added in small portions, until the addition of a further portion caused no effervescence. The orange solution was then evaporated until solid began to separate, and the solution left to cool. The product was recrystallised from water.

These two methods do not differ essentially from those quoted in PASCAL⁶, and it seems that the same product is obtained irrespective of whether the ruthenium is added to an initial excess of nitrite, or nitrite to an excess of ruthenium.

EXPERIMENTAL

(1) *Preparations and electrophoretic analyses*

All paper electropherograms were carried out with 250 V for 20 min (unless otherwise mentioned) with $N/2$ NaNO_2 as electrolyte on paper strips 40 cm long (Papier Arches No. 302), which were sandwiched between glass plates 31 cm long.

We repeated the syntheses mentioned above on a micro-scale, so as to be able to analyse the reaction mixture before crystals are separated.

For the sodium salt, about 50 mg of commercial RuCl_3 were dissolved in about 1 ml of water in a 5 ml beaker. Solid NaNO_2 was added till the solution, which was kept on the water bath, gave no effervescence. On evaporating, yellow crystals formed, which were filtered off, recrystallised from water and dissolved in about 1 ml of water.

When these three fractions (*i.e.* mother liquor, mother liquor from the recrystallisation and solution of the crystals) are subjected to paper electrophoresis, they all yield a slower orange spot and a faster yellow spot. Both spots react with H_2S to give an intense purple coloration which fades rapidly to a brown stain. The slow orange fraction is most intense in the mother liquor and is only present in traces in the once recrystallised substance. Crystals prepared from the once recrystallised material were found to be the pure yellow fraction.

The potassium salt was prepared by adding commercial RuCl_3 in small amounts to 0.4 ml of 10% aqueous KNO_2 on the water bath till a precipitate appears, and then a crystal of KNO_2 was added to redissolve this precipitate. During this operation it was realised that it is rather difficult to assess the exact point at which sufficient RuCl_3 had been added. We therefore took another lot of KNO_2 to which we added approximately half the amount of RuCl_3 added to the first tube, to ensure that KNO_2 was present in excess. When electrophorised, both solutions, separated into a slower orange and a faster yellow band with mobilities identical to those of the sodium salt.

The samples of Dr. VENANZI were also examined by paper electrophoresis. The sodium salt was found to be the pure yellow compound, while the potassium salt contained some of the orange compound.

Preliminary experiments showed us that a mixture of the orange and the yellow compounds, as formed in the two syntheses, could be converted to an almost pure solution of the yellow compound by simply heating with an excess of $N/2$ NaNO_2 on the water bath.

In order to investigate whether a complete conversion is possible, 150 mg of RuCl_3 were refluxed with excess NaNO_2 (522 mg) in about 14 ml of water (*i.e.* $N/2$ NaNO_2) and samples withdrawn at intervals and electrophorised. Already after 5 min refluxing, only a single yellow band could be detected by paper electrophoresis. A similar experiment was carried out by mixing excess KNO_2 with RuCl_3 . Here two species persisted until the solution was heated for 20 min or more.

Since ruthenium is often present as the nitroso-nitrato complexes in solution, we also investigated if these could be converted to the yellow complex by refluxing with excess NaNO_2 . A solution of the nitroso-nitrato complexes was prepared by evaporating some crystals of the yellow compound with concentrated nitric acid. The residue was taken up in $N/2$ NaNO_2 and yielded initially two anionic fractions. It is only after refluxing for at least 2 hours that only one yellow band is obtained in electrophoretic analysis.

We also carried out the reaction between carrier-free ^{106}Ru (in HNO_3) and $N/2$ NaNO_2 . When the tracer is evaporated on the water bath and taken up in NaNO_2 , its electropherogram shows two anionic peaks (Fig. 1). If it is left at room temperature only one peak may be observed after some time, however, with an electrophoretic mobility which is not identical with that of the yellow band. On the other hand, if the solution of the tracer is refluxed for about half an hour, it is converted to a single species which, when mixed with the yellow compound, shows a complete coincidence between the visible band and the activity peak, as shown in Fig. 2. The time of electrophoresis for this experiment was prolonged to 1 hour and the distance moved by the peak was 80 mm.

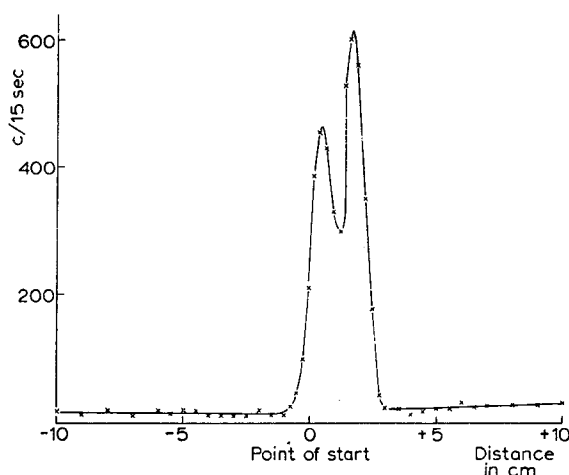


Fig. 1. Distribution of radioactivity on the electropherogram of a mixture of ^{106}Ru tracer and $N/2$ NaNO_2 (without heating). The tracer was originally in a nitric acid solution.

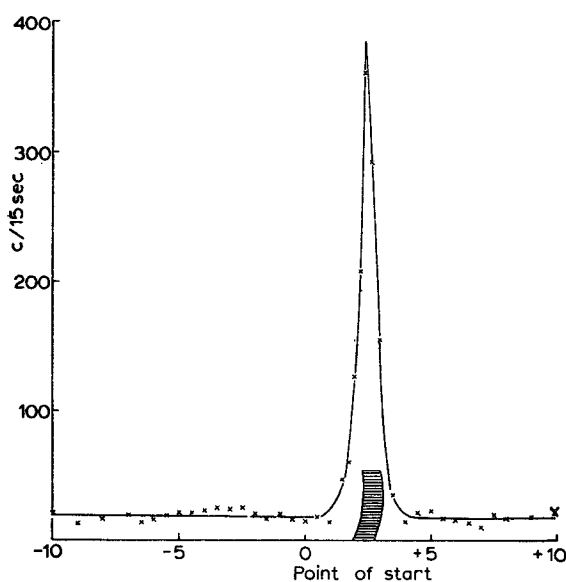


Fig. 2. Electropherogram of a mixture of ^{106}Ru tracer (boiled with $N/2 \text{ NaNO}_2$ for 30 min) and pure $\text{Na}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})]$.

(2) Absorption spectra

In Figs. 3 and 4, the spectra and electropherograms of the sodium and the potassium salt (supplied by Dr. VENANZI) are shown. The spectrum of the yellow band isolated from electropherograms, or obtained by refluxing ruthenium chloride with KNO_2 for 30 min is identical to that of VENANZI's sodium salt, but differs from the impure potassium salt. The difference between the spectra is best shown in Fig. 5 where the yellow band isolated from an electropherogram and the original mixture are superposed.

The slower orange band could only be isolated from electropherograms in small amounts even when large amounts of the mixture were separated on thick (Whatman

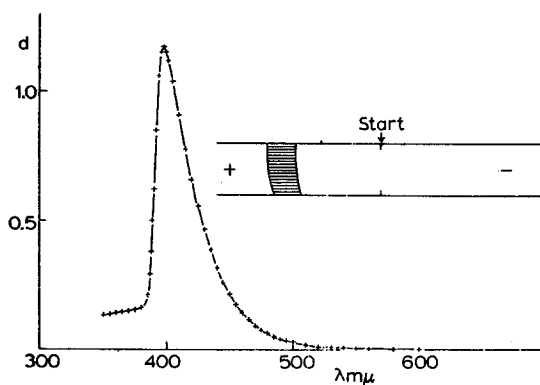


Fig. 3. Spectrum and electropherogram of a sample of $\text{Na}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})]$ prepared by Dr. VENANZI.

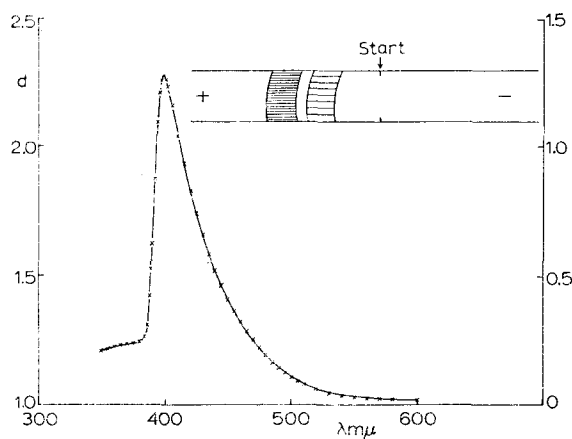


Fig. 4. Spectrum and electropherogram of a sample of $\text{K}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})]$ prepared by Dr. VENANZI.

No. 3 MM) paper. Fig. 6 shows the spectra of two different extractions as well as the spectrum of a solution of the orange compound aged in $N/2$ NaNO_2 for 3 days. The change indicates that some decomposition had taken place. By suitable dilutions of a solution prepared from pure yellow crystals it could be shown that Beer's law is obeyed for the wavelength $398 \text{ m}\mu$ as shown in Fig. 7.

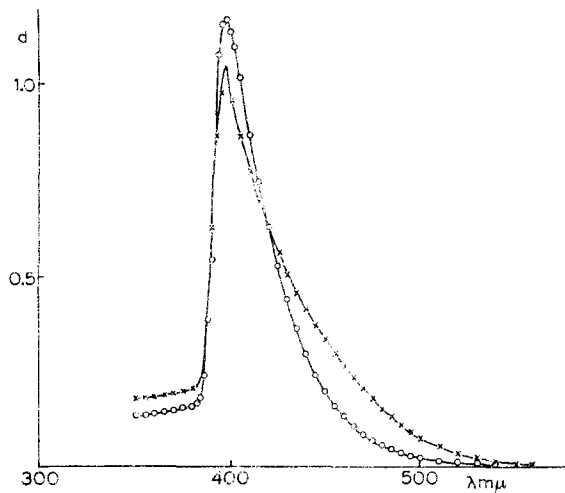


Fig. 5. Superposition of the spectra of a yellow band isolated from a paper electropherogram and an impure sample of $\text{Na}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})]$.

(3) Paper chromatography

The impure products of the syntheses of the Na and of the K salt were examined by paper chromatography.

No adsorption could be noted when they were developed with aqueous NaNO_2

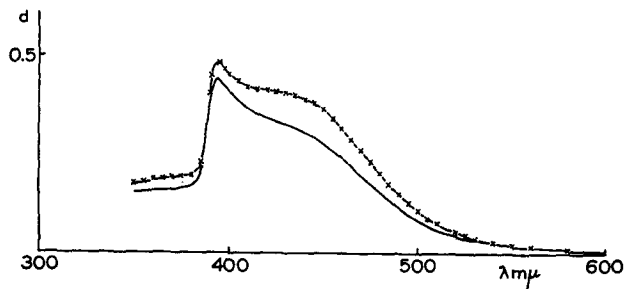


Fig. 6. The spectrum of the orange fraction isolated from a paper electropherogram immediately and after ageing 3 days in $N/2$ NaNO_2 .

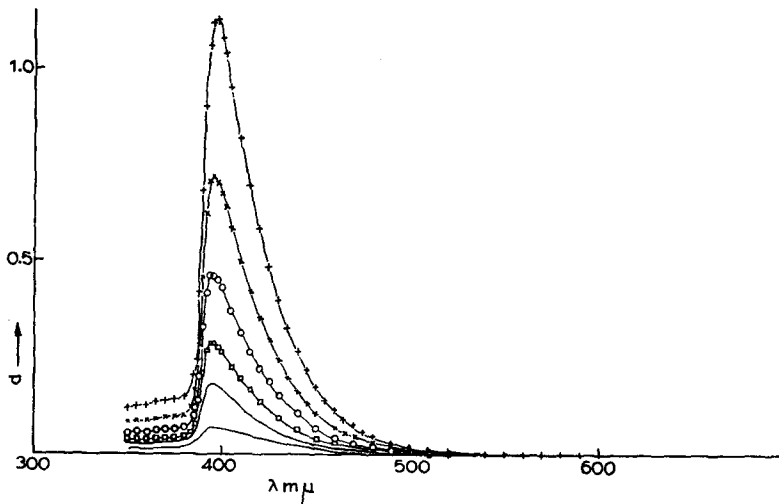
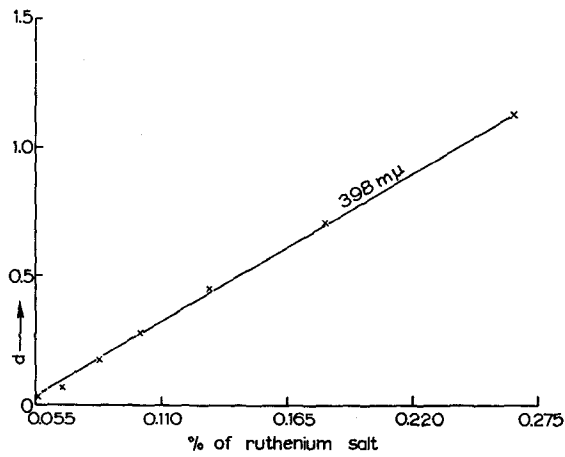


Fig. 7. Verification of Beer's law for the pure yellow $\text{Na}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})]$.

on Whatman No. 1 paper. In butanol-water there is a spot (R_F ca. 0.1) with a forward comet. In butanol-acetic acid-water (5:1:4) the product separates into an orange spot (R_F 0.21) and a yellow spot (R_F 0.28), but both are rather elongated with decomposition trails to the liquid front.

Acetone-water (4:1) and acetone-hydrochloric acid-water (90:5:5) yield two adjacent spots on the acetone front. We had the impression that decomposition occurred during partition chromatography, especially when the solvent is acid.

(4) Ion exchange chromatography

Good separations of the orange and the yellow compounds were obtained on Whatman DEAE (diethylaminoethyl-cellulose) paper using aqueous NaNO_2 as solvent. The yellow compound moved as a well defined round spot followed by the orange which had a tendency to streak. In 1 N NaNO_2 the yellow spot moved with an R_F of 0.51-0.53 and the orange with one of 0.27-0.32. Since ion exchange data can often be used for determining the charge on ions⁷, we compared the movement of the two compounds with that of ferrocyanide, ferricyanide and nitroprusside using NaNO_2 and NaCl of various concentrations as eluants.

TABLE I
 R_F VALUES OF SOME ANIONIC Fe AND Ru COMPLEXES ON WHATMAN DEAE PAPER

	Concentration of NaNO_2			
	0.1 N	0.25 N	0.5 N	1.0 N
Ferricyanide		0.13 (comet)	0.22 (comet)	0.43
Ferrocyanide		0.4	0.64	0.89
Nitroprusside		0.11	0.26	0.47
$[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})]$	0.05		0.33	0.51
Orange Ru complex	0		streak	0.27-0.32

	Concentration of NaCl		
	0.25 N	0.5 N	1.0 N
Ferricyanide	0.04	0.09	0.25
Ferrocyanide	0.16	0.57	0.85
Nitroprusside	0.09	0.21	0.37

As shown in Table I, the tetravalent ferrocyanide is less adsorbed than the trivalent ferricyanide and the divalent nitroprusside. It seems that such anions show too great a tendency for the formation of ion pairs to make a determination of the charge possible. The observations here recorded seem to be the first separations of such anions on DEAE paper or other modified cellulose paper, and the few results obtained indicate that such separations are of analytical interest.

CONCLUSION

In controlling the reaction between sodium or potassium nitrite and ruthenium salts by paper electrophoretic analysis, it was possible to show that the methods of JOLY AND VÈZES⁴ and JOLY AND LEIDIÉ⁵ yield a mixture of an orange and a yellow compound. The yellow one is obtained in a pure form if recrystallised twice from water. It is also possible to carry the reaction to completion by refluxing an excess of nitrite with ruthenium chloride or nitrate and controlling the time necessary by paper electrophoresis.

By comparison with analysed samples obtained from Dr. VENANZI it could be established that the spectrum and the electrophoretic mobility of our yellow compound is identical with that of $\text{Na}_2[\text{Ru}(\text{NO})(\text{NO}_2)_4(\text{OH})]$.

The orange by-product was found to be unstable in nitrite solution and is most likely a complex with some unconverted OH or Cl groups or perhaps a polymer linked by OH groups. A compound of this kind $\text{K}_8\text{Ru}_2\text{O}(\text{NO}_2)_{12}$ is mentioned by PASCAL⁶. It does not seem to be identical with the one isolated by us, since it is not orange but yellow, and is supposed to be formed with an excess of nitrite. Like the compound observed by us, it is destroyed by boiling with nitrite.

SUMMARY

The reaction between alkali nitrites and ruthenium salts was studied by means of paper electrophoresis. Conditions for obtaining a single electrophoretic species are described.

REFERENCES

- ¹ H. GÖTTE AND D. PÄTZE, *Z. Elektrochem.*, 58 (1954) 636; *Angew. Chem.*, 69 (1957) 608.
- ² J. M. FLETCHER, P. M. G. BROWN, E. R. GARDNER, C. J. HARDY, A. G. WAIN AND J. L. WOODHEAD, *J. Inorg. & Nuclear Chem.*, 12 (1959) 154; A. G. WAIN, P. M. G. BROWN AND J. M. FLETCHER, *Chem. & Ind. (London)*, (1957) 18.
- ³ B. B. MURRAY, *U. S. Atomic Energy Comm.*, DP-391 (1959); *C. A.*, 54 (1960) 5254e.
- ⁴ A. JOLY AND M. VÈZES, *Compt. rend.*, 109 (1889) 668.
- ⁵ A. JOLY AND E. LEIDIÉ, *Compt. rend.*, 118 (1894) 469.
- ⁶ P. PASCAL, *Nouveau traité de chimie minérale*, Vol. XIX, Masson & Cie, Paris, 1958, p. 123.
- ⁷ M. LEDERER AND A. S. KERTES, *Anal. Chim. Acta*, 15 (1956) 226.