results of Faurholt[13] and the calculations of Olson and Youle.[14]

It would be interesting to determine the equilibrium constant of reaction 3 where SbF_5 and AsF_5 replace BF_3, in reactions involving fluoride salts and interhalogens such as those represented by equations 10 and 11.

CHICAGO 16, ILLINOIS

[13] C. Faurholt, *J. chim. phys.*, **22**, 1 (1925).

[14] A. R. Olson and P. V. Youle, THIS JOURNAL, **62**, 1027 (1940).

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY, UNIVERSITY OF ILLINOIS]

Polarography of Iron Oxalates, Malonates and Succinates[1a,b]

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RECEIVED JUNE 7, 1954

The polarographic method was employed to study the iron(II) and iron(III) complexes that exist in oxalate, malonate and succinate solutions. With oxalate solutions, evidence for the existence of $Fe(C_2O_4)_2^{-2}$, $Fe(C_2O_4)_3^{-4}$ and $Fe(C_2O_4)_3^{-3}$ is presented together with dissociation constants evaluated from polarographic and solubility data. With malonate solutions, $Fe(C_3H_2O_4)_2^{-2}$ and $Fe(C_3H_2O_4)_3^{-3}$ are identified and their dissociation constants calculated. The studies with succinate solutions were inconclusive since most of the waves could not be shown to be reversible.

Previous polarographic investigation of the complexes of iron with anions of this homologous series of dicarboxylic acids is limited to the oxalato complexes. Stackelberg and Freyhold[2] report that the polarographic half-wave potentials remain constant at −0.24 volt (*vs.* S.C.E.) in oxalate solutions ranging from 0.01 to 1.0 *M* concentration, concluding that the complexes present in this concentration range are the trioxalatoferrate(III) ion and its reduction product, the trioxalatoferrate(II) ion. Lingane[3] found, however, that the half-wave potentials remain constant at about −0.242 volt only when the oxalate ion concentration is greater than 0.15 *M*. At lower oxalate concentrations the data indicate the reduction product to be the dioxalatoferrate(II) ion. Using the solubility data of Schaper,[4] Lingane recalculated the dissociation constant of the trioxalatoferrate(II) complex to be 6.1×10^{-7}, and with the ratios between the dissociation constants of the iron(III) and iron(II) complexes obtained polarographically, calculated the dissociation constants of the other two complexes to be 8×10^{-6} and 6×10^{-20} for the dioxalatoferrate(II) and the trioxalatoferrate(III) ions, respectively. Toropova[5] reports dissociation constants which vary considerably from those of Lingane, *i.e.*, for the dioxalatoferrate(II) ion, $K_d = 2.7 \times 10^{-10}$ and for the trioxalatoferrate(III) complex, $K_d = 1.2 \times 10^{-24}$. Lingane[6] also studied the analytical aspects of the iron–oxalate system, finding that well-developed, reversible waves are obtained with acidic and neutral solutions, while in basic solutions the waves disappear due to precipitation of the iron(III) hydroxide.

The present paper reports the results of a reinvestigation of the polarography of iron in oxalate solutions together with results of a systematic study with malonate solutions and an attempted study with succinate solutions. These dicarboxylate anions constitute a series of symmetrical chelating agents with gradually increasing ring size and of highly polar character.

Experimental

Apparatus.—All polarograms were made with a Sargent Model XXI Recording Polarograph. Potentials were measured against the saturated calomel electrode (S.C.E.) with a portable Rubicon potentiometer. The *p*H values of solutions were measured with a glass electrode and a Beckman Model G *p*H meter.

Polarograms of oxalate and dilute malonate solutions were made using an H-type cell with a temporary agar plug (3% agar and 0.5 *M* $NaClO_4$). The resistance of such cells together with that of the dropping mercury electrode was found to be about 500 ohms. The more concentrated solutions used in the malonate and succinate studies were found to shrink the agar plug rapidly, so for these solutions an H-type cell with a 20-mm. fine sintered glass plug and a resistance of about 700 ohms was used. All polarograms were run at 25.0 ± 0.2°. The capillary constant ($m^{2/3}t^{1/6}$) for the electrode used was 2.25 at −0.4 v., the potential at which most diffusion currents were measured. Purified nitrogen was used to remove dissolved oxygen from cell solutions.

Materials.—A standard iron(III) perchlorate solution was prepared by dissolving crystalline iron(III) perchlorate-6-hydrate in distilled water and standardized by titrating a reduced sample with a standard cerate solution. The potassium oxalate solution was prepared from the reagent grade salt and standardized by titration with standard cerate solution. Potassium malonate and potassium succinate were not available and were prepared from the acids. The technical grade acids were washed with ether and then crystallized twice from water. The recrystallized acid was dissolved in water, excess potassium hydroxide added and the solution heated and filtered to remove heavy metal hydroxides. The salt was crystallized from the filtrate by evaporation and cooling and then recrystallized from distilled water. The purified salts were dried to constant weight in a vacuum desiccator over P_2O_5. Carbon and hydrogen analyses were made to verify the composition of the anhydrous salts. Weighed amounts of these salts were used to prepare the standard malonate and succinate solutions.

In the more dilute solutions, reagent grade sodium perchlorate was added to bring the ionic strength up to a minimum value of 0.5. No maximum suppressors were required or used throughout this work.

Procedure.—All solutions were made up to contain 1.00×10^{-3} *M* iron(III) perchlorate and varying amounts of the dicarboxylate salts. The actual concentration of the dival-

[1] (a) Presented by Ward B. Schaap in partial fulfillment of the requirements for the degree of Doctor of Philosophy to the Graduate College of the University of Illinois, 1950. (b) Presented at a symposium on "Equilibrium and Rate Behavior of Complex Ions," University of Chicago, February 21–23, 1951. (c) Graham, Crowley and Associates and Burgess Battery Company Fellow, 1948–1949; Atomic Energy Commission Predoctoral Fellow, 1949–1950. Present address, Department of Chemistry, Indiana University, Bloomington, Indiana.

[2] M. v. Stackelberg and H. v. Freyhold, *Z. Elektrochem.*, **46**, 120 (1940).

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

[4] C. Schaper, *Z. physik. Chem.*, **72**, 308 (1910).

[5] V. Toropova, *J. Gen. Chem.* (*U.S.S.R.*), **11**, 1211 (1941).

[6] J. J. Lingane, THIS JOURNAL, **68**, 2448 (1946).

ent dicarboxylate anion was calculated by correcting the total amount of added salt for the amount complexed (usually 3 × [Fe(III)]) and the amount present as incompletely ionized acid forms at the *p*H measured for that particular solution. This latter correction was especially important in the more dilute dicarboxylate solutions, since the acidity of the standard iron solution lowered the *p*H significantly in those solutions.

The recording of the polarogram was interrupted at five to seven points along the rising portion of the wave to permit an accurate, non-interpolated measurement of the potential (E) with the potentiometer. At each point, following the potential reading, a reading of the average current was made with a highly damped galvanometer ("damp 2" position). The values for the current were corrected for the residual current obtained from polarograms run on "blank" solutions containing all reagents except the reducible ion. Reversibility was tested by plotting E *vs.* log $(i_d - i)/i$ for each wave, where i is the corrected average current and i_d is the diffusion current. The values for the half-wave potentials were read from these graphs at the point where log $(i_d - i)/i = 0$. The $E_{1/2}$ values reported have been corrected for the cell resistance and the 1000 ohms introduced in the damping circuit.

Results and Discussion

Oxalate Solutions.—Because of photochemical reduction of the iron(III) in oxalate solutions, consistent values for the cathodic diffusion currents were obtained only when the preparation of the solutions and the recording of the polarograms were carried out in the absence of light. All polarographic waves correspond to reversible, one-electron reduction reactions. To correct the total concentration of added oxalate for the amount present in incompletely ionized acid forms, the ionization constants of oxalic acid are taken to be $K_1 = 6.5 \times 10^{-2}$ and $K_2 = 6.1 \times 10^{-5}$.[7] The data and results obtained with oxalate solutions are presented in Table I.

TABLE I

OXALATE SOLUTIONS—DATA AND POLAROGRAPHIC RESULTS

Added $K_2C_2O_4$, M	pH	Calcd. excess $[C_2O_4^{--}]$ M	Ionic[a] strength, μ	$E_{1/2}$ (*vs.* S.C.E.) V	K_d(III)/ K_d(II)[b] $\times 10^{-4}$	I[c]
0.954	7.71	0.951	2.9	−0.255	18	1.45
.503	7.70	.500	1.5	− .255	18	1.58
.167	6.65	.164	0.5	− .251	3.4	1.55
.103	6.10	.100	.5	− .237	3.5	1.56
.053	5.60	.048	.5	− .217	3.7	1.54
.023	5.09	.018	.5	− .187	4.4	1.51
.008	4.40	.003	.5	− .136	5.5	1.55

[a] $NaClO_4$ was added to the dilute solutions to give ionic strength of 0.5. [b] Ratio of the dissociation constant of the iron(III) complex to that of the iron(II) complex. [c] I = diffusion current constant = $i_d/Cm^{2/3}t^{1/6}$ μamp. mmole^{-1} liter mg.$^{-2/3}$ sec.$^{1/2}$.

The reaction occurring at the dropping mercury electrode in the dicarboxylate solutions can be represented as

$$[Fe(C_nH_{2n-4}O_4)_p]^{3-2p} + e^- \rightleftarrows [Fe(C_nH_{2n-4}O_4)_q]^{2-2q} + (p - q)C_nH_{2n-4}O_4^{--} \quad (1)$$

The quantity $(p - q)$ and the ratio of the dissociation constant of the iron(III) complex to that of the iron(II) complex can be evaluated by application of equation 2, as described by Kolthoff and Lingane[8] and others.

$$E_{1/2} = E_S^\circ + 0.059 \log (K_d(III)/K_d(II)) - (p - q)0.059 \log [C_nH_{2n-4}O_4^{--}] \quad (2)$$

If $E_{1/2}$ values are plotted as a function of the logarithm of the anion concentration, slopes of 0.00, −0.059 and −0.118 correspond to values of 0, 1 and 2, respectively, for $p - q$.

The variation of $E_{1/2}$ with log $[C_2O_4^{--}]$ is shown in Fig. 1, and from the slopes of the lines it may be concluded that $p - q = 0$ in solutions containing more than about 0.2 M $C_2O_4^{--}$ and that $p - q = 1$ in solutions containing less than about 0.2 M $C_2O_4^{--}$. If it is assumed, in accordance with much previous evidence, that the iron(III) complex is $Fe(C_2O_4)_3^{-3}$, then it follows that the iron(II) complex formed at the d.m.e. in solutions containing >0.2 M $C_2O_4^{--}$ is $Fe(C_2O_4)_3^{-4}$, and that $Fe(C_2O_4)_2^{-2}$ is formed when $C_2O_4^{--} < 0.2$ M. These results substantiate the findings of Lingane.

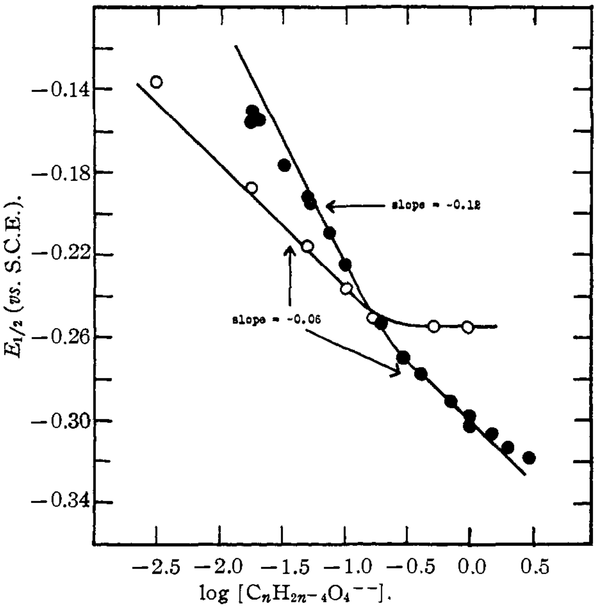

Fig. 1.—Plot of $E_{1/2}$ *vs.* log dicarboxylate anion concentration: ○, oxalate solutions; ●, malonate solutions.

For the calculation of the ratio K_d(III)/K_d(II) using equation 2, the formal potential of the iron(III)–iron(II) electrode at $\mu = 0.5$ is used as the value for E_S° rather than the standard potential of 0.771 v. at $\mu = 0$. Schumb, Sherrill and Sweetser[9] measured the potential of the iron(III)–iron(II) electrode in perchlorate solutions and report that the potential is approximately constant at 0.741 v. (0.495 v. *vs.* S.C.E.) over the range $\mu = 0.5$ to 1.0. The dissociation constant ratio is calculated to be 18×10^{-14} in solutions with $C_2O_4^{--} > 0.2$ M and 4×10^{-14} in solutions with $C_2O_4^{--} < 0.2$ M.

When the reduction reaction proceeds between two complexes in different valence states, the polarographic data yield only the *ratio* of the dissociation constants and an independent method must be used to evaluate one of the dissociation constants before the value of the other can be obtained. In this present work, an independent value for K_d of the trioxalatoferrate(III) complex was obtained

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(7) I. M. Kolthoff and V. A. Stenger, "Volumetric Analysis," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1942.

(8) I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers, Inc., New York, N. Y., 1946.

(9) W. C. Schumb, M. S. Sherrill and S. B. Sweetser, THIS JOURNAL, 59, 2360 (1937).

by measuring the solubility of iron(III) hydroxide in oxalate solutions. If equilibrium is assumed, the expressions for the dissociation constant of Fe-$(C_2O_4)_3^{-3}$ and the K_{sp} of $Fe(OH)_3$ may be combined to yield equation 3, in which the quantities on the right-hand side are known or measurable.

$$K_d(\mathrm{III}) = \frac{K_{sp}(C_2O_4^{--}]^3}{[Fe(C_2O_4)_3^{-3}][OH^-]^3} \qquad (3)$$

For these measurements, varying amounts of NaOH were added to solutions containing iron(III) and known concentrations of $C_2O_4^{--}$ causing *partial* precipitation of iron as iron(III) hydroxide. After several days standing with intermittent shaking, the value for $[OH^-]$ was obtained by *p*H measurement, $[C_2O_4^{--}]$ was calculated from the amount added minus the amount complexed and $[Fe(C_2O_4)_3^{-3}]$ was obtained by running a polarogram on the resulting solution and measuring the diffusion current. The K_{sp} of iron(III) hydroxide is taken to be 3×10^{-37}.[10] On the basis of results from several solutions, the average value and probable error calculated for the K_d of $Fe(C_2O_4)_3^{-3}$ is $1.1\ (\pm 0.5) \times 10^{-18}$. Combining this value with the ratios $K_d(\mathrm{III})/K_d(\mathrm{II})$ given above, the dissociation constants of the iron(II) complexes are calculated to be 6×10^{-6} for $Fe(C_2O_4)_3^{-4}$ and 3×10^{-5} for $Fe(C_2O_4)_2^{-2}$.

The half-wave potentials in oxalate solutions will be a function of *p*H when the *p*H is low enough so that all the oxalate is not present as the $C_2O_4^{--}$ ion and when the total $C_2O_4^{--} < 0.2$ *M*. In Fig. 2, the experimental points are compared with a curve calculated from equation 2, in which $E_s{}^\circ = 0.495$ v., $K_d(\mathrm{III})/K_d(\mathrm{II}) = 4 \times 10^{-14}$ and the actual $[C_2O_4^{--}]$ is calculated at each *p*H assuming the ionization constants of oxalic acid to be $K_1 = 6.5 \times 10^{-2}$ and $K_2 = 6.1 \times 10^{-5}$. The $E_{1/2}$ values were measured on solutions containing 1.00×10^{-3} *M* iron(III), 0.05 *M* added $K_2C_2O_4$, varying amounts of $HClO_4$ and sufficient $NaClO_4$ to give $\mu = 0.5$.

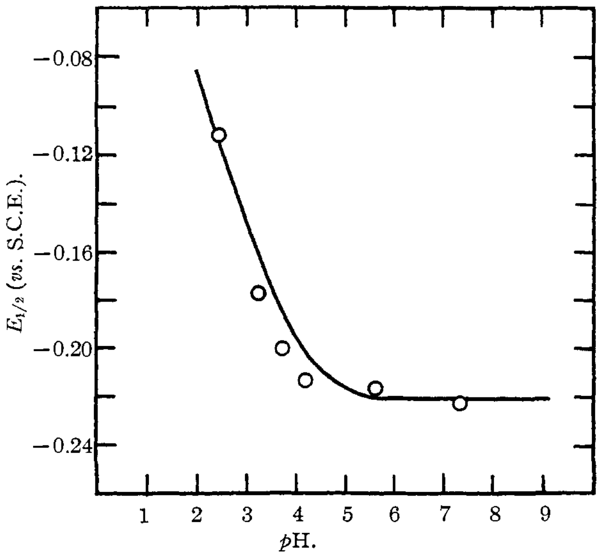

Fig. 2.—Comparison of experimental and calculated values of $E_{1/2}$ as a function of *p*H. All solutions contained 0.05 *M* added potassium oxalate.

The diffusion current constants calculated from the waves in all these solutions fall within experimental error of the value 1.55 observed previously for the trioxalatoferrate(III) ion. This, together with the trend shown in Fig. 2, indicates that the divalent $C_2O_4^{--}$ anion is the complexing species over the *p*H range investigated and that the reduction proceeds from $Fe(C_2O_4)_3^{-3}$ to $Fe(C_2O_4)_2^{-2}$ at the d.m.e. under these conditions.

Malonate Solutions.—Previous investigators present abundant evidence for the existence of the trimalonatoferrate(III) ion on the basis of preparative data,[11,12] potentiometric titration curves[13,14] and dialysis experiments.[15] In addition, a dimalonatoferrate(III) complex[13] and a hydroxomalonato ion,[12] $Fe_3(C_3H_2O_4)_3(OH)_2^+$, are reported but have not been verified.

In the case of iron(II), the complexes $Fe(C_3H_2O_4)_2^{-2}$[11,16,17] and $FeC_3H_2O_4$[17] are reported. The dissociation constant of the dimalonatoferrate(II) ion is given as 6×10^{-2} by Franke.[17] Binuclear $Fe_2(C_3H_2O_4)^{-4}$ is claimed to exist on the basis of dialysis measurements.[15]

The procedure with malonate solutions was similar to that used in the oxalate studies except that it was not necessary to eliminate light, since no indication of a photochemical reaction was noticed. For the calculation of the actual concentration of the divalent $C_3H_2O_4^{--}$ ion at any *p*H, the ionization constants of malonic acid are taken as $K_1 = 1.5 \times 10^{-3}$ and $K_2 = 2 \times 10^{-6}$.[18] Data and results are shown in Table II.

All polarographic waves in malonate solutions correspond to reversible, one-electron reductions. The variation of the half-wave potentials with the logarithm of the malonate ion concentration is shown in Fig. 1. With solutions in which $C_3H_2O_4^{--} > 0.3$ *M*, the experimental points fall quite well along the line with a slope corresponding to a value of $p - q = 1$. If the formula of the iron(III) complex is taken to be $Fe(C_3H_2O_4)_3^{-3}$ (see below), then the iron(II) complex formed at the electrode is $Fe(C_3H_2O_4)_2^{-2}$ in this concentration range.

With solutions in which $C_3H_2O_4^{--} < 0.3$ *M*, the experimental points fall between the lines drawn with slopes corresponding to $p - q = 1$ and $p - q = 2$. The reason for the intermediate slope is not clear, for if the reduction were proceeding from the trimalonatoferrate(III) complex to a mixture of iron(II) complexes, *e.g.*, $Fe(C_3H_2O_4)_2^{-2}$ and $FeC_3H_2O_4$, then a trend with opposite curvature should result rather than the trend observed over that large a concentration range. It is more probable that the reduction is from $Fe(C_3H_2O_4)^{-3}$ to $FeC_3H_2O_4$, and that the usual

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(10) P. Kriutkow and G. Awsyewitch, *Z. Elektrochem.*, **39**, 884 (1933).

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(13) W. D. Treadwell and W. Fisch, *Helv. Chim. Acta*, **13**, 1219 (1930).

(14) W. Reinders and C. de Minjer, *Rec. trav. chim.*, **57**, 594 (1938).

(15) H. Brintzinger and F. Jahn, *Z. anorg. allgem. Chem.*, **235**, 115 (1937).

(16) R. Scholder, *Ber.*, **60**, 1499 (1927).

(17) W. Franke, *Ann.*, **491**, 30 (1931).

(18) R. Gane and C. K. Ingold, *J. Chem. Soc.*, 2153 (1931).

TABLE II

MALONATE SOLUTIONS—DATA AND POLAROGRAPHIC RESULTS

Added $K_2C_3H_2O_4$, M	pH	Calcd. excess $[C_3H_2O_4^{--}]$, M	Ionic[a] strength, μ	$E_{1/2}$ (*vs.* S.C.E.) V	$K_d(III)/K_d(II)$[b] $\times 10^{14}$
3.00	..	3.00	9	−0.318	..
2.00	..	2.00	6	− .313	4.0
1.50	..	1.50	4.5	− .306	4.0
1.00	..	0.997	3	− .298	3.6
1.00	8.20	.997	3	− .303	2.8
0.703	..	.700	2	− .291	3.3
.403	..	.400	1.2	− .277	3.2
.303	7.92	.298	0.9	− .270	3.0
.203	7.63	.198	0.6	− .254	
.103	7.29	.098	0.5	− .225	
.103	7.32	.098	.5	− .225	
.078	7.27	.073	.5	− .210	
.053	7.21	.051	.5	− .193	
.053	7.20	.051	.5	− .195	
.053	7.17	.050	.5	− .193	
.053	7.02	.048	.5	− .192	
.053	6.98	.048	.5	− .190	
.053	6.95	.048	.5	− .197	
.053	6.9	.048	.5	− .192	
.038	6.78	.032	.5	− .177	
.023	6.70	.020	.5	− .155	
.023	6.72	.018	.5	− .151	
.023	6.50	.017	.5	− .157	

[a] $NaClO_4$ was added to the dilute solutions to give ionic strength of 0.5. [b] The ratios of the dissociation constant of the iron(III) complex to that of the iron(II) complex are calculated only in the concentration range where $p - q = 1$.

approximations regarding activity and diffusion coefficients are poor when the oxidized species is triply charged and the reduced species is uncharged.

The average ratio of the dissociation constant of the trimalonatoferrate(III) complex to that of the dimalonatoferrate(II) complex is 3.4×10^{-14} in solutions containing > 0.3 M malonate ion. This value is nearly identical to the ratio found for the corresponding oxalato complexes, indicating that with these anions the difference in stability of the iron(III) complexes as compared to the iron(II) complexes is due predominantly to the nature (size, charge, etc.) of the central metal ion.

The formula and dissociation constant of the iron(III) complex and the precipitate present in neutral or basic solutions were determined on the basis of solubility studies. The data were treated in a general way to take into account the possible existence of a hydroxomalonate complex or precipitate. If the precipitate is assigned the general formula $Fe(C_3H_2O_4)_a(OH)_b$ and the complex written $Fe(C_3H_2O_4)_c(OH)_d^{-x}$, then the dissociation constant of the complex can be expressed

$$K_d = \frac{[Fe^{+3}][C_3H_2O_4^{--}]^c[OH^-]^d}{[Fe(C_3H_2O_4)_c(OH)_d^{-x}]} \qquad (4)$$

Combining with the expression for the K_{sp} of the precipitate, $Fe(C_3H_2O_4)_a(OH)_b$,

$$K_d = \frac{K_{sp}[C_3H_2O_4^{--}]^n}{[Fe(C_3H_2O_4)_c(OH)_d^{-x}][OH^-]^m} \qquad (5)$$

where $n = c - a$ and $m = b - d$. Equation 5 can be rewritten

$$\log (K_d/K_{sp}) = n \log [C_3H_2O_4^{-2}] - m \log[OH^-] - \log[Fe(C_3H_2O_4)(OH)_d^{-x}] \qquad (6)$$

Application of equation 6 to the data in Table III allows graphical evaluation of m and the ratio m/n to be made. It is not possible to evaluate n directly because the pH is not held sufficiently constant. A plot of log $[Fe(C_3H_2O_4)_c(OH)_d^{-x}]$ *vs.* log $[OH^-]$ gives a value of 3.4 for m. Similarly, plotting log $[C_3H_2O_4^{--}]$ *vs.* log $[OH^-]$ gives a value of 0.9 for m/n. That these values are not whole numbers is due to the fact that it is not possible to select series of data in which one of the variables remains exactly constant. Taking $m = 3$ and $m/n = 1$, it follows that $a = 0$, $b = 3$, $c = 3$ and $d = 0$. Thus, the precipitate appears to be $Fe(OH)_3$ and the complex $Fe(C_3H_2O_4)_3^{-3}$. Further proof of the correctness of this formula for the complex is provided by the constancy of the values calculated for its dissociation constant when this formula is assumed (Table III). The average, and probable error, of the calculated values for the dissociation constant of the trimalonatoferrate (III) ion is $2.2(\pm 0.5) \times 10^{-16}$. Combining this with the ratio between the dissociation constants of the iron(III) and iron(II) complexes, the dissociation constant of the dimalonatoferrate(II) ion, $Fe(C_3H_2O_4)_2^{-2}$, is calculated to be 6×10^{-3}.

TABLE III

DISSOCIATION CONSTANT OF THE TRIMALONATOFERRATE(III) COMPLEX[a]

$[OH^-]$, $M \times 10^8$	$[C_3H_2O_4^{-2}]$, $M \times 10^2$	$[Fe(C_3H_2O_4)_3^{-3}]$, $M \times 10^4$	$K_d(III) \times 10^{16}$
214	40.2	0.42	1.7
38.0	10.1	1.22	1.7
16.2	5.12	1.06	3.3
5.01	2.03	2.31	3.2
20.9	9.83	9.05	1.3
8.91	4.77	9.21	1.8
3.16	1.75	8.95	2.1
42.4	19.9	6.25	1.8
18.6	7.39	7.39	1.0
6.03	3.30	7.79	2.3
9.44	4.84	7.21	2.0
10.5	4.97	3.55	3.3
15.9	5.11	1.23	3.0
11.8	5.00	3.22	2.6

[a] Ionic strength not less than 0.5.

Diffusion current constants, I, were measured in malonate solutions and were found to attain a limiting value of 1.44 in dilute solutions with $\mu = 0.5$. In more concentrated solutions the values for I dropped off sharply. It has been reported[19] that the diffusion current constants vary with the viscosity, η, of solutions according to the relation

$$I \times \eta^{1/2} = \text{constant} \qquad (7)$$

and that this relation holds when the viscosity increase is due to substances in true solution. Viscosities (relative to water) and diffusion current constants measured for a series of malonate solutions are shown in Table IV.

Equation 7 is seen to hold well ($\pm 3\%$) except for the most concentrated solution. For analytical purposes, viscosity effects can be of considerable significance when salts with large anions are used.

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(19) J. J. Lingane, *Anal. Chem.*, **21**, 45 (1949).

TABLE IV

EFFECT OF VISCOSITY ON DIFFUSION CURRENT CONSTANTS

$K_2C_3H_2O_4$, M	Relative viscosity (η)	$\eta^{1/2}$	$\frac{i_d}{Cm^{2/3}t^{1/6}}$ (I)	$I \times \eta^{1/2}$
3.0	2.53	1.59	0.80	1.27
2.0	1.98	1.40	1.03	1.45
1.5	1.64	1.28	1.14	1.47
1.0	1.35	1.16	1.25	1.45
0.70	1.25	1.12	1.36	1.52
.40	1.10	1.05	1.42	1.49
.10[a]	1.04	1.02	1.44	1.47
.05[a]	1.04	1.02	1.44	1.47

[a] Ionic strength adjusted to 0.5 with $NaClO_4$.

In the present case, for example, the diffusion current is more than 15% lower in 1 M potassium malonate solutions than in 0.1 M solutions.

Succinate Solutions.—Previous experimenters[14,17,20] agree that any complexes formed between iron and succinate ions are much weaker than those involving oxalate or malonate ions. Franke[17] reports the dissociation constant of the disuccinatoferrate(II) ion to be approximately 13 on the basis of solubility studies. Hydroxosuccinato complexes have been claimed to exist on the basis of preparative studies[11,21] and also on the basis of breaks in potentiometric titration curves.[13]

Polarographic studies were attempted with solutions ranging from pH 5.5 to 9.5 and from 0.1 to 4.0 M potassium succinate. Of the more than thirty solutions studied, the reversibility test could be applied to less than half the resulting polarograms. At the higher pH values all or most of the iron(III) precipitated from solution, either preventing the appearance of a wave or causing the wave to be too small for analysis. At lower pH values, where no precipitation occurred, many of the waves followed so closely after the anodic mercury dissolution wave that residual current corrections could not be made accurately. In the cases where the reversibility test was applied, the slopes of the plots of $E_{d.e.}$ *vs.* log $(i_d - i)/i$ showed considerable variation, ranging from 0.05 to 0.085. Double waves, indicating the presence of two complexes in sluggish equilibrium, were observed in a few cases. Because of the failure to establish with certainty the reversibility of the reductions occurring in succinate solutions, detailed presentation and interpretation of the data are not warranted at this time. However, the data obtained, such as they are, indicate the dissociation constant for the iron(III) complex to be on the order of 10^{-9}, and that of the iron(II) complex to be about unity. This latter value is of a similar order of magnitude as that reported by Franke.

It is apparent that the succinato (7-ring) complexes are considerably weaker than the malonato (6-ring) and oxalato (5-ring) complexes. Furthermore, succinic acid is a rather weak acid, so that in acidic solutions below pH 4 virtually no $C_4H_4O_4^{--}$ ions are present in solution. At higher pH values at which the $C_4H_4O_4^{--}$ concentration becomes appreciable, the large and weakly bound succinate groups tend to be replaced by OH^- ions causing partial or complete hydrolysis of the iron(III). This situation explains why several workers[14,20] have reported no noticeable complex formation occurring between iron and succinate ions.

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Higher Oxides of Terbium and Praseodymium from High Pressure Molecular Oxygen Treatment

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RECEIVED JUNE 25, 1954

Terbium and praseodymium oxides have been treated with molecular oxygen of pressures up to 282 atmospheres at temperatures as high as 450°. The compositions of the higher oxides thus produced were determined by weight changes on reduction to the sesquioxides with H_2 and CO, and by iodometric titration. X-Ray diffraction patterns were observed for some of the phases produced. It was found that when the reaction vessel was desiccated carefully all the methods of analyses were in agreement. Treatment of the lower oxides of terbium and praseodymium at 282 atmospheres oxygen pressure at 400° yielded $TbO_{1.86}$ and $PrO_{2.00}$, respectively.

Introduction

The higher oxides of terbium and praseodymium are interesting examples of non-stoichiometric compounds. An investigation of these oxide systems in equilibrium with oxygen up to one atmosphere pressure has been completed,[2-4] and an equilibrium study of the region up to 10 atmospheres is underway. Below one atmosphere of oxygen pressure the oxides have compositions in the range $TbO_{1.50}$ to $TbO_{1.81}$ and $PrO_{1.50}$ to $PrO_{1.83}$.

Higher oxides of terbium have been known for a long time, but only a few investigations have been made on their exact compositions. Prandtl and Rieder[5] found that air oxidized samples had an average composition of about $TbO_{1.76}$, and samples treated with 30 atmospheres of oxygen at 340° had the composition $TbO_{1.83}$. TbO_2 has been re-

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