$$\log_{10} P_{\mathrm{mm}} = 6.8637 - \frac{1075.6}{212.82 + t(^{\circ}\mathrm{C})} (\text{for } n\text{-}\mathrm{C_6F_{14}})$$

$$\log_{10} p_{\mathrm{mm}} = 6.8825 - \frac{1093.77}{215.59 + t(^{\circ}\mathrm{C})}$$

(for perfluoro-2-methylpentane)

The normal boiling points for the two compounds as shown by vapor pressures are 57.23 and 57.74; respectively. Their molar heats of vaporization at the boiling points are 7307 and 7273 cal., and at 20° they are 7793 and 7740 cal. (Data for n-C_6F_{14} are given first in each case.) When calculating the heats of vaporization by the Clapeyron equation it was assumed that the vapors were ideal. Molar volumes of the liquids were obtained from their densities.

Discussion

These two isomeric perfluorohexanes compare with each other much as do perfluoro-*n*-pentane and perfluoroisopentane. The isomers are much alike but they differ from each other slightly in directions opposite to those for the corresponding hydrocarbons. Evidence appears to be accumulating that chain branching in fluorocarbons results in higher density, higher viscosity, higher boiling point, higher index of refraction and higher surface tension. Apparently the branched molecules can pack together more closely than the normal ones.

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SEATTLE 5, WASHINGTON

[CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY]

Polarography of Ethylenediamine Tetraacetate Complexes of Europium[1,2]

BY E. I. ONSTOTT

RECEIVED FEBRUARY 11, 1952

In the presence of a large excess of anions of ethylenediamine tetraacetic acid, europium(III) is reversibly reduced to europium(II) at the dropping mercury electrode in the *p*H range of 6 to 13.6. Complex ions identified from half-wave potential and diffusion current data are: *p*H 6 to 8, $[\mathrm{EuHY}]^{-1}$; *p*H 11 to 13.6, $[\mathrm{EuY}]^{-2}$; *p*H 6 to 8, $[\mathrm{Eu(HY)_2}]^{-3}$; *p*H 11 to 12, $[\mathrm{EuY_2}]^{-5}$; *p*H 13 to 13.6, $[\mathrm{EuY(OH)}]^{-2}$. Evidence is given for the existence of $[\mathrm{EuHY}]^{-1}$ and $[\mathrm{EuY(HY)}]^{-4}$, in the *p*H range of 8.5 to 10.3. The ratios of dissociation constants for several of the complex ions are calculated. The equilibrium constant for the reaction $[\mathrm{EuY_2}]^{-5} + \mathrm{OH}^- \rightleftarrows [\mathrm{EuY(OH)}]^{-2} + \mathrm{Y}^{-4}$ is calculated to be approximately 2.

Few of the known complexing agents are coördinated strongly to rare earth ions. Citrate has been used extensively in ion exchange separations,[3] and recently it has been shown that anions of ethylenediamine tetraacetic acid form stable complexes with rare earth ions.[4–8]

Of the rare earths which show oxidation states other than (III), europium and ytterbium appear to be the most suitable for studying complex formation by the polarographic method, since they are reduced to the (II) state at the dropping mercury electrode.[9–11] This report gives the results obtained in investigating the polarography of europium complexed by anions of ethylenediamine tetraacetic acid.

Laitinen and Blodgett[12] have used the dropping mercury electrode as an indicator electrode to show the presence of ytterbium(II) and absence of neodymium(II) when complexed by ethylenediamine tetraacetate.

For simplicity, the symbol proposed by Schwarzenbach and Ackermann[13] for ethylenediamine tetraacetic acid, H_4Y, will be used.

Experimental

Spectrographically pure europium oxide, obtained from Johnson, Matthey and Co., Limited, was weighed and dissolved in dilute hydrochloric acid to make a stock solution. The concentration of europium was based on the weight of the oxide after igniting at 900°. Ethylenediamine tetraacetic acid was precipitated from a solution of the sodium salt (Bersworth Chemical Co.) with concentrated hydrochloric acid, then recrystallized twice from 6 *N* hydrochloric acid, washed with alcohol and dried under a heat lamp. This product was weighed and dissolved in sodium hydroxide to give a stock solution. Sodium hydroxide was used for the reason that potassium hydroxide and tetrabutylammonium hydroxide gave irreversible reductions. Boric acid was used as a buffer for solutions having a *p*H of 8 to 10, and sodium dihydrogen phosphate was used for the *p*H range of 6 to 8. Citrate was not a suitable buffer, as irreversible behavior was observed when it was used. The ionic strength of the solutions was adjusted with sodium chloride. Sodium nitrate was tried as an indifferent electrolyte, but a reduction wave at about −1.5 volts when europium was present precluded its use.

A modified H-cell having a middle compartment separated by 20 mm. fine sintered glass discs was used. The first compartment and middle compartment contained the solution to be analyzed and in the third compartment was placed saturated potassium chloride, used as a bridge solution to a bulb type S.C.E. The a.c. resistance of the four cells used was 710, 990, 1500 and 1750 ohms, as measured with a General Radio impedance bridge in conjunction with the dropping mercury electrode and S.C.E.

A Sargent Model XXI polarograph was used to record polarograms. Potential measurements were made with a Rubicon Type B potentiometer. A Beckman Model G *p*H meter was used for *p*H measurements. For highly alkaline solutions, a Type E electrode was used.

The polarograph was operated manually. Average current data were taken along the polarographic wave and in

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(1) Work done under the auspices of the A.E.C.

(2) Data used in plotting the graphs in this article can be obtained by writing the author or by ordering Document 3612 from American Documentation Institute, 1719 N Street, N. W., Washington 6, D. C., remitting $1.00 for microfilm (images 1 inch high on standard 35 mm. motion picture film) or $1.00 for photocopies (6 × 8 inches) readable without optical aid.

(3) F. C. Nachod, *et al.*, Academic Press, Inc., New York, N. Y., p. 167.

(4) H. Britzinger, H. Thiele and U. Muller, *Z. anorg. allgem. Chem.*, **251**, 285 (1943).

(5) T. Moeller and J. C. Brantley, THIS JOURNAL, **72**, 5447 (1950).

(6) G. Schwarzenbach and E. Frietag, *Helv. Chim. Acta*, **34**, 1503 (1951).

(7) J. K. Marsh, *J. Chem. Soc.*, 1819 (1950).

(8) R. C. Vickery, *ibid.*, 1817 (1951).

(9) W. Noddack and A. Bruckl, *Angew. Chem.*, **50**, 362 (1937).

(10) H. A. Laitinen and W. A. Taebel, *Ind. Eng. Chem., Anal. Ed.*, **13**, 825 (1941).

(11) H. A. Laitinen, THIS JOURNAL, **64**, 1133 (1942).

(12) H. A. Laitinen and Eva Blodgett, *ibid.*, **71**, 2260 (1949).

(13) G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **30**, 1796 (1947).

the diffusion current region. All current values were corrected for residual current and potential values were corrected for *iR* drop of the cell. Plots of log $(i_d - i)/i$ *vs.* E were made to determine the reversibility of the electrode reaction. Half-wave potentials were taken directly from the logarithmic plots.

Measurements were made at 25 ± 0.1°. Nitrogen, which was passed through a chromous chloride solution to free it of oxygen, was used to purge the solutions of oxygen. A maximum suppressor was not used, as no maxima were observed.

The capillary used had a m value of 1.471 mg. sec.$^{-1}$ for a mercury column height of 52.1 cm.

Discussion

Reversibility of the electrode reaction is demonstrated by the values of the slopes for plots of log $(i_d - i)/i$ *vs.* E shown in Table I.

TABLE I

*p*H range	No. of log plots	Slope of log plot Av. value	Low value	High value
6 to 8	16	0.065	0.063	0.068
8 to 11	8	.065	.064	.067
11 to 12	9	.066	.061	.074
>12	10	.065	.056	.071

These values are close to the theoretical value of 0.059 volt for a one-electron reduction. The diffusion current constant (Fig. 5) also is of the right order of magnitude for a single electron reduction.

In Figs. 1, 2, 3 and 4 are plots of log C_x *vs.* $E_{1/2}$. Values of C_x, the concentration of complexing anion, were calculated from the acid dissociation constants measured by Schwarzenbach and Ackermann[13] ($k_1 = 0.01$; $k_2 = 2.14 \times 10^{-3}$; $k_3 = 6.92 \times 10^{-7}$; $k_4 = 5.50 \times 10^{-11}$).

Log C_x is the parameter which determines $E_{1/2}$ of the following electrode reaction

$$[\mathrm{Eu\ X}\ p]^{(pb+3)+} + \mathrm{e}^- \longrightarrow [\mathrm{Eu\ X}\ q]^{(qb+2)+} + (p - q)X^b$$

The equation relating C_x and $E_{1/2}$ is[14] for 25°.

$$(E_{1/2})_c - (E_{1/2})_s = 0.05915 \log K_3/K_2 - (p - q)\ 0.05915 \log C_x f_x \quad (1)$$

Superscript b denotes the charge on the ligand X, while p and q are symbols for the number of ligands attached to europium(III) and europium(II), respectively. The subscript c refers to the complex ion and s to the simple ion. The dissociation constant of the europium(III) complex is designated by K_3, that of the europium(II) complex by K_2. C_x expresses the concentration of complexing agent, and f_x is the activity coefficient of the complexing agent. Although equation (1) is not exact due to the assumption that the ratio of the diffusion coefficients and the ratio of activity coefficients of the europium(III) and europium(II) complex ions are unity, it can be used as a good first approximation.

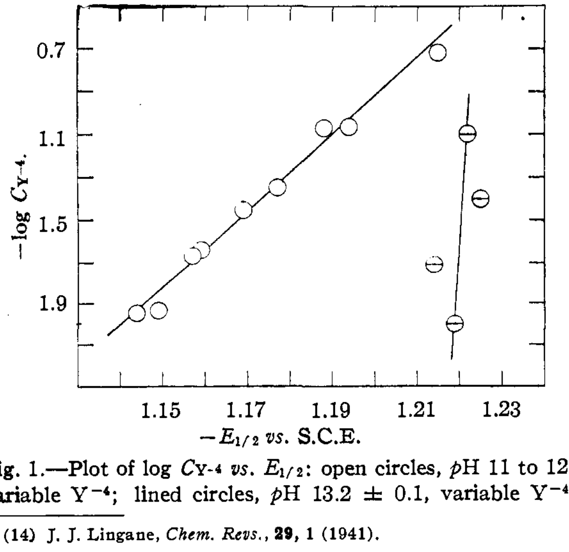

Fig. 1.—Plot of log $C_{Y^{-4}}$ *vs.* $E_{1/2}$: open circles, *p*H 11 to 12, variable Y^{-4}; lined circles, *p*H 13.2 ± 0.1, variable Y^{-4}.

pH 11 to 12.—At a *p*H of 11 to 12 the complexing ion is ethylenediamine tetraacetate ion. Figure 1 shows that $E_{1/2}$ varies linearly with the logarithm of the ethylenediamine tetraacetate concentration. The reciprocal slope of the plot is 0.055 volt, a value close to the theoretical value of 0.059 volt for $(p - q)$ in equation (1) equal to one. Therefore, europium(III) must have one more ligand attached than does europium(II). Since europium(II) should behave like barium(II) in complexing ethylenediamine tetraacetate[13,15] and coördinate one ligand, then two ligands are attached to europium(III) ion. No report has been made in the literature of trivalent rare earths coördinating more than one ethylenediamine tetraacetate group. However, the experiments that have been carried out[4-8] were not of such a nature as to employ a large excess of the complexing ion, as is used in polarographic measurements.

pH > 12.8.—Above a *p*H of about 12.8, the half-wave potential becomes essentially independent of the ethylenediamine tetraacetate concentration (Fig. 1), but varies linearly with the logarithm of the hydroxide ion activity (Fig. 2).

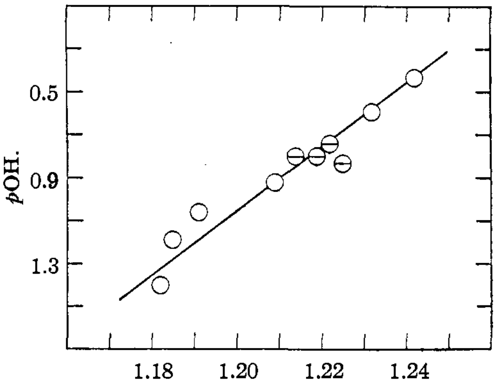

Fig. 2.—Plot of *p*OH *vs.* $E_{1/2}$. Open circles, variable *p*H, constant Y^{-4}; lined circles, *p*H 13.2 ± 0.1, variable Y^{-4}.

Equation (1) is not valid for interpreting these data, since it is apparent that the europium is complexed by two different ligands. The correct equation can be derived by using the same line of reasoning as was used by Lingane[14] in deriving equation (1). Consider the electrode reaction

$$[\mathrm{Eu\ X_pZ_u}]^{(pb+ud+3)+} + \mathrm{e}^- \longrightarrow [\mathrm{Eu\ X_qZ_v}]^{(qb+vd+2)+} + (p - q)\mathrm{X}^b + (u - v)\mathrm{Z}^d$$

The derived equation for 25° is

$$(E_{1/2})_c - (E_{1/2})_s = 0.05915 \log K_3/K_2 - (p - q)\ 0.05915 \log C_x f_x - (u - v)\ 0.05915 \log C_z f_z \quad (2)$$

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[14] J. J. Lingane, *Chem. Revs.*, **29**, 1 (1941).

[15] G. Schwarzenbach and H. Ackermann, *Helv. Chim. Acta*, **31**, 1029 (1948).

Here the symbols have the same meaning as those outlined for equation (1). The second ligand is designated as Z; u and v are the number of attached groups and d is the charge on Z.

Independence of $E_{1/2}$ with respect to the ethylenediamine tetraacetate concentration shows that $(p - q)$ in equation (2) is zero, and thus the same number of ethylenediamine tetraacetate ions is coördinated to europium(III) as is coördinated to europium(II). The most probable number is one. If no group were coördinated, the europium(III) would precipitate as the hydroxide, and if two or more groups were coördinated, the charge probably would be too high for stability of such a complex ion. From the reciprocal slope of 0.066 volt for the plot in Fig. 2, it is ascertained that the predominant species of europium(III) coördinates one more hydroxide ligand than does europium(II). The electrode reaction can be written

$$[\mathrm{EuY(OH)}]^{-2} + e^- \longrightarrow [\mathrm{EuY}]^{-2} + \mathrm{OH}^-$$

This reaction appears to be the most logical, since europium(II), like barium(II), should not be sufficiently strong as an acid to coördinate hydroxide ions readily. Hydroxo-ethylenediamine tetraacetate complexes are not unusual; Schwarzenbach and co-workers have shown the existence of transition metal complexes of this type.[13,16–18] Quite recently Schwarzenbach and Heller[18] have given quantitative interpretation to the study of iron(II) and iron(III) complexed by both hydroxo and ethylenediamine tetraacetate ligands.

***pH* 6 to 8.**—In the *p*H range of 6 to 8 the complexing anion appears to be monohydrogen ethylenediamine tetraacetate. Figure 3 shows the variation of $E_{1/2}$ with the logarithm of the ligand concentration. The straight line is drawn with the five closed circles as a foundation, these circles representing data taken at a *p*H of 6.7 ± 0.1 with variable total ethylenediamine tetraacetic acid concentration. The reciprocal slope of the plot is 0.057 volt, indicating that europium(III) is complexed by one more ligand than is europium(II). If the same reasoning is used as was used in establishing the formulas of the complexes present at a *p*H of 11 to 12, it follows that two ligands should be attached to europium(III) and one to europium (II).

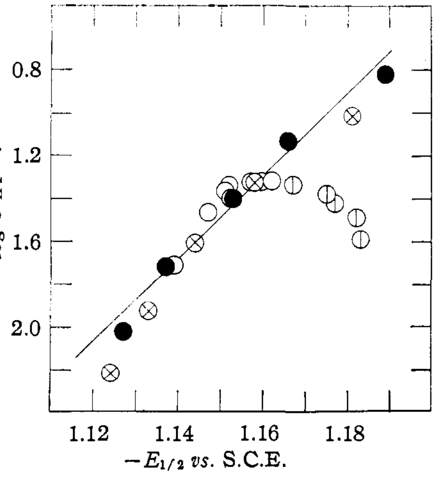

Fig. 3.—Plot of log $C_{\mathrm{HY}^{-3}}$ vs. $E_{1/2}$. Open circles, *p*H 6 to 8; crossed circles, *p*H 6.15 ± 0.05; closed circles, *p*H 6.7 ± 0.1; lined circles, *p*H 8.5 to 10.3.

***pH* 8.5 to 10.3.**—Above a *p*H of about 8.5 but less than 10.3, the behavior of $E_{1/2}$ with respect to log C_x is not well defined. The five vertical lined circles which deviate from the straight line in Fig. 3 are also plotted in Fig. 4. A straight line is obtained by plotting the logarithm of the concentration of ethylenediamine tetraacetate ion as the ordinate, but the reciprocal slope of 0.018 volt is not indicative of definite complex species. Such deviation from ideality would be expected if the europium(III) complex and/or europium(II) complex were being neutralized in this *p*H region. A consideration of the magnitude of $E_{1/2}$ helps to establish the principal electrode reaction. For the same concentration of ethylenediamine tetraacetate ion, $E_{1/2}$ at a *p*H of 8.5 to 10.3 is more negative than it is at a *p*H of 11 to 12. This can be explained by assuming the following electrode reaction to be the principal one at a *p*H of 8.5 to 10.3

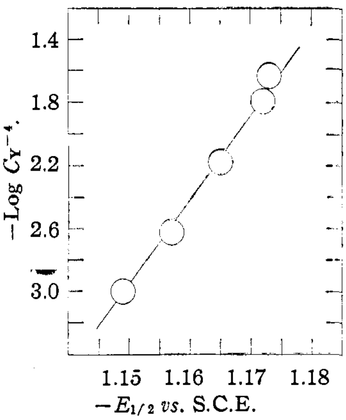

Fig. 4.—Plot of log $C_{\mathrm{Y}^{-4}}$ vs. $E_{1/2}$; *p*H 8.5 to 10.3.

$$[\mathrm{Eu(HY)Y}]^{-4} + e^- \longrightarrow [\mathrm{EuHY}]^{-1} + \mathrm{Y}^{-4} \quad (3)$$

The half-wave potential of this reaction should be more negative than that of the reaction

$$[\mathrm{EuY_2}]^{-5} + e^- \longrightarrow [\mathrm{EuY}]^{-2} + \mathrm{Y}^{-4} \quad (4)$$

for the reason that K_3/K_2 for reaction (3) would be expected to be a smaller number than K_3/K_2 for reaction (4). The addition of one hydrogen ion to (ethylenediamine tetraacetate) europate(II) ion should make it proportionately more unstable than the addition of one hydrogen ion to bis-(ethylenediamine tetraacetate) europate(III) ion.

Diffusion Current Data.—The diffusion coefficient of an ion varies directly with its equivalent ionic conductance and inversely with its charge.[19] Thus the diffusion current constant often can be used to distinguish different ionic species diffusing to a dropping mercury electrode. Two ions of approximately the same structure and size but having different charges have similar equivalent ionic

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[16] G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 459 (1948).

[17] G. Schwarzenbach, *ibid.*, **32**, 839 (1949).

[18] G. Schwarzenbach and J. Heller, *ibid.*, **34**, 576 (1951).

[19] J. J. Lingane and I. M. Kolthoff, THIS JOURNAL, **61**, 825 (1939).

conductances due to the fact that the higher charge is in part compensated for by more hydration. Since a diffusion coefficient varies with the degree of hydration of the ion, the diffusion current constant indirectly measures the charge on the ion. In Fig. 5 is plotted the diffusion current constant *vs.* the *p*H of solutions having a constant total ethylenediamine tetraacetic acid concentration and constant europium concentration. There are three distinct regions of constancy corresponding to the europium(III) complex ions postulated for these *p*H ranges. The relative order of magnitude of the diffusion current constant that is expected for these ions is: $[EuY_2]^{-5} < [Eu(HY)_2]^{-3} < [Eu\ Y(OH)]^{-2}$. The complex ion, (ethylenediamine tetraacetate)-(monohydrogen ethylenediamine tetraacetate) europate(III) ion, is not shown distinctly by the plot in Fig. 5, but neither was it identified positively by $E_{1/2}$ data.

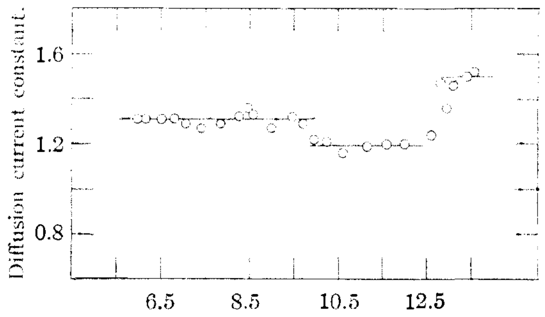

Fig. 5.—Plot of diffusion current constant *vs.* *p*H: total H_4Y, 0.05 molar; europium, 0.46 millimolar; μ, 0.5 for *p*H $\leq$ 12, 1.0 for *p*H > 12.

Reduction to the Amalgam.—Further reduction of the europium(II) complexes to the amalgam could possibly be observed if the electrode reaction were reversible and the polarographic wave were not obliterated by discharge of other ions. Several experiments were performed in which tetrabutylammonium ion was used as the indifferent cation and the *p*H was kept high to prevent a hydrogen wave, but no wave for the reduction to the amalgam was observed. Probably the reduction process is irreversible under the conditions tried, since the europium(III) to europium(II) reduction was found to be irreversible when tetrabutylammonium ion was present.

Calculations.—Data obtained in this investigation are not of such a nature so as to permit calculation of individual dissociation constants of the complex ions identified, but the ratio K_3/K_2 can be calculated from equations (1) and (2). In Table V are listed the complex ions, the extrapolated $E_{1/2}$ values, and calculated values of K_3/K_2. In making these calculations the value of −0.671 volt *vs.* S.C.E. measured by Laitinen and Taebel[10] was used for $E_{1/2}$ of the simple ion reduction.

TABLE II

Eu(III) complex	Eu(II) complex	$-E_{1/2}$ at 1 *M* C_x *vs.* S.C.E.	$K_3/K_2 \times 10^{10}$
$[Eu\ (HY)_2]^{-3}$	$[Eu\ HY]^{-2}$	1.223	4.7
$[Eu\ Y_2]^{-5}$	$[Eu\ Y]^{-2}$	1.250	1.6
$[Eu\ Y\ (OH)]^{-2}$	$[Eu\ Y]^{-2}$	1.270[a]	0.74

[a] $C_x f_x = 1$.

By combining the values of K_3/K_2 for the second and third entries in Table V and eliminating K_2, the equilibrium constant, K_{eq}, for the following reaction can be calculated

$$[EuY_2]^{-5} + OH^- \rightleftarrows [EuY(OH)]^{-2} + Y^{-4}$$

A value of $K_{eq} \cong 2$ is found.

LOS ALAMOS, NEW MEXICO

[CONTRIBUTION FROM THE AVERY LABORATORY OF THE UNIVERSITY OF NEBRASKA]

Polarographic Reduction of the Copper Derivatives of Several 1,3-Diketones in Various Solvents[1]

BY HENRY F. HOLTZCLAW, JR., KARL W. R. JOHNSON AND FRANK W. HENGEVELD

RECEIVED JANUARY 31, 1952

The polarographic reductions of the copper chelate derivatives of 2,4-pentanedione, 1-phenyl-1,3-butanedione, 1,3-diphenyl-1,3-propanedione, 3-methyl-2,4-pentanedione, 3-ethyl-2,4-pentanedione and 3-*n*-propyl-2,4-pentanedione are studied. Solvents used are water and aqueous solutions of ethanol, 2-methoxyethanol and dioxane. The effects of the solvents upon the half-wave potential and upon the diffusion current constant and the trends within each solvent are discussed.

Introduction

The choice of solvent is difficult in the polarographic study of metal chelate compounds of the 1,3-diketones because of their insolubility. A satisfactory solvent must not only dissolve the chelate in satisfactory concentration but must also fulfill the other requirements for polarographic analysis.

Calvin and Bailes[2] have reported half-wave potentials for a considerable number of copper chelate compounds in 50% aqueous pyridine solution Evidence of two reduction steps in pyridine was shown. These authors, in reporting qualitative trends of half-wave potential in that solvent, point out that the coördinating ability of the pyridine constitutes an obstacle to any interpretation other than the observation of orders of magnitude.

The purpose of the present investigation is to study polarographic reductions of copper derivatives of several 1,3-diketones in water and in aqueous solutions of ethanol, 2-methoxyethanol and dioxane.

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(1) Abstracted from the M.A. Theses of Karl W. R. Johnson, August, 1950, and Frank W. Hengeveld, August, 1951, University of Nebraska.

(2) M. Calvin and R. H. Bailes, THIS JOURNAL, **68**, 949 (1946).