sq. m./g. These observations show that (1) increasing the degassing temperature increases the apparent nitrogen surface area, and (2) the surface of a sample was lowered upon exposure to normal laboratory air after it had previously been degassed sufficiently to produce a high surface area.

The behavior of the nitrogen surface areas may be interpreted on the basis of the persorption mechanism described previously. When a sample of nickel fluoride, which has been completely converted from nickel oxide and from which the excess chlorine trifluoride has been carefully evacuated, is exposed to normal laboratory air, the sample increases in weight over a long period of time. This sorbed material, believed to be water vapor from the air, may also be removed on evacuation. It may be assumed here that the initial rapid uptake is due to surface adsorption, and the slow sorption process due to persorption which was noted previously with chlorine trifluoride. Before determining the amount of nitrogen which the sample would adsorb, it was first evacuated under various conditions as previously shown in Table III. The 16-hour evacuation at room temperature apparently removed the water vapor from the surface but only very little from the internal structure. The nitrogen was then adsorbed over the surface, while the water molecules blocked the pore structure. Increasing the temperature removed increasing amounts of water from the pores and allowed more nitrogen to enter giving a higher apparent surface area.

If the water molecules were chemisorbed on the surface, the adsorption of nitrogen should proceed just as readily over the occupied chemisorbed sites as over the uncovered surface. This was the conclusion of Brunauer and Emmett[12] who investigated the adsorption of nitrogen on an iron catalyst with and without chemisorbed oxygen.

[12] S. Brunauer and P. H. Emmett, THIS JOURNAL, **62**, 1732 (1940).

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

Rhenium(IV) Compounds: Synthesis and Properties

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Hypophosphorous acid has been used, in place of iodide, for the reduction of perrhenate in an improved synthesis of several hexahalorhenates(IV). Solubility measurements and spectrophotometric absorption data are presented for a number of rhenium(IV) complex salts. The hydrolysis of hexachlororhenate(IV) ion has been studied conductimetrically, and the existence of the species $[Re(OH)_3(H_2O)_3]^+$ is postulated as the final intermediate prior to precipitation of the dioxide.

Aqueous solutions of the four halides, K_2ReX_6, hydrolyze to varying degrees, depending on the halogen in the complex. The most general method used for the preparation of these salts involves iodide reduction of potassium perrhenate in the presence of a large excess of the appropriate halogen acid.[2] The iodine product and large excesses of potassium halide must be removed in the purification. The only accurate solubility data recorded on these salts are measurements by the Noddacks[3] on two hexachloride salts in rather strong hydrochloric and sulfuric acid. The only well characterized absorption spectrum is that of the chloride in the visible region.[4,5] Little is known concerning the hydrolysis products of the hexahalorhenates. Maun and Davidson[5] have shown that there are several varieties of yellow-brown rhenium(IV) complexes. They postulate that the several varieties might be accounted for by a series of complexes of the type $[ReCl_{6-n}(OH)_n]^{-2}$.

Syntheses

Hydrazine dihydrochloride has been found to reduce small amounts of perrhenate quantitatively.[6] For the macro synthesis of hexahalorhenates, however, neither hydrazine, formaldehyde nor sulfur dioxide proved suitable. Controlled quantities of hypophosphorous acid gave good yields of the chloride and bromide salts. In the case of the fluoride a black precipitate, similar to that obtained with the bromide when too much reducing agent is used, was obtained. With the iodide, the hydriodic acid reduced the perrhenate in preference to the hypophosphorous acid.

Reagents.—Distilled water and C.P. or reagent-grade chemicals were employed throughout this investigation, as were University of Tennessee 99.8% grade potassium perrhenate, and Mallinckrodt 50% hypophosphorous acid in the modified synthesis.

Procedure.—Approximately 3 g. of potassium perrhenate and a stoichiometric amount of potassium chloride (0.77 g.) are added to 100 ml. of hydrochloric acid in a 250-ml. beaker. Twenty milliliters of 50% hypophosphorous acid is added and the beaker is covered with a watch glass. The solution is kept just below boiling until it becomes a clear light green; it will turn brown first, then dark green and finally light green. The hydrochloric acid lost by evaporation is replaced periodically to keep the salt from precipitating. The hot solution is filtered to remove any rhenium dioxide or rhenium metal which has formed. The solution is evaporated down to 20 ml., preferably by a heat lamp to prevent spattering, and placed in an ice-bath. The bright green salt is filtered onto a sintered glass filter and suction dried. The salt is washed twice with small volumes of ice-cold dilute hydrochloric acid and then, twice each, with ethyl alcohol and diethyl ether. The salt is air-dried by drawing air through the filter by means of suction, and is finally dried in an oven at 110° for one hour.

The preparation of the bromide differs only in that 5 ml. of hypophosphorous acid is used for the same amount of potassium perrhenate, and all chloride reagents are replaced by bromide reagents.

The reactions for the preparation of both the chloride and the bromide require approximately three hours up to the isolation of impure product. If a recrystallization is added,

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[1] Abstracted from a dissertation submitted by R. J. M. in partial fulfillment of the requirements for the Ph.D. degree.

[2] L. C. Hurd and V. A. Reinders in H. S. Booth (ed.), "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., New York, N. Y., 1939, pp. 178–180.

[3] I. and W. Noddack, *Z. anorg. allgem. Chem.*, **215**, 129 (1933).

[4] H. Schmid, *ibid.*, **212**, 187 (1933).

[5] E. K. Maun and N. Davidson, THIS JOURNAL, **72**, 2254 (1950).

[6] R. J. Meyer and C. L. Rulfs, *Anal. Chem.*, in press.

the process can be completed in less than four hours. The purity of the chloride is approximately 96% or better without recrystallization, with a yield of about 80%. With the bromide, a yield of 70% is obtained and the salt is approximately 92% pure. Both salts may be obtained 99.5% pure with one recrystallization.

Analyses.—The hexahalorhenates(IV) were hydrolyzed to give rhenium dioxide. The filtrates, after acidification with nitric acid, were treated with silver nitrate and assayed for halide by conventional gravimetric techniques. Peroxide resolution of the dioxide suspension gave perrhenate solutions, aliquots of which were assayed for rhenium spectrophotometrically.[6]

Absorption Spectra

The ultraviolet absorption of solutions of hexachlororhenate (99.9% purity) and of hexabromorhenate (99.7% purity) is shown on Fig. 1. These salts were prepared by the hypophosphite procedure and were assayed for both halogen and rhenium content.

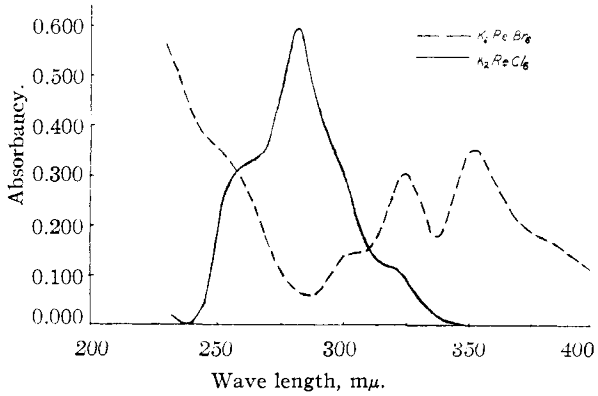

Fig. 1.—Absorption spectra of hexahalorhenates: 0.05 mM hexachlororhenate(IV) in 4 N hydrochloric acid and 0.04 mM hexabromorhenate(IV) in 1 N hydrobromic acid; 1 cm. cells at 25°.

Table I lists the molar absorbancy indices, for 1 cm. path and at 25°, at the wave lengths of principal interest for solutions of three hexahalorhenates. The slit widths were varied as necessary on the Beckman instrument, using 1 N solutions of the corresponding hydrohalide acids for zero-setting with two of the halides, and 2.8 N hydroiodic acid with the third. The potassium hexaiodorhenate was prepared by the conventional iodide reduction and recrystallized once from hydroiodic acid. It assayed 98% purity based on halogen, but only 90% based on rhenium content.

TABLE I

MOLAR ABSORBANCY INDICES OF THE POTASSIUM HEXAHALORHENATES(IV) (1 cm. path at 25°)

Wave length, mμ	K_2ReCl_6 (in 1 N HCl)	K_2ReBr_6 (in 1 N HBr)	K_2ReI_6 (in 2.8 N HI)
281.5	1.18×10^{4a}	2.68×10^3	
310	3.08×10^3	4.81×10^3	1.13×10^{4a}
325	1.8×10^3	9.45×10^{3a}	1.11×10^4
350	20	1.04×10^4	1.41×10^{4a}
353	20	1.08×10^{4a}	1.34×10^4
385	x	5.41×10^3	8.85×10^{3a}
430	2.3	2.20×10^3	6.91×10^{3a}
530	<1	18.9	6.26×10^{3a}
570	<1	1.15	5.20×10^{3a}
640	2.6^a	8.90	2.16×10^3
665	1.1	11.8^a	2.12×10^3
710	2.8^a	1.2	1.42×10^3
755	<1	11.3^a	5.55×10^2

[a] Designates an absorbancy peak.

Solubilities

To measure the solubility of easily hydrolyzed salts it is usually necessary to find a means of measuring the concentration of the saturated solution directly. The sensitivity of the ultraviolet absorption of solutions of the salts of hexahalorhenates(IV) offers an accurate method for measurements of this type.

Solubility data were obtained after equilibrations in a small jacketed cell. Water controlled at 25.0 ± 0.1° was pumped through the jacket. Stirring of the solution during saturation was accomplished by slowly bubbling nitrogen through the solution. The nitrogen was presaturated by passing it through a bubbler containing the solvent used in the measurement.

The potassium salts of the chloride and the bromide complex were prepared by the method outlined previously. The silver hexachlororhenate was prepared by dissolving the potassium salts in dilute sulfuric acid and adding dilute silver nitrate solution. The precipitate was filtered off and washed with water, ethyl alcohol and diethyl ether.

The salt to be measured was introduced into the constant temperature cell in excess of the amount which would dissolve in the amount of solvent to be used. The solvent solution was introduced and allowed to remain in contact with the salt for 24 hours with constant stirring. After the 24-hour saturation period a portion of the solution was removed and filtered. An aliquot portion of the filtrate was placed in a volumetric flask and diluted sufficiently to permit reading on the spectrophotometer. From this reading the concentration of the dilute solution was calculated by comparison with the reading given by the standard solution. The concentration of the saturated solution was then calculated. The remainder of the solution in the constant temperature cell was allowed to equilibrate for another 24-hour period before another measurement was made.

It is felt that the data recorded in Table II represent the attainment of true equilibrium to within at least 1%, for a 24-hour period. Unfortunately, data for pure water were not attainable because of the tendency for hydrolysis to occur. In the case of potassium hexachlororhenate, however, some runs were made in 0.001, 0.01 and 0.1 N acid; solubili-

TABLE II

SOLUBILITIES OF COMPLEX RHENIUM SALTS AT 25°

Salt	Media	Satd. soln., M	Solubility, g./l.	Av.
K_2ReCl_6	0.01 N	0.175	83.5	83.3
K_2ReCl_6	HCl	.174	83.0	
K_2ReCl_6		.175	83.5	
Ag_2ReCl_6	0.01 N	.000262	0.187	
Ag_2ReCl_6	H_2SO_4	.000264	0.189	0.188^a
Ag_2ReCl_6		.000261	0.187	
K_2ReBr_6	3.0 N	.144	107	
K_2ReBr_6	HBr	.144	107	107
K_2ReBr_6		.145	108	

[a] This corresponds to a solubility product of 7.2×10^{-11}.

ties in these media were identical within experimental error (1%). Hence, the data shown for the first two salts should closely approximate their "water solubility," in the absence of hydrolysis. From a consideration of the spectrophotometric, volumetric and temperature control errors, it is estimated that these data should be valid within, at least, 2%.

Rhenium(IV) Hydrolysis

An aliquot portion of a 1% hexachlororhenate(IV) solution was transferred into a 100-ml. beaker and diluted to 40 ml. This solution was titrated with 0.1 *N* base while reading with a conductance bridge. Equilibrium was established very slowly after the addition of each increment of titrant, and in the first titration an attempt was made to achieve a constant reading before another increment of titrant was added. It was found that very little change occurred after 15 minutes; in all subsequent titrations, readings were taken 15 minutes after the addition of titrant. Similar solutions of potassium hexachlororhenate(IV) were titrated in another beaker with potassium hydroxide in conjunction with a *p*H meter. Equilibrium readings were taken after 15 minutes here also. Air oxidation to perrhenate was avoided by presaturating the solutions with nitrogen and passing a slow stream of nitrogen over the surface throughout the run. It was necessary to purify the nitrogen by pretreatment with potassium hydroxide solution before passing it into the titration cell.

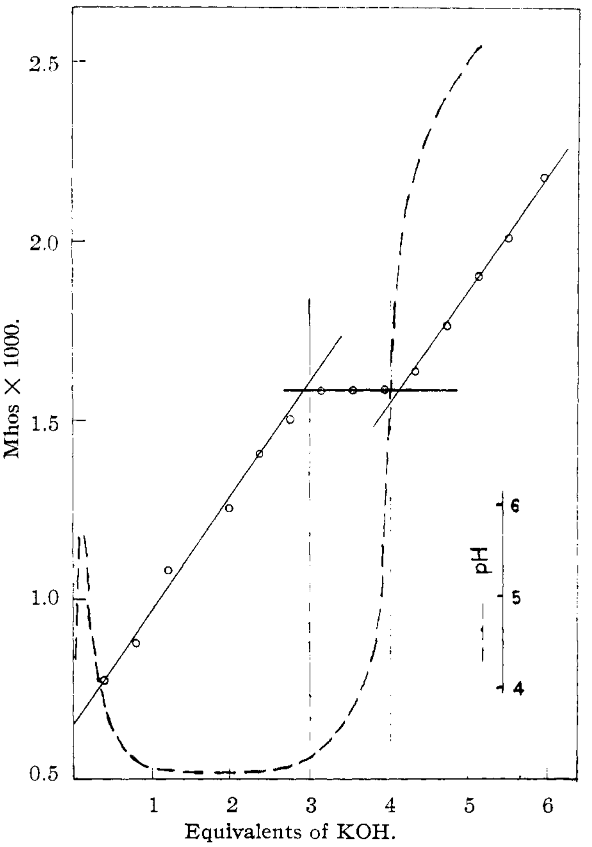

Fig. 2.—Hydrolytic titration of K_2ReCl_6, conductance and *p*H plot. The conductivity has been corrected for dilution during the titration.

Figure 2 shows the data obtained by the conductance titration technique, which indicate that a stable complex is formed upon addition of three equivalents of hydroxyl ion. Considering the type of complex postulated by Maun and Davidson,[5] the intermediate would have a formula in which *n* has the value of three. The following equation represents a stepwise reaction of the hexachlororhenate(IV) with hydroxyl ion

$$[ReCl_6]^{=} \xrightarrow{OH^-} [Re(OH)Cl_5]^{=} \xrightarrow{OH^-} [Re(OH)_2Cl_4]^{=} \xrightarrow{OH^-} [Re(OH)_3Cl_3]^{=} \quad (I)$$

Upon addition of the fourth hydroxyl group to this type of complex rhenium chloride is obtained

$$[Re(OH)_3Cl_3]^{=} \xrightleftharpoons[2H_2O]{OH^-} \begin{array}{c}\underline{Re(OH)_4 \cdot 2H_2O} + 3Cl^- \\ \downarrow \\ \underline{ReO_2} + 4H_2O\end{array} \quad (II)$$

With this type of complex a large increase in the conductance would be observed upon addition of the fourth hydroxyl ion to the complex, due to the liberation of the three chloride ions upon the formation of rhenium dioxide. Since this increase in conductance is not observed one must conclude that there are no chloride ions in the intermediate.

The conclusion to be drawn from these data is that the complex formed as an intermediate in the hydrolysis of hexachlororhenate(IV) is cationic in nature. The three chloride ions which have not been replaced by hydroxyl ions are most probably replaced by water molecules since this reagent is in excess. Equations I and II now become

$$[ReCl_6]^{=} \xrightarrow[3H_2O]{3OH^-} [Re(OH)_3(H_2O)_3]^+ + 6Cl^- \quad (III)$$

and

$$[Re(OH)_3(H_2O)_3]^+ \xrightleftharpoons{OH^-} \begin{array}{c}\underline{[Re(OH)_4(H_2O)_2]} + H_2O \\ \downarrow \\ \underline{ReO_2} + 2H_2O\end{array} \quad (IV)$$

The data obtained from the *p*H titration indicate that no further reaction between the rhenium and hydroxyl takes place after four equivalents of base have been added. This is to be expected on the basis of equations III and IV. The unusual behavior of the *p*H after addition of the first increment of base is also compatible with these equations.

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