

# Some Properties of Ruthenium (III) and (IV) in Acid Solution

## A REVIEW OF RECENT RESEARCH

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The solution chemistry of the lower oxidation states of ruthenium has attracted considerable attention in recent years from an applied viewpoint, but remains incompletely understood as far as basic considerations are concerned. Much of the contradictory information in the literature is a result of tendencies to oversimplify the exceedingly complex processes which ruthenium compounds can undergo in aqueous media. It is becoming more and more apparent that such phenomena as oxidation-reduction, polymerisation and complexation must be taken into account when dealing with ruthenium species in solution, even for seemingly simple overall processes.

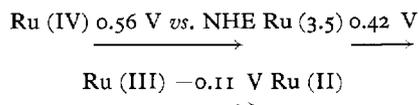
The older literature on ruthenium compounds is summarised by Mellor (1) and also by Sidgewick (2). The most recent general review in this field seems to be the excellent comprehensive summary of DeFord (3), who has given a critical discussion of the literature up to 1948. Much important work has been reported since 1948, however, because of the interest in ruthenium as a long-lived product of fission wastes.

### Reduction Potentials

Despite repeated efforts to establish reliable information on the oxidation-reduction potentials of the lower oxidation states of ruthenium, considerable confusion and ambiguity still exist in the literature on this aspect of ruthenium chemistry. According to DeFord (3), the lack of reproducible experimental data on oxidation-reduction potentials

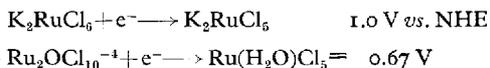
is due to the lack of rapid, reversible reactions suitable for this type of measurement.

Wehner and Hindman (4) have placed limits on the formal potential for the Ru (IV)-Ru (III) couple in perchloric acid solution with values ranging from 0.55 to 1.17 V *vs.* the normal hydrogen electrode (NHE) depending on whether zero-current potentials were approached by reduction or oxidation, respectively. It is likely, however, that equilibrium was not attained. More recently, Atwood (5) has given some potential values obtained in perchloric acid media by potentiometric titration of Ru (IV) with vanadium (II) sulphate:



The potential of the Ru (IV)-Ru (III) couple has also been evaluated polarographically as 0.65 V *vs.* NHE in 1M perchloric acid (6).

Pshenitsyn and Ezeiskaya (7) studied the chloro-complexes of Ru (III) and Ru (IV) and reported the following potentials:



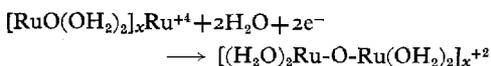
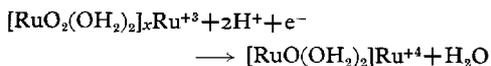
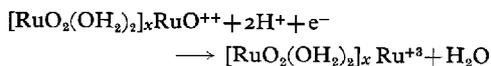
Backhouse and Dwyer (8) measured the Ru (IV)-Ru (III) potential in both hydrochloric and hydrobromic acids, finding depression of potentials with increasing halide and hydrogen ion concentrations. Their potential values, extrapolated to zero acid concentration, were 0.96 V in hydrochloric acid and 0.82 V in hydrobromic acid solutions

(presumably *vs.* NHE). The potential of the Ru (III)–Ru (II) couple in hydrochloric acid medium is given by Backhouse as 0.084 V and stated as being independent of acid concentration in the 1.5 to 6.8M range.

## Polarography

In 1945 Willis (9) found no published information on the polarography of ruthenium except for a paper dealing with the effect of ruthenium on catalytic hydrogen discharge waves (10). Willis was unable to obtain reduction waves for  $K_2RuCl_6$  or  $K_2RuCl_5$  in KCNS, KCN,  $NH_3-NH_4Cl$  or pyridine-HCl mixtures. Niedrach and Tevebaugh (6) investigated the polarography of Ru (IV) in perchloric acid media and reported three reduction waves at potentials of 0.57 to 0.65, 0.40 to 0.45, and  $-0.14$  to  $-0.10$  V *vs.* NHE respectively. The first two waves were thought to be due to the reduction of two different hydrolysis species of Ru (IV); the third wave due to the reduction of Ru (III) to Ru (II). Chloride ion was found in the polarographic solutions after electrolysis, an indication that perchlorate might have been reduced by the electrolysis products. Susic (11) also found three polarographic waves in perchloric acid solutions of mixtures of Ru (IV) and Ru (III), but concluded that these were actually catalytic hydrogen waves because both wave heights and half-wave potentials were pH dependent.

Recently, Atwood (5) restudied the polarography of Ru (IV) in perchloric acid. His potential values of 0.59, 0.39, and 0.11 V *vs.* NHE compare well with those of Niedrach and Tevebaugh (6). The polarographic waves were found to be pH dependent and rate controlled. The author proposes an intermediate average oxidation state of 3.5 to explain his polarographic and potentiometric data. Gortsema (12) showed that Ru (IV) in perchloric acid solution can exist as a  $RuO^{++}$  monomer or as polymers of the type  $[RuO_2(OH_2)_2]_xRuO^{++}$ . Atwood (5) used this information to propose half reactions for three observed reduction steps:



Polarographic studies of ruthenium in hydrochloric acid using a rotating platinum electrode have been carried out by Turk (13) who found variations in half-wave potentials from 0.55 to 0.48 V *vs.* NHE in 0.03 to 2.0 M acid. A similar study by Simpson (14) yielded only an ill-defined wave. Investigations of the polarographic behaviour of several ruthenium complexes containing chloride were reported by Pshenitsyn (7). This author prepared the compound  $K_2Ru(OH)Cl_5$  which was irreversibly reduced to  $RuCl_5(H_2O)^-$  at a stationary platinum electrode with a half-wave potential of about 0.66 V *vs.* NHE in a 2 M HCl–1M NaCl electrolyte. The fact that the limiting current obtained equalled only one-half of the expected current for a one electron process suggests that  $K_2Ru(OH)Cl_5$  exists in solution as a binuclear complex of the type  $Ru_2OCl_{10}^{-4}$ .

## Spectra and Solution Chemistry

Ruthenium (IV) chloro-complexes have been studied by Wehner and Hindman (16) who gave spectra for Ru (IV) in 10 M HCl with maxima at 460, 380 and 360 m $\mu$ . Mixed aquo, hydroxy and chloro-complexes of Ru (IV) in perchloric acid were also studied by these workers. Ru (IV) was prepared in perchloric acid by reduction of  $RuO_4$  at a potential of 1.10 V *vs.* NHE on a platinum electrode. Solutions of Ru (IV) in 1 M  $HClO_4$  showed no spectral evidence of decomposition after 120 days, but solutions in 6 and 9 M acid were found to be unstable. Gortsema and Cobble (17), however, suggest that Wehner and Hindman were not working with monomeric Ru (IV) species. Atwood (5) transformed polymeric Ru (IV) to monomeric species by ion exchange techniques and

attributed an absorption band at 300  $m\mu$  to the species  $RuO^{++}$  in perchloric acid solution. Spectra of Ru (IV) in 2 *M* HCl and 2*M*  $H_2SO_4$  solutions with maxima at 240, 380, 460, and 690  $m\mu$  and 238, 300, 420 to 480, and 610 to 640  $m\mu$ , respectively, have been reported by workers at the Argonne National Laboratory (13, 18).

Spectra of Ru (III) complexes in acid solution seem to depend on the source or method of preparation of Ru (III) as well as the nature and concentration of the solvent species. As a result, information concerning the nature and properties of Ru (III) in acid solution remains ambiguous and contradictory. Interpretation of available data is further complicated by possible polymer formation and oxidation-reduction processes. Jorgensen (19) produced Ru (III) by the oxidation of ruthenium metal to  $K_2RuO_4$ , reduction of this compound with ethanol to  $Ru(OH)_4$ , followed by further reduction with metallic silver in concentrated HCl. In 10 *M* HCl maxima were found at 307, 313, 349, 388, and 521  $m\mu$ , presumably due to  $RuCl_6^{\equiv}$ . A species presumed to be  $RuBr_6^{\equiv}$  was prepared in an analogous manner in 6 *M* HBr and yielded absorption maxima at 400, 485, and 655  $m\mu$ .

Fine (20) investigated the chloro-complexes of Ru (III) by ion-exchange methods and found predominantly cationic and neutral species in solutions less than 2 *M* in HCl and anionic complexes in more acid solutions. The author succeeded in determining equilibrium constants for the various mononuclear forms of Ru (III) present in hydrochloric acid solution. Evidence was presented for the existence of highly charged polymeric species which could not be eluted from the ion exchange resin.

A number of investigators have claimed that commercially available Ru (III) compounds contain Ru (IV). Halpern (21) reported that  $(NH_4)_2RuCl_5 \cdot H_2O$ ,  $RuCl_3 \cdot H_2O$  and  $(NH_4)_2RuCl_6$  all show the same absorption spectra when dissolved in hydrochloric acid. The resulting spectra correspond to

those obtained by Wehner and Hindman (4) for Ru (IV). The presence of Ru (IV) in these solutions was confirmed by titration with stannous chloride and measurement of hydrogen up-take. The spectra of the resulting reduced solutions agreed with those reported by Jorgensen (19) for Ru (III). Sawyer (22) reported that  $RuCl_3$  contains 85 per cent Ru (IV) as determined by the method of Crowell and Yost (23).

Connick and Fine (24) investigated the species  $Ru^{+3}$ ,  $RuCl^{+2}$ ,  $RuCl_2^+$  by ion exchange techniques and determined the charge per metal ion and charge per species for these three ions. These authors report absorption maxima for  $RuCl^{+2}$  and  $RuCl_2^+$  between 300 and 320  $m\mu$  and  $Ru^{+3}$  at 220  $m\mu$ . Two neutral species of the type  $RuCl_3$ , having absorption maxima at 320 and 290 (360)  $m\mu$  respectively, were also identified. Rehn and Wilson (25) carried out a similar study using trifluoroacetic acid as a non-complexing medium. While these authors agree with Connick and Fine in assigning formulae to the species present, the actual observed spectra show considerable differences.

## Analysis

Most of the volumetric methods for the determination of ruthenium depend on the reduction of Ru (IV) to Ru (III). Oxidation-reduction titrations involving ruthenium are complicated by uncertainties in the oxidation state of the final titration product. Reliable potential data are needed to clarify this problem. Ru (IV) may be titrated with stannous chloride (26) using visual or potentiometric end point detection. Alternately, an excess of iodide may be added and the liberated iodine titrated with thiosulphate. Ru (IV) can also be titrated potentiometrically under nitrogen with  $TiCl_3$  in dilute hydrochloric acid (27). The titration curve is reported to pass through an intermediate break requiring 0.5 equivalents of  $TiCl_3$ . A review of recent advances in oxidation-reduction methods for the determination of ruthenium has been given by MacDonald (41).

Many spectrophotometric methods for the determination of ruthenium with both inorganic and organic complexing agents have been reported. Most of these methods require a preliminary separation of ruthenium as  $\text{RuO}_4$ , a toxic material. Careful control of solution pH is usually required, and traces of nitrate or chloride may prevent colour formation.

Sandell (28) has evaluated several of the older methods.

Ruthenium can be determined spectrophotometrically using the yellow-green colour of  $\text{KRuO}_4$ , formed by distillation of  $\text{RuO}_4$  into  $\text{KOH}$  (4, 28, 29). The orange-red colour of  $\text{K}_2\text{RuO}_4$  has also been used as the basis for a colorimetric method (30, 31). The colour is measured at  $465 \text{ m}\mu$  and is reported to be stable for thirty minutes in  $2 \text{ M NaOH}$ .

Several investigators have used thiocyanate as a colorimetric reagent for ruthenium. In the method of Below (32), ruthenium is

### Spectrophotometric Methods for Determination of Ruthenium

Reagent	Remarks	Reference
1, 4-diphenylthiosemicarbazide	$\text{CHCl}_3$ extraction-colour time dependent .. ..	34
Anthranilic acid ..	pH 5.2 to 6.0, green colour	35
Acetyl acetone ..	$\text{CHCl}_3$ extraction — pH dependent; $505 \text{ m}\mu$ ..	36
2-nitroso-1-naphthol	$\text{HCl-SO}_2$ solvent .. ..	37
p-nitrosodimethylaniline	$\text{HAc-NaAc}$ buffer; $610 \text{ m}\mu$	38
Dithiooxamide ..	$\text{HCl-alcohol}$ ; $650 \text{ m}\mu$ ..	39
1, 10-phenanthroline	$\text{NH}_2\text{OH}$ solution; $448 \text{ m}\mu$ ..	40

oxidised to  $\text{RuO}_4$  with  $\text{AgO}$ , absorbed in  $\text{CCl}_4$  containing  $\text{SCN}^-$ , and determined as  $\text{Ru}(\text{SCN})^{++}$ , a red complex. Forsythe (33) investigated the nature of the complexes formed in this reaction and found evidence of anionic species. Ru (II) may also be present under these conditions.

Thiourea gives a blue colour with ruthenium compounds in hydrochloric acid, forming the basis of an analytical method studied by DeFord (3). Several other common spectrophotometric methods for the determination of ruthenium are outlined in the table.

### References

- 1 J. W. Mellor, *A Comprehensive Treatise on Inorganic and Theoretical Chemistry*, London: Longmans, Green & Co, 1937
- 2 N. V. Sidgwick, *The Chemical Elements and Their Compounds*, Oxford: Clarendon Press, 1950
- 3 D. D. DeFord, Ph.D. Thesis, University of Kansas, May 1948
- 4 P. Wehner and J. C. Hindman, *J. Amer. Chem. Soc.*, 1950, **72**, 3911
- 5 D. K. Atwood, Ph.D. Thesis, Purdue University, August 1960
- 6 L. W. Niedrach and A. D. Tevebaugh, *J. Amer. Chem. Soc.*, 1951, **73**, 2835
- 7 N. K. Pshenitsyn and N. A. Ezeiskaya, *Russ. J. Inor. Chem. (in trans.)*, March 1961, **3**, 510
- 8 J. R. Backhouse and F. P. Dwyer, *J. Proc. Royal Soc., N. S. Wales*, 1949, **83**, 134-137. *C. A.* 45:8389
- 9 J. B. Willis, *J. Amer. Chem. Soc.*, 1945, **67**, 547-550
- 10 P. Hcrasymenke and I. Slendyk, *Coll. Czech. Chem. Comm.*, 1936, **5**, 479-496
- 11 M. V. Susic, *Bull. Inst. Nuclear Sci.*, 1958, **8**, 53-57
- 12 F. Gortsema, Ph.D. Thesis, Purdue University, January 1960
- 13 E. Turk, Argonne National Laboratory Report No. 4292 (March 1949)
- 14 R. B. Simpson, R. L. Evans, H. A. Saroff, *J. Amer. Chem. Soc.*, 1955, **77**, 1438
- 15 N. K. Pshenitsyn, *Zhur. Anal. Chem.*, 1961, (2), 196-200
- 16 P. Wehner and J. C. Hindman, *J. Phys. Chem.*, 1952, **56**, 10
- 17 F. P. Gortsema and J. W. Cobble, *J. Amer. Chem. Soc.*, 1961, **83**, 4317
- 18 Argonne National Lab. Report No. 372, p. 49
- 19 C. K. Jorgensen, *Acta Chem. Scand.*, 1956, **10**, 518-534
- 20 D. A. Fine, Ph.D. Thesis, University of California (Berkeley), February 1960

- 21 J. F. Harrod, S. Ciccone and J. Halpern, *Can. J. Chem.*, 1961, **39**, 1372
- 22 D. Sawyer, R. George, J. Bagger, *J. Amer. Chem. Soc.*, 1959, **81**, 5893
- 23 W. R. Crowell, D. M. Yost, *J. Amer. Chem. Soc.*, 1928, **50**, 374
- 24 R. E. Connick, D. A. Fine, *J. Amer. Chem. Soc.*, 1961, **83**, 3414
- 25 I. M. Rehn, A. S. Wilson, private communication
- 26 J. L. Howe, *J. Amer. Chem. Soc.*, 1927, **49**, 2393
- 27 N. K. Pshenitsyn, *Iv. Sektora Platiny ION. Kh. Akad. Nauk U.S.S.R.*, 1955 (33), 20-30 [*Anal. Abstr.*, 1957, 2214]
- 28 E. B. Sandell, *Determination of Traces of Metals*, 3rd ed., New York, Interscience, 1959
- 29 F. E. Beamish, W. A. E. McBryde, *Anal. Chim. Acta.*, 1958, **18**, 551
- 30 E. D. Marshall, R. R. Rickard, *Anal. Chem.*, 1950, **22**, 79
- 31 R. Larsen, L. Ross, *Anal. Chem.*, 1959, **31**, 1768
- 32 W. L. Below, G. R. Wilson, L. T. Corbin, *Anal. Chem.*, 1961, **33**, 886
- 33 J. H. W. Forsythe, R. J. Magee and C. L. Wilson, *Talanta*, 1960, **3**, 324
- 34 T. Hara, E. B. Sandell, *Anal. Chim. Acta.*, 1960, **23**, 65
- 35 A. K. Majumdar, J. G. Sen Gupta, *Z. Anal. Chem.*, 1961, **178**, 401
- 36 A. Brandostetr, *Coll. Czech. Chem. Comm.*, 1961, **26**, 392
- 37 D. L. Manning, O. Menis, *Anal. Chem.*, 1962, **34**, 94
- 38 J. E. Curran, A. Fischel, *Anal. Chem.*, 1952, **24**, 1980
- 39 G. H. Ayers, F. Young, *Anal. Chem.*, 1950, **22**, 1281
- 40 C. V. Banks, J. M. O'Laughlin, *Anal. Chem.*, 1957, **29**, 1412
- 41 A. M. G. MacDonald, *Ind. Chem.*, 1959, **35**, 293

## Magnetic Transformations in Iron-Rhodium Alloys

### ANOMALOUS CHANGES AT MODERATE TEMPERATURES

The saturation intensity of ferromagnetic materials generally decreases slightly with heating until at temperatures approaching the Curie point a rapid decline occurs. A notable exception to this rule is afforded by alloys containing approximately equal numbers of iron and rhodium atoms which are non-magnetic at room temperature and become suddenly ferromagnetic when heated to 60°C. Above this temperature they respond as normal ferromagnetic materials, the Curie point being at 400°C. Hocart and Fallot (1, 2) who first reported this behaviour attributed it to a sudden ordering reaction. Recent X-ray (3) and neutron-diffraction (4) measurements have shown that the magnetic transformation is due to a rapid yet uniform expansion of the CsCl type ordered structure which exists above and below critical temperature. The state below this temperature is antiferromagnetic with the magnetic unit cell doubled in all directions (5, 6). In the ferromagnetic region above the characteristic temperature the magnetic and crystallographic unit cells coincide.

A field of 5 Koe is sufficient to saturate the 52 atomic per cent rhodium alloy which has a peak magnetic intensity at 77°C of 115 emu/gm. (7). Rhodium has in this region an appreciable magnetic moment, and it is probable that the magnetic moment of the iron atoms in this alloy is higher than in alpha iron (6). The temperature hysteresis asso-

ciated with the magnetic and electrical resistance changes of this alloy has been interpreted as evidence of a first order phase change (7). Complete confirmation of this hypothesis would require the demonstration of a crystallographically discrete phase.

The remarkable magnetic characteristics of the alloy are likely to be of considerable utility. Thermal switching is an obvious application, although more sophisticated devices will undoubtedly suggest themselves to the development engineer.

A. S. D.

### References

- 1 M. Fallot, *Ann. Phys.*, 1938, **10**, 291
- 2 M. Fallot and R. Hocart, *Rev. Sci.*, 1939, **77**, 498
- 3 F. de Bergevin and L. Muldower, *Compt. rend.*, 1961, **252**, 1347
- 4 F. de Bergevin and L. Muldower, *Bull. Amer. Phys. Soc.*, 1961, **6**, 159
- 5 E. F. Bertaut, A. Delapalme, F. Forrat, G. Roult, F. de Bergevin and R. Pauthenet, *Proceedings of International Conference on Magnetism and Crystallography*, 1961, vol. III. (*J. Phys. Soc. Japan*, 1962, **17**, Supplement B.III)
- 6 E. F. Bertaut, A. Delapalme, F. Forrat and G. Roult, F. de Bergevin and R. Pauthenet, *J. Applied Physics*, 1962, Supplement to Vol. 33, No. 3, 1123-1124
- 7 J. S. Kouvel and C. C. Hartelius, *J. Applied Physics*, 1962, Supplement to Vol. 33, No. 3, 1343-1344