CATALYTIC EFFECT OF RUTHENIUM COMPOUNDS ON THE REDUCTION OF PERCHLORIC ACID BY HYDROBROMIC ACID

Thesis

by

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CATALYTIC EFFECT OF RUTHENIUM COMPOUNDS ON THE REDUCTION OF PERCHLORIC ACID BY HYDROBROMIC ACID.

Purpose. The purpose of the present investigation has been to determine the nature of the catalytic effect shown by ruthenium compounds on the reduction of perchloric acid by hydrobromic acid; and, if possible, to determine the mechanism of the reaction.

Underlying theory. The reaction just mentioned is a good case of homogenious catalysis, and offers possibilities of discovering more about both the oxidizing power of perchloric acid and the chemistry of ruthenium. In fairly dilute solution, perchloric acid is extraordinarily stable, even when hot. A few metallic ions, (Ti^{+++}, Cr^{++}, Mo^{+++}) besides ruthenium ion, are the only substances that have a reducing effect on it in cold dilute solution. It is known to oxidize ruthenium compounds to the tetroxide in hot, fairly concentrated solution(1); the fact of catalysis indicates a possibity of this in dilute solution as well. Investigation therefore seems of value as offering information on the nature of oxidation by perchloric acid, as well as the relative stabilty of different compounds of ruthenium towards oxidizing and

1) System of Qualitative Analysis now in preparation by Dr. A. A. Noyes and Dr. W. C. Bray.

reducing agents.

Previous work on the problem. Mr. R. H. Dalton of this laboratory, while working on the complete system of qualitative analysis now in preparation by Dr. A. A. Noyes discovered the catalytic action of ruthenium salts. At one point in the procedure for the preparation of the solution for analysis, hydrobromic acid is removed by adding perchloric acid and boiling. Mr. Dalton noticed that with a sample containing ruthenium, free bromine was given off on boiling; and a repetition confirmed this fact. Dr. Noyes suggested a more complete investigation of the fact as a research problem which I have undertaken.

Discussion

The reaction between perchloric and hydrobromic acids: $HClO_4 + 8HBr = HCl + 4H_2O + 4Br_2$ (1) must go to completion in a thermodynamic sense; no reversal is possible. However, blank experiments showed that no reaction took place even with 3N perchloric acid and small amounts of hydrobromic acid on boiling the solution. On the addition of very small quantities of ruthenium tri-chloride or tri-bromide, bromine immediately began to be produced. Since ruthenium shows every valence from one to eight, (the pentavalent oxide has recently been shown to exist)(2) it appears that it may here act as a carrier catlyst, being alternately oxidized and reduced.

It is evident that much might be learned by an investigation of the rate at which reaction (1) proceeds, and of the effect of changes in concentration that the e reacting substances and the catalyst have on the rate. Also, since the ruthenium is presumably oxidized during the course of the reaction, an investigation of the action of perchlric acid on ruthenium salts, and of the effect of bromide ion and free bromine on them, should also be of great interest.

Experimental Methods

For measuring the rates, it is most convenient to determine the bromine produced in a definite time. Preliminary work showed that the rate was easily measurable at 100 degrees, using moderately dilute concentrations. In the method first used, the solution containing the reacting substances was placed in a glass-stoppered distilling flask provided with a gas inlet tube leading to the bottom of the flask. The bromine produced could then be swept out with a stream of carbon dioxide and led into a solution of potassium iodide, in which the iodine liberatd could be detrmined with a thiosulphate solution. By changing the receiving vessel containing the iodide a t regular intervals, the rate could be followed.

2) H. Remy, Z. anorg. chem. 126 185-92 (1923)

The reaction falsk was immersed in a steam bath; the carbon dioxide before entering was led through a simlar flask containg hydrobromic acid at the same concentration as that used in the reaction. This was done to prevent evaporation and loss of hydrobromic acid and water.

This arrangement proved very unsatisfactory, however, as evaporation and loss of hydrobromic acid and water with the subsequent changes in concentration could not be avoided. This and other disadvantages led to the adoption of another method for following the rates.

A method offering few disadvantages found. The reaction solution was made up at room temperature, by measuring definite volumes of the reacting substances into a volumtric flask by means of precision pipettes. The total volume was then made up to 100 ml, thoroughly mixed, and small portion removed into test tubes, which were then sealed off and placed in a water bath at 100 degrees. Tubes were removed after varying lengths of time, cooled to room temperature and broken under iodide solution. The Iodine was then titrated against thiosulphate. The size of the samples could be adjusted to suit the time of reaction, 20 ml being convenient for samples heated for less than half an hour, and 5ml for samples heated for longer periods.

An exactly similar method was used for following the rection between perchloric acid and ruthenium chloride.

Preparation of Solutions

Ruthenium. Ruthenium tri-bromide was prepared by converting a weighed quantity of the tri-chloride into hydroxide and dissolving in hydrobromic acid. The solution was made up to be 8.710 N in acid andto contain 2.50 mgm of ruthenium perml.

Later ruthenium tri-chloride solution was made up by dissolving a weighed quantity of the anhydrous solid in 50.00 ml of water and adding 5.00 ml of 6N hydrochloric acid. This solution contained 8.88 mgm of ruthenium per ml , and was slightly over 0.5N in acid. The acid was found necessary to prevent hydrolysis.

A solution made up by Mr. Dalton was also used for several experiments. It contained 10.00 mgm of ruthenium per ml, but the acid content was unknown. It was probably nearly the same as in my solution.

Perchloric Acid. The 60% C.P. acid was diluted to about 3N and titrated against sodium hydaoxide solution. It gave no test for free chlorine nor chloride ion.

Hydrobromic Acid. The C.P. acid of sp. gr. 1.49 was used. It was also titrated against hydroxide solution. The color was almost water white; only very inapprciable amounts of bromine.

Potassium tribromide. A solution made up by Mr. Yost was analyzed for bromide ion with silver nitrate, and for free bromine with thiosulphate, after the addition of potassium iodide.

Iodine and Thiosulphate. Tenth normal solution were made up and compared with each other. The iodine was then standardized against arsenious oxide.

Other chemicals used. The othr chemicals used were potassium iodide, bromine and carbon tetrachloride. C.P. materials were used throughout.

Experimental Data on the Rate Experiments.

Results of the rate experiments are given below. The results for one experiment using the flask method are given, not so much for the information of the rate, but as an example of a reaction the has gone to completion. In the first column is given the total time elapsed, and in the second, the volume of thiosulphate solution required for the titration of the iodine liberated by the bromine formed during the interval preceding.

Series A. Experiment 2.

Volume 12.56 ml Ru as $RuCl_3$ 28.5 mgm 0.28 milli-mol

HBr 7.90 N $HClO_4$ 0.251 N

15 min	8.80 ml	135min	13.60ml	255min	4.44ml
30	13.29	150	8.57	270	4.43
45	24.65	165	18.81	285	6.50
60	15.73	180	8.76	300	2.56
75	16.18	195	10.17	315	1.56
90	16.50	210	8.20	330	1.21
105	17.90	225	55.3		
120	16.35	240	4.16		

Experiment 2 continued

Total thiosulphate used 211.43 ml Br_2 evolved 24.2 milli-equivalents.

Oxidizing equivalents of $HClO_4$ in solution 25.2

Equivalents Br per mole of Ru $\overset{860.}{865.}$

This experiment shows the enormous catalytic effect of the ruthenium, and also the fact that the reaction will proceed to completion if the bromine is removed as it is formed. The other experiments of this series are not worth much in a quantitative way, as the errors from evaporation losses and changes in concentration are very large. The only conclusion that could be drawn was that the rate varied probably as the concentrations of Ru and ClO

In table I are given the results of the rate experiments by the second method as well as several blank experiments. In the first column the time of heating in the water bath is given, in the second the bromine evolved for a 100 ml sample, in milli-equivalents.

Table I

Experimental Data of the Reaction Rate Experiments.

Exp. I

$HClO_4$ o.1562 N HBr 0.936 N $RuBr_3$ 0.00132 M

15 min	0.458 milli-eq.	60 min	0.940 milli-eq.
30	0.505	75	I.03
45	0.825	90	1.I4

Table I

Exp. 2

$HClO_4$ 0.2905 N. HBr 0.871 N.
$RuBr_3$ 0.00123 M

15 min	0.505milli-eq
30	1.10
45	1.32
60	1.56
75	1.79
90	2.04
120	2.46
150	2.84
24 hr.	5.68

Exp.3

$HClO_4$ 0.7362 N, HBr 0.871 N
$RuBr_3$ 0.00123 M

15 min	1.25 milli-eq
30	2.28
45	3.12
60	3.96
75	4.86
90	5.32
120	6.24
150	7.33
24 hr.	15.19

Exp. 4

$HClO_4$ 0.2905 N. HBr 0.871 N.
$RuBr_3$ 0.00246 M

15	0.929
30	1.53
45	2.08
60	2.38
75	2.62
90	2.94
120	3.39
150	3.65

Exp. 5

$HClO_4$ 0.2905 N, HBr 0.871 N
$RuBr_3$ 0.00246 M, KI 0.06 N

15	0.908
30	1.65
45	2.29
60	2.75
75	3.12
90	3.32
120	3.76
150	4.17

Table 1

Exp. 6

Same as for Exp. 5

Except KI 0.00120 N

15 min	0.874 milli-eq
30	1.74
45	2.61
60	3.16
75	3.58
90	4.01
120	4.56
150	4.88

Exp. 7

Same as for Exp. 5

Except KI 0.0301 N

15 min	0.938 milli-eq
30	1.88
45	2.74
60	3.62
75	4.51
90	5.38
120	6.70
150	7.25

Exp. 8

$HClO_4$ 1.395 N, HBr 0.940 N,

$RuCl_3$ 0.00246 M, KI 0.0301 N

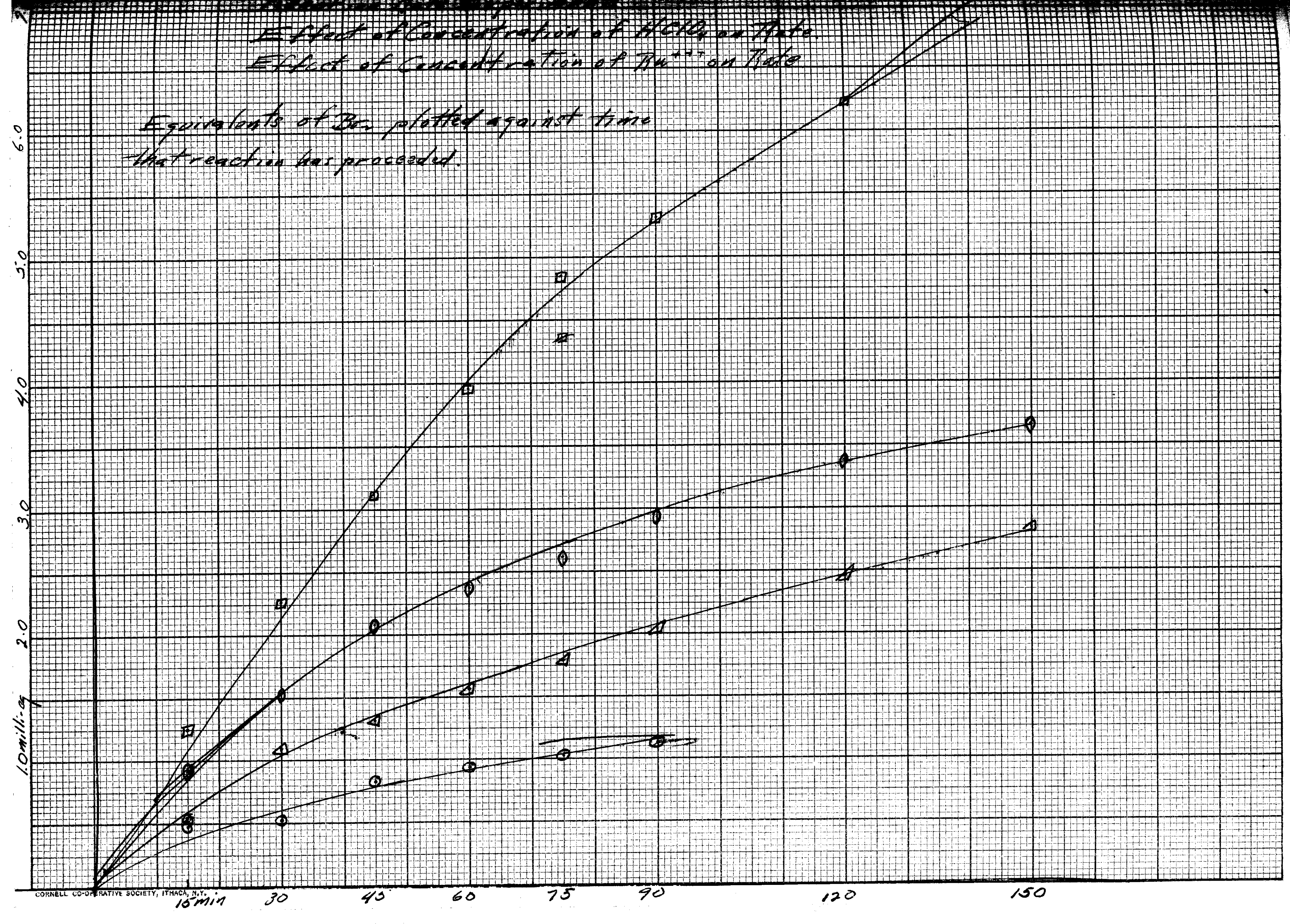
15	20.1
30	27.1
45	30.9
60	33.8
75	35.6

Exp. 9

$HClO_x$ 1.395 N, HBr 0.940 N,

$RuCl_3$ 0.000874 M, KI o.0301 N

15	10.5
30	15.80
45	19.6
60	22.4
90	26.8
120	32.4



Effect of Concentration of $HClO_4$ on Rate.

Effect of Concentration of Ru^{++} on Rate

Equivalents of Br_2 plotted against time that reaction has proceeded.

Effect of Removal of Drain Plate.

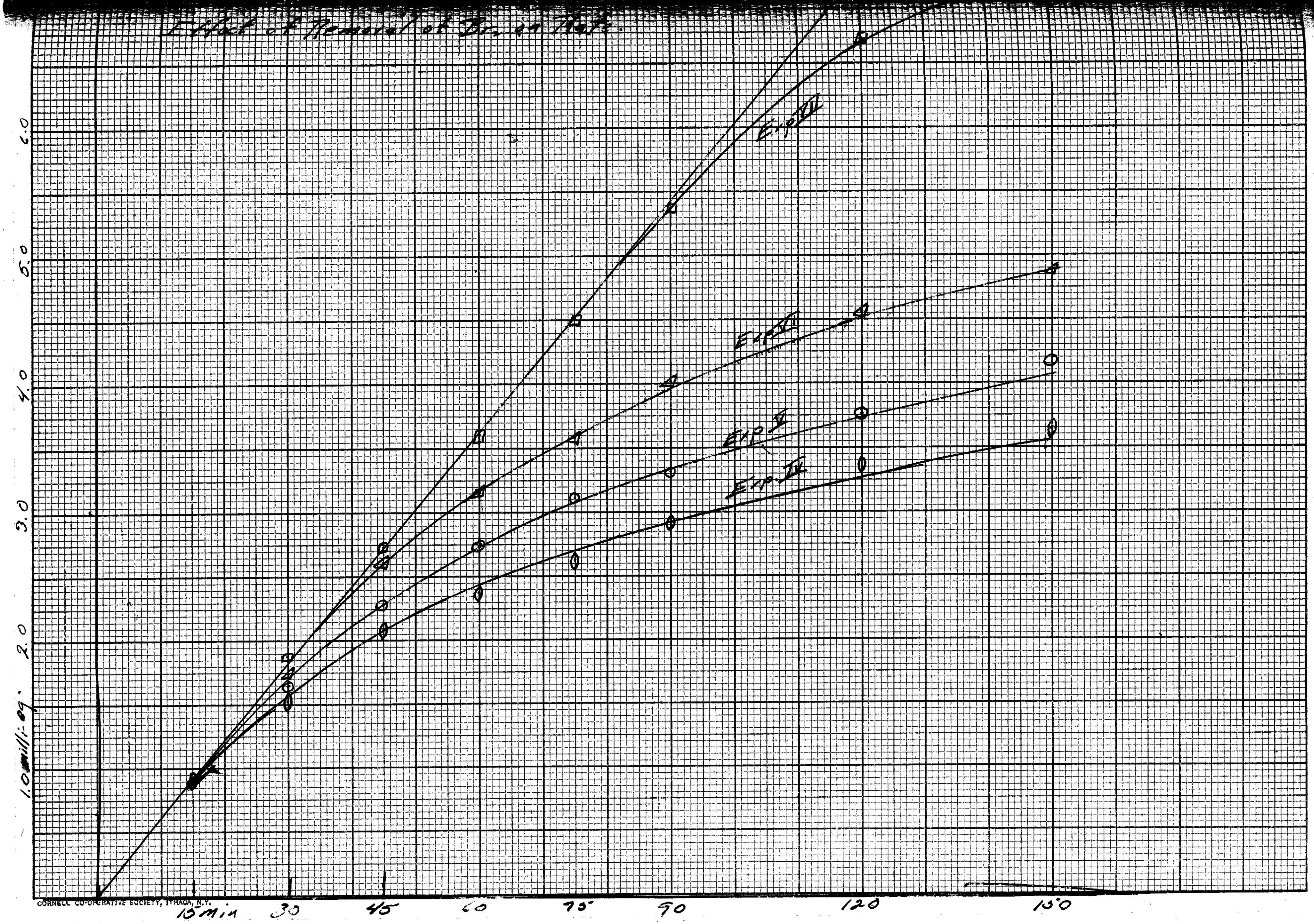


Table I

Exp. 10		Exp. 11	
Remainder of solution from		$HClO_4$	0.2905 N
Exp. 8. Run at 25 degrees		HBr	0.871 N
95.5 hr.	2.43 milli-eq	3.5 hr.	0.00 milli-eq.

Interpretation of the Rate Experiments.

The effect of the concentration of perchlorate ion is easily determined. In Experiments 1, 2, and 3 the ratio of perchlorate ion is very nearly 1;2:5. A comparison of the relative amounts of bromine formed in the same time shows thatthey also are very nearly in the same ratios Hydrogen ion does not vary greatly in these experiments.

The effect of the concentration of the ruthenium is also easily determined. A comparison of the rate curves for Experiments 2 and 4, shows that the rate varies linearly with the concentration of ruthenium. This fact can also be deduced from experiments in which the perchloric acid concentration varies by reducing the results to the same concentration in accordance with the way the rate varies with the perchloric concentration. The results are quite consistent throughout.

The effect of removal of bromine from the solution is shown by the graphs of Experiments 4,5,6, and 7. In these experiments, small amounts of potassium iodide were introduced. It is seen that the rate continues at its initial value until all the iodide has been oxidized, butᴍ that as soon as bromine started to accumulate, the rate decreases as in the other experiments. This indicates possibly an equilibrium between the ruthenium and bromine to form some inactive ruthenium compound. It was planned to increase the amount of iodide in the solution, but the precipitation of ruthenium tri-iodide made this impractical.(3) The iodide does not effect the reduction of ruthenium below the trivalent state, however, so that any objection on this ground is met.

The effect of the concentration of hydrogen ion is not yet determined, although it is evident that it has som some effect. A comparison of the rates in Experiments 4 and 8 shows that while the concentration of perchlorate ion has been changed by a factor of about five, and that of the hydrogen ion by a factor of about two, the rate has increased by about twenty times. (twenty six, if the extrapolated initial rate is taken in Experiement 8). It seems that the rate is dependent to a large degree upon the concentration of hydrogen ion.

Temperature Coefficient of the Reaction.

From the data of Experiment 10 compared with Experiment 8, the temperature coefficient can be calcualated, and is found tobe equal to 2.91 for a ten degree rise in temperature.

3) Gutbier and Trenckner, Z. anorg. chem. 45, 166, (1905)

Reaction of Ruthenium Chloride and Perchloric Acid

An investigation of the action of ruthenium trichloride and perchloric acid was undertaken, to determinne if possible to what state ruthenium is oxidized during the reaction, and in the hope of finding an intermediate compound.

First it was attempted to prepare ruthenium trichloride, but because of the hydrolysis of ruthenium salts at low hydrogen ion concentration or high temperatures, (above 50 degrees) it was found impractical. The formation of an oxychloride on hydrolysis makes the removal of all the chloride almost impossible.

Later, it was thought that it might be possible to follow the course of the reeaction between the ruthenium and the perchloric acid by determining the increase in chloride ion on heating a mixture of the two. However, silver nitrate even under the best conditions could never remove all of the chloride, even in quite acid solution.

Finally, it was found possible to use the same method as in the rate experiments. As mentioned before iodide ion does not reduce ruthenium below the tri-valent state, so that the ruthenium is at the end in the same stae as in the beginning. A time correction had to be made from the time that the iodide was added, however, as of course as soon as it was added, the reaction (1) , given on page 2 began to occur.

In the first column of the table are given the times of reaction at 100 degrees,; in the second the oxididation equivalents as determined by titration of the iodine liberated; and in the third the ratio of the eqivalents of iodine liberatd to the moles of ruthenium present.

Experiment 12

10.00 ml samples containing $RuCl_3$ and $HClO_4$

$RuCl_3$ 0.427 milli-mols $HClO_4$ 13.92 milli-mols

4 days	0 hr	0.317	0.742
8	0	0.342	0.800
2I	0	0.430	I.005

Tubes that were heating for a longer time broke in the water bath andhence no information could be obtained as to whether the oxidation proceeded past the value found. As time was limited it was decided to run another experiment, but to heat the mixture to a higher temperature, and speed up the reaction. This method is open to objection, as it is quite possible that other reaction will take place at a higher temperature, but any information that can be obtained is of use.

A tube of solution the same as that used in the other experiements was heated for six days in xylene vapor, (b.p. 140 degrees). At the end of that time, there was a clear, brown liquid and a black precipitae in the tube. It was desired to keep the liquid and the precipitate separate, so that the tube was not opened under iodide solution, but the end was cut off. There was considerable gas pressure in the tube, and the odor of chlorine was quite strong on opening. On this account, the titration does not represent an accurate value of the oxidation of the ruthenium, but is too low by an unknown amount.

After opening the tube, the liquid was removed with a pipette, and poured into potassium iodide solution. The precipitate was washed and the washings added to the liquid. The solid was then divided into two parts; to one of them potassium bromide in water was added. No bromine was formdd. To the other potassium iodide was added, and iodine was immediately formed. That this was due to reduction of the solid and not to small quantities of the liquid remaining was proved by the fact that the last wash water barely colored potassium solution. Potassium iodide was finally added to the first part of the solid, and the total iodine liberated by the solid titrated against thiosulphate. A solid residue of black metallic scales remained after the treatment with iodide, and did not dissolve after several days.

Milli- mols of $RuCl_5$ in solution	0.874
Equivalents of I_2 from liquid	0.876
" " " from solid	0.127
Total eqivalents of I_2 per mol Ru	1.13

These experiments would seem to indicate that perchloric acid oxidizes the ruthenium to some state higher than the pentavalent. Further work on this should be of interest.

Reaction of Ruthenium Chloride and Bromine.

From the effect of the accumulation of bromine on the rate found in the rate experiments, it might be supposed that an equilibrium existed between tri-valent ruthenium ion and bromine, to give some more highly oxidized state and bromide ion. In order to measure the supposed equilibrium a series of experiments were undertaken.

In carrying out the experiments, solutions containing known amounts of ruthenium trichloride, potassium bromide, and bromine were placed in stoppered bottles in contact with a measured volume of carbon tetrachloride. At the same time blanks containing no ruthenium were treated in the same way. The bottles were rotated in the thermostat at 25 degrees for several days, then portions of the carbon tetrachloride were removed with a pipette, and after addition of potassium iodide were titrated against thiosulphate. From the difference in the concentrations of bromine in the sample containing the ruthenium and the blank, it should be possible to calculate the amount of bromine reacting with the ruthenium. From several sets of experiments, with different amounts of ruthenium and bromine, it should then be possible to prove the existance of an equilibrium if one exists and to measure its constant.

The results yielded no quantitative measurements, partly because of leakage from the bottles, which was almost impossible to avoid; and also because of the fact discovered later that there was no equilibrium, but that ruthenium trichloride and bromine react irreversibly.

It was noticed that the bromine in the carbon tetrachloride phase of one of the samples that had stood for several days had disappeared. To decide whether this was due to leakage of to an irreversible reaction more bromine was added and the mixture let stand for sever al days. At the end of this time the sample was repeatedly shaken with carbon tetrachloride until no test for bromine was obtaind. The solution retained the wine color it had assumed in the addition of the bromine, and showed no signs of giving up bromine after standing in contact with carbon tetrachloride for two days.

Experiments on the Brominated Ruthenium Compound.

Since the preceding experiment indicated a complete oxidation of ruthenium by bromine, which appeared to be irreversible, it was decided to test portions of the solution containing this oxidized compound with a view of determining its state of oxidation and its properties. The solution was known to contain 0.0437 milli-mols of ruthenium per ml, or slightly less because of losses in shaking with carbon tetrachloride in removing free bromine.

a. A 10.00 ml sample was treated with an excee of potassium iodide. The color changed rapidly from the characteristc wine shade of the qxidized compound to the yellow brown color corresponding to the tri-valent ion. The iodine liberated was shaken out with carbon tetrachloride, and titrated against thiosulphate solution. Because of the large excess of iodide ion , the iodine was removed with difficulty, and probably not all of it was removed.

An excess of bromine was then added to the reduced solution to reoxidize it. The removal of the excess of free brominewas attempted after the mixture Has stood for four days, but the harge concentration of bromide already referredto, reduced the distribution ratio between the solution and carbo tetrachloride to such an extent that the removal was very difficult. For this reason when iodide was again added, a large excess of iodine was formed by oxidation with the unremoved bromine.

Another sample, of 20.00 ml that had been in contact with bromine for five days was reduced with potassium iodide in the same manner as the first sample, except that care was taken to add only a very slight excess. After all the iodine formed had been removed a small additional amount of iodide was added, but no further iodine was formed.

Experiment 13

In the first column are given the milli-equivalents of I_2 formed; in the second the ratio of the I_2 formed to the Ru present.

0.357	0.82
---- n.g.	
0.683	0.78

The actual ratios of the equivalents of iodine formed to the mols of ruthenium present should probably be slightly higher, as some of the ruthenium was unavoidably lost in repeated shaking with carbon tetrachloride.

It appears that tri-valent ruthenium is oxidized to the tretra-valent state by bromine, and that this compound is quite stable as it does not give off bromine at room temperature.

b. A small volume of this sme solution used in the previous experiment was ditilled, and the distillate collected in potassium solution. No trace of color appeared in this solution, showing that the oxidized compound is stable even at 100 degrees.

c. Reducing agents such hydrazine sulphate and potassium iodide, (already noted) reduce the ruthenium apparently giving the original tri-valent form.

d. Alkalies precipitate all of the ruthenium to give a black or very dark solid.

Ho Howe(4) mentions the oxidation of the sodium or other alkali aquo-brom-ruthenates to form the chlor-ruthenates by means of bromine. The present case may be something similar, although there is nothing in the literature concerning the oxidation of tri-valent ruthenium chloride alone. Apparently the alkali ruthenites and ruthenates, or rather the brom-ruthenits and ruthenates, are much less subject to hydrolysis than the simple salts, so that most of the work concerning the ruthenium halides has been done on these compounds rather than on those which were used in the present case.

Catalytic Effect of the Oxidized Ruthenium

A rate experiment was run as in the series made previously, except that the oxidized ruthenium solution was used. The solution was made up to 100 ml, and samples sealed into test tubes and heated for different times

Experiment 14

$HClO_4$ 0.2785 N   HBr 0.9404 N

Ruthenium 0.00218 (approx)

15 min	0.0795 milli-eq.
30	0.159
60	0.487
90	0.748
150	1.22
122 hr. 25 min	16.30

To one sample was added a small amount of potassium iodie, about a 50% excess over that required to reduce the ruthenium to the tri-valent form; it was then sealed in a tube and heated for 15 minutes in the water bath.

15 min 2.64 milli-eq.

This represents an increase in the rate by a factor of 20.

These two experiments show that the oxidized form of ruthenium has no catlytic action. The slow rate found in the first experiment can be explained by the presence of only four per cent of the total ruthenium in an unoxidized, state. This is quite probable, as the reaction between the tri-valent ruthenium and bromine is slow.

Miscallaneous Qualitative Experiments.

A. Experiments on the dark solid residue remaining in the flask at the end of rate experiments conducted by the first method. Small amounts, as nearly equal as possible were treated with various reagents.

1. $KClO_3$ added --- no action
2. " solution heated--- no action
3 " and HCl added; solution heated --no action
4. H_2O_2 added --- no action
5. Wet solid let stand in the air-- wine color developed in the solution on addition of water
6. Solution of RuBr treated with $KClO_3$ -- assumed wine color, same as 5
7. Sodium sulphite, hydroxylamine, hydrazine sulphate, all caused reduction with appearance of

Qualitative Experiments

A.7. the yellow brown tri-valent rutheunium ion

B. Experiments on the solid residue remaining in the reaction of RuCl and $HClO_4$ at 140 degrees.

1. KBr added--- no action
2. KI added -- I_2 liberatdd immediately. Not all of the precipitate dissolved; small metallic scales remained.

Conclusions.

Not enough facts are known to formulatea mechanism for the reaction (I) on page 2 with any degree of surety. From the facts known, however, a tentative mechanism may be suggested. Further work will serve to either prove or overthrow the theory suggested.

From the experiments on ruthenium and perchloric acid, it is shown that puthenium is oxidized to some valence higher than three, possibly five.

Bromine is shown to oxidize tri-valent ruthenium to a higher valence which seems to be four. (See note on work of Howe).

The following mechanism is then suggested:

$$Ru^{+++} + ClO_4^- = Ru^{+++++} + ClO_3^- \qquad (I)$$

$$Ru^{+++++} \quad ClO_4^- - Ru^{6,7\text{ or }8} + ClO_3^- \text{ or } ClO_2 \text{ or } CL_2 \qquad (2)$$

$$Ru^{6,7\,or\,8} + Br^{-} = Ru^{++++} + Br_2 \qquad (3)$$

$$Ru^{+++} + Br_2 = Ru^{++++} + Br^{-} \qquad (4)$$

Argument. Reaction (1). This folllws from the experiments on ruthenium tri-chloride and perchloric acid.

Reaction (2). Perchloric acid is know to oxidize ruthenium salts to the tetroxide in hot fairly concentrated solution. (See note on Dalton's work). It seems quite likely that this may take place slowly in more dilute solution, and that the oxidation will not stop at the pentavalent form shown in (1), but will go further.

Reaction (3). The six, sevem, and eight valent states of ruthenium do not appearto be stable in acid solution,(5) h but decompose in the presence of hydrochloric or hydrobromic acids to give chlorine or bromine. Since in the first reaction rate data given, it is seen that the reaction goes to completion when the bromine is removed, it is evident that the tetravalent form is not formend in the decompsition, as this has been shown to have no catalytic action. Of course the end product in reaction(30 might be the tri-valent form.

Reaction (4). This follows from the experiments on the action of bromine on tri-valent ruthenium.

5). Textbook of Inorg. Chem. (J.N.Friend, Ed.)
Vol. IX Part I page 147
Gutbier u. Ransohoff, Z.anorg. chem. <u>45</u>,243

Conclusions.

Proposed experimentsto determine the mechanism.

1. Continuance of the rate experiments up to a longer period of time. The mechanism suggested would give a constant rate, as when no tri-valent ruthenium was any longer present, the decrease in the rate due to the removal by bromine would cease.

2. Use of ruthenium pentoxide as a catalyst in place of the trichloride. The rate should in this case not be affected by the accumulation of bromine.

3. The effect of the concentration of hydrogen ion and of bromide ion on the rate should yield interesting results.

This work has been carried out under the direction of Mr. Don M. Yost. Thanks are due him for many valuable and helpful suggestions, and also to Dr. Noyes, who suggested the investigation.

Summary.

1. The reaction $HClO_4 + 8HBr = HCl + 4H_2O + 4Br_2$ has been found to be catalyzed by salts of tri-valent ruthenium.

2. The rate of the reation has been measured at 100 degrees and at 25 degrees under certain condition, and the temperature coefficient of the reaction determined.

3. Both Ru^{+++} and ClO_4^- have been found to affect the rate, within the limits of error, directly as the first power of their concentrations.

Summary

4. H^+ ion has also been shown to affect the rate.

5. Perchloric acid has been shown to oxidize tri-valent ruthenium to a higher state, possibly the penta-valent.

6. Bromine has been shown to oxidize tri-valent ruthenium irreversibly to the tetra-valent state.

7. The tetra-valent ruthenium has been shown to have no catalytic actiom.

8. Potassium iodide has been shown to reduce tetra-valent ruthenium to the tri-valent. This shows that the reduction potential lies between that of bromine and iodine.

9. A tentative mechanism has bee sugested for the catalytic effect of ruthenium on the reaction under investigation, and experiments outlined which should settle the matter.

4). (Should have been included on page 18)

Howe, J. Am. Che,m. Soc. 26, 543, (1904)