

[CONTRIBUTION FROM PURDUE UNIVERSITY AND THE PURDUE RESEARCH FOUNDATION]

Oxidation Levels of Rhenium. I. Polarographic and Coulometric Reduction of Perrhenate<sup>1</sup>BY CHARLES L. RULFS<sup>2</sup> AND PHILIP J. ELVING<sup>3</sup>

The reduction of perrhenate ion has been investigated polarographically and coulometrically in 4 *N* perchloric acid and in 2 *N* potassium chloride solutions. The observed reductions are apparently all highly irreversible; the most positive potential at which any reduction occurs is still too negative for a reversible perrhenate couple. Reduction in perchloric acid approximates that expected for a 3-electron diffusion-controlled process and in potassium chloride solution for an 8-electron process; there are objections to such interpretation. The current behavior is actually quite complex with the concurrent evolution of hydrogen being a factor under some circumstances. The behavior of perrhenate in lanthanum chloride and other media was observed; the reduction of rhenium(IV) was attempted.

A previous polarographic survey of the reduction of perrhenate ion<sup>4</sup> led to the tentative assignment of the reduced states in several media. Reductions in 4 *N* acid media appeared to proceed to the rhenium(IV) state; in 2 *N* potassium chloride, to the rhenide state. The present investigation was concerned with a critical examination of the reductions reported<sup>4</sup> in 4 *N* perchloric acid and in 2 *N* potassium chloride. Other media were briefly examined and the reduction of rhenium(IV) was attempted.

It does not seem possible to reconcile the observed behavior of perrhenate reduction waves with explanations invoking any simple combinations of diffusion, kinetic or adsorption processes. The concurrent evolution of hydrogen appears to be a current-contributing factor in some cases; perrhenate itself may have a catalytic effect on this action. Such an effect has been postulated<sup>4,5</sup> to account for the abnormally large waves obtained in certain buffer media. All of the observed perrhenate reductions are evidently highly irreversible; the most positive potential at which any reduction could be obtained, *ca.* -0.35 v. *vs.* the S.C.E., is still too negative to be regarded as a reversible potential involving a perrhenate couple.

## Experimental

Potassium perrhenate (University of Tennessee, stated purity 99.8%) was used without further purification; assay showed 64.2% Re and 13.5% K (theoretical, 64.4 and 13.5). Potassium hexachlororhenate(IV) was prepared by iodide reduction in excess hydrochloric acid, using the standard synthesis<sup>6</sup> plus an additional recrystallization from concentrated hydrochloric acid; the oxidation level of the rhenium was verified by titration. Laboratory grade distilled water was redistilled from permanganate for most of the experiments.

The major part of the polarographic work was done by manual measurement with a calibrated Fisher Electrode. Several curves were recorded with the Sargent Models XII and XXI. Voltage settings and slidewires of all instruments were checked with a potentiometer. All potential measurements have been corrected to 1 mv. A jacketed H-type cell with a saturated calomel electrode was usually employed; all potentials, unless otherwise stated, are given relative to the S.C.E. Since the resistance of the entire assembly, from the anode contact to the mercury reservoir, was usually *ca.* 80 ohms, corrections for *iR*-drop were not applied. The temperature, unless otherwise stated, was 25.0 ± 0.1°. Purified nitrogen, which was used to remove

air from the test solutions, was presaturated in a bubbler containing either water or a portion of the test solution.

The coulometric assembly used did not differ in principle from the original descriptions of Lingane.<sup>7</sup> A water-jacketed cell was employed because of the desirability of maintaining low temperatures in some of the work. Since an external anode was required, a large salt bridge was inserted through the top of the cell; the cell-end of the bridge was stoppered with an agar plug seated on a fritted glass disc.

## Discussion

## Diffusion Coefficient of the Perrhenate Ion.—

The equivalent conductance of perrhenate ion at 25° and infinite dilution shows values of 49.2 to 60.0. 51.3<sup>8</sup> was used in the previous polarographic study.<sup>4</sup> The conductivity and temperature coefficient of conductivity were measured, giving values in agreement with those of Jones and Monk.<sup>9</sup> It is sufficient for polarographic purposes to use 54.8 as the perrhenate conductance at 25°, and 0.025 per degree as the temperature coefficient. The diffusion coefficient may then be calculated as 14.6 × 10<sup>-6</sup>. The square root of this appears in the Ilkovic equation which may then be written as  $i_d/C = 2.32nk$ , where  $k$  is the capillary constant,  $m^{2/3}t^{1/6}$ .

## Reduction of Perrhenate Ion in Acid Media.—

Lingane<sup>4</sup> observed well-defined reduction waves for perrhenate in either hydrochloric or perchloric acids. The reductions proceed more reversibly (*i.e.*, at less negative potentials) and farther (*i.e.*, larger diffusion currents are obtained) as the concentration of acid is increased. Approximately constant values of  $i_d$  for a given perrhenate concentration are observed for acidities greater than *ca.* 2.5 *N*; to permit direct comparison with Lingane's results, 4 *N* concentrations of acid were used. In 4 *N* hydrochloric acid the early inception of the calomel discharge lessens the accuracy with which the wave height can be determined. For this reason 4 *N* perchloric acid was the preferred medium.

A readable current plateau is normally found in perchloric acid, though this is somewhat distorted at high perrhenate concentrations. Values for  $i_d/C$  show good constancy over a wide range of perrhenate concentrations. Calculation from the Ilkovic equation leads to a reproducible *n*-value of 3.04 at 25° as reported.<sup>4</sup> The slope of the waves is highly irreversible, an average value of ( $E_{1/4} - E_{3/4}$ ) being *ca.* 0.08 v. A consistent shift is also

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(4) Lingane, *THIS JOURNAL*, **64**, 1001 (1942).

(5) Heyrovsky, "Polarographie," Julius Springer, Wien, 1941, p. 141.

(6) "Inorganic Syntheses," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939.

(7) Lingane, *THIS JOURNAL*, **67**, 1916 (1945); Lingane, Swain and Fields, *ibid.*, **65**, 1348 (1943).

(8) Puschin and Tutundzic, *Z. anorg. allgem. Chem.*, **193**, 420 (1930).

(9) Jones, *THIS JOURNAL*, **68**, 240 (1946); Monk, *ibid.*, **70**, 3281 (1948).

observed in the  $E_{1/2}$  values as the perrhenate concentration is increased, *i.e.*,  $-0.360$  v. at  $0.08$  mM  $KReO_4$  to  $-0.394$  v. at  $1.00$  mM. Despite certain other peculiarities, the waves seem to meet all of the essential requirements to form the basis of an analytical method.

The waves in solutions more concentrated than about  $0.4$  mM perrhenate were always distorted. An additional current rise started at about  $-0.55$  v. and was followed by a marked current decrease which reached a minimum at about  $-0.84$  v. These phenomena were not altered when the curve was recorded automatically at either slow or rapid rates of polarization. Perchloric acid from several sources gave the same results as did the use of an internal mercury pool anode. Prolonged degassing made no difference. A typical photographically recorded curve is shown in Fig. 1. The fact that potassium hexachlororhenate(IV) reduced at  $-0.55$  v. would seem to correlate nicely with the interpretation of the primary process as the 3-electron reduction of perrhenate to rhenium(IV). On the other hand, there are serious objections to this interpretation.

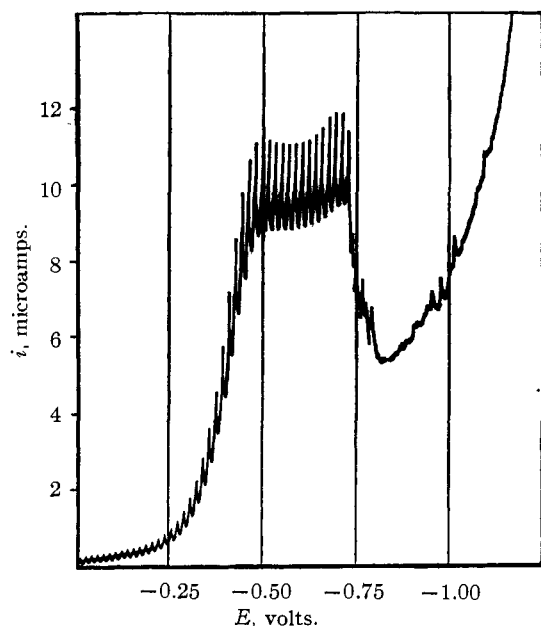


Fig. 1.—Perrhenate reduction in perchloric acid:  $0.80 \times 10^{-3}$  M perrhenate ion in  $4$  N perchloric acid at  $25^\circ$ ;  $k = 1.67$  mg.<sup>2/3</sup> sec.<sup>-1/2</sup> at  $-0.6$  v.

Although  $i_d$  for the initial current step varies with  $h$  in the manner expected for a diffusion-controlled process, the temperature coefficient is zero or even slightly negative which is characteristic for an adsorption wave; since the perrhenate ion shows a normal temperature coefficient of conductivity, it is evident that  $n$ -values of 3 would not be obtained at any temperature other than  $25^\circ$ . The possible adsorption nature of the wave correlates with the unusually strong depressant effect of gelatin on the wave,  $0.013\%$  of gelatin practically obliterating the wave.<sup>4</sup>

The coulometric reduction of perrhenate in acid media also indicates that the simple interpretation of the wave as a 3-electron process is not valid.

Reduction in  $4$  N perchloric acid at  $25^\circ$  and at potential settings of  $-0.45$  to  $-0.55$  v., always gave rise to a continuous process. In a typical run conducted at  $-0.52$  v., the reduction was continued until the gas coulometer showed a volume of gas equivalent to a current consumption of 7 times the theoretical value for 3 electrons. There was no indication of any diminution in the rate of the process at the end of this time. Titration of the cell solution indicated that the original perrhenate had only suffered a reduction equivalent to 0.2 electron. Gas evolution at the mercury-solution interface indicated that the reduction of hydrogen ions played a major role in the current consumption.

There is interesting similarity in the behavior of perrhenate and of periodate. An increase was observed<sup>10</sup> in the normally 2-electron periodate reduction wave as the acid concentration was increased beyond pH 0.8; gelatin had a pronounced effect on the wave. A current decrease was observed<sup>11</sup> beyond the periodate wave which, however, appeared to be favored by more alkaline media.

Most of the phenomena observed in perchloric acid are duplicated in comparable concentrations of hydrochloric acid. The only distinction is that the  $E_{1/2}$  values under similar conditions are *ca.* 0.1 volt more positive in hydrochloric acid.

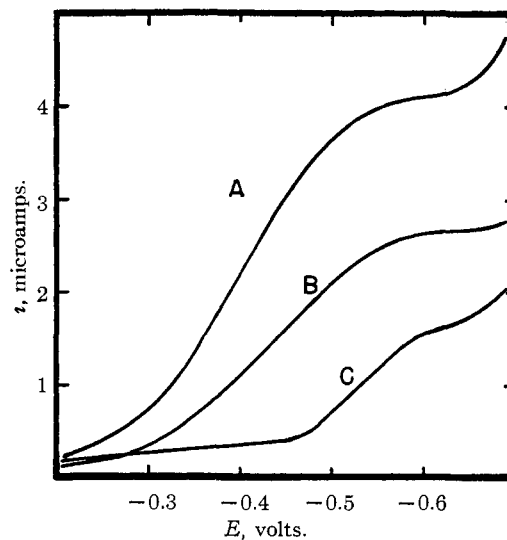


Fig. 2.—Perrhenate and rhenium(IV) reductions in hydrochloric acid:  $2.4$  N hydrochloric acid at  $15^\circ$  which is (A)  $0.4$  mM in perrhenate, (B)  $0.2$  mM each in perrhenate and in hexachlororhenate(IV), (C)  $0.4$  mM in hexachlororhenate(IV);  $k = 1.66$  mg.<sup>2/3</sup> sec.<sup>-1/2</sup> at  $-0.6$  v.

Interesting curves were obtained in  $2.4$  N hydrochloric acid at  $15^\circ$  for solutions of perrhenate, hexa-

TABLE I  
REDUCTION OF RHENIUM(VII) AND RHENIUM(IV) IN  $2.4$  N HCl AT  $15^\circ$

Composition, mM	$(k = 1.66$ at $-0.6$ v.)		
	$E_{1/2}$ , v.	$i_d$ , $\mu$ a.	$E_{1/4} - E_{3/4}$ , v.
$0.4$ in $KReO_4$	$-0.398$	$3.74$	$0.109$
$.4$ in $K_2ReCl_6$	$-.528$	$1.13$	$.061$
$.2$ in each	$-.432$	$2.42$	$.119$

(10) Coe and Rogers, *THIS JOURNAL*, **70**, 3276 (1948).

(11) Souchay, *Anal. Chim. Acta*, **2**, 17 (1948).

chlororhenate(IV), and a mixture of these two states (Fig. 2 and Table I);  $i_d$  for the mixed solution is in agreement with that calculated from the other runs. The reduction of a rhenium(IV) salt within the bounds of the perrhenate reduction does not, of course, either prove or disprove the perrhenate reduction as a 3-electron process. The slope for the rhenium(IV) wave is not in complete accord with the theoretical value of 0.055 for a 1-electron process. Subsequent work on the anodic oxidation of rhenide solutions indicates that the reversible potential of the (IV)/(III) couple must be more positive than  $-0.5$  v. The observed slope for the perrhenate reduction is in accord with that calculated<sup>12</sup> for a one-electron reduction involving dimerization and adsorption at the electrode.

**Reduction of Perrhenate Ion in Neutral Medium.**—Lingane<sup>4</sup> observed a perrhenate wave in 2 *N* potassium chloride solution at  $-1.41$  v. which approximated to that expected for an 8-electron process over a limited range of concentration; this was followed by a catalytic hydrogen discharge wave at  $-1.7$  v. The present studies in this medium are essentially in accord; the perrhenate wave was found at  $-1.43$  v. *vs.* the S.C.E. and calculation from the Ilkovic equation indicates an 8.4-electron reduction. The agreement for an 8-electron transition shows greater constancy over a wider concentration range than in the prior study.<sup>4</sup> This could be ascribed either to the use of a capillary of widely different character or of manual measurement in the present study. The slope of curves obtained manually or automatically shows an average value for  $(E_{1/4} - E_{3/4})$  of *ca.* 0.09 v.

Coulometric studies in 2 *N* KCl at 25° revealed a continuous electrode process comparable to that found in acid media, even at a potential setting of only  $-1.5$  v. (to ensure exclusion of the following catalytic hydrogen wave). In a typical run five times the anticipated gas-coulometer reading (for an 8-electron reduction) was reached without any evidence that the process was slowing down; the pH of the solution rose from 6 to 9 during the run. The perrhenate, meantime, had only been reduced by 1.1 electron.

**Reduction of Perrhenate Ion in Lanthanum Chloride.**—The purported 8-electron reduction of the nitrate anion in this medium suggested its application in the present case. Perrhenate concentrations from 0.08 to 1.0 mM were examined in 0.05 *M* LaCl<sub>3</sub> solution at 25°. A very poorly defined double wave usually resulted with the first wave at *ca.*  $-1.15$  v. and the second at *ca.*  $-1.40$  v. In a few cases a small third wave at *ca.*  $-1.57$  v. was obtained. The curves are not highly reproducible, and the definition between the waves is poor; *n*-values vary from 3.4 to 5.5 for the first wave and 4.3 to 6.5 for the second (Table II). With the continuous polarization of automatic recording (Sargent Model XXI) sporadic, sharp current increases were often obtained. These were sometimes followed by marked current decreases reminiscent of

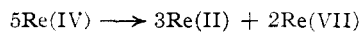
the phenomena observed in acid media. The *n*-values for the second wave were calculated on the assumption that  $D^{1/2}$  for the substance being reduced would approximate  $D^{1/2}$  for perrhenate.

Freshly prepared solutions of hexachlororhenate(IV) exhibited only a minute portion of the first wave and about one-half of the anticipated second wave.

TABLE II  
PERRHENATE REDUCTIONS IN 0.05 *M* LaCl<sub>3</sub> AT 25° (*k* = 1.47 AT  $-1.25$  v.)

KReO <sub>4</sub> , mM	$i_d/C$		<i>n</i> , calcd. from Ilkovic equation		
	Wave 1	Wave 2	Wave 1	Wave (1 + 2)	Wave 2
1.0	19.5	36.3	5.5	10.3	4.8
0.8	..	28.3	...	8.0	...
.6	..	27.2	...	7.7	...
.4	16.8	37.8	4.8	10.7	5.9
.2	17.8	40.6	5.0	11.5	6.5
.08	12.1	27.0	3.4	7.7	4.3

After standing for 20 to 30 min. a sizeable first wave developed and the second wave approached its normal height. After standing overnight, the solution showed the typical double wave of proper height for an equivalent concentration of perrhenate. The initial result implies that rhenium reductions are probably involved in both waves, the second wave being confined to oxidation levels lower than (IV). The effects observed on standing probably reflect the progress of the disproportionation reaction



concurrent with a gradual approach to complete oxidation.

The attainment of calculated total *n*-values as high as 11.5, the greatly decreased size of the second wave for a non-oxygenated (IV) state, the erratic steep current steps sometimes obtained, and analogies with the cases previously discussed seem to indicate (1) that catalytic hydrogen discharge contributes to one or both waves, and (2) that electrolytic perrhenate reduction probably proceeds through an oxygenated (IV) state comparable with the rhenite ion, ReO<sub>3</sub><sup>=</sup>.

**Perrhenate Reductions in Other Media.**—Of numerous other media examined, only three are worth noting as being potentially useful. In 2 *M* potassium thiocyanate a small wave of moderately good definition is found at *ca.*  $-1.20$  v. In 0.1 *M* barium chloride a wave at  $-1.35$  v. is followed by a large wave beginning at about  $-1.6$  v. In sodium sulfite, with or without potassium chloride present, two waves are obtained, at potentials of  $-1.5 \pm 0.1$  v. and  $-2.2 \pm 0.1$  v. *vs.* a mercury pool anode.

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(12) Tishkoff, "Dimerization and Adsorption at the Dropping Mercury Electrode," U. S. Atomic Energy Commission, MDCC-1390.

(13) Original manuscript received August 6, 1949.