to thank Professor Kleinberg for the samples of sodium oxides and for his interest in the problem. This research was supported in part by the Atomic Energy Commission.

## Summary

1. The crystal structure of sodium superoxide has a face-centered cubic lattice with $a = 5.490 \pm 0.005$ Å. The structure is like that of sodium chloride with $O_2^-$ ions occupying halide positions with disorderly orientation.

2. The bond distance in the superoxide ion in this crystal is $1.33 \pm 0.06$ Å.

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[CONTRIBUTION FROM THE GATES AND CRELLIN LABORATORIES OF CHEMISTRY, CALIFORNIA INSTITUTE OF TECHNOLOGY, No. 1318]

# Investigations in the Chemistry of Rhenium. I. Oxidation States IV, V and VII[1,2]

BY EUGENE K. MAUN AND NORMAN DAVIDSON

Part of the interest of the chemistry of rhenium is due to the large number of oxidation states in which this metal occurs—in fact, compounds of rhenium for all oxidation numbers between +7 and −1 have been reported. It was the object of this research to characterize more precisely some of the oxidation states of rhenium in aqueous solution. Since many of the rhenium compounds encountered were colored, they were studied by measuring their light absorption with a Beckman spectrophotometer. The various rhenium compounds studied were also characterized by their reactions with some common oxidizing and reducing agents. The present communication describes our studies of the IV, V and VII oxidation states; in a subsequent paper we will report on our observations of the lower oxidation states $Re^{-1}$ and $Re^{+1}$.

## Experimental

**Materials.**—Samples of rhenium metal powder and of potassium perrhenate were obtained from the University of Tennessee. The rhenium metal was reported to assay 99.5% or better, the chief impurity being silver; the potassium perrhenate was stated to assay 99.8% or better, the chief impurity being rubidium. Solutions of perrhenic acid were prepared by heating the powdered metal with excess 30% hydrogen peroxide.[3,4] In agreement with experiments of Hölemann[5] and Geilmann and Weibke,[6] the perrhenic acid found in 0.025 to 0.05 formal solutions was 3–5% less than expected from the weight of metal taken, as shown by titrations to a methyl red end-point with potassium hydroxide and by precipitation as nitron perrhenate.[7] No molybdate was present and the hydrogen peroxide contained no non-volatile acidic or basic impurities. To detect oxide impurity, a 100-mg. sample of rhenium was treated with hydrogen at 1000°. After cooling under pure nitrogen, it had lost only 1.5 mg. in weight. In view of these experiments, the stated purity of the rhenium, and the similar experience of other investigators[5,6] it appears that the low results for perrhenic acid are due to either (a) volatility or (b) loss in a spray during the solution process.

Potassium hexachlororhenate(IV) was prepared from potassium perrhenate.[8] The $Re^{IV}$ in a 24.71 mg. sample was determined with hot ceric sulfate.[9] A blank of chloride consumed 0.003 meq. of cerium(IV) and the Re(IV) found after correction for this was 0.122 meq. (theory 0.120 meq.). The $ReCl_6^{=}$ in the preparation was determined as $Cs_2ReCl_6$[10,11] by addition of 0.10 ml. of 0.5 *F* cesium chloride solution to 0.300 ml. of solution containing 7.25 mg. of the preparation of $K_2ReCl_6$. The resulting precipitate of $Cs_2ReCl_6$ was washed with concentrated hydrochloric acid and dried at 120°. Its weight was 10.0 mg. (theory 10.1 mg.).

Where not otherwise specified, reagent grade chemicals were used. Ceric ammonium sulfate was used as a standardized *ca.* 0.05 *F* solution in 0.5 *F* sulfuric acid. Solutions of 0.05–0.1 *F* sodium thiosulfate, 0.3 *N* iodine in 7.5% potassium iodide, 0.07 *F* copper sulfate, and 0.1 *N* chlorine in 4 *F* hydrochloric acid were standardized by iodometric titrations, using 0.0150 *F* potassium iodate solutions. Solutions of 0.05–0.15 *F* ferric ammonium sulfate in 0.1 *F* sulfuric acid were also standardized iodometrically using the optimum conditions given by Swift.[12] Stannous chloride solutions 0.05 *F* (0.1 *N*) were standardized just before use against excess iodine, working under carbon dioxide and rinsing out all equipment with this gas. Cuprous chloride was reprecipitated by dilution of a solution in concentrated hydrochloric acid, and the purified solid thus obtained was used to prepare 0.1 *F* solutions in 4 *F* hydrochloric acid which were standardized with ceric sulfate (*o*-phenanthroline end-point). An approximately 0.1 *F* chromic chloride solution in 4 *F* hydrochloric acid was prepared from the solid. For detection of chlorine, a 0.1% solution of *o*-tolidine was prepared in 1.2 *F* hydrochloric acid[13] and stored in the dark.

**Spectrophotometry.**—Light absorption measurements were made at room temperature on solutions in 3-ml. quartz or corex cells of calibrated path length, 1.00 cm., using a Beckman spectrophotometer. For protection of solutions from oxygen of the air, a number of long-stemmed corex cells capped with ground joints were used. The extinction coefficient $\epsilon$ was calculated for a given wave length from the readings of the optical density *D* relative

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(1) Presented before the Physical and Inorganic Division at the 115th meeting of the American Chemical Society, San Francisco, California, March 28, 1949.

(2) A more detailed account of this research is contained in the Thesis by Eugene K. Maun, submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, California Institute of Technology, June, 1949.

(3) W. Feit, *Angew. Chem.*, **46**, 216 (1933).

(4) J. T. Dobbins and J. K. Colehour, THIS JOURNAL, **56**, 2054 (1934).

(5) H. Hölemann, *Z. anorg. Chem.*, **202**, 277 (1931).

(6) W. Geilmann and F. Weibke, *ibid.*, **195**, 289 (1931).

(7) W. Geilmann and A. Voigt, *ibid.*, **193**, 311 (1930).

(8) L. C. Hurd and V. A. Reinders, "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 178.

(9) W. Geilmann and F. W. Wrigge, *Z. anorg. Chem.*, **222**, 56 (1935).

(10) W. and I. Noddack, *ibid.*, **215**, 129 (1933).

(11) E. Enk, *Ber.*, **64**, 791 (1931).

(12) E. H. Swift, THIS JOURNAL, **51**, 2682 (1929).

(13) F. J. Welcher, "Organic Analytical Reagents," D. Van Nostrand Co., New York, N. Y., 1947, Vol. II, p. 464.

to a blank (usually water or hydrochloric acid) and the formal concentration $c$ (in moles/liter) and path length $l$ of 1.00 cm.

$$D = \log_{10} I_0/I = \epsilon c l \qquad (1)$$

The spectral band width used was shown to be just sufficient at each wave length to permit readings to 0.1%[14] and hence gave good resolution.

## Results

**Rhenium(VII).**—The nitron test[7,15,16] was verified to be quite sensitive for perrhenate, but cannot be used effectively in solutions containing chloride, since an appreciable white precipitate was given with nitron reagent and hydrochloric acid or ammonium chloride. No precipitate was observed in a mixture of 0.1 $F$ cesium ion and 0.01 $F$ perrhenate in water or in 4 $F$ hydrochloric acid in a short time after mixing. The solubility of $CsReO_4$ was exceeded[17] but supersaturation may have occurred.[15] Since $ReCl_6^=$ solutions gave an immediate yellow-green precipitate of $Cs_2ReCl_6$ with cesium chloride solutions, this reagent could be used to distinguish $ReO_4^-$ and $ReCl_6^=$.

The light absorption of 0.025 and 0.05 $F$ perrhenic acid solutions agreed with Custers' measurements.[18] The absorption spectrum of perrhenic acid is given in Fig. 1. The extinction coefficient remained less than 0.5 from 400 to 1000 mμ.

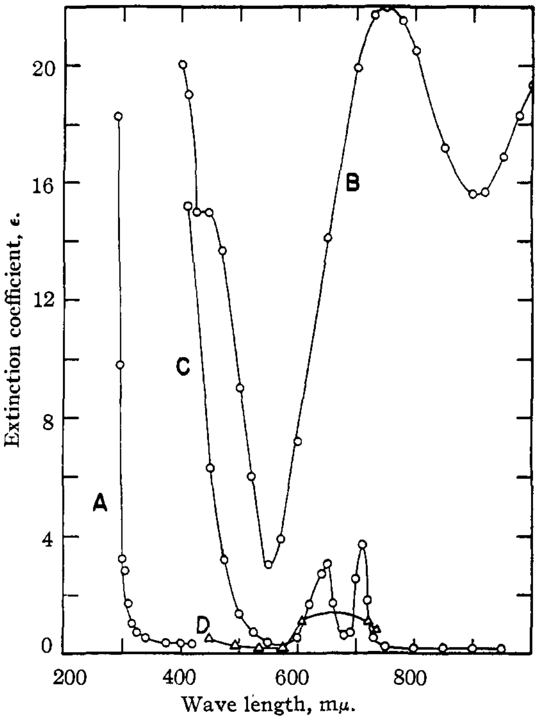

Fig. 1.—Absorption spectra: A, aqueous $HReO_4$ (0.025 and 0.05 $F$); B, $Re^V$ (0.005 and 0.01 $F$) from $HReO_4$ with $SnCl_2$ in 4 $F$ HCl; C, $K_2ReCl_6$ (0.05 $F$) in 4 $F$ HCl (present work); D, $K_2ReCl_6$ (0.04 $F$) in 3 $F$ HCl (Schmid's data).

**Rhenium(V) from the Reaction of Perrhenate with Stannous Chloride.**—Previous potentiometric studies[19,20,21,22] of the reduction of perrhenate by stannous chloride have shown the formation of rhenium(V) followed by formation of rhenium (IV). Figure 2 contains a spectrophotometric record of this reaction. The optical densities of the light green solutions were a linear function (to ±3%) of the amount of added reducing agent until two equivalents of reducing agent had been added. Further addition of stannous chloride caused gradual formation of a more strongly colored yellow-brown substance. The light absorption of the yellow-brown solutions with three or more equivalents of reducing agent reached the same limiting value after fifteen hours. These observations show that rhenium(V) was formed

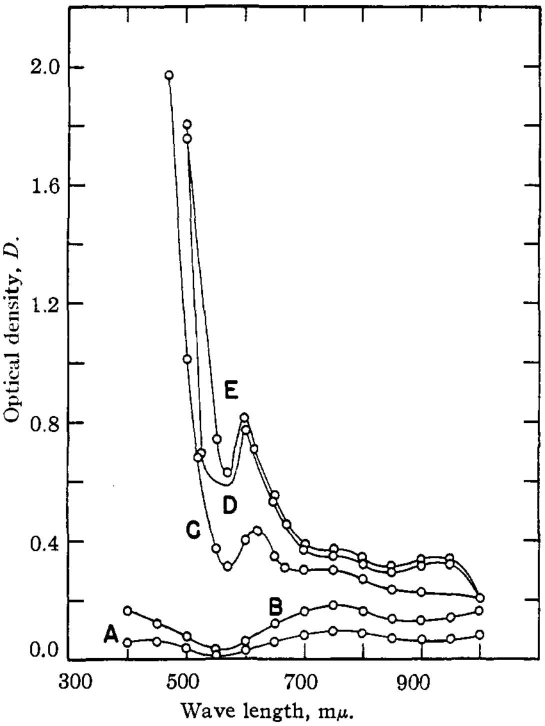

Fig. 2.—Light absorption of one to three day old reaction mixtures of 3 ml. of 0.0100 $F$ $HReO_4$ in 4 $F$ HCl with: A, 0.030 meq. $SnCl_2$; B, 0.060 meq. $SnCl_2$; C, 0.075 meq. $SnCl_2$; D, 0.090 meq. $SnCl_2$; E, 0.120 meq. $SnCl_2$.

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[14] H. H. Cary and A. O. Beckman, *J. Optical Soc. Am.*, **31**, 682 (1941).

[15] W. Geilmann and K. Brünger, *Z. anorg. Chem.*, **199**, 77 (1931).

[16] L. C. Hurd, *Anal. Chem.*, **8**, 11 (1936).

[17] I. and W. Noddack, *Angew. Chem.*, **44**, 215 (1931).

[18] J. F. H. Custers, *Physica*, **4**, 426 (1937).

[19] E. Turkiewicz, *Roczniki Chem.*, **12**, 589 (1932); "Gmelins Handbuch der anorganischen Chemie," 8th ed., Vol. 70, p. 130.

[20] W. F. Jakób and B. Jeżowska-Trzebiatowska, *Ber.*, **66**, 461 (1933); *Z. anorg. Chem.*, **214**, 337 (1933); **220**, 16 (1934).

[21] H. Hölemann, *ibid.*, **217**, 105 (1934); **220**, 33 (1934); **235**, 1 (1937).

[22] S. Tribalat, *Compt. rend.*, **220**, 881 (1945) **222** 1388 (1946); **223**, 34 (1946).

rapidly, followed by slow formation of rhenium(IV) if excess stannous chloride was present.

Rhenium(V) solutions were found to have the same absorption for hours after their preparation. The extinction coefficients calculated from measurements on several rhenium(V) solutions have been plotted in Fig. 1 for the wave length region where tin in its different oxidation states has negligible absorption.[23]

Jakób and Jeżowska-Trzebiatowska[20] and Hölemann[21] have reported preparation of a compound $K_2ReOCl_5$. The chemical reactivity of rhenium(V) solutions prepared from stannous ion with perrhenate agreed with the reported reactivity of solutions of $K_2ReOCl_5$, for example, the rhenium in both solutions was completely oxidized to perrhenate by hydrogen peroxide.

Table I contains titration experiments showing that rhenium(V) is completely oxidized by cold dilute ceric sulfate but is unaffected by five minutes treatment with bubbling oxygen. To obtain the rhenium solutions used for these analyses, perrhenic acid, stannous chloride, and hydrochloric acid were mixed in a closed cell to give 3 ml. of a solution 0.01 *F* in rhenium and in 4 *F* acid. In some of these experiments excess stannous chloride was used, forming some rhenium (IV). Spectrophotometry permitted estimation of both the rhenium(V) and the rhenium(IV) concentrations. A 0.01 *N* solution of stannous chloride in 4 *F* hydrochloric acid was largely oxidized to the stannic state after bubbling oxygen through the solution five minutes. Since a five-minutes treatment of $Re^V$ solutions with oxygen caused no loss of reducing agent, the results in Table I show that the reaction of $Sn^{II}$ with $Re^{VII}$ to give $Re^V$ is quantitative. Other results in Table I show that rhenium(V) is largely but not completely oxidized to perrhenate by iodine, and completely oxidized to perrhenate by potassium iodate.

Analyses with $Ce^{IV}$ were done by pipetting 0.50-ml. portions of the $Re^V$ solutions into excess $Ce^{IV}$ and titrating the excess with ferrous sulfate to an *o*-phenanthroline end-point. The volume of 0.05 *F* cerium(IV) was varied from 0.30 to 0.80 ml. with no effect, and blanks showed no oxidation of the 1.5 to 2.5 *F* acid furnished by the rhenium solution. In the iodine analyses, typically a 0.50 ml. portion of the 0.010 *F* rhenium(V) solution was added to 10 ml. of 0.2 *F* potassium iodide solution containing 0.018 to 0.036 meq. of iodine. The resultant acidity of hydrochloric acid was 0.2 *F*. The iodate analyses were done by pipetting 0.50 to 1.00 ml. of rhenium(V) solution into 1 to 2 ml. of 0.007 *F* potassium iodate, giving iodine monochloride (identified by color changes and a starch test) in the 1.1 to 1.5 *F* acid. Excess iodide was then added and the iodine formed was titrated by thiosulfate.

Solutions of rhenium(V) containing no excess stannous chloride gave a white precipitate with mercuric chloride, and the green color of the rhenium(V) disappeared. The reaction is therefore

$$Re^V + 2HgCl_2 + 4H_2O = ReO_4^- + Hg_2Cl_2(s) + 8H^+ + 2Cl^- \quad (2)$$

Rhenium(V) solutions were also instantly decolorized by hydrogen peroxide. Excess chlorine solution completely decolorized rhenium(V), thus forming perrhenate. A reaction mixture with a limited amount of chlorine gave no *o*-tolidine test for chlorine several minutes after mixing the reactants. Also the amount of unreacted rhenium(V) determined by remeasuring the light absorption agreed roughly with that expected from reaction with all of the added chlorine to form perrhenate. Thus, there is no evidence for the formation of $Re^{VI}$ in these solutions.

TABLE I

ANALYSIS OF RHENIUM(V)

| Soln. | Meq. reducing agent added | Meq. $Ce(SO_4)_2$ | Meq. $I_2$ | Meq. $KIO_3$ |
|---|---|---|---|---|
| 1[a] | 0.0100 | 0.0105 | 0.0073 | |
| | .0100 | | .0093 | |
| | .0100 | | .0091 | |
| 2[a] | .0105 | .0113 | | 0.0115 |
| 3[a] | .0105 | .0110 | | .0111 |
| | .0105 | .0110 | | |
| 4[a] | .0194 | | .0145 | .0180 |
| 1[b] | .0100 | .0105 | | |
| 2[c] | .0102 | .0111 | | |

[a] Calculated from light absorption data to contain: 1, 0.0100 *F* $Re^V$, 45 min. old; 2, 0.0087 *F* $Re^V$, 0.0010 *F* $Re^{IV}$, 0.0002 *F* $SnCl_2$, 2.5-hr. old; 3, 0.0096 *F* $Re^V$, 0.0005 *F* $Re^{IV}$, 2.25-hr. old; 4, 0.0097 *F* $Re^V$, 12 hr. old. [b] Bubbled $O_2$ through Re soln. 1 min., then added to excess $Ce^{IV}$. [c] Bubbled $O_2$ through Re soln. 5 min., then added to excess $Ce^{IV}$.

Attempts to prepare rhenium(V) from equivalent amounts of the reactants in 1.9 *F* hydrochloric acid gave a black precipitate. The supernatant liquid contained perrhenate but no stannous chloride. Therefore, the black precipitate was some lower state than rhenium(V). Its behavior with hydrochloric acid as well as the light absorption and the behavior of its hydrochloric acid solutions with oxidizing agents were those found for freshly precipitated rhenium dioxide as described later. Hence this confirms the disproportionation of rhenium(V) into rhenium dioxide and perrhenate observed by Tribalat[22] in low concentrations of hydrochloric acid. This disproportionation was also observed in the present work in 3 *F* acid. Tribalat also reported a slow disproportionation in 4 *F* acid over a period of twenty-four hours, but this was not observed in the present work. After standing for twenty days in the absorption cells, there was a slight decrease in the light absorption by rhenium(V). This was proved, by adding more stannous chloride and following the light absorption, to be entirely due to oxidation to perrhenate. Moreover, an increase in the absorption with time would have been expected for formation of highly colored rhenium(IV). The acid used in the present work was within 5% of 4.0 *F*, perhaps slightly high; if the acid used by Tribalat were 5 or 10% low, this might account for slow dis-

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[23] C. I. Browne, Master's Thesis, California Institute of Technology, 1948.

proportionation. No influence of temperature upon the stability of rhenium(V) solutions was found in that the light absorption of a 0.007 $F$ rhenium(V) solution was unchanged by heating for an hour at 55 ± 5°.

**Rhenium(IV) from the Reaction of Perrhenate with Stannous Chloride.**—Rhenium(IV) solutions were prepared in a manner similar to that used for rhenium(V). Figure 2 shows agreement between the absorption spectra of solutions with $Sn^{II}:Re^{VII}$ in the ratios 3:1 and 4:1 milliequivalents per millimole, while the absorption of a solution with ratio 2.5:1 is halfway between the absorption of a 2:1 mixture and that of a 3:1 mixture. Other solutions with three or more equivalents of stannous chloride had identical absorption spectra. Therefore, in all cases with three or more equivalents of stannous ion, rhenium(IV) was formed as a well-defined species. The absorption remained nearly constant with time for several days after completion of the reaction (after fifteen to twenty hours). At acidities lower than 4 $F$ the light absorption of the product was significantly higher than that of the species in 4 $F$ acid. Some indication was found that formation of rhenium(IV) is quite slow in the last stages with equivalent amounts of the reactants, as seen by comparison of curves D and E, Fig. 2.

An experiment was performed in which oxygen was bubbled through a rhenium(IV) solution. This experiment showed that no unreacted stannous ion was present and that a long time would be required for complete oxidation of rhenium(IV) to perrhenate. In another series of experiments, analysis by ceric sulfate was done in a manner similar to that described for rhenium(V). Table II shows that all the reducing agent added as stannous chloride was recovered even after sixty-five hours, thus proving that no oxidation of the solutions in capped cells had occurred, and establishing quantitative oxidation of rhenium(IV) to perrhenate by cerium(IV). Iodine had but slight effect on rhenium(IV). Rhenium(IV) was oxidized to colorless perrhenate by excess potassium iodate. Rhenium(IV) in 4 $F$ hydrochloric acid was rapidly oxidized to perrhenate by chlorine with no intermediate formation of rhenium(V), as shown by iodine titrations and by the yellow-brown color remaining for rhenium(IV) solutions oxidized with one equivalent of chlorine.

TABLE II

ANALYSIS OF $Re^{IV}$ BY CERIC SULFATE

| Solution | Meq. reducing agent added | Meq. $Ce^{IV}$ used |
|---|---|---|
| 1[a] | 0.0149 | 0.0151 |
| 2[a] | .0403 | .0398 |

[a] Calculated from light absorption to contain: 1, 0.0094 $F$ $Re^{IV}$, 0.0007 $F$ $Re^{V}$, 22 hr. old soln.; 2, 0.0100 $F$ $Re^{IV}$, 0.0051 $F$ $SnCl_2$, 64.5 hr. old.

To obtain the cerium(IV) analyses, 0.50 or 1.00 ml. portions of the rhenium solution in 4 $F$ hydrochloric acid were added to 0.80 ml. or 1.00 ml. of 0.0462 $F$ cerium(IV) solution. In the analyses with iodine, typically 0.036 meq. of iodine was present in a volume of 16 ml. of 0.1 $F$ hydrochloric acid after adding the rhenium solution. The hydrochloric acid was 1–2 $F$ in the iodate analyses.

In agreement with the results of previous investigators,[19,21,22] it was found that chromium(II) reduced perrhenic acid to yellow-brown rhenium(IV). Excess chromous solution was added to known amounts of perrhenic acid in 4 $F$ acid, and the excess destroyed by treatment with oxygen for one to two minutes. The solution was then titrated with cerium(IV) to an *o*-phenanthroline end-point. The reducing agent thus found ran 5–10% less than theoretical for formation of rhenium(IV); some oxidation of the rhenium(IV) by the gaseous oxygen may have occurred. The chromium(II) was prepared by shaking 0.1 $F$ chromic chloride in 4 $F$ hydrochloric acid with 30-mesh zinc in a loosely stoppered vessel.

**Potassium Hexachlororhenate(IV).**—Extinction coefficients calculated from measurements on a 0.05 $F$ $K_2ReCl_6$ solution in 4 $F$ hydrochloric acid are plotted in Fig. 1. Within the errors for the weakly-absorbing solutions, the same results were obtained for 0.01 to 0.05 $F$ hexachlororhenate in 4 to 6 $F$ acid, and a 0.01 $F$ solution in 4 $F$ acid had the same light absorption for three hours in a closed cell. For comparison, Schmid's data[24] are also plotted; rough agreement is seen over the wave length intervals where Schmid gave measurements.

Acidic solutions of potassium hexachlororhenate(IV) are known to be resistant to such oxidizing agents as hydrogen peroxide,[10] potassium permanganate,[11] dichromate, and ferric sulfate.[9,10] This inertness was confirmed in the present work and it was shown that the hexachlororhenate ion at room temperature is stable against oxygen, stannous chloride, ferrous or ferric ions, chlorine, iodine or potassium iodide, potassium iodate, and cupric or cuprous ions. In agreement with Geilmann and Wrigge[9] quantitative oxidation of potassium hexachlororhenate(IV) to perrhenate resulted after a twenty-minute treatment with hot cerium(IV), but no oxidation was found in a few minutes at room temperature.

The experimental data showing the inertness of hexachlororhenate are given in Table III. As indicated there, the lack of reaction was shown either by analyzing for the oxidizing or reducing agent added or by determining the $K_2ReCl_6$ by its light absorption. The reaction time was several minutes where not otherwise noted.

We may note that $Cs_2ReCl_6$ is quite insoluble especially in hydrochloric acid solutions. It was used in the analysis of the $K_2ReCl_6$ preparation and the following section describes its use to

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(24) H. Schmid, *Z. anorg. Chem.*, **212**, 187 (1933).

distinguish between $ReCl_6^=$ and other forms of $Re^{IV}$.

**Rhenium(IV) Prepared from Rhenium Dioxide.**—The marked contrast between the highly colored reactive yellow-brown rhenium(IV) prepared by stannous chloride reduction of perrhenate, Fig. 2, and the light green inert hexachlororhenate, Fig. 1, suggested that the reactive yellow rhenium(IV) differs from $ReCl_6^=$ by containing some rhenium–oxygen bonds instead of only rhenium–chlorine bonds. Therefore, the kind of rhenium(IV) obtained by dissolving freshly precipitated rhenium dioxide in acid was studied. The Noddacks[10] treated rhenium dioxide with 20% hydrochloric acid to obtain a brown solution which was not colloidal, gave no precipitate with cesium chloride, was easily oxidized to perrhenate, and was converted into hexachlororhenate upon heating. These observations were confirmed and extended in the present work. Thus rhenium dioxide solutions appeared to have the same reactivity as the kind of rhenium(IV) formed from perrhenate with stannous ion, and similar but not identical light absorption.

Rhenium dioxide was prepared by adding base to hexachlororhenate ion.[10,25] The brown-black precipitate was readily centrifuged and up to 0.2 millimole dissolved at room temperature in 35 ml. of 12 $F$ hydrochloric acid. Warming caused changes in the form of the rhenium(IV). The 12 $F$ acid solutions could be diluted to 4 $F$ with no precipitation.

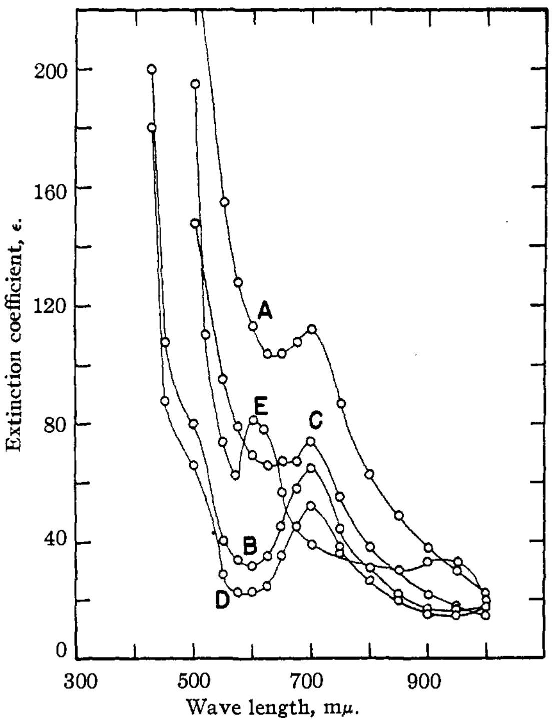

Fig. 3.—Absorption spectra of solutions of $ReO_2$ in HCl (concentrations by analysis with iodate): A, $0.0027_7$ $F$ $Re^{IV}$ in 6 $F$ HCl, 2-hr. old; B, previous solution, 44-hr. old and $0.0020_3$ $F$ $Re^{IV}$; C, $0.0026_7$ $F$ $Re^{IV}$ in 6 $F$ HCl, 2-hr. old; D, previous solution, 49-hr. old and $0.0019_7$ $F$ $Re^{IV}$; E, 0.0100 $F$ $Re^{IV}$ from $HReO_4$ with $SnCl_2$ in 4 $F$ HCl.

TABLE III

EFFECT OF OXIDIZING OR REDUCING AGENTS UPON $K_2ReCl_6$

| Agent used | Concentrations in mixture, $F$ | | | Observations |
|---|---|---|---|---|
| | Agent | $K_2ReCl_6$ | Acid | |
| $O_2$ | (air) | 0.010 | 4 (HCl) | Light absorption same after 11 hr. exposure |
| $Sn^{II}$ | 0.018 | .0064 | 4.7 (HCl) | Light absorption same |
| $Ce^{IV}$ | .0398 | .00720 | 0.6 (HCl) + .4 ($H_2SO_4$) | All $Ce^{IV}$ recovered |
| $Fe^{III}$ | .0069 | .0091 | .01 ($H_2SO_4$) | Strong red with KSCN |
| $Cl_2$ | .01 | .010 | 4 (HCl) | Light absorption same. Strong $Cl_2$ test with *o*-tolidine, starch-iodide |
| KI | .18 | .0033 | Neutral | No color formed |
| $I_2$ | .0032 | .00059 | 0.01 (HCl) | All $I_2$ recovered |
| $KIO_3$ | .0050 | .00278 | 2 (HCl) | All $KIO_3$ recovered |
| $KIO_3$ | .0076 | .00418 | Neutral | All $KIO_3$ recovered |
| $Cu^{II}$ | .0257 | .0065 | Neutral | No color change, no ppt. No ppt. with KSCN |
| $Cu^{I}$ | .0220 | .0085 | 0.7 (HCl) | No $Cu^{II}$ formed |

Geilmann and Wrigge[9] obtained quantitative oxidation of anhydrous rhenium dioxide to perrhenate by ferric sulfate, potassium dichromate or ceric sulfate in 1 $F$ sulfuric acid. In the present work hydrochloric acid solutions of rhenium dioxide were oxidized to colorless perrhenate by ceric sulfate, potassium iodate, ferric sulfate or cupric sulfate, in 3 to 4 $F$ acid. The reducing agent found in these analyses was 60–85% of that expected from the amount of potassium hexachlororhenate(IV) taken to prepare the rhenium dioxide. Some oxidation of the rhenium(IV) by air may have occurred while washing the precipitate, or small amounts of inert hexachlororhenate may have formed gradually. Decreases in the amount of reducing agent were found after forty-five hours of standing. The strongly brown rhenium(IV) was decolorized by cerium(IV) or iodate thus giving a concentration for interpreting the spectrophotometric results. From 10–30% of the rhenium(IV) was oxidized by iodine in 0.3 $F$ acid.

Examination of the light absorption curves of two $ReO_2$ solutions, Fig. 3, shows the following facts: (1) the two solutions did not have the same absorption initially, although their concentrations were practically identical, (2) after correcting for decreases in concentration as determined with iodate over a forty-five-hour period, the absorption for each solution was lower than for either initially, and (3) the absorptions of the two solutions were close after forty-five hours although they were different initially. From this it is concluded that rhenium dioxide in solution exists in more than one absorbing form, that one or more of the initial colored forms is converted into less absorbing forms upon standing, and that since the initial forms are not reproducible, the substance

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(25) W. Biltz, *Z anorg. Chem.*, **214**, 225 (1933).

is not one well-defined species. Figure 3 also displays, for comparison, the absorption spectrum of $Re^{IV}$ prepared by reduction of perrhenic acid with $Sn^{II}$.

Solutions of rhenium dioxide in 8 to 12 *F* hydrochloric acid were converted into hexachlororhenate(IV) by heating in an evacuated oxygen-free tube for twelve hours at 130°. A precipitate of $Cs_2ReCl_6$ was then obtained upon addition of cesium chloride and the light absorption was similar to that of a potassium hexachlororhenate(IV) solution, although slightly higher, perhaps because of the presence of some of the unconverted brown form of rhenium(IV).

## Discussion

It is shown in the preceding sections that there are several varieties of rhenium(IV) which can be prepared in hydrochloric acid solution. The hexachlororhenate ion is chemically the least reactive of these and also the least colored.

We propose the hypothesis that the yellow-brown rhenium(IV) prepared by reduction of perrhenate with stannous ion and the varieties of yellow-brown rhenium(IV) obtained by dissolving rhenium dioxide in hydrochloric acid differ from $ReCl_6^{=}$ in that they contain some rhenium–oxygen bonds instead of only rhenium–chlorine bonds. The evidence that suggests this hypothesis is: (a) the conversion of the rhenium(IV) prepared by dissolving rhenium dioxide in hydrochloric acid into hexachlororhenate upon treatment with hot concentrated hydrochloric acid[26]; (b) the formation of the yellow-brown varieties of rhenium(IV) from compounds containing rhenium–oxygen bonds ($ReO_4^-$ and$ReO_2$) by relatively gentle reactions, and also the ease with which these species may be oxidized to perrhenate, as compared to the inertness of $ReCl_6^{=}$ (c) the analogy between the strong color of these ions (as compared to $ReCl_6^{=}$) and the strong color of solid rhenium dioxide.

Since the absorption spectra show that there are several yellow-brown varieties of rhenium(IV) we may suppose that there are either a series of hydroxo ions of the type $ReCl_{6-n}(OH)_n^{=}$, or a series of polymers with rhenium–oxygen–rhenium bonds. In this connection it may be noted that solid compounds $K_4Re_2^{IV}OCl_{10}$ and $K_2Re^{IV}Cl_5(OH)$ have been reported.[27] Indeed, our results do not preclude the possibility that the yellow-brown kinds of rhenium(IV) are colloidal solutions, but the reproducibility of the extinction coefficients of rhenium(IV) obtained from perrhenate with stannous chloride makes this seem unlikely. An ultra-filtration experiment by the Noddack's[10] also argues against this possibility.

In considering the chemical evidence as to the magnitudes of the oxidation potentials of the various $Re^{IV}$–$Re^{VII}$ couples, one may mention the following facts. (a) $ReCl_6^{=}$ is prepared from $ReO_4^-$ by reduction with hot iodide ($E_0$ *ca.* − 0.5 v.). It is oxidized at an appreciable rate only by strong oxidizing agents like cerium(IV) in hot solutions. (b) Yellow-brown rhenium(IV) is obtained from $ReO_4^-$ by $Sn^{II}$ ($E_0$ *ca.* − 0.2 v.) and is readily oxidized by strong oxidizing agents like chlorine, but not at an appreciable rate by iodine.[28] Since the failure of some reagents to attack $Re^{IV}$ may be due to rate phenomena rather than equilibrium conditions, the chemical evidence serves only to bracket the several $Re^{IV}$–$Re^{VII}$ potentials between widely spaced limits.

As regards the stability of rhenium(V), we note that it is formed from rhenium(VII) by tin(II) but it is oxidized to rhenium(VII) by iodine in dilute acid. It is interesting to note that Jakób and Jeżowska-Trzebiatowska report that in concentrated hydrochloric acid the first step in the reduction of perrhenate by iodide is the formation of a form of rhenium(V).[28] At lower acidities, rhenium(V) disproportionates to $ReO_4^-$ and $ReO_2$ but it does not do so at an appreciable rate in 4 *F* hydrochloric acid. However, rhenium(IV) does not react with rhenium(VII) to give rhenium(V), so there is no evidence as to the equilibrium conditions among these three oxidation states in 4 *F* hydrochloric acid.

Pauling[29] has pointed out the special stability associated with a half-filled subgroup of electrons and the close similarity in properties to the corresponding structure with a full subgroup. Hence it might be expected that the hexachlororhenate(IV) ion would be at least as stable as the hexachlorosmate or hexachloroplatinate ions corresponding to −0.7 v.[30] or a more positive potential for formation from the element. Indeed, a more positive value of this potential has been estimated by Latimer[30] from the reported heat of formation of perrhenate and other data, but further work is required to establish the rhenium–hexachlororhenate and the hexachlororhenate–perrhenate potentials more precisely.

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[26] Unfortunately, we did not determine whether the $Re^{IV}$ by stannous reduction of perrhenate also undergoes this conversion but we believe it probable that it does.

[27] B. Jeżowska-Trzebiatowska and C. Jodko, *Rocsniki Chem.*, **19**, 187 (1939); "Gmelins Handbuch der anorganischen Chemie," 8th ed., Vol. 70, p. 132.

[28] It would be interesting to know whether any of the reactive yellow-brown kinds of rhenium(IV) are formed as intermediates in the reduction of $ReO_4^-$ by iodide to $ReCl_6^{=}$. Extensive studies were not made, but it was observed that the reaction of perrhenate with the equivalent amount of potassium iodide in 12 *F* HCl at room temperature gave initially a form of rhenium that was not precipitated by cesium ion and hence was not $ReCl_6^{=}$. However, the absorption spectrum of this product was similar to that of $ReCl_6^{=}$, but about twice as intense. For other evidence supporting the intermediate formation of a reactive $Re^{IV}$, see W. F. Jákob and B. Jeżowska-Trzebiatowska, *Z. anorg. Chem.*, **220**, 16 (1934).

[29] L. Pauling, Victor Henri Memorial Volume, Desoer, Liege, 1948.

[30] W. M. Latimer, "The Oxidation States of the Elements," Prentice-Hall, New York, N. Y., 1938, pp. 194, 195, 218, 226.

## Summary

The absorption spectra of rhenium(VII), rhenium(V), and various rhenium(IV) species have been determined, and the reactivity of these valence states determined for common oxidizing and reducing agents. Reduction of rhenium(VII) in 4 formal hydrochloric acid with tin(II) gives first green rhenium(V) and then a yellow-brown variety of rhenium(IV). A similar but not identical yellow-brown form of rhenium(IV) may be obtained by dissolving freshly precipitated rhenium dioxide in hydrochloric acid, and this form is converted to hexachlororhenate(IV) by digestion with hot concentrated hydrochloric acid. The hexachlororhenate ion has a different absorption spectrum and is much less reactive toward oxidizing agents than the yellow-brown varieties of rhenium(IV).

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

# Reactions of Some Thorium and Uranium Compounds in Liquid Ammonia

BY GEORGE W. WATT, W. A. JENKINS, JR., AND JANE M. MCCUISTON[1]

A need for simple compounds of thorium and uranium that are appreciably soluble in liquid ammonia without reaction more extensive than solvation has led to the study of the behavior of a number of compounds of these elements. In the course of this work several solvolytic reactions have been observed and a few solubility determinations have been made. These and other related studies are described below.

## Experimental

**Materials.**—Aside from the following starting materials, all chemicals employed were reagent grade and were used without further purification or analysis.

**Thorium(IV) Nitrate 4-Hydrate.**—(A. D. Mackay Co.) *Anal.* Calcd. for $Th(NO_3)_4 \cdot 4H_2O$: Th, 42.0. Found: Th, 42.0.

**Thorium(IV) Sulfate.**—(City Chemical Corporation) *Anal.* Calcd. for $Th(SO_4)_2$: Th, 54.7. Found: Th, 54.4.

**Thorium(IV) Iodate.**—This salt was prepared by the reaction between pure thorium(IV) nitrate and potassium iodate. *Anal.* Calcd. for $Th(IO_3)_4$: Th, 24.9. Found: Th, 24.6.

**Thorium(IV) Oxalate 2-Hydrate.**—Thorium(IV) oxalate 6-hydrate was prepared from thorium(IV) nitrate and oxalic acid and dehydrated at 110° to afford the 2-hydrate. *Anal.* Calcd. for $Th(C_2O_4)_2 \cdot 2H_2O$: Th, 52.3. Found: Th, 52.3.

**Uranium(IV) Chloride.**—This compound was prepared by the method described by Moore[2] and purified by sublimation. *Anal.* Calcd. for $UCl_4$: U, 62.7; Cl, 37.3. Found: U, 62.2; Cl, 37.2.

The origin and composition of uranium peroxide 2-hydrate, uranyl nitrate 6-hydrate and 2-hydrate used in this work are given elsewhere.[3]

**The Ammonolysis of Thorium(IV) Nitrate 4-Hydrate.**—Because of a strongly exothermal reaction with ammonia gas and resultant caking of the solid, thorium(IV) nitrate 4-hydrate could not be treated satisfactorily with liquid ammonia in an apparatus of the type described by Watt and Moore.[4,5] Consequently, 5.1818 g. of the salt was added to 70 ml. of vigorously agitated liquid ammonia in a Dewar flask, the ammonia was then evaporated, and the resulting gross solid was dried *in vacuo* over barium oxide. A sample (5.4207 g.) of this material was then placed in the reactor,[4] and treated with anhydrous liquid ammonia for a total of four hours (including the time required for filtration and nine washings).

The ammonia-insoluble product consisted of an amorphous white solid which was insoluble in water but soluble in hot concentrated acids. Qualitative tests for nitrate ion were negative. A typical solid product contained 74.3% thorium and 1.3% nitrogen.

The solid residue from the combined filtrate and washings consisted of a small amount of white water-insoluble solid, but the major portion was water-soluble. The water extract yielded 2.38 g. of ammonium nitrate (or 3.2 moles/mole of thorium nitrate used), m. p. 169–170°, and this melting point was not depressed upon admixture with an authentic specimen (m. p. 169.6°).

These results indicate (but do not finally prove) that the thorium(IV) nitrate 4-hydrate was converted to ammonium nitrate and hydrated thorium(IV) oxide, the latter probably containing a small amount of ammonia of solvation. Complete conversion requires 2.99 g. of ammonium nitrate, but mechanical losses are considered sufficient to account for the fact that only 2.38 g. was recovered. Attention is called to the fact that these results do not necessarily depend upon the solvolytic action of ammonia. The water content of the hydrate is sufficient to permit the reactions

$$Th(NO_3)_4 \cdot 4H_2O + 4NH_3 \longrightarrow Th(NO_3)_4 + 4NH_4OH$$
$$Th(NO_3)_4 + 4NH_4OH \longrightarrow ThO_2 \cdot 2H_2O + 4NH_4NO_3$$

Alternatively, it is possible that the nitrate is directly ammonolyzed. In any event, the present results stand in sharp contrast to a report by Shatenshtein[6] that thorium (IV) nitrate 12-hydrate is soluble to the extent of 26 g./100 g. ammonia at room temperature, and to Audrieth and Yntema's statement[7] that thorium(IV) nitrate is soluble in liquid ammonia at −33°.

**The Action of Liquid Ammonia upon Thorium(IV) Sulfate.**—This salt (3.4667 g.) was treated with excess liquid ammonia for about three hours. Filtration could not be accomplished owing to clogging of the filter medium and take-off lines. Consequently, the ammonia was evaporated and the solid residue was dried *in vacuo* ($10^{-3}$ mm.) for eighteen hours. A 1.0142-g. sample was leached eight times with 5–10-ml. portions of water and made up to a known volume for analysis. This solution gave a negative test for thorium but was found to contain ammonium and sulfate ions in a 2:1 ratio. Ammonium sulfate was crystallized from the aqueous extract and identified through its X-ray ($CuK_\alpha$) diffraction pattern in

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[1] Present address: Chemistry Division, U. S. Naval Ordnance Test Station, China Lake, California.

[2] Moore, *J. Am. Electrochem. Soc.*, **43**, 317 (1923).

[3] Watt, Marley and Achorn, THIS JOURNAL, in press.

[4] Watt and Moore, *ibid.*, **70**, 1197 (1948).

[5] Unless otherwise indicated, all reactions in ammonia were carried out in this type of equipment.

[6] Shatenshtein, "Liquefied Gases as Solvents," Government Chemical-Technical Publishing Office, Leningrad Division, 1934.

[7] Audrieth and Yntema, *J. Phys. Chem.*, **34**, 1902 (1930).