

tory. Such media would be expected to have a constant distribution of polymer sizes and shapes and the effective concentration of active sites would be dependent on total Cr(III) concentrations.

An unusual feature of our results is the observation that the h -function provides an exact correlation of the rate data in both KOH and NaOH media varying from 0.5 to 6.0 M , even though other properties in the media vary widely and irregularly both with change of concentration and change of cation. This indicates that, insofar as the rate of this reaction is concerned, the basic function of the Cr(III) polymer behaves as a mononegative base of the type used in the determination of the h -function. If this interpretation is correct, it implies that charged sites are sufficiently removed from one another to prevent effective interaction

through the solvent and that the insulating properties of the Cr-OH-Cr bonds¹⁵ are such that interaction through the particle is small.

The non-integral exponent of the acidity factor in the rate law may be interpreted in terms of an equilibrium in which μ -hydroxo bridges between adjacent Cr(III) atoms are broken by abstraction of protons from the medium. Inhibition by carbonate may be understood as an effect on this equilibrium. Rate determining attack by peroxide on Cr(III) after bridge rupture is in agreement with the observed rate law. A slow coordination number change of Cr(V)^{6c,16} is also a possibility.

Inhibition by bases indicates that protonated intermediates are involved in basic as well as acidic media.

(15) A. Earnshaw and J. Lewis, *J. Chem. Soc.*, 396 (1961).

(16) J. Y. Tong and E. L. King, *J. Am. Chem. Soc.*, **82**, 3805 (1960).

[CONTRIBUTION FROM THE BELL TELEPHONE LABORATORIES, INCORPORATED, MURRAY HILL, NEW JERSEY, AND THE DEPARTMENT OF CHEMISTRY, COLUMBIA UNIVERSITY, NEW YORK 27, NEW YORK, AND THE DEPARTMENT OF CHEMISTRY, BROWN UNIVERSITY, PROVIDENCE 12, RHODE ISLAND]

Transition Metal-Hydrogen Compounds. I. Dipotassium Octahydridorhenate(VI)

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The preparation, characterization and some properties of the unusual ternary transition metal hydride K_2ReH_8 are described. Evidence is given to show that the hydride anion ReH_8^- is the only such species formed by reduction of perrhenate with alkali metals or of rhenium heptoxide with lithium aluminum hydride.

In a recent note^{1b} we presented chemical and nuclear magnetic resonance evidence showing the existence of a soluble potassium rhenium hydride, the first example of a transition metal hydride complex which does not also contain electron donating groups such as $C_5H_5^-$, CO or CN^- attached to the metal ion. In the present paper we give the results of further work which demonstrates that a compound having the composition K_2ReH_8 has been isolated from the products of the reduction of aqueous ethylenediamine solutions of perrhenate with potassium metal. The infrared spectrum of this compound suggests that it is essentially identical with the substance prepared initially by Bravo, Griswold and Kleinberg² and later by Floss and Grosse,³ and described as the rhenide $KRe \cdot 4H_2O$. The latter authors, in the light of our earlier work^{1,4} and the independent work of Wilkinson,⁵ have recently revised their formula to $KReH_4 \cdot 2H_2O$.⁶ Since there is evidence that Floss and Grosse's $KReH_4 \cdot 2H_2O$ is really the same as our K_2ReH_8 , at least in regard to the nature of the hydride anion, we appear to be faced with a discrepancy

between our results and those of Floss and Grosse. In view of this and the rather unexpected nature of our results, we consider it desirable to present this work in somewhat greater detail than would ordinarily be necessary.⁷

The important question of the relation between the hydride formed by reduction of perrhenate with alkali metals, and Lundell and Knowles rhenide, obtained by reduction of acid perrhenate solutions with zinc amalgam, is discussed in a separate paper.⁸

Experimental

Preparation of Dipotassium Octahydridorhenate(VI).
(1) **Reduction of Potassium Perrhenate in Aqueous Ethylenediamine with Potassium Metal.**—For each batch of product one gram of powdered potassium perrhenate (99.8% pure or better) was suspended in 8 ml. of water and the mixture made up to 100 ml. with anhydrous ethylenediamine.⁹ When the perrhenate had completely dissolved, the solution was reduced with 8.5 grams of potassium metal (freed of oil and weighed under benzene) using the apparatus and procedure of Bravo, Griswold and Kleinberg.^{2,4} The crude product was a dark brown solid. After draining off the ethylenediamine and washing once with 100 ml. of anhydrous ethyl ether, the solid was dried with a nitrogen stream and transferred to a 250 ml. polyethylene bottle. The bulk of the potassium hydroxide now was removed by extracting with deaerated, anhydrous 2-propanol until a viscous brown liquid appeared beneath the alcohol.^{2,4} (Requires extrac-

(1) (a) Summer 1960 research student, Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey. (b) A. P. Ginsberg, J. M. Miller, J. R. Cavanaugh and B. P. Dailey, *Nature*, **185**, 528 (1960).

(2) J. Bravo, E. Griswold and J. Kleinberg, *J. Phys. Chem.*, **58**, 18 (1954).

(3) J. G. Floss and A. V. Grosse, *J. Inorg. & Nuclear Chem.*, **9**, 318 (1959).

(4) A. P. Ginsberg, Ph.D. Dissertation, Columbia University, New York, N. Y., 1959.

(5) R. Colton, J. Dalziel, W. P. Griffith and G. Wilkinson, *Nature*, **183**, 1755 (1959).

(6) J. G. Floss and A. V. Grosse, *J. Inorg. & Nuclear Chem.*, **16**, 36 (1960).

(7) In ref. 4, where the hydridic nature of the reduction product of aqueous perrhenate with alkali metals is reported for the first time, the product described had the composition $K_2ReH_7 \cdot 3H_2O$, where the water was assigned by difference. It is now known to have actually been a mixture of $K_2ReH_8 + KReO_4 + K_2CO_3 + H_2O$.

(8) A. P. Ginsberg and E. Koubek, to be published.

(9) Prepared by refluxing Eastman 98% ethylenediamine over potassium hydroxide pellets and then distilling in a nitrogen atmosphere. This procedure also reduces the carbonate content.

tion with ~150 ml. of 2-propanol for 5 to 10 minutes.) The 2-propanol then was drained off, the brown liquid mixed with 4 ml. of 2 *N* potassium hydroxide (carbonate free, prepared from the metal) and the resulting solution filtered through a medium porosity disk to remove the suspended brown material (probably $\text{Re} + \text{ReO}_2$) as well as some of the unreacted perrhenate. The clear brown filtrate was extracted to dryness with 2-propanol (polyethylene bottle) and the resulting brown solid washed with ether, dried with nitrogen and dissolved in 2 ml. of 2 *N* potassium hydroxide. After adding 8 ml. of ice-cold, deaerated methanol, the solution was centrifuged to settle out the remaining brown solid. Addition of the clear, colorless supernatant to ~30 ml. of 97–98% ethylenediamine (prepared by adding water to the anhydrous material) in a glass capped centrifuge tube, gave a white precipitate of K_2ReH_8 contaminated with K_2CO_3 , KReO_4 and H_2O . (From this point on the product must be protected from oxygen and moisture; so all further operations were carried out in a dry nitrogen or argon atmosphere.) The contaminants were removed by repeated extraction with 25 ml. batches of 97–98% ethylenediamine. The progress of the extraction was followed by washing the solid with 2-propanol and ether, then drying with nitrogen and taking the infrared spectrum. Extraction was continued until the bands due to perrhenate, carbonate and water were negligible (*cf.*, the results section). Six to twelve extractions of several hours duration usually were required. After the impurities had been extracted, the solid was washed successively with 2-propanol (twice) and ether (twice), dried with nitrogen and dissolved in 2 ml. of 2 *N*, CO_2 -free potassium hydroxide. After addition of 8 ml. of ice-cold, deaerated methanol, the solution was centrifuged to settle out any insoluble matter present and the clear supernatant added to 30 ml. of oxygen-free 2-propanol in a capped centrifuge tube. The resulting precipitate was extracted three times with anhydrous 2-propanol, two times with ether and then dried for 0.5 to 1 hr. in a dry nitrogen stream. The final product was a white, microcrystalline solid which is quite deliquescent and decomposes slowly on exposure to the atmosphere. Its purity was always checked by taking an infrared spectrum prior to use. Yield was ~150 mg. of K_2ReH_8 or 16% of the total rhenium.

An alternative procedure sometimes used for removing the carbonate impurity involved treatment of the solid with barium hydroxide solution. When this is done only perrhenate need be removed by ethylenediamine extraction, and this is accomplished more easily (usually three or four 3-hour extractions). The details are as follows: After the ethylenediamine precipitation step the solid was washed with alcohol and ether, dried, and then divided into portions not exceeding ~40 mg. Each portion was dissolved in 2 ml. of saturated barium hydroxide solution and 8 ml. of ice-cold methanol was added. The barium carbonate precipitate was settled by centrifugation and the clear supernatant precipitated by addition to ~30 ml. of 2-propanol. After washing with alcohol and ether, the dry precipitate was treated with 2 ml. of 0.5 *N* potassium sulfate solution. To the resulting suspension, 10 ml. of ice-cold methanol was added (excess potassium sulfate precipitates at this point) and after centrifuging, the clear supernatant was precipitated by adding to ~30 ml. of 97–98% ethylenediamine. The remainder of the purification procedure is the same as already described.

(2) **Reduction of Aqueous Potassium Perrhenate with Lithium Metal.**^{3,10}—Solutions containing the rhenium octahydride ion also were prepared by slowly adding 5 g. of oil-free lithium metal wire (99.8% pure, from A. D. Mackay), in small pieces, to a solution of 0.2 g. of potassium perrhenate in 100 ml. of water while stirring with an argon or hydrogen stream. Undissolved lithium hydroxide as well as some rhenium metal or rhenium dioxide was separated by filtration. To the clear filtrate excess tetraphenylarsonium hydroxide was added to precipitate unreduced perrhenate. The solution was then evaporated under vacuum to ~10 ml., after which it was centrifuged and the clear supernatant used as indicated below. This reaction is very inefficient, only about 3% of the total rhenium being obtained as hydride.

(3) **Reduction of Rhenium Heptoxide with Lithium Aluminum Hydride.**—A solution of ~200 mg. of rhenium heptox-

ide¹¹ in ~30 ml. of anhydrous tetrahydrofuran was slowly dropped into 100 ml. of a solution of ~2 g. of lithium aluminum hydride in diethyl ether while stirring constantly with a magnetic stirrer. The product of the reaction was a white solid consisting of the rhenium hydride mixed presumably with lithium oxide and aluminum oxide. We were unsuccessful in attempts to isolate the hydride from this mixture, so that it was necessary to carry out experiments on the mixture. After thoroughly washing with ether and drying with nitrogen, the hydride (and also the aluminum oxide) was extracted with ~25 ml. of 4 *N* potassium hydroxide plus several ml. of 0.1 *N* tetraphenylarsonium chloride (to precipitate any perrhenate which might be present). Remaining lithium aluminum hydride was destroyed in this process. After filtering, the solution was used as described below.

Attempted Preparation of a Rhenium Hydride by Reduction of Rhenium Pentachloride with Lithium Aluminum Hydride.—Working in an argon filled dry box, ca. 100 mg. of solid rhenium pentachloride¹² was added slowly to 100 ml. of an ether solution of lithium aluminum hydride, while stirring rapidly with a magnetic stirrer. Unlike the reduction of rhenium heptoxide with lithium aluminum hydride, no reaction was observed, but a slight brown turbidity was present at the end; this was centrifuged down and tested for rhenium hydride.

Chemical Characterization of the Hydride. Determination of Potassium and Rhenium.—Samples of the solid hydride weighing¹³ between 25 and 60 mg. were oxidized to perrhenate by slow addition to 15 ml. of 5% hydrogen peroxide. The resulting solution then was diluted to 50 ml. with CO_2 -free water and titrated to about 10 drops past the potentiometric end-point (glass indicator electrode, calomel reference electrode, Beckmann pH meter) with 0.1 *N* hydrochloric acid in a weight buret. The back titration then was made with 0.01 *N* sodium hydroxide.

After the titration, the neutral solution was evaporated to dryness on a steam bath and the rhenium content of the residue determined by the tetraphenylarsonium perrhenate procedure of Willard and Smith.¹⁴

$$\text{mmoles K} = \text{mmoles KOH} + \text{mmoles KReO}_4$$

In one case the potassium determination was checked by decomposing the sample in excess of standard acid, filtering off the rhenium metal and determining the remaining acid by titration with 0.1 *N* sodium hydroxide to a phenolphthalein end-point. As a further check on the potassium determination, one sample was analyzed as follows: ~0.15 g. of the hydride was oxidized with 5% hydrogen peroxide. The resulting perrhenate solution was diluted with water, made acid with hydrochloric acid and evaporated to dryness on a steam-bath. The residue was dissolved in water and diluted to 50 ml. One-half of this solution was used for a perrhenate determination while potassium was determined on the remainder by conversion to the sulfate (ion exchange) and weighing as such after ignition at ~600°. That the material weighed was K_2SO_4 was confirmed by a sulfate determination.

Oxidation in Alkaline Solution, Reducing Power and Hydrogen Evolution.—Weighed samples of the solid hydride (~50 mg.) contained in small glass tubes were suspended inside a flask above the surface of 50 ml. of standard 0.06 *N* calcium hypochlorite solution.¹⁶ The ground-glass-

(11) Prepared according to the procedure in "Inorganic Syntheses," 3, 188 (1950).

(12) Obtained from A. D. Mackay. Stated to have been prepared according to the procedure in "Inorganic Syntheses," 1, 180 (1939). This material probably contains traces of oxychlorides of +7 rhenium.

(13) Samples were transferred to the weighing vessels inside an argon filled dry box. During this process they picked up a static charge which made it difficult to obtain the correct weights: A weight too high by 4 or 5 mg. was usually observed if the weighing was made soon after the transfer. The weight then decreased slowly over a period of several hours. This difficulty was largely overcome by exposing each sample to a strong radium-D source after the transfer operation. Great care must still be taken in making the weighing.

(14) H. H. Willard and G. M. Smith, *Ind. Eng. Chem., Anal. Ed.*, 11, 305 (1939).

(15) I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," revised edition, The Macmillan Co., New York, N. Y., 1949, p. 410.

(16) Ref. 15, pp. 639–640. The iodometric procedure was used in standardizing the solution.

(10) A. V. Grosse, *Z. Naturforsch.*, 8b, 533 (1953).

joint mouth of the flask was connected to a Fisher Precision Universal Model Gas Measuring Unit. When the manometer showed all parts of the apparatus to be at atmospheric pressure, the sample was allowed to fall into the hypochlorite solution which was then stirred with a magnetic stirrer. After all of the brown-black solid (Re metal?), which forms as an intermediate in the reaction, had been oxidized to perrhenate by the hypochlorite, and temperature equilibrium had been reached (0.5 to 1 hr.), the volume of hydrogen evolved was measured. The unconsumed hypochlorite in the flask then was determined iodometrically.¹⁶ In correcting the measured volume of hydrogen to standard temperature and pressure, the vapor pressure of the hypochlorite solution was taken as that of water at the temperature of the experiment.

For the solutions of rhenium hydride obtained from the lithium metal reduction reaction and from the product of the lithium aluminum hydride reduction of rhenium heptoxide, only the reducing power was determined, the H₂ evolved not being measured. Hence, in these experiments, an aliquot of sample solution was merely added to a known excess of standard hypochlorite, and after standing for 1 hr. the unreacted hypochlorite was determined iodometrically. Blanks having the same composition as the sample, except for the rhenium hydride, were run and found to consume a negligible amount of hypochlorite. The rhenium content of each sample was determined on a separate aliquot by the usual procedure¹⁴ after oxidation with hydrogen peroxide.

Acid Decomposition, Hydrogen Evolution.—The hydrogen evolved on decomposing samples of the solid hydride with acid was determined in the same way as just described for the hypochlorite oxidation, using ~50 mg. samples and 50 ml. of 3 *N* hydrochloric acid. The gas volume was measured when the buret reading became steady (*ca.* 1 hr. from start of reaction). In correcting the observed volume to standard temperature and pressure, the vapor pressure of 3 *N* hydrochloric acid was taken to be the same as that of water at the temperature of the experiment.

The hydrogen evolved on acid decomposition of the solution of the product from the lithium aluminum hydride reduction was determined by a slight modification of the above technique, in which the alkaline sample solution was in the reaction flask while 6 *N* hydrochloric acid was added slowly with stirring from an attached sample bulb. After cooling the reaction flask to room temperature, the volume of hydrogen was measured. To find the rhenium content of the sample, the metal formed in the decomposition reaction was filtered off, oxidized to perrhenate with 30% peroxide and determined in the usual manner. The filtrate from the reaction flask always contained a small amount of perrhenate (3 or 4% of the total) due to air oxidation of the finely divided moist rhenium metal.¹⁷ This was precipitated as the tetraphenylarsonium salt after neutralizing the solution and the precipitate was added to the main precipitate from the metal.

Direct Determination of the Hydrogen Content of the Solid by Proton Magnetic Resonance; Rate of the H⁻-D⁺ Exchange.—All spectra were obtained with a Varian high-resolution nuclear magnetic resonance spectrometer operating at 60 Mc. Peak areas were measured by tracing the recorded spectra on tracing paper and then cutting out the peaks and weighing on a Mettler balance.

Two types of experiments were performed. In the simplest a weighed sample of the hydride was dissolved in about 1 ml. of D₂O containing 15% KOD. The solution was weighed and a portion of it placed in a weighed n.m.r. tube which then was weighed again. The areas under the high field proton resonance peak, due to the hydridic hydrogens, as well as the low field water peak were measured, taking the average of four traces for each and repeating the measurements at a second attenuation setting in order to be able to calculate the saturation factor. 15% KOD in D₂O containing a known quantity of normal isotopic water was now prepared, and an amount sufficient to give a water peak area of about the same magnitude as the hydride peak area weighed into the sample tube. The area measurements were repeated as before. The rhenium content of the sample solution was determined by oxidizing with hydrogen peroxide, neutralizing with hydrochloric

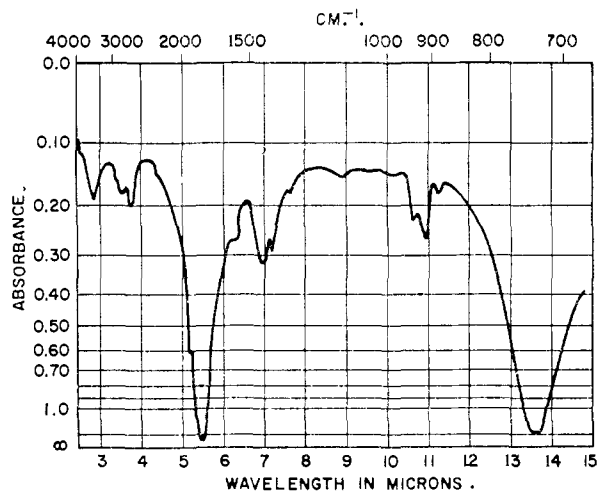


Fig. 1.—Infrared spectrum of impure K₂ReH₈.

acid, evaporating to dryness to destroy excess peroxide and then precipitating and weighing the rhenium.

The small H₂O content of the KOD-D₂O solvent was determined by comparing the water peak height measured in an adiabatic fast-passage experiment with the water peak height, measured in a similar manner, for KOD-D₂O to which a known amount of H₂O had been added. This procedure was adopted because the extreme narrowness of the water line in the pure solvent makes it difficult to avoid strongly saturating it at ordinary sweep rates. This difficulty is not encountered in the sample solution since the presence of small amounts of paramagnetic impurities broadens the line sufficiently to make it possible to carry out the measurements with only little saturation at ordinary sweep rates.

In a more elaborate experiment a sample of the hydride in D₂O containing 15% KOD was prepared as above. The areas under the water and hydride peaks were then measured and their change over a period of about one month followed, keeping the samples and making the measurements at 25.0 ± 0.2°. Each peak was observed at two sweep settings and on one of the sweep settings at two attenuation settings. Each area was taken as the average of *at least* six traces, three with increasing and three with decreasing field, in order to eliminate any effect due to field drift. At the beginning and end of each day's measurements a standard was run to calibrate the instrument; this consisted of a little H₂O in D₂O containing some Cu⁺⁺ to broaden the water line. After about one month, H⁻-D⁺ exchange had reduced the hydride line to about 0.1 of its original intensity. At this point enough of the H₂O in 15% KOD-D₂O standard was weighed into the sample tube to increase the water peak area by a factor of ~1.5, and then the water peak area was measured again. The rhenium content of the sample solution was determined as above.

Infrared Spectra.—The infrared spectra shown in the next section were recorded with a Perkin-Elmer model 137 Infracord using a rock salt prism. Samples were prepared by the potassium bromide pressed-pellet technique using an evacuable die which was loaded in a dry box. The disks were pressed at ~20,000 lb. per in.² and contained ~0.5 mg. sample in 200-300 mg. of potassium bromide. A more careful and extensive study of the infrared spectrum of K₂ReH₈ has also been made¹⁸ and interpreted in terms of the structure of the octahydrorhenate(VI) ion.

Results and Discussion

Figure 1 shows an example of an infrared spectrum of the impure solid hydride after the first precipitation step but before extraction with ethylenediamine or treatment with barium hydroxide. The bands at 1846 and 735 cm.⁻¹ are due to the rhenium hydride,^{18,19} the others are

(18) A. P. Ginsberg, to be published.

(19) The band positions quoted are taken from spectra calibrated with a polystyrene film.

(17) G. E. F. Lundell and H. B. Knowles, *J. Research Natl. Bur. Standards*, **18**, 629 (1937).

TABLE I: RESULTS OF EXPERIMENTS ON SOLID SAMPLES OF POTASSIUM RHENIUM OCTAHYDRIDE

| Sample | Infrared | | | Comments | K/Re | % K | % Re | % K + % Re | $\frac{n}{\text{mmoles Re}}$ (meq. OCl ⁻ /mmoles Re) | Alkaline meq. H ₂ evol./mmoles Re | Acid meq. H ₂ evol./mmoles Re | n.m.r. ^h H ⁻ /Re | % H ⁻ | % K + % Re + % H ⁻ |
|--------------------------------------------|--------------------------------|---------------------------------------------|-------------------------------|-------------------------------------------|-------------------|------|------|------------|-----------------------------------------------------------------|----------------------------------------------|------------------------------------------|----------------------------------------|-------------------|-------------------------------|
| | KReO ₄ ^a | K ₂ CO ₃ ^b | H ₂ O ^b | | | | | | | | | | | |
| Theor. for K ₂ ReH ₈ | | | | | 2 | 28.7 | 68.4 | 97.1 | 12 | 5 | 10 | 8 | 2.96 | 100 |
| 1 | Present | Present | Small | B _a Proc. without EDA extrac. | 1.99 | 27.7 | 66.1 | 93.8 | ... | .. | ... | .. | .. | .. |
| 2 | Small | 2.3 | 1.2 | B _a Proc. without EDA extrac. | .. | .. | .. | .. | 11.81 ^e | .. | ... | .. | .. | .. |
| 3 | Present (6.2%) ^g | 2.7 | 0.6 | B _a Proc. without EDA extrac. | .. | .. | 64.0 | .. | 12.10 ^d | .. | ... | .. | .. | .. |
| 4 | Small | 0.4 | 0.8 | EDA extraction proc. | 1.93 | 27.3 | 67.3 | 94.6 | ... | .. | ... | 8.12 | 2.96 | 97.6 |
| 5 | Small | 3.0 | 0.8 | EDA extraction proc. | 2.04 | 27.3 | 63.6 | 90.9 | ... | .. | ... | .. | .. | .. |
| 6 | Absent | 1.9 | 1.5 | EDA extraction proc. | 2.10 | 28.5 | 64.7 | 93.2 | 12.12 | 5.01 | 10.10 ^f | .. | 2.80 ^f | 96.0 |
| 7 | Absent | 1.2 | 0.8 | EDA extraction proc. | 2.06 | 28.8 | 66.6 | 95.5 | 12.32 | 4.88 | ... | 7.96 | 2.88 | 98.4 |
| 8 | Absent | 1 | 1 | EDA extraction proc. | 2.07 | 28.6 | 66.0 | 94.6 | 12.26 | 5.01 | 10.12 ^e | .. | 2.88 ^f | 97.5 |
| 9 | Absent | 0.5 | 0.3 | EDA extraction proc. | .. | .. | .. | .. | .. | .. | ... | .. | .. | .. |
| | | | | Absorbed H ₂ O during weighing | 2.01 | 26.4 | 62.7 | 89.1 | ... | .. | ... | .. | .. | .. |
| 10 | Absent | Present | Present | EDA extraction proc. | 2.17 ⁱ | .. | .. | .. | ... | .. | ... | .. | .. | .. |

^a Present > small. ^b Relative intensities with respect to the intensity in Fig. 2 (sample 8) taken as unity and normalized to the hydride peak intensity of Fig. 2. ^c Determined by dissolving sample in 2 *N* potassium hydroxide (de-aerated), oxidizing an aliquot with hypochlorite and determining the rhenium content of the remainder. ^d Corrected for perchlorate content. ^e The gas evolved was tested with limewater, after its volume had been measured, and found to contain only a very small amount of CO₂ (1% or less). No correction for this was applied in calculating H₂evol./Re. ^f Calculated from acid hydrogen evolution and % K. ^g Determined by decomposing a sample in concentrated, air free, hydrochloric acid, filtering off the rhenium metal and determining the perchlorate in solution. ^h Our use of the symbol H⁻ for the hydrogen present in the solid hydride is not meant to imply that we believe H⁻ ions are actually present. ⁱ Potassium determined by weighing as the sulfate.

SUPPLEMENT TO TABLE I

ANALYTICAL DATA FOR SAMPLES LISTED IN TABLE I

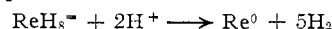
| Sample no. | Sample wt. (mg.) | K and Re determination | | | Alkaline hypochlorite oxidation | | Acid decomposition H ₂ at S.T.P., ml. |
|------------|------------------|---------------------------|-----------------------------|-----------------------------------------------------------------------------|----------------------------------------------------------------------|-------------------------------|--------------------------------------------------|
| | | Std. HCl, ^a g. | Std. NaOH, ^b ml. | (C ₆ H ₅) ₃ AsReO ₄ ppt. (mg.) | Std. Na ₂ S ₂ O ₈ , ^d g. | H ₂ at S.T.P., ml. | |
| 1 | 20.2 | 0.767 | 0.62 | 45.4 | ... | ... | ... |
| 2 | ... | ... | .. | 13.01 ^e | 24.868 ^f | ... | ... |
| 3 | 21.68 | ... | .. | 47.18 | ... | ... | ... |
| | 8.85 | ... | .. | ... | 41.250 | ... | ... |
| 4 | 43.28 | 1.928 | 5.02 | 99.07 | ... | ... | ... |
| 5 | 46.67 | 1.828 | 2.35 | 100.93 | ... | ... | ... |
| 6 | 40.97 | 1.876 | 3.62 | 90.18 | ... | ... | ... |
| | 52.88 | ... | .. | ... | 33.772 | 10.32 | ... |
| | 78.35 | ... | .. | ... | ... | ... | 30.80 |
| 7 | 26.31 | 1.333 | 3.53 | 59.62 | ... | ... | ... |
| | 48.85 | ... | .. | ... | 37.447 | 9.56 | ... |
| 8 | 17.87 | 1.073 | 3.94 | 40.07 | ... | ... | ... |
| | 54.50 | ... | .. | ... | 26.870 | 10.84 | ... |
| | 33.95 | ... | .. | ... | ... | ... | 14.34 |
| 9 | 22.71 | 1.295 | 5.13 | 48.40 | ... | ... | ... |

^a *N* = 0.1008₉ meq./g. for sample 1; 0.1062₂ meq./g. for all other samples. ^b *N* = 9.929 × 10⁻³ meq./ml. for sample 1; 0.01180 meq./ml. for all other samples. ^c *N* = 0.05812₂ meq./ml. Aliquot volumes (ml.): 9.986 for sample 2; 19.972 for sample 3; 49.981 for other samples. ^d *N* = 0.02008₂ meq./g. ^e Volume of sample solution = 29.95 ml. ^f Volume of sample solution = 10.00 ml.

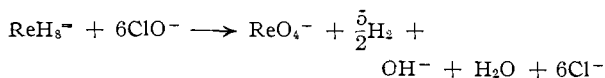
attributed to impurities. The relative intensities of the impurity bands varied considerably at this stage, but Fig. 1 may be regarded as typical and shows all of the features observed. The band at $3425 \pm 5 \text{ cm.}^{-1}$ and the shoulder at 1636 cm.^{-1} are due to water.²⁰ The doublet at 915 and $\sim 935 \text{ cm.}^{-1}$ appears as a triplet in many of the spectra, the third band being at 925 cm.^{-1} . Since in the rock salt region potassium perrhenate shows a triplet at 915 , 920 and 935 cm.^{-1} , these bands must be due to perrhenate. The 915 cm.^{-1} band in the perrhenate spectrum is quite intense and serves as a sensitive test for perrhenate in the rhenium hydride, easily indicating the presence of amounts of the order of 1%. The bands at 1440 cm.^{-1} , 1387 cm.^{-1} and the small peak at 890 cm.^{-1} are attributed to carbonate. (Potassium carbonate in a KBr disk has intense bands at 1450 and 1380 cm.^{-1} , and a medium one at 878 cm.^{-1} .) This is confirmed by the fact that the gas evolved on acid decomposition of the impure hydride contains carbon dioxide. Also, the barium hydroxide treatment greatly reduces the intensity of these two absorptions. The doublet at 2810 and 2670 cm.^{-1} was present in only some of the impure samples. It has not been identified but was of negligible intensity in spectra of the final samples.

Figure 2 shows a typical infrared spectrum of a solid hydride sample after it has been put through the complete purification procedure (the spectrum shown is that of sample 8 in Table I). Perrhenate is completely absent but small amounts of carbonate and water still are present.

In Table I are summarized the results of the experiments performed on the solid hydride. The K/Re ratio together with either the n value and the ratio $H_{\text{evolved}}/\text{mmoles Re}$ on alkaline oxidation or the value of $H_{\text{evolved}}/\text{mmoles Re}$ on acid decomposition and the fact that the rhenium is reduced to the metal are sufficient to determine uniquely the stoichiometry of the hydride. (That the black solid formed in the acid decomposition experiments is metallic rhenium is indicated by its qualitative behavior (some deposits as a bright mirror, it is insoluble in hydrochloric acid but soluble in hydrogen peroxide) as well as quantitative analysis which shows it to contain 98% rhenium. The deviation from 100% is to be expected on account of the great ease with which moist finely divided rhenium is oxidized.) Both sets of data require that the empirical formula be K_2ReH_8 ; the equation for the acid decomposition is



for which $H_{\text{evolved}}/\text{Re} = 10$. The hypochlorite oxidation follows the course



for which $H_{\text{evolved}}/\text{mmoles Re} = 5$ and $n = 12$. The deviations of %K, %Re and %H⁻ found from what is expected for K_2ReH_8 are explained by the small amounts of impurities (K_2CO_3 , H_2O and, in 4 cases, KReO_4) shown to be present by the infrared spectra. The deviations from the theoretical com-

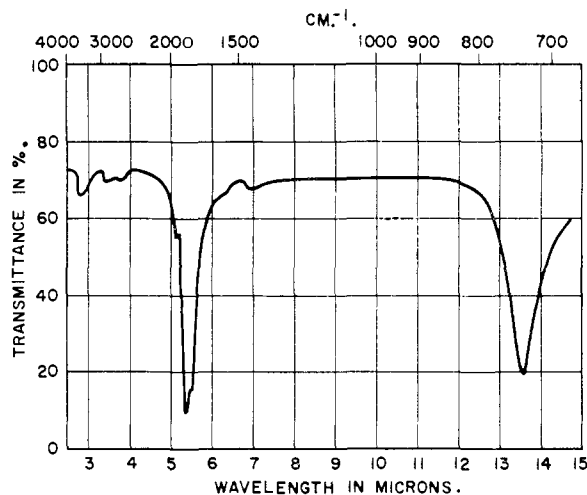


Fig. 2.—Infrared spectrum of purified K_2ReH_8 .

position correlate well with the relative amounts of impurities present as indicated in columns 2, 3 and 4 of Table I. In Table II are shown, for the perrhenate-free samples, the amount of K_2CO_3 and H_2O impurities that would be required to give the observed percentage composition.

TABLE II
CARBONATE AND WATER CONTAMINANTS PRESENT IN THE
PERRHENATE FREE SAMPLES

| Sample no. | % K_2CO_3 | % H_2O |
|------------|---------------------------|------------------------|
| 6 | 2.3 | 2.7 |
| 7 | 1.5 | 0.95 |
| 8 | 1.5 | 1.65 |

The ratio $\text{H}^-/\text{Re} = 8$ is directly confirmed by the results of the two proton resonance experiments shown in column 13 of Table I. We give now a detailed discussion of the second experiment, which we regard as quite reliable.

The sample solution was prepared by dissolving 59.80 mg. of sample 7 in enough solvent to give a total weight of 1070.03 mg. A small amount of white material remained undissolved. After centrifuging, 827.46 mg. of the supernatant was transferred to the n.m.r. sample tube, while 98.98 mg. of supernatant was analyzed for rhenium. The analysis showed that there was 0.1524 mmole of rhenium in the n.m.r. sample tube, while from the known composition of sample 7 there should have been 0.1654 mmole. This indicates that the insoluble solid contains rhenium. An infrared spectrum showed it to be potassium perrhenate. Since sample 7 is perrhenate free (Table I), the perrhenate presumably was formed by reaction with oxygen during the dissolution procedure, which was carried out without special precaution. A part of the hydric hydrogen should then be present as water and hydroxide ion (*cf.*, the second preceding equation). In agreement with this we found more water in the sample solution at zero time than the total water in the solvent and solid sample.

The first spectra were taken 25 minutes after adding the solvent to the solid. No change in the relative heights of the water and hydride lines was observable during the approximately 2 hr.

(20) F. A. Miller and C. A. Wilkins, *Anal. Chem.*, **24**, 1253 (1952).

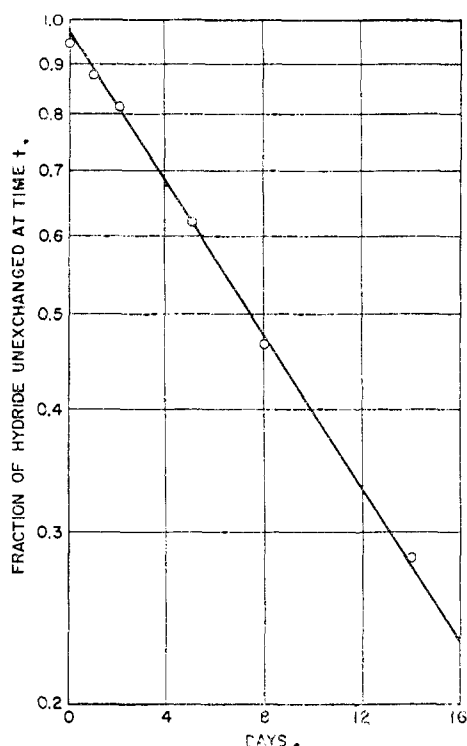


Fig. 3.—Exponential exchange law plot for K_2ReH_8 in 15% KOD- D_2O at 25.0° .

period over which spectra were taken, indicating that the exchange with D_2O is quite slow. In Table III are shown the final corrected peak areas in mg. These numbers have all been adjusted to the same instrument settings and corrected for the change in area of the reference standard, taking the first measurement as standard. They also include a correction for the saturation factor $(1 + \gamma^2 H_1^2 T_1 T_2)^{1/2}$, so that the corrected areas given are strictly proportional to the number of nuclei present in the active volume. The saturation factors were, for the hydride line at $H_1 = 1.1 \times 10^{-4}$ gauss, 1.029, and for the water line 1.028 at $H_1 = 1.1 \times 10^{-5}$ gauss and 1.108 at $H_1 = 2.2 \times 10^{-5}$ gauss. (The actual weights of the peaks generally ranged between 10 and 30 mg.)

That the diminution in hydride line area, and the accompanying increase in water line area, are due to an exchange reaction with the solvent rather than decomposition of the hydride is shown by:

(1) Alkaline solutions of K_2ReH_8 which are carefully protected from oxygen do not change appreciably in reducing power on standing for several weeks.

(2) A solid potassium rhenium deuteride may be isolated from alkaline D_2O solutions of K_2ReH_8 after several weeks standing.¹⁸

After adding 66.88 mg. of a water standard containing 1.120 meq. H_2O per mg. of solution,²¹ the increase in water line area amounted to $7.000 - 5.154 \left(\frac{827}{894} \right) = 2.232$ mg. Hence, in the final

(21) This includes both the water added in preparing the solution and the water found in the KOD- D_2O solvent. The solvent contained 4.08×10^{-4} meq. H_2O per mg.

TABLE III
FINAL CORRECTED PEAK AREAS (MG.) FOR PROTON RESONANCE MEASUREMENTS ON SAMPLE 7

| Day no. | Water line | Hydride line | Water line + hydride line |
|-------------------------------------|------------|--------------|---------------------------|
| 0 | 1.157 | 3.696 | 4.853 |
| 1 | 1.574 | 3.445 | 5.019 |
| 2 | 1.890 | 3.193 | 5.083 |
| 5 | 2.555 | 2.456 | 5.011 |
| 8 | 3.606 | 1.863 | 5.469 |
| 14 | 4.534 | 1.164 | 5.698 |
| 23 | 5.154 | 0.410 | 5.564 |
| 23 after addition of water standard | 7.000 | ... | ... |

solution, meq. H/mg. area = $0.7489/2.232 = 0.3355$. We may now use the data in several different ways to obtain the desired H^-/Re ratio. For example, from Table III the mean of the sum of the hydride peak area and the water peak area is 5.24 mg., with an average deviation of 0.28 mg.; so that there was present $(5.24)(827/894)(0.3355) = 1.626$ meq. of protons (H^+ and H^-). Extrapolating a plot of water peak area vs. t to $t = 0$ gives for the area at zero time 1.33 mg., corresponding to 0.413 meq. of H_2O-OH^- protons not due to exchange. Hence, at zero time there was present $1.626 - 0.413 = 1.213$ meq. of hydridic hydrogen. Using the result of the rhenium analysis on the sample solution, we have that $H^-/Re = 7.96$. The alternative calculations give similar results.

A semilogarithmic plot of the fraction of hydride unexchanged at time t , i.e.

$$\frac{(\text{meq. } H^-)_t - (\text{meq. } H^-)_{t \rightarrow \infty}}{(\text{meq. } H^-)_{t=0} - (\text{meq. } H^-)_{t \rightarrow \infty}}$$

vs. t gives a good straight line (Fig. 3). Since the small divergence of the intercept from unity is well within the experimental error, no significance can be attached to it. The fact that the exchange reaction follows a simple exponential law suggests that all of the hydrogens are equivalent, or at least indistinguishable by an exchange experiment. The half-time for the exchange under the conditions of the present experiment is $t_{1/2} = 7.8$ days.

The experiments just described show conclusively that the solid we have isolated from the reduction of perrhenate with potassium metal in aqueous ethylenediamine is a ternary hydride of rhenium with the empirical formula K_2ReH_8 (our best sample was 97.5% pure). The same rhenium hydride anion was found in the solution prepared by the reduction of aqueous perrhenate with lithium metal and also in the solution of the reduction product of rhenium heptoxide with lithium aluminum hydride. This is demonstrated by the results in Table IV and by the fact that these solutions showed the same high field proton resonance line characteristic of aqueous solutions of K_2ReH_8 . Also, in the case of the lithium aluminum hydride reduction product, an infrared spectrum of the solid in KBr showed two bands at frequencies close to those characteristic of K_2ReH_8 .

The treatment of rhenium pentachloride with an ether solution of lithium aluminum hydride was an attempt to form a hydride containing rhenium in a formal oxidation state lower than +6. As

TABLE IV
HYPOCHLORITE OXIDATION n -VALUES AND ACID HYDROGEN
EVOLUTION FOR RHENIUM REDUCTION PRODUCTS

| Sample | $\frac{n}{\text{meq. OCl}^-}$ mmoles Re | Acid meq. H evolved mmoles Re | |
|--------------------------------------------------------------------------------------|--------------------------------------------|----------------------------------------|------|
| Solution from Li-metal reduction of aqueous perrhenate | Sample 1 | 12.05 | |
| | Sample 2 | 12.4 | |
| | Sample 3 | 12.2 | |
| | Sample 4 | 12.3 | |
| | Sample 5 | 11.8 | |
| Solution of reduction product of Re_2O_7 with LiAlH_4 | Sample 1 | 11.9, 11.9 | |
| | Sample 2 | 12.0, 12.1 | |
| | Sample 3 | 11.8, 12.4 | |
| | Sample 4 | | 10.3 |
| | Sample 5 | | 10.1 |
| | Sample 6 | | 9.9 |

already mentioned, no reaction was observed. The sensitive thallos nitrate test,²⁻⁴ on an alkaline extract of the brown turbidity gave a *very* faint positive reaction, showing the presence of a trace of rhenium hydride, but this undoubtedly is due to small amounts of +7 rhenium impurities in the rhenium pentachloride. We conclude that if a hydride of $\text{Re}^{<+6}$ exists, it cannot be formed in this way.

We must now consider the relation between our results and the work of Floss and Grosse.^{3,6} The only explanation for the discrepancy that is at present apparent to us is, as suggested by Floss and Grosse,⁶ that we are indeed dealing with compounds in which the oxidation state and coordination number of the rhenium are different. However, this is difficult to accept in view of the almost exact coincidence of the Re-H bands in the infrared spectra measured in the two laboratories. Thus, examination of Floss and Grosse's Figs. 1 and 4⁶ (spectrum of $\text{KReH}_4 \cdot 2\text{H}_2\text{O}$) shows two intense bands, one at $1845 \pm 5 \text{ cm}^{-1}$ ²² and a broader one at 735 cm^{-1} , corresponding exactly with the two intense bands in our Fig. 2. In addition there are bands at 3390 (m), ~ 1600 (w, sh), 1415 ± 5 (m), 1390 ± 5 (m) and 885 cm^{-1} (vw).²³ Bands near these positions are

(22) The wave numbers quoted for Floss and Grosse's spectra were read from originals sent to us in 1960 by Dr. J. G. Floss.

(23) This carbonate peak is very difficult to see because of the nearby perrhenate absorption. In the spectra of the barium derivatives, which are perrhenate free, the corresponding band at 856 cm^{-1} is clearly visible.

not present, or are very weak, in Fig. 2, but they are present in appreciable intensity in Fig. 1, the spectrum of *impure* K_2ReH_8 , and, as we have already pointed out, are due to water and carbonate. However, it should be noted that the positions of the water bands in Floss and Grosse's spectra differ by $\sim 30 \text{ cm}^{-1}$ from the corresponding bands in our spectra. Also, the band at 1415 cm^{-1} is displaced by 25 cm^{-1} from what is *presumably* the corresponding band (1440 cm^{-1}) in Fig. 1; the remaining two carbonate bands are in good agreement with their congeners in Fig. 1.

In conclusion we remark that although the minimum n value possible for ReH_3^- is 9, corresponding to oxidation of all the hydrogen to H^0 and the Re^{+6} to ReO_4^- , results in the vicinity of 8 are obtained if the determination is made by oxidation in strongly acid solution, as was done by Bravo, Griswold and Kleinberg² and by Floss and Grosse^{3,6} who found $n \approx 8$ for their hydride. The lower value of n is a consequence of the unmeasured oxidation by hydrogen ion.

In addition we wish to point out that a monomeric ion containing $\text{Re}^{+6}(d^1)$ and no other paramagnetic species should be paramagnetic. However, magnetic measurements which we are in the process of making¹⁸ show that, at least at room temperature, solid K_2ReH_8 is diamagnetic. Similarly, the proton resonance spectra we have obtained^{1,18} indicate that in solution the rhenium containing species is also diamagnetic, or at most only very slightly paramagnetic. There are two possible explanations for these results: (1) The rhenium hydride anion is dimeric and contains an Re-Re bond. (2) Spin-orbit coupling could under certain circumstances reduce the magnetic moment of the unpaired electron sufficiently so that when combined with the relatively large diamagnetic contribution to be expected from 8H^- the effective susceptibility of ReH_3^- is very small or even negative. X-Ray diffraction studies on single crystal K_2ReH_8 and a study of the temperature dependence of the magnetic susceptibility, both of which are now in progress, should distinguish between these two possibilities.

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