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.

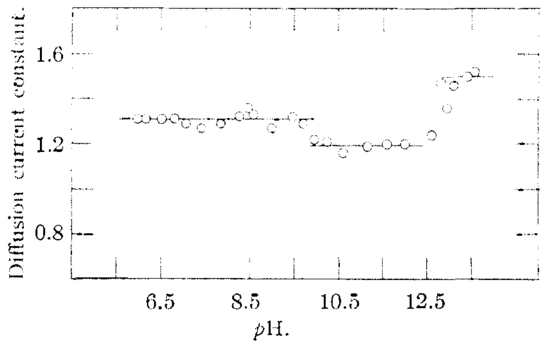

Fig. 5.—Plot of diffusion current constant *vs.* *p*H: total H_4Y, 0.05 molar; europium, 0.46 millimolar; μ, 0.5 for *p*H ≦ 12. 1.0 for *p*H > 12.

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.

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[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]

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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).

Experimental

Apparatus.—A Sargent Model XII photographic-type polarograph was used with a cell of the type described by Lingane and Kolthoff.[3] Oxygen-free nitrogen was passed through the cell before each electrolysis. The potentials of the dropping mercury electrode during electrolysis were measured against an external saturated calomel electrode by means of a standard potentiometer circuit. Cell temperature was maintained at 25.0 ± 0.1° by means of a water thermostat. Reversibility of the electrode reactions was tested by determining the slopes of the plots of log $i/(i_d - i)$ *versus* potential. Half-wave potentials were taken from the logarithmic plots.

Preparation of Materials.—Solutions were prepared immediately before use in terms of per cent. by volume. Tenth molar potassium nitrate was used as supporting electrolyte in every determination. Reagent grade materials were used throughout.

Dioxane, for use as a solvent, was refluxed over sodium and distilled immediately before each use. Ethanol and 2-methoxyethanol were distilled prior to use.

1,3-Diketones.—Reagent grade 2,4-pentanedione, 1-phenyl-1,3-butanedione and 1,3-diphenyl-1,3-propanedione were purchased for use. Alkylation of the number three carbon atom of 2,4-pentanedione was accomplished by heating its sodium salt with the appropriate alkyl iodide under pressure.[4] The operation was carried out in a stoppered Pyrex tube immersed in methanol and agitated within a micro-hydrogenator. Temperature was controlled by a Variac and measured with a chromel–alumel thermocouple connected to a Leeds and Northrup portable potentiometer. The product was separated by fractional distillation under vacuum.

The sodium salt of 2,4-pentanedione was prepared by adding, dropwise, freshly distilled 2,4-pentanedione to a solution of sodium ethoxide.

Copper Chelates. Method (1).—A known amount of diketone was added to water and dissolved by addition of ammonium hydroxide. Precipitation of the chelate occurred upon addition, with stirring, of a solution of copper(II) nitrate and neutralization with nitric acid. Precipitation was carried out at room temperature for chelate (A), at 50° for chelate (B), and on a steam-bath for chelate (C).

Method (2).—Tetramminecopper(II) nitrate solution was added to a solution of a known amount of diketone dissolved in absolute alcohol. The precipitated chelate was filtered and recrystallized. This method was used for chelates (D), (E) and (F).

Chelate (A) was purified by sublimation at 200° under 1 mm. pressure. All other chelate derivatives were purified by recrystallization from alcohol except the highly insoluble derivative of 1,3-diphenyl-1,3-propanedione (C).

Copper analyses of each chelate were made by standard methods.

Results and Discussion

A one-step reduction is obtained in each case. Slopes of the log plots indicate irreversible reduction throughout. Table I shows polarographic values obtained in the various solvents.

The chelate compounds (A) bis-(2,4-pentanediono)-copper(II), (B) bis-(1-phenyl-1,3-butanediono)-copper(II) and (C) bis-(1,3-diphenyl-1,3-propanediono)-copper(II) differ from each other in the groupings at the ends of the respective 1,3-diketone molecules. In 75% dioxane–25% water solution (hereafter referred to as 75% dioxane solution), the half-wave potentials become more negative, indicating more difficult reduction, for (C), (B) and (A) in the order named. The same order pertains for the latter two in 50% dioxane solution and in 50% ethanol solution. Chelate (C) was studied only in 75% dioxane because of its limited solubility in the other solvents. The solubility of (C) was not tested in 2-methoxyethanol. Copper(II) nitrate is reduced at much more positive potentials in all solvents used. This may indicate that for the chelates in dioxane and in ethanol solution the covalent character of the bond to the copper is increased in the order (C), (B), (A). The fact that the melting points for the copper derivatives decrease in the same order is compatible with this idea. Steric effects may arise as the bulky phenyl groups are substituted on the carbonyl carbon atoms. Such effects could conceivably cause (1) distortion of the chelate with resultant lessening of the covalent character of the bond to the copper, (2) an effect upon orientation of the chelate at the dropping mercury electrode.

The diffusion current constants decrease in the order (A), (B), (C) in 75% dioxane solution and decrease in the corresponding order for the chelates which are sufficiently soluble for measurement in 50% dioxane and in 50% ethanol solution. This trend indicates that the diffusion rate in dioxane and in ethanol, as might be expected, decreases as the size of the chelate molecule increases. In 50% ethanol and in water, the diffusion current constant for copper(II) nitrate is larger, indicating more rapid diffusion than for chelate (A). The low diffusion current constant for copper(II) nitrate in dioxane seems anomalous. A comparison of 0% dioxane–100% water with the other two dioxane–water solutions shows a minimum in the diffusion current constant values for copper(II) nitrate and for chelate (A) in 50% dioxane.

The chelate compounds (A) bis-(2,4-pentanediono)-copper(II), (D) bis-(3-methyl-2,4-pentanediono)-copper(II), (E) bis-(3-ethyl-2,4-pentanediono)-copper(II) and (F) bis-(3-*n*-propyl-2,4-pentanediono)-copper(II) differ from each other with respect to the groups attached to the number three carbon atom in the respective 1,3-diketones. Table I indicates that in 75% ethanol, 75% 2-methoxyethanol and 75% dioxane the diffusion current constant decreases as 2,4-pentanedione, 3-methyl-2,4-pentanedione and 3-ethyl-2,4-pentanedione are used as the chelating 1,3-diketone in the order named. An increase in diffusion current constant occurs, however, when 3-*n*-propyl-2,4-pentanedione is used. It has previously been established that the per cent. enol in a keto–enol equilibrium mixture also decreases as first a methyl and then an ethyl group is substituted for a hydrogen on the number three carbon atom of 2,4-pentanedione[5,6] and then seems to increase somewhat when a *n*-propyl group is introduced.[6] The apparent correlation between per cent. enol content of the parent 1,3-diketone and the diffusion current constant of the corresponding copper chelate may have significance. Wheland[7] points out that generalization is difficult, even with regard to enol content, upon the effect of an alkyl substituent on the carbon atom to which the enolic hydrogen atom is attached in β-ketoesters and in 1,3-diketones. Re-

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[3] J. J. Lingane and I. M. Kolthoff, This Journal, **61**, 825 (1939).

[4] G. T. Morgan and A. E. Rawson, *J. Soc. Chem. Ind.*, **44**, 462T (1925).

[5] J. B. Conant and A. F. Thompson, Jr., This Journal, **54**, 4039 (1932).

[6] K. von Auwers and H. Jacobsen, *Ann.*, **426**, 161 (1922).

[7] G. W. Wheland, "Advanced Organic Chemistry," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1949, p. 603.

TABLE I

POLAROGRAPHIC REDUCTION OF COPPER COMPOUNDS

0.1 *N* potassium nitrate as supporting electrolyte, temperature 25.0 ± 0.1°

Copper compound	Identification letter	Concn., millimoles/l.	Half-wave potential, $E_{1/2}$ vs. S.C.E.	i_d, μa	$\frac{i_d}{Cm^{2/3}t^{1/6}}$
Water as solvent					
Copper(II) nitrate	..	1.30[a]	+0.018	6.27	3.42
Bis-(2,4-pentanediono)-copper(II)	A	0.20	−0.184	0.823	2.94
50% Ethanol-50% water as solvent					
Copper(II) nitrate	..	1.10	+0.04	3.48	2.26
Bis-(2,4-pentanediono)-copper(II)	A	1.00	− .28	2.57	1.82
Bis-(2,4-pentanediono)-copper(II)	A	0.50	− .27	1.30	1.83
Bis-(1-phenyl-1,3-butanediono)-copper(II)	B	0.20	− .22	0.485	1.73
75% Ethanol-25% water as solvent					
Copper(II) nitrate	..	1.00[a]	+0.07	3.83	2.20
Bis-(2,4-pentanediono)-copper(II)	A	1.00[a]	− .31	4.23	2.46
Bis-(3-methyl-2,4-pentanediono)-copper(II)	D	1.00[a]	− .42	2.83	1.63
Bis-(3-ethyl-2,4-pentanediono)-copper(II)	E	1.00[a]	− .42	2.60	1.49
Bis-(3-*n*-propyl-2,4-pentanediono)-copper(II)	F	0.50[a]	− .43	1.59	1.85
75% 2-Methoxyethanol-25% water as solvent					
Copper(II) nitrate	..	1.04[a]	+0.07	3.12	1.72
Bis-(2,4-pentanediono)-copper(II)	A	1.00[a]	− .34	3.13	1.80
Bis-(3-methyl-2,4-pentanediono)-copper(II)	D	1.00[a]	− .44	2.20	1.27
Bis-(3-ethyl-2,4-pentanediono)-copper(II)	E	1.00[a]	− .44	1.97	1.13
Bis-(3-*n*-propyl-2,4-pentanediono)-copper(II)	F	Satd. soln.[a,b]	− .43	...	...
50% Dioxane-50% water as solvent					
Copper(II) nitrate	..	1.20	+0.04	2.60	1.55
Bis-(2,4-pentanediono)-copper(II)	A	1.00	− .46	2.70	1.93
Bis-(1-phenyl-1,3-butanediono)-copper(II)	B	0.50	− .31	1.10	1.58
Bis-(1-phenyl-1,3-butanediono)-copper(II)	B	0.50[a]	− .31	1.08	1.55
75% Dioxane-25% water as solvent					
Copper(II) nitrate	..	1.31	+0.06	3.19	1.77
Copper(II) nitrate	..	1.05[a]	+ .07	3.26	1.79
Bis-(2,4-pentanediono)-copper(II)	A	0.50	− .49	1.81	2.64
Bis-(2,4-pentanediono)-copper(II)	A	1.00[a]	− .49	3.58	2.08
Bis-(1-phenyl-1,3-butanediono)-copper(II)	B	0.50	− .38	1.35	1.92
Bis-(1,3-diphenyl-1,3-propanediono)-copper(II)	C	.50	− .38	0.735	1.05
Bis-(1,3-diphenyl-1,3-propanediono)-copper(II)	C	.50[a]	− .38	0.613	0.87
Bis-(3-methyl-2,4-pentanediono)-copper(II)	D	1.00[a]	− .56	3.38	1.96
Bis-(3-ethyl-2,4-pentanediono)-copper(II)	E	1.00[a]	− .56	3.33	1.92
Bis-(3-*n*-propyl-2,4-pentanediono)-copper(II)	F	1.00[a]	− .56	3.36	1.96

[a] In presence of 0.001% methyl red; all other experiments in the absence of maximum suppressors. [b] In presence of 0.004% Aerosol T in addition to methyl red.

mick[8] presents what appears to be a plausible explanation of the effect on enol content that comes from substitution of an alkyl group on the methylene carbon of 1,3-diketones. Additional factors, however, complicate the situation with the chelates. Before generalizations can be made for their diffusion current constants more compounds should be studied, among them the chelates of 3-phenyl-2,4-pentanedione and 3-benzyl-2,4-pentanedione, each of which have relatively high enol content. Solvation of the copper, varying with the amount of ionic character, may have a bearing on the diffusion current constant trends.

Table I shows no pronounced trend in the half-wave potentials for (A), (D), (E) and (F) in any one solvent and indicates that the numerical values do not differ from each other very much.

The nature of the solvent has an effect upon both the diffusion current constant and upon the half-wave potential. A general trend in the data is difficult to establish for the diffusion current constants of the individual copper compounds in the various solvents. The half-wave potential for each chelate becomes more negative in water, 50% ethanol, 75% ethanol, 75% 2-methoxyethanol, 50% dioxane and 75% dioxane in the order named. This order is in agreement with the probable general order of increased coördinating ability of the molecules listed.

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[8] A. E. Remick, "Electronic Interpretations of Organic Chemistry," 2nd edition, John Wiley and Sons, Inc., New York, N. Y., 1950, p. 456.