

obtaining curve a (0.0002%) is far below what experience has shown to be needed for the complete suppression of maxima. The remaining curves in Fig. 4 demonstrate that the apparent agreement between the theoretical predictions and experimental results of Kivalo, Oldham and Laitinen<sup>10</sup> is attributable to their accidentally having chosen a concentration of maximum suppressor that happened to produce a log plot conforming to their predictions. Attempts to duplicate their results under exactly the same conditions that they employed (0.5 mM nickel(II) in 0.20 *F* potassium nitrate containing 0.005% gelatin, *t* = 3.5 sec.) gave instead a strictly linear log plot like curve b in Fig. 4.

**Acknowledgment.**—It is a pleasure to acknowledge the helpful advice of Professor Joseph Jordan.

**Summary.**—From the results of computations by Koutecký as applied to the form of a totally irreversible polarographic wave involving a single rate-determining electron-transfer step, it is shown that a plot of  $E_{d.e.}$  versus  $\log i/(i_d - i)$ , where *i* and  $i_d$  represent maximum currents during the drop lives, is linear over nearly the entire rising portion of the wave provided that *t* is constant. It is suggested that  $\alpha n_a$  and  $k_{t,1}^0$  can best be evaluated from the slope and intercept, respectively, of a plot of  $E_{d.e.}$  versus  $[\log i/(i_d - i) - 0.546 \log t]$ , which prevents errors that might otherwise result from variations of *t* with  $E_{d.e.}$ . Both this deduction and the results of experimental measurements are in disagreement with another description of the form of the current-potential curve for such a process, and what has been taken to be experimental confirmation of that description is shown to be merely fortuitous.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, GEORGETOWN UNIVERSITY, WASHINGTON, D. C.]

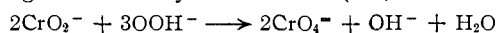
## The Kinetics of the Oxidation of Cr(III) to Cr(VI) by Hydrogen Peroxide<sup>1</sup>

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The rate of the oxidation of Cr(III) to Cr(VI) by aqueous alkaline hydrogen peroxide is first order in total Cr(III) concentration and in total hydrogen peroxide concentration. The base dependence is interpreted in terms of a Hammett-type acidity function: the rate is half order in effective hydrogen ion activity. The rate of the reaction is slowed by prior aging of Cr(III) in the basic medium and by the presence of CO<sub>2</sub>.<sup>3</sup> Mechanistic implications of these results are noted.

Acid dependencies of the rates of oxidation-reduction reactions of oxyions in acid solution have been interpreted in terms of protonated intermediates.<sup>3</sup> This investigation was undertaken in order to obtain information on oxidation mechanisms in highly basic media. The system chosen is the oxidation of Cr(III) to Cr(VI) by alkaline hydrogen peroxide. This reaction often is used in analysis for Cr.<sup>4</sup> The stoichiometry of the reaction, assuming minimum hydration of Cr(III), is



### Experimental

Distilled water used in these studies was passed through a mixed-bed ion exchange resin to remove traces of metal ions. Cr(H<sub>2</sub>O)<sub>6</sub>(ClO<sub>4</sub>)<sub>3</sub> was prepared by the method of Phipps and Plane.<sup>5</sup> Stock solutions were kept at pH 2.5 to control colation (polymerization).<sup>6</sup> Solutions of NaOH and KOH were prepared by dissolving NaOH and KOH pellets in water. Some of these solutions then were saturated with Na<sub>2</sub>CO<sub>3</sub> or K<sub>2</sub>CO<sub>3</sub>. Carbonate-free NaOH solutions were prepared by precipitating carbonate as barium carbonate followed by filtration in a carbon dioxide free atmosphere. Excess barium was removed as the chromate after digestion at 90–95° for 1 hr. The chromate concentration in the resulting solution was determined spectrophotometrically at 374 mμ. Carbonate-free base was stored in polyethylene bottles fitted with air-tight serum caps from

which solution was removed by means of a hypodermic syringe. Carbon dioxide-free air was forced into the bottles to maintain a slight positive pressure.

Stock solutions of H<sub>2</sub>O<sub>2</sub> were prepared by dilution of 30% hydrogen peroxide which contained no stabilizers. These solutions were kept under refrigeration and standardized daily with Ce(IV).<sup>7</sup> Reaction mixtures prepared by dilution of these H<sub>2</sub>O<sub>2</sub> stock solutions gave an H<sub>2</sub>O<sub>2</sub> analysis within 1% of that calculated from the concentration of the stock solutions.

Rate measurements were made spectrophotometrically at 594 mμ. At this wave length CrO<sub>4</sub><sup>2-</sup> does not absorb. Spectrophotometric measurements were made using Beckman model DK and DU spectrophotometers. A Varian model 11 recorder and Beckman ERA 5800 were used in conjunction with the DU for rate measurements. The sample compartment of the DU was thermostated to ±0.1° by circulation of thermostated water. Quartz spectrophotometer cells of 1, 5 and 10 cm. length were used. Alkaline samples of Cr(III) exhibited absorption peaks at 594 and 425 mμ. Beer's law was obeyed at both wave lengths. The measured extinction coefficient at 594 mμ was 27.1, which compares favorably to that which Symons<sup>8</sup> observed in KOH glasses containing Cr(III) (26.9 ± 0.2). The peak at 425 mμ was more sensitive to changes due to aging of Cr(III) than was the peak at 594 mμ. After aging for four days, further peaks appeared between 360 and 400 mμ (Fig. 1). These peaks appeared to be related to the peaks in the reflectance spectrum of basic chromium rhododithionate observed by Schaffer.<sup>9</sup> Schaffer interpreted these peaks as being due to the Cr–O–Cr grouping. The red color of peroxy-chromium compounds was not observed in the concentration ranges used in this study<sup>10</sup> but does appear when more concentrated H<sub>2</sub>O<sub>2</sub> is employed.

The reaction medium was prepared in the form of two solutions; A, an aged solution 0.080 *M* in chromium(III) and 0.050 *M* in sodium hydroxide and, B, an alkaline hydrogen peroxide solution of varying composition.

A was aged at 25°, usually for 1 hr., before initiating the reaction by mixing of solutions A and B. Heating effects

(1) Taken from a portion of a thesis to be submitted by Michael Baloga to the Graduate School of Georgetown University in partial fulfillment of the requirements for the Ph.D. Degree. Presented in part at the May 1961 meeting of the Chemical Society of Washington.

(2) Research grants from the National Science Foundation and the Smith, Kline and French Foundation are gratefully acknowledged.

(3) (a) F. R. Duke, *Anal. Chem.*, **31**, 527 (1959); *J. Chem. Ed.*, **38**, 161 (1961); (b) J. O. Edwards, *Chem. Revs.*, **50**, 455 (1952).

(4) G. W. Haupt, *J. Research Natl. Bur. Standards*, **48**, 414 (1952).

(5) A. L. Phipps and R. A. Plane, *J. Am. Chem. Soc.*, **79**, 2458 (1957).

(6) (a) H. T. Hall and H. Eyring, *ibid.*, **72**, 782 (1950); (b) N. Bjerrum, *Z. physik. Chem.*, **59**, 336 (1907); **73**, 724 (1910); **110**, 656 (1924); (c) C. Altman and E. L. King, *J. Am. Chem. Soc.*, **83**, 2825 (1961).

(7) H. H. Willard and P. Young, *J. Am. Chem. Soc.*, **55**, 3260 (1933).

(8) N. Bailey and M. C. R. Symons, *J. Chem. Soc.*, 202 (1957).

(9) C. E. Schaffer, *J. Inorg. and Nuclear Chem.*, **8**, 149 (1958).

(10) M. Haggett, P. Jones and W. F. K. Wynne-Jones, *Discussions Faraday Soc.*, **29**, 153 (1960).

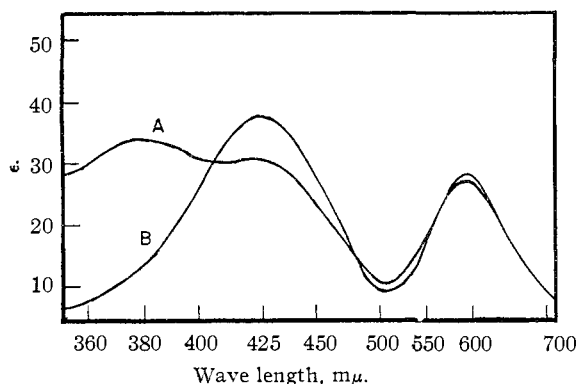


Fig. 1.—The change in spectrum of Cr(III) solutions upon aging in aqueous NaOH at 25°. Curve A represents the spectrum measured after an aging period of 4 days and curve B within 5 minutes after mixing.

on mixing were controlled by thermostating solution B in the reaction cell at 24°. Rapid mixing was achieved by injecting solution A into the cell by means of a hypodermic syringe. Initial Cr(III) concentrations were determined spectrophotometrically at 594 mμ for each run. Sodium hydroxide concentrations were determined by titration with standard perchloric acid. In a majority of runs the ionic strength was approximately 2 M due to the high concentration of NaOH employed.

In the series of runs in which the concentration of NaOH was varied the carbonate concentration was kept constant by preparing solution B from a stock solution which was essentially carbonate-free and by maintaining solution A at a constant carbonate concentration. After mixing the carbonate concentration in the reaction medium was  $0.020 \pm 0.002 M$ . In this concentration range slight variations of the carbonate concentration have a negligible effect on the initial reaction rate (see below). In KOH medium, the carbonate concentration was kept constant by preparing solutions A and B from stock solutions of KOH, 0.114 M in  $K_2CO_3$ , and by diluting with water having a  $K_2CO_3$  concentration of 0.114 M. During the preparation of solution A with KOH,  $KClO_4$  precipitated, and was removed from the mixture by decantation of the supernatant alkaline Cr(III) solution.

Initial rates were measured directly from the recorder traces of % transmission as a function of time. These were arithmetically converted to the corresponding initial rates in units of moles  $l^{-1} sec^{-1}$ . When the Cr(III) was aged for 1 hr. in concentrated solution before dilution to run conditions and peroxide was in large excess, the runs follow pseudo first order kinetics for about one half time. When aging was allowed to proceed for longer periods, a pseudo first order rate law was followed for a greater fraction of the reaction. In one experiment the Cr(III), A, was aged for 75 hr. prior to mixing to run conditions. Equivalent concentrations of Cr(III) and  $H_2O_2$  were used in this experiment. A pseudo-second order law was followed for three half times. The explanation for this effect appears to be that the aging process continues during the course of the run. The seriousness of this effect depends on the extent to which aging has occurred prior to dilution. When prior aging has been extensive, dilution essentially stops further aging and simple kinetics are observed.

The rate of reaction was not affected by illumination, by saturation with oxygen gas or by packing with glass wool. Serious effects would be expected if a free radical mechanism were important.<sup>11</sup>

## Results

The rate of reaction decreased markedly as the time of aging of Cr(III) solution A was increased. Figure 2 shows the effect of changing aging times on the rate of oxidation in NaOH media, all other conditions being constant. The same type of

(11) S. W. Benson, "The Foundations of Chemical Kinetics." McGraw-Hill Book Co., Inc., New York, N. Y., 1960.

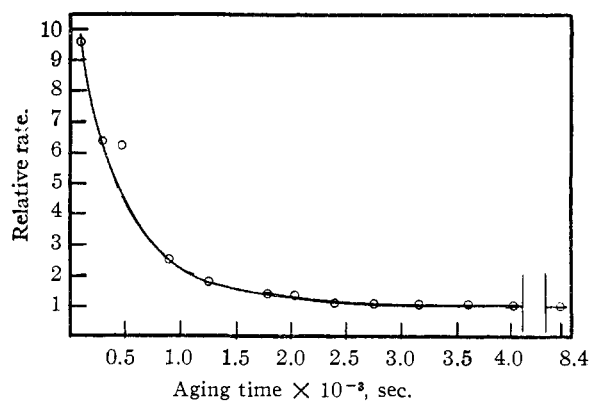


Fig. 2.—The variation of initial rate with time of aging. Concentrations in aging and reaction mixtures kept constant; temperature =  $25 \pm 0.1^\circ$ .

curve was obtained in KOH but longer aging times were required to produce the same effect. No detailed study was made of the effect of changing the concentrations of Cr(III) or of hydroxide which prevailed during aging; it was noted however, that the rate of oxidation increased if either of these concentrations was increased. When care was taken to reproduce aging conditions, good (3%) reproducibility of rate was obtained.

The reaction was slowed by dissolved  $CO_3^{2-}$  as shown in Fig. 3. Because of the difficulty in working with rigorously carbonate-free base in the concentration range required for this work, the reaction medium was kept at a high constant  $CO_3^{2-}$  concentration.

TABLE I

INITIAL RATE OF OXIDATION OF Cr(III) BY  $H_2O_2$  AT  $25.0 \pm 0.1^\circ$

[Cr] $\times 10^3$ , M	$[H_2O_2]^{-1}$ , M	$[OH^-]^{-1}$ , M	$h_e \times 10^{14}$ , M	Initial rate $\times 10^3$ , M	$k \times 10^{-4}$ , $(M^{-1/2})sec^{-1}$
A. NaOH and 0.020 $\pm$ 0.002 M $Na_2CO_3$					
2.58	0.153	2.00	0.501	10.3	3.67
1.02	.153	2.00	.501	3.41	3.54 <sup>a</sup>
0.501	.153	2.00	.501	2.03	3.74
.257	.153	2.00	.501	0.983	3.55 <sup>a</sup>
.666	.158	0.482	3.17	6.85	3.68
.666	.158	0.970	1.25	4.33	3.68
.666	.158	2.00	0.501	2.74	3.67
.666	.158	3.45	.132	1.37	3.58
.666	.158	6.06	.0437	0.815	3.70
Av. $3.64 \pm 0.07$					
B. KOH and 0.114 $\pm$ 0.006 M $K_2CO_3$					
0.600	0.147	0.473	2.14	6.67	5.17
.600	.147	0.963	1.00	4.21	4.88
.600	.147	1.94	0.339	2.64	5.14
.600	.147	3.96	.0758	1.34	5.52
.600	.147	5.95	.0170	0.626	5.44
Av. $5.23 \pm 0.23$					

<sup>a</sup> Average of two runs. Aging conditions, [Cr] = 0.080 M,  $[OH^-] = 0.050 M$ , time of aging,  $60 \pm 5$  minutes in NaOH and  $120 \pm 2$  minutes in KOH.

Table I and Fig. 4 show the results of a number of experiments in which the concentrations of Cr(III),  $H_2O_2$  and  $OH^-$  in the final reaction medium

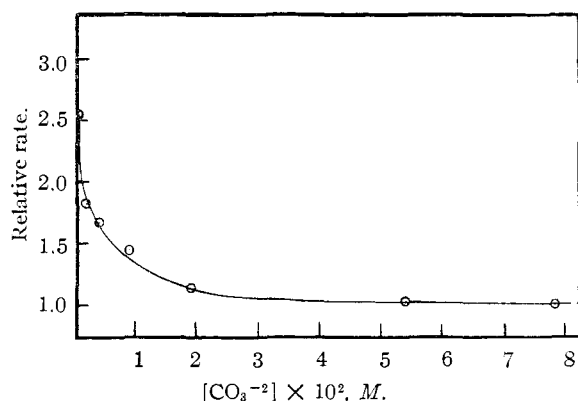


Fig. 3.—The variation of initial rate with carbonate concentration. Concentrations in aging and reaction mixtures kept constant; temperature  $25 \pm 0.1^\circ$ ;  $[\text{CrO}_4^{2-}] = 0.014 M$ .

varied. The time of aging was generally  $60 \pm 5$  min. for NaOH media,  $120 \pm 2$  min. for KOH systems. The data indicate that the reaction is first order in both total Cr(III) and in total  $\text{H}_2\text{O}_2$  concentrations.

The reaction rate was not a simple function of the hydroxide ion concentration when the reaction medium was maintained at a constant ionic strength of  $4.0 M$  with  $\text{NaClO}_4$ . Between  $0.5$  and  $2.0 M$  NaOH the rate is approximately inverse one half order in hydroxide ion concentration, while in more basic media a larger inhibition was noted. This behavior might be due to the noninterchangeability of  $\text{NaClO}_4$  and NaOH as electrolytes in the region of high NaOH concentration where the activity coefficients of the two differ considerably. The dependence of the initial reaction rate on the inverse half power of the hydroxide ion concentration in the lower concentration range appears to be an indication of a real hydroxide ion dependence rather than an inhibition due to salt effects since in this concentration range the activity coefficients of the two electrolytes do not differ greatly.<sup>12</sup> Another series of runs was made in which the hydroxide ion concentration was varied in the absence of added  $\text{NaClO}_4$ . Both NaOH and KOH were used as sources of  $\text{OH}^-$ . The results of these experiments can be correlated most conveniently by use of the  $h_-$ -function of Schwarzenbach and Sulzberger<sup>13</sup> where the term in paren-

$$h_- = (f_{\text{B}^-}/f_{\text{HB}})a_{\text{H}^+}$$

theses is the ratio of activity coefficients of a mononegative base and its uncharged conjugate acid. The tabulated values of this function were measured using a series of indicators. The function would be expected to be useful whenever bases which behave in a manner similar to the indicators are involved (see below). The  $h_-$ -function serves as a measure of the tendency of highly alkaline media to provide protons to such bases.

Table I shows that the one half power of the  $h_-$ -function gives a satisfactory correlation of the rate over the entire range investigated ( $0.5$  to  $6.0 M$ ). Although the values of  $h_-$  for KOH are lower

(12) (a) J. H. Jones, *J. Phys. Chem.*, **51**, 516 (1947); (b) G. Akerlof and G. Kegeles, *J. Am. Chem. Soc.*, **62**, 620 (1940).

(13) G. Schwarzenbach and R. Sulzberger, *Helv. Chim. Acta*, **27**, 348 (1944).

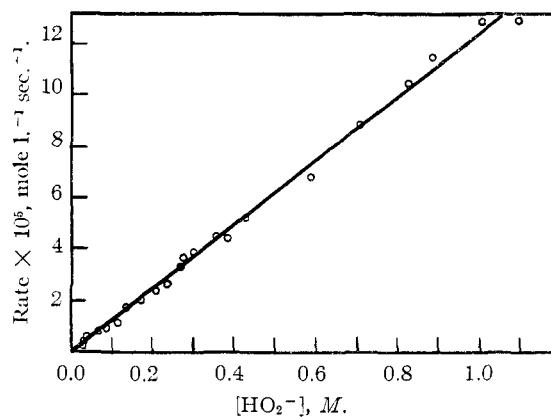


Fig. 4.—The variation of initial rate with total peroxide concentration. Aging conditions:  $[\text{Cr(III)}] = 0.080 M$ ,  $[\text{OH}^-] = 0.050 M$ , aging time =  $60 \pm 15$  min., temperature =  $25 \pm 0.1^\circ$ . Reaction conditions:  $[\text{Cr(III)}] = 0.00666 M$ ,  $[\text{OH}^-] = 2.00 M$ ,  $[\text{CO}_3^{2-}] = 0.020 \pm 0.002 M$ , temperature =  $25 \pm 0.1^\circ$ .

than those of NaOH for solutions of the same molar concentration and the difference becomes much greater in the higher concentration range, the dependence of the reaction rate on  $h_-$  is the same in both cases. This is a strong indication of a half order dependence of rate on  $h_-$ .

At  $25.0^\circ$ ,  $[\text{CO}_3^{2-}] = 0.020 \pm 0.002 M$  in NaOH medium (with prior aging for  $60 \pm 5$  min. under the aging conditions,  $[\text{Cr(III)}] = 0.080 M$ ,  $[\text{OH}^-] = 0.50 M$ ), the simplest rate law which fits our data is

$$\text{Rate} = k[\text{Cr(III)}][\text{HO}_2^-](h_-)^{-1/2}$$

where  $k = 3.64 \pm 0.07 \times 10^4 M^{-3/2} \text{ sec.}^{-1}$ , brackets refer to molar concentrations.

### Discussion

The detailed nature of Cr(III) in basic media is obscure.<sup>14</sup> Freshly prepared  $\text{Cr(OH)}_3$  "dissolves" in excess  $\text{OH}^-$  to give an emerald green, apparently homogeneous mixture. After long standing or upon heating, however, a bluish green precipitate forms. Precipitation occurs more slowly in KOH medium than in NaOH. Many investigators<sup>6a,b</sup> have concluded that, in moderately acidic solutions, Cr(III) is polymerized due to the formation of Cr-OH-Cr and Cr-O-Cr bridges. A similar situation is evident in basic media. A variety of Cr(III) species ranging up to macroscopic particles exists, the distribution depending on the aging history of the sample.

Confirmatory evidence for this view is found in the eventual precipitation and also in the kinetic data reported here. The decrease of the rate of oxidation with aging time is connected with inactivation or shielding of Cr(III) atoms by inclusion in polymer particles. The shape of the aging curve is consistent with this interpretation.

Aging would not be expected to complicate the dependence of initial rate on total Cr(III) concentration since reaction media having different final Cr(III) concentrations were prepared by dilution of samples with identical prior aging his-

(14) H. J. Emeleus and J. S. Anderson, "Modern Aspects of Inorganic Chemistry," D. Van Nostrand Company, Inc., New York, N. Y., 1960.

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 bonds<sup>15</sup> 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  $\mu$ -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)<sup>6c,16</sup> 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<sup>1b</sup> 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 Kleinberg<sup>2</sup> and later by Floss and Grosse,<sup>3</sup> and described as the rhenide  $KRe \cdot 4H_2O$ . The latter authors, in the light of our earlier work<sup>1,4</sup> and the independent work of Wilkinson,<sup>5</sup> have recently revised their formula to  $KReH_4 \cdot 2H_2O$ .<sup>6</sup> 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.<sup>7</sup>

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.<sup>8</sup>

### 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.<sup>9</sup> 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.<sup>2,4</sup> 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 decaerated, anhydrous 2-propanol until a viscous brown liquid appeared beneath the alcohol.<sup>2,4</sup> (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  $K_2ReH_8 \cdot 3H_2O$ , 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.