The point that a change in solvent from H_2O to CH_3OH causes a considerable change (four-fold decrease) in rate, but yet no effect on the rate is admitted arising out of altering the solvent water by compressing it to a molar volume of 15 ml., requires some comment. It can be argued that because the solvent in the neighborhood of an ion of high charge is already highly compressed, no large change in the solvent in this region is effected by increasing the pressure. Change from one solvent to another does, however, alter the immediate environment of the cation. Thus, the change in rate caused by changing solvent does not appear to be incompatible with the assumption that the pure solvent effect caused by increase in pressure does not give rise to a large change in rate.

In a number of substitution reactions, it has been observed that the rate of aquation or hydrolysis increases as the acidity decreases. The marked decline in rate of exchange for ROH_2^{+++} as alkali is added, therefore, seems surprising at first sight. Closer examination of the system shows that the result is not inconsistent with the observations on other complexes. A specific rate ratio of 10^3 to 10^5 has been estimated[16] for the replacement of X in $(NH_3)_4CoNH_2X^+$ as compared to $(NH_3)_5CoX^{++}$, and a similar ratio can be assumed for $(NH_3)_4CoNH_2OH_2^{++}$ as compared to $(NH_3)_5CoOH_2^{+++}$. However, in a solution in which $(NH_3)_5CoOH^{++}$ is the dominant form, only a small fraction is present as $(NH_3)_4CoNH_2OH_2^{++}$, this fraction being determined by the relative acidities of coördinated H_2O as compared to coördinated NH_3. The fraction in question may be as small as 10^{-7}; therefore, the specific rate of exchange when $(NH_3)_5CoOH^{++}$ is dominant is expected to be 10^{-4} to 10^{-2} times that for $(NH_3)_5CoOH_2^{+++}$. Experimentally, it is found that this ratio is no greater than 2×10^{-2}.

Acknowledgments.—We wish to express our gratitude to Professor A. W. Lawson for placing the high pressure equipment at our disposal; to the office of Naval Research for financial support (Contract N6ori-20) and to Allied Chemical and Dye Corporation and E. I. du Pont de Nemours and Company for providing fellowship awards for H.R.H.

[16] R. G. Pearson and F. Basolo, THIS JOURNAL, **78**, 4878 (1956).

CHICAGO 37, ILLINOIS

[CONTRIBUTION FROM RADIATION LABORATORY AND DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA, BERKELEY]

The Determination of the Formulas of Aqueous Ruthenium(III) Species by Means of Ion-exchange Resin: Ru^{+3}, $RuCl^{+2}$ and $RuCl_2^+$

BY HOWARD H. CADY AND ROBERT E. CONNICK

RECEIVED OCTOBER 7, 1957

The formulas of some aqueous ruthenium(III) species have been determined by a method which utilizes the properties of ion-exchange resins. The method is applicable when equilibria between the species of interest and other species of significant concentration are established slowly, and when the species of interest can be isolated in solution, as for example certain complex ions. In one experiment the charge per metal atom is found from the equivalents of charge exchanged with an ion-exchange resin per gram atom of the metal. In a second experiment the total charge per species is determined from the concentration dependence of the ion-exchange equilibrium of the unknown species with an ion of known charge. The total charge divided by the charge per atom gives the degree of polymerization of the species. The stoichiometric formula can be inferred when a single anion is involved in complexing. The method has been employed to establish the formulas of the species Ru^{+3} and $RuCl^{+2}$. A species shown to have a total charge of +1 is probably $RuCl_2^+$. The separation of the ruthenium species was accomplished by "pushing" with cerous ion a dilute mixture of species on an ion-exchange column, with the result that nearly pure bands of the individual species were obtained at high concentration.

Little is known regarding the formulas of aqueous ruthenium species in the +2, +3 and +4 oxidation states.[1,2] Preparations customarily yield mixtures of species corresponding to different complexes and varying degrees of polymerization, as well as mixtures of oxidation states. Because equilibria between the species are established slowly it is impractical in most cases to use equilibrium measurements to establish the formulas. Colligative determinations are not employed because of the difficulty of preparing pure species.

It was desirable to have as general a method as possible for the identification of ruthenium species. One has been developed which makes use of ion-exchange measurements.[3] Two experiments are performed. First, the charge on the species per ruthenium atom, a, is found. Second, the total charge per species, b, is measured. The ratio b/a equals the number of ruthenium atoms per species. If the oxidation number of the ruthenium is known, the number of negative charges contributed to the species by anions can be inferred. If only one anion is involved, the complete formula of the species is determined. The method has been used to identify Ru^{+3} and $RuCl^{+2}$. A chloride complex of the +3 oxidation state with b equal to +1 was detected and it is presumed to be $RuCl_2^+$.

Determination of Charge per Metal Atom.—The method is based on the fixed exchange capacity of the resin, measured in equivalents of charge. The charge per metal atom, a, is equal

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[1] (a) The older literature is summarized in Gmelin's Handbuch der anorganischen Chemie, System No. 63, 8th Edition, Verlag Chemie, Berlin, 1938; (b) more recently D. D. Deford has critically reviewed the literature in his doctoral thesis at the University of Kansas (May, 1948), which has been reproduced by the United States Atomic Energy Commission as an unclassified document, NP-1104, Nov. 30, 1949.

[2] Recent work is to be found in: (a) P. Wehner and J. C. Hindman, THIS JOURNAL, **72**, 3911 (1950); (b) P. Wehner and J. C. Hindman, *J. Phys. Chem.*, **56**, 10 (1952); (c) L. W. Niedrach and A. D. Tevebaugh, THIS JOURNAL, **73**, 2835 (1951); (d) J. R. Backhouse and F. P. Dwyer, *Proc. Roy. Soc. New South Wales*, **83**, 138 (1949); **83**, 146 (1949).

[3] R. E. Connick and H. H. Cady, THIS JOURNAL, **79**, 4242 (1957).

to the equivalents of charge displaced from the resin divided by the gram atoms of metal atom taken up by the resin, when ion exchange occurs.

For the ruthenium experiments it was convenient to use a column method[4] rather than a batch exchange, because, in addition to the determination of a, the ruthenium species could be separated and concentrated. The procedure was to place the ruthenium at the top of a cation-exchange column and elute with a cerous perchlorate solution containing some perchloric acid. The cerous ion is held sufficiently strongly to the resin to displace essentially completely hydrogen ion and the ruthenium species of interest. As the ruthenium species are displaced they separate into bands with the least easily held species at the head. These bands consist of essentially pure ruthenium species which occupy nearly all of the exchange sites within each band. As each band emerges from the column a number of samples are taken for analysis of ruthenium and free hydrogen ion. The value of a is given by the expression

$$a = \frac{(\mathrm{H}^+)_\mathrm{i} + 3(\mathrm{Ce}^{+3})_\mathrm{i} - (\mathrm{H}^+)_\mathrm{f}}{(\mathrm{Ru})_\mathrm{f}} \qquad (1)$$

where parentheses are used to indicate concentration in moles per liter of solution, i and f designate the elutriant and eluate, respectively, and the ruthenium concentration in the eluate is in gram atoms per liter.

In the above treatment it is assumed that the unknown cation has the same charge when on the resin as in solution. If changes in complexing occur during the exchange process, the value of a cannot be calculated from equation 1.

Changes in hydrolysis on exchange constitute a special case for which it can be shown that equation 1 holds. By way of example, assume that the following exchange involving the metal cation M^{+3} and hydrogen ion occurs

$$\mathrm{M}^{+3} + \overline{2\mathrm{H}^+} + \mathrm{H_2O} = \overline{\mathrm{MOH}^{+2}} + 3\mathrm{H}^+ \qquad (2)$$

where the bar over a formula designates the resin phase. It is seen that the number of hydrogen ions appearing in the solution corresponds to the charge on M in the solution. It is simple to show that this result is generally true, even when other reference cations in addition to hydrogen ion are involved in the reaction. Any cation which has changed its degree of hydrolysis on entering the resin will occupy one less exchange site per OH^- group added. Consequently, it displaces from the resin one less equivalent of charge per OH^- group. Simultaneously it has produced in the aqueous phase one more hydrogen ion per OH^- group added, in the act of hydrolysis. Therefore the equivalents of positive charge released in solution correspond to the case of no change in hydrolysis and equation 1 applies. Equation 1 gives always the charge per atom on the species in the aqueous phase, regardless of hydrolysis.

Should there be a change in the complexing (other than hydrolysis) of the unknown cations in the exchange process, equation 1 will not yield the correct value of a. In principle it would be possible to measure the aqueous concentration of the anion forming the complex, thereby giving the data necessary for a correct calculation of a, but in practice this would be difficult experimentally. In the case of the ruthenium species in the +3 oxidation state studied here, it is believed that there is little likelihood that such a change in complexing (other than hydrolysis)[5] could occur during an experiment, because it is known that these complexes form and break up only slowly.

When changes in complexing of the unknown cation do occur, one obtains from equation 1 the charge per metal atom of the species in the resin, if the anion in the aqueous phase does not combine with hydrogen ion. This may be seen from the following type reaction where X^- is a complexing anion

$$\mathrm{MX}^{+2} + \overline{3\mathrm{H}^+} = \overline{\mathrm{M}^{+3}} + 3\mathrm{H}^+ + \mathrm{X}^- \qquad (3)$$

If the acid HX is dissociated in the aqueous phase, as shown in the equation, the equivalents of positive charge displaced by M are equal to the charge on M in the resin phase. Equation 1 then yields a for the species in the resin. When HX is undissociated in the aqueous phase, equation 1 yields a for the species in the aqueous phase because only the free hydrogen ion concentration is to be used in (1). Hydrolysis is an example of such a case.

When the reference cation (*e.g.*, Ce^{+3}) undergoes hydrolysis or other forms of complexing, equation 1 will yield a for the aqueous species if the coefficient multiplying the concentration of the reference ion in equation 1 corresponds to the number of exchange sites occupied by the reference ion in the resin phase, regardless of the complexing in the aqueous phase. In this case $(\mathrm{H}^+)_\mathrm{i}$ should be the stoichiometric hydrogen ion concentration calculated assuming the degree of hydrolysis found for the reference ion in the resin phase.

Changes in degree of polymerization can affect the a values of equation 1 only when changes in complexing (other than hydrolysis) occur simultaneously.

Determination of Charge per Species.—The charge per species is determined from the dependence of the equilibrium distribution of the unknown ion on the concentration of the known exchangeable ion in the resin and aqueous phases. Consider for example the reaction

$$\mathrm{M}^{+b} + \overline{b\mathrm{H}^+} = \overline{\mathrm{M}^{+b}} + b\mathrm{H}^+ \qquad (4)$$

$$Q = \frac{\overline{(\mathrm{M}^{+b})}(\mathrm{H}^+)^b}{(\mathrm{M}^{+b})(\overline{\mathrm{H}^+})^b} = K\,\frac{\gamma_{\mathrm{M}^{+b}}\gamma^b_{\overline{\mathrm{H}^+}}}{\gamma_{\overline{\mathrm{M}^{+b}}}\gamma^b_{\mathrm{H}^+}} \qquad (5)$$

where Q is the equilibrium quotient expressed in concentrations, K is the equilibrium constant, and γ signifies an activity coefficient. It is seen that the distribution of M, given by $\overline{(\mathrm{M}^{+b})}/(\mathrm{M}^{+b})$ varies as the b power of the hydrogen ion distribution, $(\overline{\mathrm{H}^+})/(\mathrm{H}^+)$. Equilibration at two different hydrogen ion concentrations and substitution

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[4] Analogous to the method used by D. A. Everest and J. E. Salmon for determining the charge per metal atom in pentagermanate ion. *J. Chem. Soc.*, 1444 (1955).

[5] Hydrolysis can occur rapidly since only a proton has to be moved off the oxygen of a water molecule attached to the ruthenium. Changes in complexing, other than hydrolysis, require the replacement of atoms in the first coördination sphere of the ruthenium, which is a relatively slow process.

into equation 5 permits the simultaneous solution for the two unknowns b and Q, if their values are the same for the two experiments. Actually Q will vary because of activity coefficient changes, as shown on the right of equation 5. In practice this variation was minimized in two ways. First, the mole fractions of ruthenium and hydrogen ion in the resin were kept at very nearly the same absolute value in the two experiments so that the activity coefficients in the resin phase would not change appreciably. This was done by keeping the ruthenium mole fraction in the resin very small. There is an additional effect on activity coefficients in the resin caused by the change in activity of water in the aqueous phase, but at the concentrations of perchloric acid employed (<1.0 M) these effects should be small.

Secondly, the concentration of perchloric acid in the aqueous phase was kept in the region of 0.2 to 1.0 M. Aqueous activity coefficients generally are not varying rapidly in this region. It is hoped that this procedure minimized aqueous activity coefficient changes, although it is recognized that they would not be eliminated. The saving feature of the method is that for a single species b should be an integer and a multiple of a. Therefore a highly precise value of b is not necessary for the determination of the charge per species.

In making the measurements, the concentrations in the aqueous phase were determined experimentally and those in the resin phase obtained by difference. To achieve maximum accuracy the fraction of the total ruthenium in the resin phase was made much larger than that in the aqueous phase.

Although the concentrations of ruthenium are known only in terms of gram atoms, only the ratio appears in equation 5, and this ratio is equal to the molar concentration ratio. To calculate the hydrogen remaining on the resin it is necessary to know a. In practice an accurate value is not necessary as long as the mole fraction of ruthenium on the resin is kept small.

In principle any reference ion could be used in equation 4. In practice the accuracy of the determination of b is greatest with singly charged reference ions and falls off badly with higher charges.

Changes in complexing of the unknown metal ion between the aqueous and resin phases invalidate equation 5. Again hydrolysis is a special case where the correct answer is obtained, as may be seen from equation 2. The equilibrium expression for equation 2 is identical with that of equation 4 except that the hydrogen ion concentration on the resin appears to a different power, depending on the hydrolysis. Since the experiments were performed with practically constant concentration of hydrogen ion in the resin, the power of $\overline{(H^+)}$ is not important.

Changes in complexing of the unknown ion between the two phases will result in values of b corresponding to neither the resin nor aqueous phase. Assuming only one type of anion to be present and $\overline{(H^+)}$ to be constant, it can be deduced from equation 3 that the value of b obtained by the use of equation 5 will equal the actual value of b in the aqueous phase plus twice the anionic charge lost by the unknown ion in passing from the aqueous to the resin phase. Intermediate cases of complexing will give intermediate values of b.

Experimental

Apparatus.—All absorption spectra were measured on either a Cary Recording Spectrophotometer Model 11, Serial 4, or a Beckman Model DU Spectrophotometer using quartz cells. A Beckman Model G *p*H meter was employed to determine the hydrogen ion concentration in solutions where direct titration was not possible.

Solutions.—The water used in all experiments was either normal distilled water or conductivity water prepared by redistillation of distilled water from alkaline permanganate solution. In neither case could evidence of chloride ion be obtained by addition of silver nitrate. The perchloric acid solutions were prepared from G. F. Smith doubly vacuum distilled perchloric acid.

Cerous perchlorate was prepared from recrystallized G. F. Smith primary standard ammonium hexanitrato cerate. This ceric salt was dissolved in dilute hydrochloric acid solution and boiled until the ceric was reduced to cerous chloride and there were no ammonium or nitrate ions remaining in solution. The resulting solution was fumed with perchloric acid to remove the chloride ion as HCl. Traces of ceric ion were removed by reaction with hydrogen peroxide.

Chromic and cupric solutions were prepared by dissolving the nitrate salts.

The source of hydrogen peroxide was a 30% solution with no preservatives added. The sodium periodate was $Na_3H_2IO_6$ from the Fisher Scientific Company, and the ammonium persulfate (peroxydisulfate) was J. T. Baker Analyzed reagent.

Stock solutions of ruthenium tetroxide were prepared from ruthenium chloride by fuming the chloride with sulfuric acid, after which the ruthenium was oxidized to RuO_4 by permanganate and the RuO_4 distilled over into a solution of dilute perchloric acid.

The ruthenium tetroxide was added slowly to a cold, rapidly stirred solution of stannous ion in perchloric acid to prepare solutions containing Ru^{+3}. This technique prevented excessive formation of Ru(IV). Satisfactory reaction occurred when the stannous ion was between 0.01 and 0.1 M, the RuO_4 was about 3×10^{-3} M, and the perchloric acid was about 0.1 M. The RuO_4 solution could be added until the preparation just began to show signs of Ru(IV) formation although an excess (10 to 50%) of stannous was usually maintained to eliminate Ru(IV) and to stabilize the Ru(III) with respect to oxidation by perchloric acid or oxygen. The stock solution of Ru(III) was oxidized by $HClO_4$ within a day unless stored in a refrigerator at about 0°. Under these conditions it would last as long as one week.

To prepare the chlorides $RuCl^{++}$ and $RuCl_2^+$, hydrochloric acid was added to the stannous solution before the reduction reaction so that the solution was about 0.05 M in HCl after the reduction.

Analysis.—The ruthenium concentration in acidic solutions was determined by oxidation of the ruthenium to RuO_4 with sodium periodate or ammonium persulfate, followed by spectrophotometric analysis for the ruthenium.[2a,6] Sodium periodate oxidation was used unless there was an undesirable side reaction involving iodate or periodate. The molar absorptivities ϵ used for these analyses were ϵ_{385} 930 and ϵ_{310} 2960,[7] where the wave length in millimicrons is indicated by the subscript.

A qualitative test for the presence of Ru(IV) in a Ru(III) solution was based on the reduction of the higher oxidation states of ruthenium to Ru(III) by iodide ion.[8,9,2a] Sodium iodide was added to the ruthenium solution which was about 1 M in hydrogen ion. After about twenty seconds a solution of colloidal starch was added. Evidence of iodine in this

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(6) J. L. Swanson and A. S. Wilson, Hanford Atomic Works Quarterly Report of the Chemistry Unit, HW-29619, Nov. 16, 1953 (classified report).

(7) R. E. Connick and C. R. Hurley, THIS JOURNAL, **74**, 5012 (1952).

(8) W. R. Crowell and D. M. Yost, *ibid.*, **50**, 374 (1928).

(9) O. Ruff and E. Vidic, *Z. anorg. allgem. Chem.*, **136**, 49 (1924).

solution was considered to indicate the presence of Ru(IV) in the initial ruthenium solution.

The cerous solutions were standardized by oxidation to ceric by peroxydisulfate and titration with standard ferrous solution. Chromic ion was standardized by peroxydisulfate oxidation to dichromate and analysis either by titration with standard ferrous solution, or spectrophotometric measurement as chromate ion. The molar extinction coefficient used for chromate ion was 4.88×10^3 at 373 mμ.

Cupric nitrate solutions were standardized by the iodide and thiosulfate method.

Ion-exchange Resin.—The ion-exchange resins were obtained from the Bio-Rad Laboratories as analytical grade resin. These resins had been processed from Dowex-50W and Dowex-1 ion-exchange resins. The resins used were Dowex-50W × 8, Dowex-50W × 12 and Dowex-1 × 10 in 200 to 400-mesh particle size. No evidence for the presence of iron or aluminum in these resins was noticed, although they were not analyzed spectroscopically.

The capacities of the ion-exchange resins were determined by titration of the air-dried, hydrogen ion form of the resin with standard sodium hydroxide. These results as well as other physical properties of the particular batches used are given in Table I.

TABLE I

PHYSICAL CONSTANTS OF AIR-DRIED DOWEX-50 ION-EXCHANGE RESIN IN THE HYDROGEN ION FORM

	Dowex-50W × 12 200 to 400 mesh	Dowex-50W × 8 200 to 400 mesh
Capacity (equiv./kg.)	3.52	3.86
Grams resin per ml. column vol.	0.555	..
Void vol. per ml. of column vol.	0.472	..
Density of resin (g. per cc.)	1.18	..

Procedure for Determination of Charge per Atom, *a*.—The stock solution containing the Ru(III) species and all other products of the stannous reduction reaction was stirred with enough ion-exchange resin to fill almost a column. It was found to be necessary to stir the resin–ruthenium solution for several hours in order to get most of the ruthenium into the resin phase. The reason for this slowness is unknown but is perhaps associated with the presence of the tin in the solution. Subsequent equilibrations were rapid. After stirring, the resin was separated from the solution and placed in the column over an amount of the resin in the hydrogen ion form that corresponded to about 5% of the resin stirred. The column was tapered so that the pure hydrogen ion form occupied *ca.* one-fourth of the column height.

A solution of known hydrogen ion and cerous ion concentration was then used to elute the ruthenium from the resin. Cerous ion was held so strongly by the Dowex-50W ion-exchange resin that it quantitatively displaced the Ru(III) cations, which formed in bands ahead of the cerous front in the column. Samples were collected as the ruthenium bands were pushed out of the column. The ultraviolet spectra of these samples were measured on a Cary recording spectrophotometer, and a sample was considered to contain a pure species when the spectra of the two adjacent samples were identical with that of a given sample. The ruthenium samples were collected at 0° and maintained at that temperature until the acidity of the solutions and the ruthenium concentration could be determined. Unless the samples were kept cold they tended to oxidize.

The hydrogen ion concentration of the cerous perchlorate solution was determined by direct titration. That of the eluted ruthenium solutions was read from a *p*H meter which had been set according to the acidified cerous solution used in the elution.

There were two techniques that helped in the separation of pure species. The first was to vibrate the ion-exchange column during the elution. This kept the resin tightly packed and prevented serious channeling. The second was to taper the column so that it was larger at the top than at the bottom. This permitted the addition to the column of a large amount of the species to be separated and retained the advantage of a narrow column at the bottom where the bands occupied a large vertical distance as they were emerging from the column.

The validity of the method was checked by determining the charge per chromium atom in a solution of chromic nitrate. Instead of using a column elution, the chromic nitrate solution was equilibrated with a sample of Dowex-50 × 12, 200–400 mesh, in the cupric ion form by stirring and the resulting solution analyzed for chromium(III) and cupric ion. The results are shown in Table II. In the calculations it was assumed that cupric was a +2 ion. The value of 3.07 for chromic ion agrees well with the expected value of 3.00.

TABLE II

CHARGE PER CHROMIC ION IN SOLUTION

Initial soln. (*M*)		Final soln. (*M*)		Charge per chromium atom, calcd.
Cr^{+3}	Cu^{+2}	Cr^{+3}	Cu^{+2}	
0.1045	0.000	0.027	0.116	3.07

Procedure for Determination of Charge per Species, *b*.—A solution of the pure species dissolved in perchloric acid was obtained from the charge per atom determinations. After dilution with perchloric acid this solution was equilibrated with cation-exchange resin in the hydrogen ion form by stirring in a beaker for at least six hours at approximately 0°. Following removal of a sample for analysis, water was added to lower the acidity and the equilibration was repeated. Analysis was made for the gram atoms of ruthenium per liter of the initial solution and the solutions from the two equilibrations.

The concentrations of ruthenium in the aqueous phase were known by direct analysis and those in the resin were obtained by difference, knowing the weight of resin taken for the experiment. The aqueous hydrogen ion concentration was much greater than that of the ruthenium and known from the preparation of the initial solution. The hydrogen ion concentration in the resin was approximately equal to the capacity of the resin (Table I); a small correction for the hydrogen ion displaced by ruthenium was applied using the *a* value from the charge per atom determination.

The method was tested by determining the charge on chromic ion in a chromic nitrate solution. The results are presented in Table IV with the ruthenium data.

Results and Discussion

Charge per Atom.—The experimental results are given in Table III. The numbers in the first column indicate the experiment and the sample number in the given experiment. Dowex 50W × 8, 200–400 mesh, was used. The absence of tin and cerous ions was shown by qualitative analysis. The iodide test indicated that all of the ruthenium was in the +3 oxidation state.

TABLE III

CHARGE PER RUTHENIUM(III) ATOM IN SOLUTION

Experiment	Elutriant compn. (*M*)		Eluent soln. compn. (*M*)		Charge per Ru atom
	Ce^{+3}	H^+	H^+	Ru	
			Species Ru^{+3}		
1-5	0.0420	0.040	0.040	0.0436	2.89
1-6	.0420	.040	.040	.0448	2.81
2-2	.0672	.113	.120	.0664	2.92
2-4	.0672	.113	.120	.0670	2.90
2-6	.0672	.113	.120	.0666	2.91
			Species $RuCl^{++}$		
3-2	0.0420	0.106	0.143	0.0430	2.08
3-3	.0420	.106	.141	.0484	1.89
3-4	.0420	.106	.135	.0480	2.04
3-5	.0420	.106	.135	.0486	2.01
3-6	.0420	.106	.145	.0480	1.84

In the calculation of the charge per atom it was assumed that cerious ion neutralized three exchange sites on the resin. Mr. James Finholt of this Laboratory has shown this to be true at the concentrations employed here, although less than three sites are neutralized at higher aqueous cerous perchlorate concentrations.

The results in the last column of Table III are consistent with a charge of +3 per ruthenium for the first species and +2 for the second. All results probably lie within the experimental uncertainty of these values, although the presence of small amounts of other species is not excluded by the accuracy of the measurements.

Charge per Species.—The results are given in Table IV where each pair of experiments constitutes a determination. Dowex-50W × 8, 200–400 mesh, was used in all but the first experiment where Dowex-50W × 12, 200–400 mesh, was substituted. The first column gives the total milligram-atoms of ruthenium present during the equilibration. The second column is the aqueous concentration of hydrogen ion before equilibration. In the third, fourth and fifth columns are listed the aqueous phase volume, the weight of resin (air-dried, hydrogen ion form) in grams, and the total capacity of the resin in milliequivalents, respectively. The sixth column contains the aqueous ruthenium concentration after equilibration. In the last column is the calculated value of the charge per species, *b*.

TABLE IV

CHARGE PER SPECIES DETERMINATIONS

Total Ru(III) (mg. atoms)	Initial (H^+) (*M*)	*V* (ml.)	*W* (g.)	Capacity of resin (mequiv.)	(Ru(III)) (g.atoms/l.)	Calcd. *b*
			Species Ru^{+3}			
0.0131	1.035	14.5	0.1738	0.611	2.68×10^{-4}	2.7
.0116	0.517	18	.1738	.611	4.91×10^{-5}	
.0201	1.010	15	.2256	.868	4.14×10^{-4}	2.8
.0180	0.5065	20	.2256	.868	7.42×10^{-5}	
			Species $RuCl^{+2}$			
0.0121	0.705	14.2	0.2275	0.875	6.47×10^{-4}	1.7
.00885	.235	27.2	0.2275	0.875	1.63×10^{-4}	
.0242	.750	20	3.124	12.0	4.35×10^{-4}	
.0242	.375	40	3.124	12.0	1.56×10^{-4}	1.7
			Species Cr^{+3}		Cr^{+3}	
0.540	1.00	60	3.403	11.9[a]	1.695×10^{-3}	
0.523	0.50	100	3.403	11.9[a]	2.62×10^{-4}	2.96

[a] Different batch of resin from that in Table I; capacity 3.20 mequiv. per gram.

The values of *b* for the ruthenium species lie fairly close to +3 and +2. Since they must be multiples of the *a* values for the same species it is clear that these are the correct values. Presumably the deviations reflect not only experimental inaccuracies but also appreciable activity coefficient changes in the aqueous phase, as discussed earlier.

The formula of the Ru(III) species with +3 charge is fixed unambiguously as Ru^{+3} by the *a* and *b* determinations. The Ru(III) species with +2 charge must contain one ruthenium in the +3 oxidation state and a singly charged anion. The only anions present were ClO_4^-, OH^- and Cl^-. Since ClO_4^- and OH^- showed no tendency to complex Ru(III) under similar conditions in the absence of chloride ion, it is concluded that the +2 species is a chloride complex, $RuCl^{++}$.

$RuCl_2^+$ (?).—In the charge per atom determinations with ruthenium(III) chloride species, at least one positively charged species which was held by the resin less strongly than $RuCl^{++}$ could be detected. Because this species was eluted readily with even 0.1 *M* acid, it was impossible to concentrate it into a pure band on a column. Consequently, the charge per atom determination could not be made.

The charge per species was measured using a column technique, rather than the batch method previously described. A ruthenium(III) solution containing chloride and prepared as described earlier, was passed into the top of an ion exchange column containing Dowex-50W × 8, 200–400 mesh, until the eluent appeared to have reached constant optical absorption at the wave lengths where the species being investigated absorbed most strongly. As little solution as possible was used in order that more strongly held ruthenium species would not have an opportunity to migrate far down the column. At this time the resin in the lower part of the column presumably contained only hydrogen ion and the unknown species, uniformly distributed. Next a dilute solution of hydrogen ion was passed through the column sufficient first to sweep out the void space and then to give two samples containing the unknown species. This procedure removed neutral or negatively charged species from the void spaces and gave two samples of the unknown species equilibrated with hydrogen ion. Following the dilute acid, hydrogen ion of a higher concentration was passed through the column to yield two more samples of the unknown species equilibrated with the resin at this higher hydrogen ion concentration.

In the above elutions the composition of the resin toward the bottom of the column should remain constant because the build up of the concentration of the unknown species in the perchloric acid to its equilibrium concentration occurs high in the column. Therefore equation 5 reduces to

$$Q\frac{\overline{(H^+)^b}}{\overline{(M^{+b})}} = \frac{(H^+)^{b_1}}{(M^{+b})_1} = \frac{(H^+)^{b_2}}{(M^{+b})_2}$$

where the subscripts refer to the samples with low and high acid.

The experimental results are shown in Table V. The results indicate a charge of +1 on the ruthenium(III) species. The simplest possible formula is $RuCl_2^+$, although such species as $Ru_2Cl_5^+$ are not excluded.

TABLE V

CHARGE PER SPECIES—$RuCl_2^+$ (?)

Elutriant	Ruthenium in eluent	Charge per species
0.0500 *M* $HClO_4$	2.48×10^{-4} *M* Ru(III)	0.92
0.200 *M* $HClO_4$	8.87×10^{-4} *M* Ru(III)	

Spectra.—The most convenient means of detecting aqueous ruthenium species is by their optical absorption spectra. The molar absorptivities of of the three species studied are plotted in Fig. 1 as a function of wave length. The curve for Ru^{+3} was for a solution eluted from a column with 0.5 *M* perchloric acid; elution with lower acid concentrations resulted in a somewhat higher absorption above 270 mμ, possibly because of a small amount of oxidation to the +4 state. An elution with cerous ion and 0.006 *M* perchloric acid yielded no Ru^{+3} from the column, apparently because of oxidation.

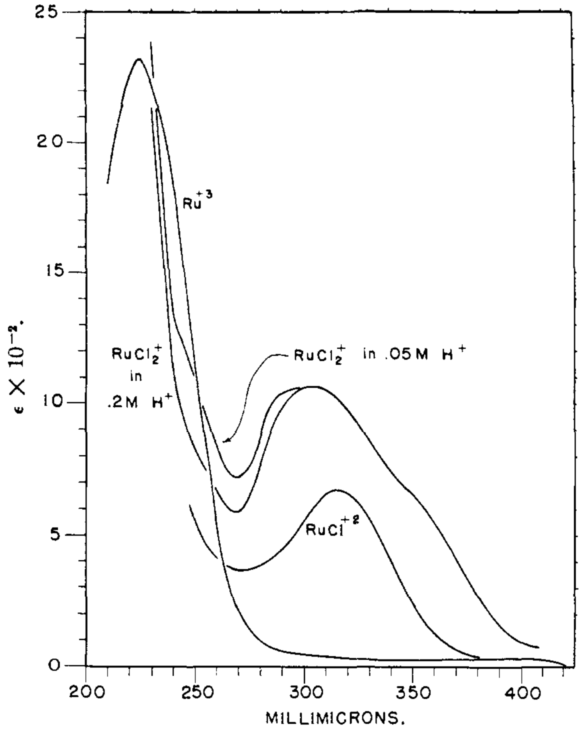

Fig. 1.—Spectra of Ru^{+3}, $RuCl^{++}$ and $RuCl_2^+$ in perchloric acid.

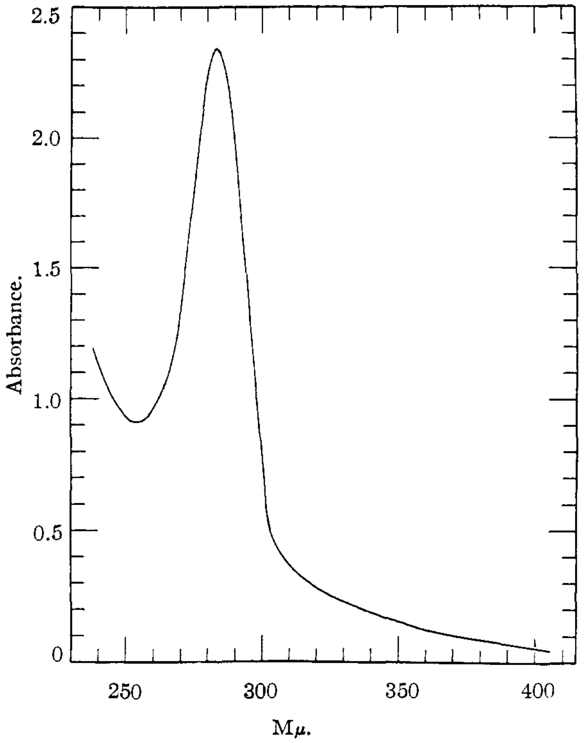

Fig. 2.—Absorbance of neutral species in dilute hydrochloric acid.

The spectra of the two $RuCl_2^+$ (?) samples at 0.05 and 0.2 *M* perchloric acid did not agree perfectly below 300 mμ. This discrepancy may arise from the presence of a small and variable amount of some other species. It might also be due to changes in the relative amounts of the two possible isomers of $RuCl_2^+$. Partial hydrolysis of $RuCl_2^+$ does not seem a likely explanation in the absence of evidence of hydrolysis of Ru^{+3} (Tables III and IV).

Other Species.—In the charge per atom determinations bands of several other species were observed visually but no identifications were attempted. In the experiments on Ru^{+3} at low acidity a species with an absorption maximum at 288 mμ followed the Ru^{+3} off the column. Other species, which might have been Ru(IV), were held too tightly to be eluted.

In the experiments on $RuCl^{++}$ there was a minimum of six additional cationic species being pushed as separate bands in addition to the $RuCl_2^+$ which was not pushed, but eluted. Some of these species may have contained Ru(IV). Additional species were not moved at appreciable rates by the cerous ions.

Separation of a neutral ruthenium chloride species was attempted using cation and anion resins. A solution 0.02 *M* in commercial ruthenium chloride and containing 0.3 *M* HCl was refluxed over mercury for 40 hours. A portion of the solution, which contained no detectable Ru(IV) species, was run through a cation column in the hydrogen ion form. The first fraction collected was then passed through an anion column in the chloride form. The spectrum of the final solution is shown in Fig. 2. The absorption is reported in terms of absorbance rather than molar absorptivity because of uncertainty in the ruthenium analysis.

Comparison with Previous Work.—There appears to be no previous work where the formulas of uncomplexed ruthenium(III) or chloride complexed ruthenium(III) species have been unambiguously identified. The many qualitative observations of colors reported in the literature are of little value when such solutions contain mixtures of several species.

Wehner and Hindman[2a] prepared Ru(III) in perchloric acid by electrolytic reduction of Ru(IV). The absorption spectrum was entirely different from that shown for Ru^{+3} in Fig. 1 and varied with time, although no oxidation had taken place and no chloride test was obtained with silver nitrate. Except below 250 mμ the molar absorptivity was higher than for Ru^{+3} and a maximum was observed in the neighborhood of 300 mμ.

Grube and Fromm[10] reported the preparation of $RuCl_3 \cdot H_2O$ which when freshly dissolved in water showed no ionic chlorine. They concluded that on standing or heating one chlorine became ionized. Their data, however, do not support such a simple stoichiometry and it seems likely that their solutions contained mixtures of species.

Rehn and Wilson[11] have attempted the separation of Ru(III) chloride complexes by means of a cation-exchange column, using the method which

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(10) G. Grube and G. Fromm, *Z. Elektrochem.*, **46**, 661 (1940).

(11) I. M. Rehn and A. S. Wilson, "Ruthenium(III) Chloride Complexes in Trifluoroacetic Acid," Hanford Atomic Works, Richland, Washington. Presented at the Northwest Regional Meeting of the American Chemical Society, June 11, 1955. We are indebted to Dr. Wilson for a copy of the talk.

King and Dismukes[12] applied to the separation of the chromic thiocyanate complexes. A 10^{-2} M solution of $K_2RuCl_5 \cdot H_2O$ in 1.00 M trifluoroacetic acid was equilibrated by heating at 64°, diluted twofold, and passed onto an ion-exchange column of Dowex-50 in the hydrogen ion form. On the basis of the ease of elution with acid they tentatively assigned formulas to three species: Ru^{+3}, $RuCl^{+2}$ and $RuCl_2^+$. Comparison with the present results may be made by means of the molar absorptivities. The spectrum of the species which they postulated to be Ru^{+3} resembles that of Ru^{+3} in Fig. 1 much more closely than it does Wehner and Hindman's Ru(III). In the wave length range covered (260 to 420 mμ) their molar absorptivities lie higher than ours by as much as a factor of three but approach ours at the two extreme wave lengths. The maximum percentage deviation occurs near 300 mμ.

Rehn and Wilson's molar absorptivities for their $RuCl^{+2}$ lie above ours at all wave lengths but approach ours closely around 340 mμ. They found a maximum at 308 mμ with a molar absorptivity of 804 compared to 315 mμ and 677, respectively, for our curve. At 260 mμ their curve was twofold higher than ours. Their curve for $RuCl_2^+$ agrees well with ours for the 0.05 M $HClO_4$ solution except that theirs shows no shoulder around 350 mμ. The spectrum which they assigned to $RuCl_3$ or $RuCl_4^-$ does not at all agree with that of the neutral species in Fig. 2.

Application of the Method to Other Systems.—The present method should be useful in establishing formulas of species in other systems. It is necessary that the species not change appreciably during the course of the measurements, except for hydrolysis. Undoubtedly the necessary experiments could be performed much more rapidly than was the case in the present work, but highly labile systems cannot be studied by this method. Anions can be studied using anion-exchange resins, as shown by preliminary measurements. Everest and Salmon[4] have already determined the charge per atom in pentagermanate ion.

The reliability of the charge per species determination for large and highly charged ions has not yet been established. As long as the variation in activity coefficients in the aqueous phase on dilution is not too great the method should be satisfactory. It should be interesting to investigate the behavior of such species as polymolybdates.

This research was supported by the United States Atomic Energy Commission.

BERKELEY, CALIFORNIA

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(12) E. L. King and E. B. Dismukes, THIS JOURNAL, **74**, 1674 (1952).

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, TEXAS SOUTHERN UNIVERSITY]

Interaction of Osmium with 1,2,3-Benzotriazole[1]

BY RAY F. WILSON AND LAWRENCE J. BAYE

RECEIVED NOVEMBER 15, 1957

Methods for the synthesis of some 1,2,3-benzotriazole coördination compounds of certain metals and of certain halides of osmium in high yield and in high purity are reported.

During the course of this study on the interaction of 1,2,3-benzotriazole with osmium, we have had occasion to prepare several 1,2,3-benzotriazole coördination compounds of osmium. In previous papers, the interaction of palladium with 1,2,3-benzotriazole has been reported.[2]

It was the purpose of this investigation to ascertain the possibility of obtaining reproducible and accurate stoichiometric results in the interaction of osmium with 1,2,3-benzotriazole.

Experimental

Materials.—The osmium stock solution was prepared by dissolving 5.0054 g. of osmium tetroxide, obtained from A. D. Mackey, Inc., in 250 ml. of 0.1 M sodium hydroxide and diluting the resulting solution to 1 liter with distilled water.

A 1.5% stock solution of 1,2,3-benzotriazole was prepared by dissolving recrystallized reagent in distilled water.

Absolute alcohol was used to reduce the tetroxide of osmium presumably to the plus 3 oxidation state; allylalcohol also may be used for the same purpose.

All other materials were reagent grade chemicals. All precipitates were filtered using medium or fine porosity, sintered-glass crucibles.

Analyses.—The osmium content in the compounds reported was determined using an inert hydrogen atmosphere according to modifications of the Gilchrist–Wichers procedure.[3] Carbon, nitrogen, hydrogen, halogen and other metals were determined using conventional methods of analyses. It was observed in the determination of carbon and hydrogen contents in osmium coördination compounds that these compounds had to be mixed first with potassium chlorate and combusted at a temperature of about 1000° instead of the usual 700°.

Preparation of $Na_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]$.—To an erlenmeyer flask which contained 5 ml. of ethyl alcohol were added 20 ml. of stock osmium tetroxide solution. The color of the system changed to a faint pink over a period of 30 seconds. This color change is apparently characteristic of some lower oxidation state of osmium or of the osmite ion. To the pink solution was added 10 ml. of 1.5% 1,2,3-benzotriazole solution and the color changed from faint pink to a deep red. The mixture was digested for about 2 hours and then upon setting for 2 hours, the red crystals were salted out using excess sodium nitrate crystals. A faint red color always is left in the flask after such a separation. The crystals, in fine porosity, sintered-glass crucibles, were washed free of sodium nitrate and 1,2,3-benzotriazole with several portions of a hot water–ethyl alcohol mixture. The precipitates were dried in an oven at 105° for three hours to constant weight. Because of the apparent non-quantitative results of the precipitation method, gravimetric precision and accuracy were not studied for this compound. *Anal.* Calcd. for $Na_3[OsO_3(C_6H_4NHN_2)_4(H_2O)_2]$: C, 35.16; H, 2.95; N, 20.51; Na, 8.41; Os, 23.20. Found: C, 35.01; H, 2.95; N, 20.32; Na, 8.30; Os, 23.23. The above de-

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(1) This work was supported by a grant from The Robert A. Welch Foundation.

(2) R. F. Wilson and L. E. Wilson, THIS JOURNAL, **77**, 6204 (1955); **78**, 2370 (1956); *Anal. Chem.*, **28**, 93 (1956).

(3) W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffmann, "Applied Inorganic Analysis," John Wiley and Sons, Inc., New York, N. Y., 1953, pp. 338-383.