reaction indicates a chain mechanism involving a free methyl group as a chain carrier. From our experimentally measured ethane concentration, further, a chain length of 10^2 may be calculated.

2. Unwarranted emphasis should not be placed upon the initial phases of the reaction, especially since the initial process appears to be more complicated than the final stage of the reaction. We believe that the entire course of the reactions should be studied rather than that conclusions should be drawn from a study of any one part.

Summary

1. A mass spectrometer has been used in a new method for following the course of kinetic reactions. This method has the advantages of direct identification and concentration measurements of all stable substances involved, including intermediates.

2. The thermal decompositions of dimethyl ether and acetaldehyde have been studied by this method.

3. A chain mechanism for the decomposition of dimethyl ether has been postulated and a chain length of 10^2 calculated. The initial rate constant is a function of the initial dimethyl ether pressure. However, the initial rate has been shown to approach the final rate at zero initial concentration.

Polarographic Investigation of Rhenium Compounds. I. Reduction of Perrhenate Ion at the Dropping Mercury Electrode

BY JAMES J. LINGANE

Since its discovery in 1925 by Walter and Ida Noddack and O. Berg, the chemistry of rhenium has been investigated diligently by numerous investigators, and compounds have been reported corresponding to all the possible oxidation states between $+ 7$ (perrhenate ion) and $- 1$ (rhenide ion).[1] However, very few quantitative data are available concerning the oxidation–reduction potentials connecting the various oxidation states of rhenium compounds in aqueous solution. In the present investigation a start in the direction of obtaining such information has been made by employing the polarographic technique to study the reduction of perrhenate ion at the dropping mercury electrode.

Experimental Technique

Polarograms were recorded according to the usual technique[2] with a Heyrovsky Polarograph, Model XI.[3] For most of the measurements the H-type cell with saturated calomel anode and the dropping electrode assembly described by Lingane and Laitinen[4] were used. In some experiments a Heyrovsky-type cell with a pool of mercury as

anode was used, and in these cases proper correction was made for the anode potential in order to refer the potential of the dropping electrode to the saturated calomel electrode. Except as otherwise noted the experiments were run with the cells in a water thermostat at 25°. Nitrogen was used to remove air from the solutions under investigation. The drop time and rate of flow of mercury from the dropping electrode were determined in the usual manner.[2]

The sample of potassium perrhenate used was kindly furnished by Dr. Max Mosesman. It was known to be of high purity and was used without further purification. Since the amount of the sample was quite small (0.5 g.) the experiments were performed with solutions as dilute as was consistent with satisfactory accuracy of measurement.

Diffusion Current Constant of Perrhenate Ion.—The oxidation states to which perrhenate ion is reduced under various conditions were determined from the observed diffusion currents by means of the Ilkovic equation in the form[5]

$$\frac{i_d}{C} = 605 n D^{1/2} m^{2/3} t^{1/6} \quad (25°) \qquad (1)$$

where i_d is the diffusion current (microamperes), D is the diffusion coefficient (cm.^{2} sec.$^{-1}$) and C

(1) W. Noddack and I. Noddack. "Das Rhenium," Leopold Voss, Leipzig, 1933.

(2) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, 1941.

(3) Manufactured by E. H. Sargent and Co., Chicago, Ill.

(4) J. J. Lingane and H. A. Laitinen, Ind. Eng. Chem., Anal. Ed., 11. 504 (1939).

(5) For a detailed discussion of the Ilkovic equation and its applications, see Ref. 2.

is the concentration (millimoles per liter) of the reducible substance, m is the rate of flow of mercury from the dropping electrode (mg. sec.$^{-1}$), t is the drop time (sec.), and n is the number of equivalents of electricity per molar unit of the electrode reaction. The diffusion coefficient of perrhenate was calculated from its equivalent conductance at infinite dilution, λ^0, by means of the relation[2]

$$D = 2.67 \times 10^{-7} \lambda^0 \text{ cm.}^2 \text{ sec.}^{-1} \text{ (infinite dilution; } 25°)$$
(2)

According to Puschin and Tutundžič,[6] $\lambda^0_{ReO_4^-} = 51.3$ ohm^{-1} cm.^{2} at $25°$, and from this value and Eq. 2 the diffusion coefficient of perrhenate ion at infinite dilution is calculated to be 1.37×10^{-5} cm.^{2} sec.$^{-1}$. Hence Eq. 1 becomes

$$\frac{i_d}{C} = 2.24 n m^{2/3} t^{1/6}$$
(3)

Reduction of Perrhenate Ion in Acid Media.— Perrhenate ion produces only a slight indication of a wave in 0.1 N hydrochloric acid, but with larger concentrations of either hydrochloric or perchloric acid a well-defined wave is obtained. With a constant concentration of perrhenate ion the height of the wave increases with increasing concentration of the acid up to about 2 N. When the concentration of hydrochloric or perchloric

Fig. 1.—Polarograms of perrhenate ion in 1.2 N perchloric acid: concentration of perrhenate ion was (a) none (residual current), (b) 0.86×10^{-4} M, and (c) 1.76×10^{-4} M; temp., $25°$; $m^{2/3}t^{1/6} = 2.40$ mg.$^{2/3}$ sec.$^{-1/2}$ at -0.9 v.

(6) N. A. Puschin and P. S. Tutundžič. Z. anorg. Chem., **193**, 420 (1930).

acid is smaller than about 2 N, the wave is distorted by a rounded maximum and the diffusion current is not well defined. This is illustrated by the polarograms of perrhenate ion in 1.2 N perchloric acid shown in Fig. 1.

As shown in Fig. 2, the wave is suppressed markedly by even very small concentrations of gelatin, and with 0.013% gelatin it is practically obliterated.
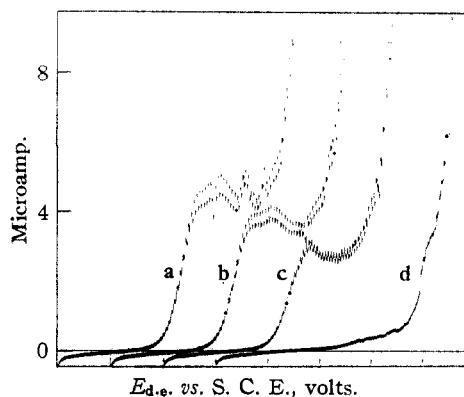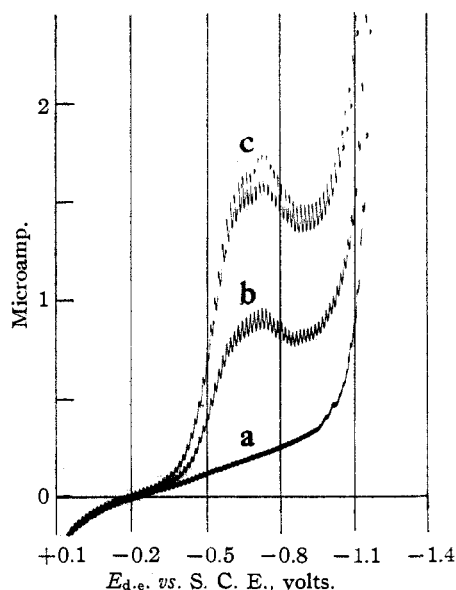

Fig. 2.—Influence of gelatin on the perrhenate wave in acid medium: 8.9×10^{-4} M perrhenate ion in 0.8 N perchloric acid containing (a) none, (b) 0.001%, (c) 0.003% and (d) 0.013% gelatin. Each curve starts at $E_{d.e.} = +0.1$ v. and distance between the voltage marks corresponds to 0.3 v.

Typical polarograms of perrhenate ion in 2 and 4.2 N hydrochloric acid are reproduced in Fig. 3. The observed diffusion currents are seen to be in satisfactory agreement with the theoretical value predicted by the Ilkovic equation (Eq. 3) for $n = 3$, which is indicated on the polarograms.
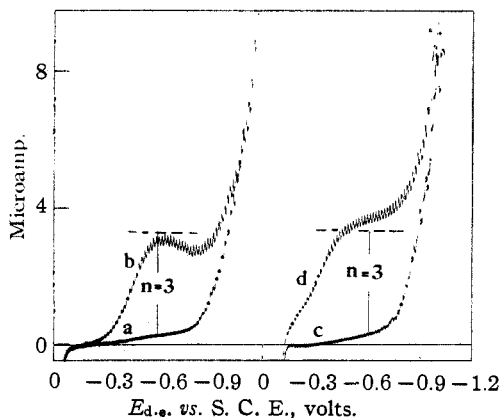

Fig. 3.—Polarograms of perrhenate ion in the presence of hydrochloric acid: 1.92×10^{-4} M perrhenate ion in (b) 2 N and (d) 4.3 N hydrochloric acid. Curves a and c are the residual current curves of the hydrochloric acid solutions alone; temp., $25°$; $m^{2/3}t^{1/6} = 2.35$ mg.$^{2/3}$ sec.$^{-1/2}$ at -0.6 v.

Hence in 2–4 N hydrochloric acid the perrhenate ion is reduced to the + 4 state. Since there is evidence from other sources that + 4 rhenium exists as $ReCl_6^-$ in hydrochloric acid solutions,[7] the most probable equation for the reduction is

$$ReO_4^- + 8H^+ + 6Cl^- + 3e = ReCl_6^- + 4H_2O \quad (4)$$
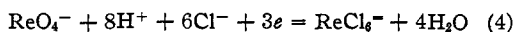
In 2 N hydrochloric acid the half-wave potential is −0.45 v., and in 4.2 N hydrochloric acid it is −0.31 v. vs. the S. C. E. From the abnormally small slope of the wave it is evident that the reduction does not take place reversibly, in a thermodynamic sense, and hence the reversible potential of reaction 4 is undoubtedly more positive (greater oxidizing ability) than these values of the half-wave potential would indicate. From the fact that perrhenate ion slowly oxidizes iodide ion in hydrochloric acid solution, Latimer and Hildebrand[7] concluded that the reversible potential of reaction 4 is in the neighborhood of the iodide–iodine potential (ca. + 0.25 v. vs. the S. C. E.).

Polarograms of various concentrations of perrhenate ion in 4 N perchloric acid are shown in Fig. 4, and the diffusion current and half-wave potential data from these polarograms are assembled in Table I. The definition of the diffusion current and all other characteristics of the wave in perchloric acid are superior to those in hydrochloric acid, and 4 N perchloric acid was found to be the best supporting electrolyte of all those investigated for the determination of perrhenate ion. After correction for the residual current (curve a in Fig. 4), the diffusion current is directly proportional to the concentration of perrhenate, as shown by the constancy of the values of i_d/C in Table I. The average value of i_d/C of 15.6 microamp./millimole/liter agrees very well with the value 15.7 predicted by the Ilkovic equation for $n = 3$. Hence the reduction proceeds to the + 4 state.

The half-wave potential in 4 N perchloric acid shows a definite shift to more positive values as the concentration of perrhenate is increased (Table I), indicating that the reduction proceeds irreversibly. The fact that the half-wave potential is about 0.1 v. more positive (easier reduction) in hydrochloric acid than in perchloric acid of the same concentration is further evidence for the formation of $ReCl_6^-$ in chloride solutions.

The reduction of perrhenate ion in dilute sul-

(7) W. M. Latimer and J. H. Hildebrand, "Reference Book of Inorganic Chemistry," Macmillan Co., New York, 1940, p. 375.
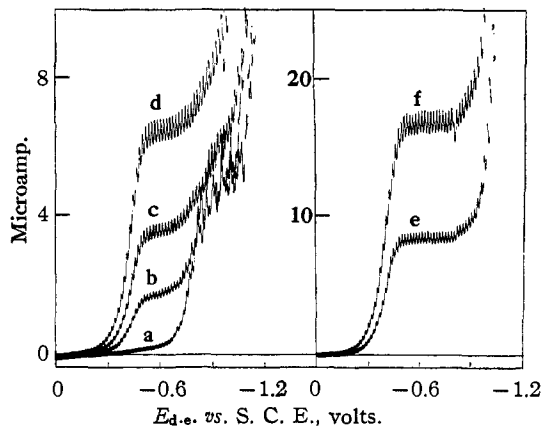

Fig. 4.—Various concentrations of perrhenate ion in 4 N perchloric acid: concentrations of perrhenate ion were (a) none, (b) 0.096, (c) 0.213, (d) 0.400, (e) 0.528, and (f) 1.055 millimoles per liter; temp., 25°; $m^{2/3}t^{1/6}$ = 2.33 mg.$^{2/3}$ sec.$^{-1/2}$at −0.6 v.

furic acid was also investigated, but the results were very unsatisfactory. In 1.8 N sulfuric acid the polarogram consists principally of a huge maximum starting at −0.6 v. which is only partially suppressed by gelatin, and the wave does not show a well-defined limiting current.

TABLE I

DIFFUSION CURRENT AND HALF-WAVE POTENTIAL OF PERRHENATE ION IN 4 N PERCHLORIC ACID AS A FUNCTION OF CONCENTRATION

The diffusion currents were measured at −0.6 v. vs. the S. C. E. (see Fig. 4), and they have been corrected for the residual current. $m^{2/3}t^{1/6}$ = 2.33 mg.$^{2/3}$ sec.$^{-1/2}$ at −0.6 v. Temp., 25°.

ReO_4^- millimolar	i_d in microamp. (cor.)	i_d/C in microamp./ mmole/l.	$E_{1/2}$ vs. S. C. E. v.
0.0960	1.49	15.5	−0.44
.213	3.34	15.7	.43
.400	6.29	15.7	.43
.528	8.15	15.4	.38
1.06	16.5	15.6	.39
Theor. (n = 3) 15.7		Av. 15.6 ± 0.1	

Reduction of Perrhenate Ion in Unbuffered Solution.

—Polarograms of various concentrations of perrhenate ion in 2 N potassium chloride as supporting electrolyte are shown in Fig. 5. With the smallest concentration of perrhenate ion a well-defined wave is obtained whose half-wave potential is −1.41 v. vs. the S. C. E., and the diffusion current is well defined (curve b). As the concentration of perrhenate is increased a second wave appears at −1.7 v. and a maximum develops in the first wave (curves b to e in Fig. 5, and curve b in Fig. 6). When a small concentration of gelatin (0.01%) was added in an attempt
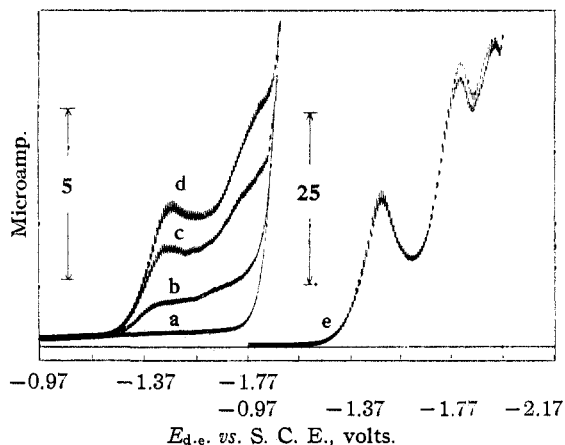
Fig. 5.—Various concentrations of perrhenate ion in 2 N potassium chloride: concentrations of perrhenate ion were (a) none, (b) 0.0192, (c) 0.0487, (d) 0.0703, and (e) 0.311 millimoles per liter; temp., 25°, $m^{2/3}t^{1/6} = 2.25$ mg.$^{2/3}$ sec.$^{-1/2}$ at -1.55 v.

to eliminate the maximum the double wave was transformed into a much larger single wave that showed an even more pronounced maximum than the original wave. This singular effect is demonstrated in Fig. 6. The characteristics of the waves were practically the same in 1 N and 2 N potassium chloride.
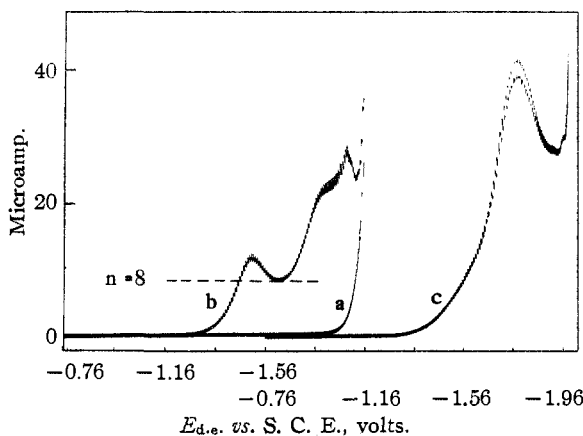

Fig. 6.—Influence of gelatin on the perrhenate wave in potassium chloride medium: (a) residual current curve of 1 N potassium chloride alone; (b) 1.92×10^{-4} M perrhenate ion in 1 N potassium chloride; (c) curve b repeated after addition of 0.01% gelatin; temp., 25°; $m^{2/3}t^{1/6} = 2.30$ mg.$^{2/3}$ sec.$^{-1/2}$ at -1.55 v. The horizontal dashed line is the theoretical diffusion current for $n = 8$.

The height of the first wave is not strictly proportional to the concentration of perrhenate ion, even after proper correction is made for the residual current. The ratio i_d/C increases considerably with decreasing concentration of perrhenate ion, as shown in Table II. From Eq. 3

TABLE II

DIFFUSION CURRENT OF PERRHENATE ION AS A FUNCTION OF CONCENTRATION IN 2 N POTASSIUM CHLORIDE

The diffusion currents were measured at -1.6 v. vs. the S. C. E. (see Fig. 5 and 6), and they have been corrected for the residual current. $m^{2/3}t^{1/6} = 2.25$ mg.$^{2/3}$ sec.$^{-1/2}$ at -1.6 v. Temp., 25°.

ReO$_4^-$ millimolar	i_d (cor.) in microamp.	i_d/C, microamp./mmole/l.
0.0192	0.97	50.5
.0487	2.38	48.8
.0703	3.39	48.3
.192	7.85	40.9
.311	12.5	40.2

Theor. ($n = 8$) = 40.3

the theoretical value of i_d/C for $n = 8$, corresponding to reduction of the ReO$_4^-$ to rhenide ion (Re$^-$), is 40.3 microamp./millimole/liter for the particular capillary that was used ($m^{2/3}t^{1/6} = 2.25$ mg.$^{2/3}$ sec.$^{-1/2}$). With the smaller concentrations of perrhenate ion the observed values of i_d/C are considerably larger than the theoretical value, but they approach the theoretical value when the concentration of perrhenate ion is larger than about 10^{-4} M. The values of i_d/C are subject to considerable uncertainty, of course, because of the pronounced maximum in the c. v. curves. However it does seem reasonable to conclude from these data that the first wave at -1.41 v. is due to reduction of the perrhenate ion to rhenide ion. In unbuffered potassium chloride solution the reduction probably follows the equation

$$\text{ReO}_4^- + 4\text{H}_2\text{O} + 8e = \text{Re}^- + 8\text{OH}^- \quad (5)$$
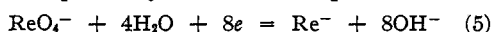
From the abnormally small slope of the first wave, it is evident that the reduction occurs irreversibly, in a thermodynamic sense, at the dropping electrode.

The existence of rhenide ion has recently been demonstrated by Lundell and Knowles,[8] who showed that it is formed when *cold and air-free* solutions of perrhenate ion in dilute sulfuric acid are reduced by amalgamated zinc in a Jones reductor. We have repeated and confirmed the experiments of these authors, and are now engaged in a polarographic study of the reduced rhenium solutions which will be reported in a later paper.

Since the second wave at -1.7 v. is much larger than corresponds to complete reduction of the perrhenate ion, and since its character is changed markedly by the presence of gelatin (Fig. 6), it appears to be a catalytic wave of the type described in the following section.

(8) G. E. F. Lundell and H. B. Knowles, *J. Research Nat. Bur. Standards,* 18, 629 (1937). See also O. Tomiček and F. Tomiček, *Collection Czech. Chem. Commun.,* 11, 626 (1939).

When a dilute solution of perrhenate ion in 1 N potassium chloride is acidified with hydrochloric acid (*ca.* 0.1 N), the original double wave disappears, and with large concentrations of hydrochloric acid (>1 N) a single wave is obtained in the neighborhood of −0.4 v., as described in the preceding section.

Catalytic Wave of Perrhenate in Buffered Solution.—Heyrovsky and his co-workers[9] found that perrhenate ion and tetrathioperrhenate ion ($ReS_4^=$) produce a catalytic wave in acetic acid–acetate buffers at about −1.2 v.; they employed this wave to demonstrate the occurrence of traces of rhenium in manganese compounds. We found that perrhenate ion also produces a catalytic wave at −1.6 v. *vs.* the S. C. E. in a phosphate buffer of pH 7 as shown in Fig. 7. The height of this catalytic wave is several times greater than corresponds to simple reduction of the perrhenate ion. This is evident from Fig. 7 in which the
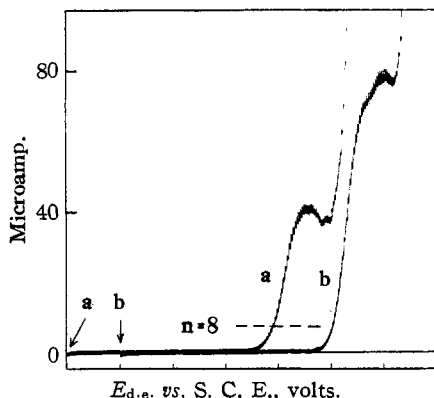

Fig. 7.—Influence of gelatin on the catalytic wave of perrhenate in a phosphate buffer of pH 7: (a) 1.76 × 10^{-4} M perrhenate ion in a 0.05 M phosphate buffer of pH 7 containing 0.2 N potassium chloride as additional supporting electrolyte; (b) repeated after addition of 0.01% gelatin. Each curve starts at $E_{d.e.}$ = +0.08 v. and distance between the voltage marks corresponds to 0.4 v. The horizontal dashed line is the theoretical diffusion current for n = 8. Temp. is 25°; $m^{2/3}t^{1/6}$ = 2.36 mg.$^{2/3}$ sec.$^{-1/2}$ at −1.2 v.

dashed horizontal line marked "$n = 8$" is the calculated diffusion current for complete reduction to rhenide ion. This catalytic wave occurs at about the same potential as the second wave in unbuffered potassium chloride solutions (compare Figs. 6 and 7), indicating the same or at least a

(9) (a) V. Dolejsek and J. Heyrovsky, *Bull. intern. acad.*, Bohème **25**, 179 (1925); *Nature*, **116**, 782 (1925); *Chem. Listy*, **20**, 4 (1926); *Rec. trav. chim.*, **46**, 248 (1927). (b) J. Heyrovsky, *Rozpravy II. tr. Ces. Akademie*, **34**, 25 (1925); *Chem. Listy*, **19**, 168 (1925); *Nature*, **117**, 16 (1926); *ibid.*, **135**, 870 (1935); J. Heyrovsky, V. Dolejsek and G. Druce, *ibid.*, **117**, 159 (1926). See also ref. 2, p. 201, p. 289.

very similar electrode reaction in both cases. However, from a comparison of Figs. 6 and 7 it is seen that the catalytic wave is much larger in the phosphate buffer than in unbuffered potassium chloride solution. This difference is probably connected with the fact that the solution at the surface of the dropping electrode becomes quite alkaline as the reduction proceeds from an originally neutral and unbuffered solution (see Eq. 5). Apparently the presence of hydroxide ion suppresses the catalytic wave.

Like the second wave in unbuffered potassium chloride solutions, the height of the catalytic wave in a phosphate buffer is increased greatly by a small amount of gelatin. This is demonstrated by curve *b* in Fig. 7.

Polarograms of various concentrations of perrhenate ion in a 0.05 M phosphate buffer of pH 7, containing 0.2 N potassium chloride as additional supporting electrolyte, are shown in Fig. 8. When the concentration of perrhenate ion is of the order of 10^{-5} M the catalytic wave shows a well-defined limiting current (curve *b*), but with greater concentrations of perrhenate a maximum develops. The relative height of this maximum increases as the concentration of perrhenate is increased, and its presence precludes accurate measurement of the wave height.
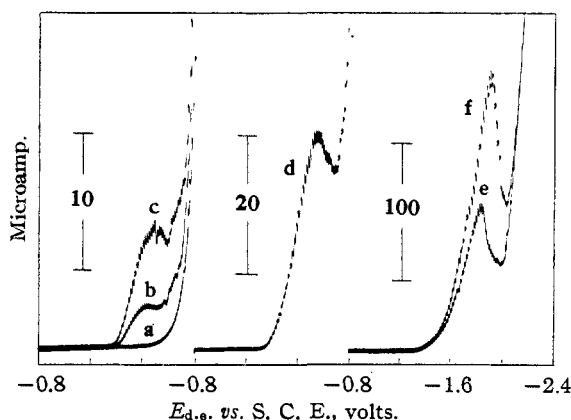

Fig. 8.—Catalytic wave of perrhenate ion at various concentrations: supporting electrolyte consisted of a 0.05 M phosphate buffer containing 0.2 N potassium chloride; concentrations of perrhenate ion were (a) none, (b) 0.0176, (c) 0.0452, (d) 0.125, (e) 0.246, and (f) 0.377 millimole per liter. Temp. is 25°; $m^{2/3}t^{1/6}$ = 2.25 mg.$^{2/3}$ sec.$^{-1/2}$ at −1.6 v.

We found that the height of the catalytic wave is very sensitive to changes in temperature. This is demonstrated by the three polarograms in Fig. 9, which were obtained with the same solution of
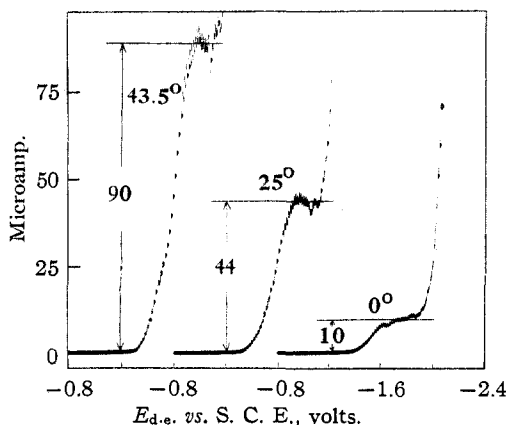
Fig. 9.—Influence of temperature on the catalytic perrhenate wave: 1.76×10^{-4} M perrhenate ion in a 0.05 M phosphate buffer of pH 7 containing 0.2 N potassium chloride as additional supporting electrolyte, at 0, 25, and 43.5°.

perrhenate ion at 0, 25, and 43.5° under otherwise identical conditions. The observed temperature coefficient of the limiting current is approximately 4.3% per degree at 25°. The temperature coefficient of a diffusion controlled limiting current at 25° is given by[10]

$$\frac{1}{i_d}\frac{di_d}{dT} = 0.0026 + \frac{1}{2\lambda^0}\frac{d\lambda^0}{dT} \quad (6)$$

From the measurements of Puschin and Tutundžić[6] the temperature coefficient of the equivalent conductance of the perrhenate ion is 0.025 deg.$^{-1}$ at 25°. From this value and Eq. 6 the temperature coefficient of a diffusion controlled limiting current of perrhenate ion should be 1.5% per degree, which is only about one third as large as the value observed for the catalytic wave.

The fact that the catalytic limiting current is much larger than for simple reduction of the perrhenate ion, together with the fact that its temperature coefficient is much greater than can reasonably be expected for a diffusion controlled current and approaches the order of magnitude of temperature coefficients of reaction rates, suggests that the catalytic current is governed to some extent by a reaction rate and that diffusion probably plays a relatively minor role. In common with other catalytic waves that have been observed in polarographic work,[11] the *net* reaction responsible for the major part of the catalytic limiting current is very likely hydrogen discharge. Catalytic hydrogen evolution may

(10) See Ref. 2, p. 76.
(11) For a review of the characteristics of various types of catalytic waves see ref. 2.

result from reduction of hydrogen ion or from any acidic ion or molecule that may be present (including H_2O).

In the present case the available evidence indicates that perrhenate ion is reduced all the way to rhenide ion at potentials at which the catalytic wave is obtained. From the experiments of Lundell and Knowles,[8] and our own experience, it is known that rhenide ion is a strong and rapid reducing agent, being easily oxidized to the +1 state (probably hyporhenous acid, HReO). Hence a likely mechanism for the catalytic current in this case can be represented by the following equations, which for simplicity's sake are written schematically in respect to the oxidation states of rhenium

$$Re^{+7} + 8e = Re^- \quad (7)$$
$$Re^- + 2H^+(H_3O^+ \text{ or } HA) = Re^+ + H_2 \quad (8)$$
$$Re^+ + 2e = Re^- \quad (9)$$
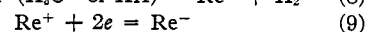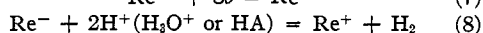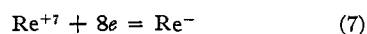
The fraction of the catalytic current due to Eq. 7 would be diffusion controlled and in accord with the Ilkovic equation (Eq. 1), and the remainder would be due to the rapid cyclic recurrence of reactions 8 and 9 at the electrode surface. The net result of reactions 8 and 9 is a lowering of the hydrogen overvoltage at the dropping electrode. Reaction 8 is doubtless the slowest reaction in this series and hence governs the catalytic current.

Acknowledgment.—The writer expresses his appreciation to Dr. Max Mosesman for his collaboration in the preliminary stages of this investigation.

Summary

In 2–4 N hydrochloric or perchloric acid as supporting electrolyte perrhenate ion is reduced to the +4 state at the dropping electrode. In 4 N perchloric acid the diffusion current is well defined and directly proportional to the concentration of perrhenate ion. In 4 N perchloric acid the half-wave potential is -0.4 v., in 2 N hydrochloric acid it is -0.45 v., and in 4.2 N hydrochloric acid it is -0.31 v. vs. the S. C. E.

In neutral unbuffered solutions of potassium chloride a double wave is produced. The first part of this wave ($E_{1/2} = -1.41$ v. vs. the S. C. E.) is due to reduction to rhenide ion, Re^-. The second part of the wave at -1.7 v. vs. the S. C. E. is due to the catalytic discharge of hydrogen.

In a phosphate buffer of pH 7, perrhenate ion produces a catalytic wave at -1.6 v. vs. the S. C. E. The limiting current and its temperature

coefficient are both much greater than for a diffusion controlled current. A mechanism is proposed for this wave which is based on the catalysis

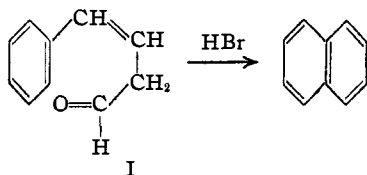of hydrogen discharge by the Re^{-1}–Re^{+1} couple.

CAMBRIDGE, MASSACHUSETTS

NOTES

Cyclization of β-Styrylacetaldehyde

BY CHARLES K. BRADSHER[1]

It has been reported by Rinkes[2] that β-styrylacetaldehyde (I) may be cyclized to give naphthalene. Inasmuch as he failed to report either the

yield or the method employed in this cyclization, we have undertaken to reinvestigate this matter.

The required aldehyde (I) was prepared by the more convenient method of Meyer,[3] involving the pyrolysis of α-methoxycinnamylacetic acid. When refluxed with hydrobromic and acetic acids, the aldehyde gave naphthalene in 25% yield.

While this is the simplest case of aromatic cyclodehydration to give a naphthalene nucleus, there are a number of other instances in which a cyclization of this type is believed or known to take place.[4]

Experimental

Naphthalene.—β-Styrylacetaldehyde was prepared in 25% yield by the method of Meyer.[3] This aldehyde (0.65 g.) was dissolved in acetic acid (13 cc.) and added dropwise to boiling 34% hydrobromic acid (6.5 cc.), the addition requiring about five hours. Refluxing was allowed to continue for a total of forty-eight hours. The mixture was then diluted with water and extracted with ether. The ethereal extract was washed, dried, concentrated and the residue sublimed in vacuo. The sublimate consisted of small white plates; m. p. 80–81°; yield, 0.14 g. (25%). This material showed no depression of melting point when mixed with an authentic sample of naphthalene.

DEPARTMENT OF CHEMISTRY
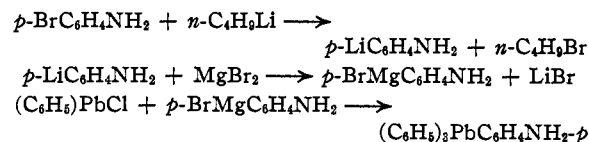DUKE UNIVERSITY,
DURHAM, N. C.　　　RECEIVED NOVEMBER 10, 1941

(1) National Research Fellow (participating basis).
(2) Rinkes, Rec. trav. chim., **39**, 200 (1920).
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Diazotization of an Aminoaryllead Compound[1]

BY HENRY GILMAN AND C. G. STUCKWISCH

p-Aminophenyllithium has been used for the introduction of the p-aminophenyl group into organoarsenic and organophosphorus compounds.[2] In attempts to effect a related transformation between triphenyllead chloride and p-aminophenyllithium, complex mixtures were obtained. The difficulty probably resides in the metal–metal interconversion reactions between organolead and organolithium compounds.[3]

However, because M–M interconversions only occur to a highly subordinated extent between Grignard reagents and organolead compounds, we first converted the RLi compound to the corresponding RMgBr compound by means of magnesium bromide.[4] The following sequence of reactions illustrates the preparation of triphenyl-p-aminophenyllead, which was obtained in a 66% yield.

$p\text{-}BrC_6H_4NH_2 + n\text{-}C_4H_9Li \longrightarrow$
$\qquad\qquad p\text{-}LiC_6H_4NH_2 + n\text{-}C_4H_9Br$
$p\text{-}LiC_6H_4NH_2 + MgBr_2 \longrightarrow p\text{-}BrMgC_6H_4NH_2 + LiBr$
$(C_6H_5)PbCl + p\text{-}BrMgC_6H_4NH_2 \longrightarrow$
$\qquad\qquad (C_6H_5)_3PbC_6H_4NH_2\text{-}p$

The p-aminophenyllead compound was diazotized by conventional procedures, despite the presence in the molecule of a supposed labilizing aminoaryl group. The diazonium compound was coupled with β-naphthol to give an azo-lead compound which was red in acid solution and green in basic solution. The general reactions described now provide the essential means for the resolution of some RM compounds, and the introduction of water-solubilizing groups to vary the lipoid-water distribution of the less chemically reactive RM compounds.

(1) Paper XLIV in the series "Relative Reactivities of Organo-metallic Compounds"; the preceding paper is in THIS JOURNAL, **63**, 2844 (1941).
(2) Gilman and Stuckwisch, ibid., **63**, 2844 (1941).
(3) Gilman and Moore, ibid., **62**, 3206 (1940).
(4) Gilman and Kirby, ibid., **63**, 2046 (1941).