584. *A Sexavalent Ruthenium Sulphate.*

By F. S. Martin.

The reduction of ruthenium tetroxide by various reducing agents in sulphuric acid has been studied. The primary reduction is thought to be from Ru(VIII) to Ru(IV) and it is shown that these two states disproportionate to form Ru(VI). Ru(VI) sulphate solutions decompose in a few hours at room temperature, probably by disproportionation to Ru(VIII) and Ru(IV). It is considered that the solution contains the complex $[RuO_2(SO_4)_2]^{--}$ rather than the ruthenyl ion RuO_2^{++}.

Sexavalent ruthenium is commonly met in the form of alkali-metal ruthenates, $M_2[RuO]_4$. These compounds are alkali stable, but unlike the analogous osmates, which yield osmyl compounds on treatment with dilute acids, the ruthenates are decomposed to salts of quadrivalent ruthenium. The ruthenyl salts are almost completely unknown and no simple salt of the type RuO_2X_2 has yet been isolated. Howe (*J. Amer. Chem. Soc.*, 1901, **23**, 775) treated dilute hydrochloric acid solutions containing rubidium or cæsium chloride with ruthenium tetroxide and obtained tetrachlororuthenates of the general formula $M_2[RuO_2Cl_4]$. Kraus (*Z. anorg. Chem.*, 1923, **132**, 301) obtained an ammino-derivative of sexavalent ruthenium by adding ammonia to cæsium or rubidium ruthenate. He formulated this as $RuO_2(OH)_2(NH_3)_2$ and thus it is to be regarded as a ruthenyl hydroxide derivative. The acid $H_2[RuO_2Cl_4]$ corresponding to Howe's tetrachlororuthenate was isolated by Aoyama (*ibid.*, 1924, **138**, 249) by passing hydrogen chloride and chlorine over anhydrous ruthenium tetroxide. Each of these compounds contains sexavalent ruthenium as the bivalent ruthenyl radical RuO_2^{++}. In the case of the tetrachlororuthenates, the reduction from the octavalent state is brought about by hydrogen chloride. The dihydroxydiammino-compound $RuO_2(OH)_2(NH_3)_2$ is derived from sexavalent ruthenium by a process involving no valency changes, *i.e.*,

$$M_2[RuO_4] + NH_4{\cdot}OH \longrightarrow \underset{\text{(possible intermediate)}}{(NH_4)_2[RuO_4]} \longrightarrow RuO_2(OH)_2(NH_3)_2.$$

Rémy and Lührs (*Ber.*, 1928, **61**, 917) observed that the reduction of Ru(VIII) by hydrogen chloride does not go to Ru(VI) in one step, but rather that the primary reduction is to Ru(IV) which reacts with excess of ruthenium tetroxide to form Ru(VI). More recently, Wehner and Hindman (*J. Amer. Chem. Soc.*, 1950, **72**, 3911) investigated the electrolytic reduction of Ru(VIII) in perchloric acid solution but found no evidence for the existence of a sexavalent state in this acid.

This paper describes the reduction of Ru(VIII) in dilute sulphuric acid solutions by means of sodium nitrite, sodium sulphite, ferrous sulphate, hydrazine, and hydroxylamine. It is shown that a sexavalent state of ruthenium is capable of existence in sulphuric acid solution. The presence of this valency state can only be due to the ruthenyl radical. Ruthenates are immediately unstable in acid solution, and in addition, the ruthenate ion has a pronounced orange colour in solution whereas the sexavalent ruthenium solution described here is green. Quadrivalent ruthenium sulphate solutions are intensely brown.

EXPERIMENTAL

Known amounts of reducing agent were added to an excess of ruthenium tetroxide dissolved in sulphuric acid. Reduction occurred immediately except in the case of hydrazine where there was frequently a variable induction period. The excess of ruthenium tetroxide was extracted from the solution by carbon tetrachloride, and analysis for ruthenium then gave directly the quantity of Ru(VIII) which had been reduced.

Results are presented in the table. The consumption of reducing agent per mole of Ru(VIII) is clearly dependent on the relative excess of Ru(VIII). With a ruthenium tetroxide concentration greater than about six-fold the amount of reducing agent, the consumption of the latter is 2 equiv. per ruthenium atom, the product evidently being Ru(VI). With smaller relative amounts of Ru(VIII), reduction involves the consumption of more than 2 equiv. per ruthenium atom, the maximum consumption of reducing agent being 4 equiv. The product is then Ru(IV), and for the intermediate cases must be a mixture of Ru(IV) and Ru(VI). The colour of the Ru(VI) solution is green, and that of Ru(IV) the familiar dark brown. The colour of the mixed solutions is intermediate.

Consumption of reducing agent per mole of RuO_4 *in sulphuric acid solution.*

Micro-moles of reducing agent	Micro-moles of RuO_4 reduced	Equiv. of reducing agent per mole of RuO_4	Original excess of RuO_4 (approx.)	Colour of product	Valency of Ru in product
$NaNO_2$					
13·4	13·6	2·0	6-fold	Green	6
13·4	13·1	2·0	5 ,,	Green	6
67·0	48·5	2·8	4 ,,	Green-brown	Mixed 4 and 6
67·0	39·8	3·4	3 ,,	,,	,, ,,
67·0	38·8	3·5	2 ,,	,,	,, ,,
67·0	36·8	3·7	1 ,,	,,	,, ,,
Na_2SO_3					
15·4	15·4	2·0	7-fold	Green	6
15·4	14·8	2·1	5 ,,	Green	Mainly 6
15·4	12·6	2·5	4 ,,	Green-brown	Mixed 4 and 6
58·0	30·6	3·9	<1 ,,	Green-brown	,, ,,
58·0	29·0	4·0	nil	Brown	4
N_2H_4,H_2SO_4					
22·2	33·0	2·7	4-fold	Green-brown	Mixed 4 and 6
22·2	28·7	3·1	3 ,,	,,	,, ,,
44·3	51·2	3·5	2 ,,	,,	,, ,,
$2NH_2{\cdot}OH,H_2SO_4$					
8·1	16·2	2·0	8-fold	Green	6
8·1	13·5	2·4	4 ,,	Green-brown	Mixed 4 and 6
8·1	13·0	2·5	3·5-fold	,,	,, ,,
$FeSO_4$					
9·4	4·8	2·0	8-fold	Green	6
9·4	4·6	2·0	6 ,,	Green	6

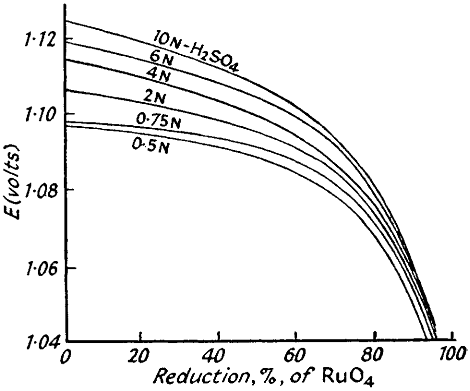
The valency of 6 for the ruthenium in the green solution was verified [after extraction of unchanged Ru(VIII) by carbon tetrachloride] by Crowell and Yost's method (*J. Amer. Chem. Soc.*, 1928, **50**, 374) in which the ruthenium is reduced to the $+3$ state by iodide ion, and the liberated iodine estimated volumetrically.

The potentiometric titration of Ru(VIII) in dilute sulphuric acid with any of the reducing agents cited above, by using a bright platinum electrode and saturated calomel reference electrode, merely showed steps in the titration curves corresponding to the consumption of 4 equiv. of reducing agent per mole of Ru(VIII). No steps were observed corresponding to the reduction to Ru(VI), although the green colour of this valency state was observed in the earlier parts of the titration.

The redox potential of the system when titrated with ferrous ion was dependent on the sulphuric acid concentration. The figure shows that the dependence is roughly of the order associated with hydrogen-ion consumption in reductions of the type $RuO_4 + 8H^+ + 4e^- \longrightarrow Ru^{4+} + 4H_2O$ and $RuO_2^{++} + 4H^+ + 2e^- \longrightarrow Ru^{4+} + 2H_2O$, where the value of the redox potential is given approximately by

$$E_{\mathrm{Ru(VIII)/Ru(IV)}} = E_{0\mathrm{Ru(VIII)/Ru(IV)}} - \frac{\boldsymbol{RT}}{\boldsymbol{4F}} \ln \frac{[\mathrm{Ru}^{4+}]}{[\mathrm{RuO_4}][\mathrm{H}^+]^8}$$

At the points on the curves corresponding to 50% reduction, the solution contains a mixture of Ru(VIII), Ru(VI), and Ru(IV), and the observed potential at these points may therefore be due to both the Ru(VIII)/Ru(IV) and the Ru(VI)/Ru(IV) couple. Since no step is observed in the potential curves corresponding to the reduction of Ru(VIII) to Ru(VI), and also since both Ru(VI) and Ru(IV) may be present in the partially reduced solution, the primary reduction may possibly be directly to Ru(IV), with subsequent formation of Ru(VI) by interaction with excess of Ru(VIII). That this interaction is possible was confirmed by taking freshly reduced Ru(IV) solution in dilute sulphuric acid and adding to it an excess of Ru(VIII). The green colour of Ru(VI) developed immediately, and after removal of excess of Ru(VIII), the sexavalency was confirmed by Crowell and Yost's method (*loc. cit.*). Solutions of Ru(IV) more than a few hours old, or solutions which have been heated, do not lead to the formation of Ru(VI) on addition of the tetroxide. The quadrivalent ruthenium ion is not stable in the simple form in solution, and its failure to disproportionate with Ru(VIII) when not freshly prepared is probably connected with the formation of either a more stable hydrolysis product, or a sulphate complex on storage, or possibly even oxygen-bridge formation.



Dependence of redox potential of Ru(VIII) *system on* H_2SO_4 *concentration.* [Ru(VIII)] = 10^{-2}M.

Ru(VI) solutions in dilute sulphuric acid decompose to Ru(IV) in a few hours at room temperature, even when excess of Ru(VIII) is present. Since it is formed by reproportionation of Ru(IV) and Ru(VIII), it would be reasonable to expect it to decompose by disproportionation to these two states. The presence of Ru(VIII) was not unambiguously shown in the decomposition products, but its transient concentration would be sufficiently low for a large amount of reduction to occur on glass surfaces or adventitious dust particles. Higher concentrations cannot be used to obviate this, since the maximum concentration of ruthenium tetroxide in dilute sulphuric acid is of the order of 2%, and as shown in the table, it is not possible to prepare from this a solution of Ru(VI) of greater concentration than about one-sixth of 2%, corresponding approximately to 2×10^{-2}M. However, if the disproportionation occurs according to $2Ru(VI) \longrightarrow RuO_4 + Ru(IV)$, then the iodine-liberating power from iodide ion should be the same for both products and reactant, and the iodine titre of the mixture should not vary with time except in so far as Ru(VIII) is decomposed by surface reactions as mentioned above. On the other hand, the possible alternative method of decomposition is $RuO_2^{++} + 2H^+ \longrightarrow Ru^{4+} + H_2O + \frac{1}{2}O_2$, and the iodine titre in this case should fall to one-third of its initial value when decomposition is complete. In practice, the iodine titre–time curves were not reproducible, but decreases of not more than 10% were observed in the titres, and this clearly obviates the alternative mode of decomposition. Additional evidence in favour of decomposition by disproportionation is obtained from the study of the potential at a platinum electrode in a solution of Ru(VI) in sulphuric acid. A saturated calomel reference electrode being used, the potentials for freshly prepared Ru(VI) solutions were of the order of 0·8 v, rising steadily for a period of about 15 minutes to a maximum value of the order of 1·0—1·1 v. As may be seen from the figure, this latter value is that associated with a solution containing both Ru(VIII) and Ru(IV) as well as Ru(VI), and it is concluded that the presence of Ru(VIII) and Ru(IV) has arisen by disproportionation of Ru(VI).

(a) *Preparation of Reagents.*—Ruthenium tetroxide was prepared by fusing ruthenium sponge or ruthenium trichloride with potassium nitrate and potassium hydroxide. If the sponge was used the melt containing potassium ruthenate was dissolved in water and acidified with sulphuric acid, and sufficient periodic acid was added to oxidise the ruthenate to Ru(VIII). In the case of the trichloride, the melt was dissolved, and hydrated Ru(IV) oxide precipitated by addition of methanol. The precipitate was filtered off, washed, dried, and re-fused. The second melt was then treated as for the sponge. After addition of the periodic acid, the ruthenium tetroxide was distilled off in a current of air with gentle heating, and was condensed into ice-cold dilute sulphuric acid. The tetroxide was redistilled from this solution and was collected as the yellow solid (m. p. 25°) on an ice-cold surface. The solid was allowed to melt and was dissolved in dilute reagent-grade sulphuric acid.

Solutions of sodium nitrite, sodium sulphite, ferrous ammonium sulphate, hydrazine sulphate, and hydroxylamine sulphate were prepared from pure or A.R. reagents and were standardised by the customary methods.

(b) *Analysis.*—The determination of ruthenium was carried out according to Marshall and Rickard's absorptiometric method (U.S.A.E.C. unclassified document number AECU 224) in which an aliquot of solution containing ruthenium is evaporated and the residue fused with potassium nitrate and potassium hydroxide. The melt is dissolved to a known volume in 2N-potassium hydroxide, and the orange ruthenate colour is measured by the absorbancy at 465 mμ. In the present case the determination was carried out by " Spekker " absorptiometer.

(c) *Confirmation of Valency.*—Crowell and Yost (*loc. cit.*) have shown that higher ruthenium valencies are reduced to the +3 state by potassium iodide. Aliquots of the ruthenium solution in 2N-sulphuric acid were treated with *ca.* 1 g. of potassium iodide, and the liberated iodine titrated with sodium thiosulphate, carbon tetrachloride being used as " indicator."

(d) *Reduction of* RuO_4 *in Dilute Sulphuric Acid.*—Aliquots of RuO_4–sulphuric acid were pipetted into 15-ml. conical centrifuge tubes held in an ice-bath. Aliquots of reducing solution were added (the tip of the pipette being below the surface of the solution for $NaNO_2$ and Na_2SO_3 solutions) and the contents were stirred for a few seconds. Reaction was immediate except in the case of hydrazine, when there was often an induction period of several minutes. An approximately equal volume of carbon tetrachloride was added, and the two phases mixed by stirring. After being allowed to settle, the organic phase was removed, and the process was repeated twice more. The partition coefficient of ruthenium tetroxide between carbon tetrachloride and water is 59 (unpublished results) in favour of the organic phase and therefore three equal-volume washes reduce the tetroxide concentration to negligible proportions. After removal of the last droplets of solvent by centrifuging the tubes for a few minutes, aliquots of solution were withdrawn for ruthenium analysis.

DISCUSSION

Since the formation of Ru(VI) in sulphuric acid solution may occur by reproportionation of Ru(VIII) and Ru(IV), it is logical to expect the decomposition of Ru(VI) by disproportionation and the equilibrium $2Ru(VI) \rightleftharpoons Ru(VIII) + Ru(IV)$ to be set up. Approximate values may be obtained from the table and substituted in the expression $[Ru(VIII)][Ru(IV)]/[Ru(VI)]^2$ and a set of evaluations lying mainly between 20 and 80 is obtained. Hence, if this expression represents the equilibrium constant for the disproportionation reaction, disproportionation should be 20—80 times as rapid as reproportionation. Since reproportionation has been shown to be immediate [where freshly prepared Ru(IV) is concerned], the solution of Ru(VI) when separated from Ru(VIII) should immediately disproportionate to the extent of approximately 90%. In fact the disproportionation to this extent takes at least 1—2 hours. It is evident then that $2RuO_2^{++} \rightleftharpoons RuO_4 + Ru^{4+}$ does not represent the true approach to equilibrium, and not only must complex species of Ru(IV) be taken into account, but also of Ru(VI). It would be expected that the Ru(VI) would not exist as the simple or hydrated RuO_2^{++} ion in sulphuric acid solution, but more probably as $[RuO_2(SO_4)_2]^{--}$ (cf. the tetrachlororuthenates). Transference experiments, however, failed to reveal the presence of anionic Ru(VI) in solution, but it is believed that this may be due to the rapid decomposition of Ru(VI) on passing into a region of zero Ru(VI) concentration, *i.e.*, into the anode or cathode compartments of the transference cell. Evidence in favour of this belief was obtained when diluting Ru(VI) solutions for spectrophotometric examination. On dilution to a ruthenium concentration of approximately 10^{-4}M and maintaining the sulphuric acid concentration at 2N, decomposition of Ru(VI) to Ru(IV) was complete in 30 minutes as compared with periods of more than 2 hours at concentrations of 10^{-2}M. The decomposition was too rapid at the lower concentrations to enable spectrophotometric data to be obtained.

Conclusions.—It has been shown that solutions of sexavalent ruthenium involving the ruthenyl radical RuO_2^{++} may be prepared in sulphuric acid solutions by reduction of ruthenium tetroxide. The ruthenyl compound may be formed by way of reproportionation of Ru(VIII) and Ru(IV) and it probably decomposes by the corresponding disproportionation reaction. Qualitative observation of the rates of reproportionation and disproportionation indicates that it is unlikely that the simple or hydrated RuO_2^{++} ion exists in solution.

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