

None of the other assumptions necessary for the mathematical analysis of the extended Ilkovic problem (sphericity of the drop, isolation of the drop, etc.) are innovations, and none should have any important effect on the results. They have all been discussed previously, *e.g.*, reference 5b.

The authors wish to thank Dr. H. Strehlow, who called to their attention while the present paper was in proof the fact

that W. Hans and W. Henne (*Naturwiss.*, 40, 524 (1953)) had demonstrated experimentally the effect of depletion on the rate of growth of the polarographic current.

Acknowledgment.—The authors wish to thank the Atomic Energy Commission, which helped support the work described.

ANN ARBOR, MICHIGAN

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

Polarographic Reduction of Copper Chelates of 1,3-Diketones. III. Solvent Effects

BY E. R. NIGHTINGALE, JR., AND HENRY F. HOLTZCLAW, JR.

RECEIVED NOVEMBER 8, 1958

The influence of the solvent upon the polarographic reduction of the copper chelates of some 1,3-diketones has been investigated. The half-wave potential is demonstrated to vary linearly with the reciprocal of the dielectric constant of the solvent, and this is attributed to the difference in the free energy necessary to charge the ionic products of the electrode reaction in the dielectric medium of the various solvents. The diffusion current constants of some chelates are observed to obey a Stokes-Einstein relation when corrected for the differences in the viscosities of the solutions. For certain of the substituted diketones, the Stokes-Einstein relationship is less satisfactory. These deviations are interpreted in terms of the size and structure of the substituted chelate molecule.

Previous articles from these laboratories^{1,2} have discussed the polarographic reduction of the copper chelates of several 1,3-diketones in various solvents. In particular, the second paper in this series has considered the relation between the polarographic half-wave potentials observed in the various solvents and the structure and electrophilic character of the chelate ligand. Considerable variation in the diffusion current constants for the reduction of the various copper chelates was reported. No over-all trend in diffusion current constants was apparent, although trends of some significance could be noted by comparing small groups of chelates possessing similar ligands. The present paper investigates the influence of the solvent upon the reduction of the copper chelates and demonstrates that the dielectric constant and viscosity of the solution play important roles in determining the ease of reduction and the magnitude of the reduction current for the electrode reaction in the various solvents.

Experimental

The polarographic procedures and experimental details have been described in the previous papers.^{1,2}

The viscosities of the ethanol, 2-methoxyethanol and dioxane solutions were measured at $25.00 \pm 0.01^\circ$ with an Ostwald viscometer. The viscometer was calibrated at 20, 25 and 30° with water and at 25° with 20 and 30% sucrose solutions. Details have been described elsewhere.³ The viscosities of the three solutions, each 0.1 M in potassium nitrate, are 75 vol. % ethanol in water, 0.0214 poise; 75 vol. % methoxyethanol in water, 0.0388 poise; and 75 vol. % dioxane in water, 0.0190 poise. The absolute viscosity of water was taken as 0.008903 poise at 25° .⁴ The dielectric constants for the ethanol, methoxyethanol and dioxane solutions have been taken as those of the pure solvents, 37.9,⁵ 27.7⁶ and 13.6,⁵ respectively.

(1) H. F. Holtzclaw, Jr., K. W. R. Johnson and F. W. Hengeveld, *THIS JOURNAL*, **74**, 3776 (1952).

(2) H. F. Holtzclaw, Jr., A. H. Carlson and J. P. Collman, *ibid.*, **78**, 1838 (1956).

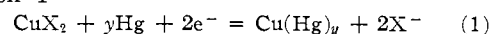
(3) E. R. Nightingale, Jr., *J. Phys. Chem.*, **63**, 742 (1959).

(4) J. R. Coe and T. B. Godfrey, *J. Applied Phys.*, **15**, 625 (1944).

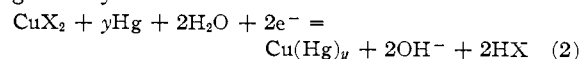
(5) H. S. Harned and B. B. Owen, "Physical Chemistry of Electrolyte Solutions," 2nd Ed., Reinhold Publ. Corp., New York, N. Y., 1950, p. 118.

Results and Discussion

When copper(II) is complexed with the various 1,3-diketones, stable chelates with the empirical formulas CuX_2 are formed^{7,8} where X is the monobasic chelate ligand. The primary electrode reaction for the reduction of these compounds at the dropping mercury electrode (DME) is given by equation 1



However, the chelate ions are the conjugate bases of very weak acids⁹ and hydrolyze rapidly in water. Hence, the over-all reaction, for which the electrode potential is a measure of the free energy, is given by



This investigation has considered the effect of the solvent upon (a) the change in the polarographic half-wave potential for the reduction of the copper chelate according to equation 2, and (b) the magnitude of the diffusion current constant for a given copper chelate in the various solvents.

Variation of $E_{1/2}$ with Solvent.—The half-wave potential, $E_{1/2}$, for a rapid (reversible) polarographic reaction is a measure of the standard free energy of the reaction. For slow (irreversible) reactions, the half-wave potential is a function of both the heterogeneous rate constant at a standard potential and the transfer coefficient and is not necessarily related in a simple manner to the free energy for the reaction. An excellent discussion of irreversible polarographic processes has been presented recently by Randles.¹⁰

(6) S. R. Phadke, N. L. Phalnikar and B. V. Bhide, *J. Ind. Chem. Soc.*, **22**, 239 (1945).

(7) M. Calvin and K. W. Wilson, *THIS JOURNAL*, **67**, 2003 (1945).

(8) L. G. Van Uitert, W. C. Fernelius and B. E. Douglas, *ibid.*, **76**, 457, 2736 (1953).

(9) L. G. Van Uitert, C. G. Haas, W. C. Fernelius and B. E. Douglas, *ibid.*, **75**, 455 (1953).

(10) G. W. C. Milner, "The Principles and Applications of Polarography and Other Electroanalytical Processes," Longmans, Green and Co., New York, N. Y., 1957, p. 53 ff.

The current-potential curves observed for the reduction of the copper chelates investigated in these studies are not reversible. Consequently, comparisons of the half-wave potentials for these reactions are meaningful only if the standard rate constants and the transfer coefficients are known, or alternately, if the half-wave potentials can independently be shown to be a function of the reaction equilibria. The significance of half-wave potentials for slow reactions has been considered by Berzins and Delahay.¹¹ For the reaction of a series of structurally similar substances, the transfer coefficients will not vary appreciably and may be assumed to be approximately constant. A recent study of the reduction of organic nitro-compounds by De Vries and co-workers has demonstrated that the transfer coefficient for the reduction of a given compound is essentially constant and independent of the nature of the solvent.¹² Although rate constants at any given potential may be calculated from the ratio of i/i_D according to the method of Koutecky,¹³ these rate constants cannot be related to those at a single standard potential since the variation of the potential in the various solvents is unknown.

The significance of the present set of half-wave potentials is supported by the pH measurements of Van Uitert for the evaluation of the acid dissociation constants and metal complex formation constants for some 1,3-diketones.^{8,9,14} In mixed water-dioxane solutions, the logarithm of the acid dissociation constant is a linear function of the mole fraction of water in the solvent. In 75 vol. % dioxane solutions, the formation constants for the copper(II) chelates are a linear function of the acid dissociation constants. The half-wave potentials for the reduction of the copper(II) chelates reported previously^{1,2} are a linear function of the logarithm of formation constants reported by Van Uitert, from which it follows that the half-wave potential for the reduction according to equation 2 provides a valid indication of the over-all change in free energy for the reaction.

According to the Born equation, the free energy necessary to charge a spherical ion of radius r in a medium with dielectric constant ϵ is given by

$$\Delta F = z^2 e^2 / 2\epsilon r \quad (3)$$

where z is the charge of the ion and e is the magnitude of the unit electrical charge. As a consequence of reaction 2, it may be assumed that the primary difference in the free energy required for the reduction of a given copper chelate in the various solvents arises from the free energy necessary to charge the ionic product of the reaction, the hydroxide ion, in one solvent as compared with another. From equation 3 the difference in the work necessary to charge the hydroxide ion in solvent 1 as compared with solvent 2 is, per mole of CuX_2 reduced

$$\Delta F = Nz^2 e^2 / r (1/\epsilon_2 - 1/\epsilon_1) \quad (4)$$

(11) T. Berzins and P. Delahay, *THIS JOURNAL*, **75**, 5716 (1953).

(12) T. De Vries, private communication.

(13) J. Koutecky, *Collection Czechoslov. Chem. Commun.*, **18**, 183, 311, 597 (1953).

(14) L. G. Van Uitert, Ph.D. Thesis, Pennsylvania State University, 1951.

or

$$\Delta F = 139 \times 10^3 z^2 / r \times \Delta(1/\epsilon) \text{ ergs} \quad (5)$$

Assuming that the radius of the hydroxide ion is 1.76 Å,^{15,16} the change in the polarographic half-wave potential is given by

$$\Delta E_{1/2} = \frac{F}{-n\bar{v}} = \frac{-139 \times 10^3 z^2}{n\bar{v}r} \times \Delta(1/\epsilon) \quad (6)$$

or

$$\Delta E_{1/2} = -4.09 \times \Delta(1/\epsilon) \text{ volts} \quad (7)$$

In this derivation, no allowance has been made for changes in the energy of solvation of the hydroxide ion in the various solvents. In solvents of relatively high dielectric constant containing nominal fractions of water, it is probable that the solvation energy does not change sufficiently to affect this approximation. Amis¹⁷ recently has considered the nature of the ionic solvation in mixed solvent systems containing water and presents evidence that, for systems containing more than about 10% water, the hydration of ions does not change appreciably in the mixed solvent systems. However, in solvents of low dielectric constant such as the dioxane solutions, this approximation may not be sufficiently rigorous, and evidence is presented (*vide infra*) that the divalent aquocopper(II) ion is more extensively hydrated in the dioxane solutions than in those with higher dielectric constants.

Figure 1 plots the reciprocal of the dielectric constant as a function of the half-wave potential for the reduction of several copper chelates. For the copper chelates of 2,4-pentanedione and the 3-substituted-2,4-pentanediones, the shift in $1/\epsilon$ is approximately constant with half-wave potential. Except for the 3-phenyl-2,4-pentanedione chelate, the experimental values for $\Delta E_{1/2} / \Delta(1/\epsilon)$ of about -3.5 v. compare favorably with the calculated value of -4.09 . The half-wave potentials for the reduction of aquocopper(II) as a function of $1/\epsilon$ have been included in Fig. 1 for comparison. The positive slope of the plot for this ion is of opposite sign to that for the reduction of the copper-chelate molecules because the difference in the free energy arises from the discharging of the ionic reactant, the aquocopper(II) ion.

Variation of D with Solvent.—In the previous papers,^{1,2} the diffusion current constants calculated on the basis of the Ilkovic equation¹⁸ were reported for a number of the copper chelates in the three solvents, but no significant over-all trends were apparent to correlate these values in a single solvent nor in comparisons between solvents.

For diffusing particles that are large compared with the size of the water molecules, the Stokes-Einstein relation predicts that the diffusion coefficient D is inversely proportional to the viscosity η of the solution or that $D\eta$ is equal to a constant. The applicability of the Stokes-Einstein relation to polarographic reactions in aqueous solutions previously has been verified for the re-

(15) L. Pauling, "The Nature of the Chemical Bond," 2nd Ed., Cornell University Press, Ithaca N. Y., 1948, p. 346.

(16) R. C. Evans, "An Introduction to Crystal Chemistry," University Press, Cambridge, 1948, p. 292 ff.

(17) E. S. Amis, *J. Phys. Chem.*, **60**, 428 (1956).

(18) I. M. Kolthoff and J. J. Lingane, "Polarography," Vol. I, Interscience Publishers, Inc., New York, N. Y., 1952, p. 70.

duction of metal ions¹⁹ and for the reduction of maleic acid, Orange II and for the oxidation of ascorbic acid.²⁰ The applicability of the relation in non-aqueous solvents has been verified²¹ for the reduction of several nitroalkanes in solvents varying in viscosity from 0.5 to 950 centipoise.

The average diffusion current, i_D , at a dropping mercury electrode is given¹⁸ by

$$i_D = 607nD^{1/2} C m^{2/3} t^{1/6} (1 + kD^{1/2} t^{1/6} m^{-1/3}) \quad (8)$$

where D is the diffusion coefficient and C is the concentration of the reacting species, m is the mass of mercury flowing per second and t is the drop-time for the electrode. The numerical value for k appears to depend upon the nature of the electro-active substance and the characteristics of the dropping electrode and has been reported variously as 17,²² 31.5²³ and 39.²⁴ Presumably, k also depends upon the nature of the solvent, but the applicability of equation 8 has not been tested rigorously for non-aqueous solvent systems. In this work, the Lingane-Loveridge value of 39 for k has been chosen for the calculation of the diffusion coefficients.

Using equation 8, the values of the diffusion coefficients have been calculated for a number of the copper chelates of the 1,3-diketones. Table I compares the values of $D\eta$ for those species for which diffusion current constants were reported in the previous papers.^{1,2} It is observed that, within experimental error, the Stokes-Einstein relation is obeyed for the reduction of the copper complexes of 2,4-pentanedione, 3-methyl-2,4-pentanedione, 3-*n*-propyl-2,4-pentanedione and 1,1,1-trifluoro-2,4-pentanedione and for the reduction of the aquocopper(II) ion. The failure of the 3-ethyl-2,4-pentanedione to exhibit the proper relation is not explained. The anomalous value for the copper(II) ion in dioxane almost certainly arises from an abnormally large hydration of the divalent ion in a solvent with low bulk dielectric constant. From equation 3, it may be seen that the free energy of solvation of an ion increases appreciably when the ion is solvated in a solvent of low dielectric constant. Because of the increase in the solvated (*i.e.*, hydrated) radius of the ion, the ion diffuses more slowly through the solution and the diffusion current constant decreases. The failure of the $D\eta$ values for the 3-phenyl and 3-benzyl derivatives to agree more closely results at least partially from the extremely low solubilities of these species in the solvents and the resulting difficulties associated with the polarographic measurements.

It is interesting to consider the change in the $D\eta$ values as various groups are substituted in the 3-position on the diketone ligand. The normal magnitude of $D\eta$ for bis-(2,4-pentanedione)-copper(II) is approximately 0.074. Upon substitution of the methyl and other groups in the 3-position, the value is lowered to 0.04 or less. The molecular

(19) D. M. Brasher and F. R. Jones, *Trans. Faraday Soc.*, **42**, 775 (1946).

(20) H. A. McKenzie, *J. Council Sci. Ind. Research, Australia*, **21**, 210 (1948).

(21) N. Radin and T. DeVries, *Anal. Chem.*, **24**, 971 (1952).

(22) H. Strehlow and M. von Stackelberg, *Z. Elektrochem.*, **54**, 51 (1950).

(23) L. Meites and T. Meites, *THIS JOURNAL*, **73**, 395 (1951).

(24) J. J. Lingane and B. A. Loveridge, *ibid.*, **72**, 438 (1950).

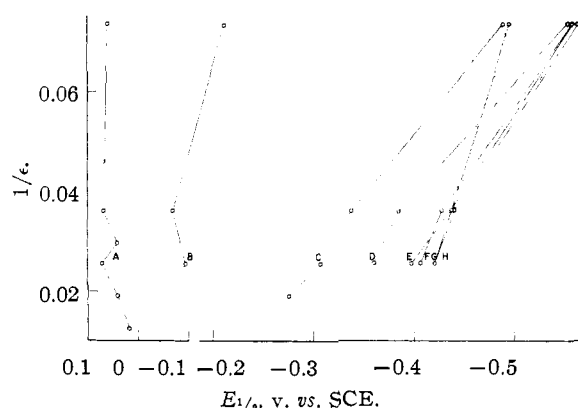


Fig. 1.—Variation in $1/\epsilon$ with $E_{1/2}$ for reduction of copper (II) complexes with 1,3-diketones: A, aquocopper(II); B, 1,1,1-trifluoro-2,4-pentanedione; C, 2,4-pentanedione; D, 3-benzyl-2,4-pentanedione; E, 3-phenyl-2,4-pentanedione; F, 3-*n*-propyl-2,4-pentanedione; G, 3-methyl-2,4-pentanedione; H, 3-ethyl-2,4-pentanedione.

radius of the copper complex with 2,4-pentanedione is calculated to be approximately 4.5 Å.^{25,26} Assuming that the solvation, if any, of the complex remains unchanged, the substitution of a methyl group in the 3-position will increase the molecular

TABLE I
STOKES-EINSTEIN PRODUCT FOR COPPER CHELATES^a

Ligand	Solvent ^b	Diffusion coefficient, D , 10 ⁶ cm. ² /sec.	Stokes-Einstein product, $D\eta$
1 (Aquocopper(II))	Water	6.00	0.054
	E	2.83	.060
	M	1.74	.067
	D	1.83	.035
2 2,4-Pentanedione	E	3.49	.075
	M	1.94	.075
	D	3.78	.072
3 3-Methyl-2,4-pentanedione	E	1.61	.035
	M	1.00	.039
	D	2.26	.042
4 3-Ethyl-2,4-pentanedione	E	1.37	.029
	M	0.80	.031
	D	2.16	.041
5 3- <i>n</i> -Propyl-2,4-pentanedione	E	2.04	.044
	D	2.27	.043
6 3-Phenyl-2,4-pentanedione	E	1.64	.035
	D	1.19	.023
7 3-Benzyl-2,4-pentanedione	M	0.57	.022
	D	1.61	.030
8 1,1,1-Trifluoro-2,4-pentanedione	E	2.22	.047
	M	1.15	.044
	D	2.03	.039

^a 0.1 M potassium nitrate supporting electrolyte. See Table II, ref. 2. ^b E = 75 vol. % ethanol; M = 75 vol. % methoxyethanol; D = 75 vol. % dioxane.

radius by 1.5 Å. or about 34%. This increase is reflected in the 45% decrease in the value of $D\eta$ for the 3-methyl complex. It is difficult to predict the effective radius for other ligand substitutions,

(25) R. E. Rundle and L. Dahl, 123rd National Meeting, American Chemical Society, Los Angeles, Calif., March, 1953, Abstract p. 33-P

(26) E. A. Shugam, *Doklady Akad. Nauk, S.S.S.R.*, **81**, 853 (1951)

however, because those species which are free to rotate or coil about in the plane of the copper chelate ring may exhibit a larger diffusion coefficient than those ligands whose rotation is restricted. For example, a phenyl group substituted in the 3-position of 2,4-pentanedione cannot become coplanar with the heterocyclic ring of the chelate

molecule and results in a marked decrease in the $D\eta$ value (Table I).

Acknowledgment.—The assistance of H. D. Russell in measuring the viscosities of the solutions is acknowledged.

LINCOLN, NEBRASKA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF BRITISH COLUMBIA]

Kinetics of the Oxidation of Uranium(IV) by Thallium(III)¹

BY A. C. HARKNESS AND J. HALPERN

RECEIVED JANUARY 21, 1959

The kinetics of the reaction $U(IV) + Tl(III) \rightarrow U(VI) + Tl(I)$ were examined in aqueous perchloric acid solution and found to be of the form $-d[U(IV)]/dt = [U^{4+}][Tl^{3+}](k_1[H^+]^{-1} + k_2[H^+]^{-2})$. The two rate constants were identified with reaction paths involving activated complexes of the compositions $(U \cdot OH \cdot Tl)^{\ddagger+}$ and $(U \cdot O \cdot Tl)^{\ddagger+}$, respectively. The corresponding heats and entropies of activation, evaluated from rate measurements over the temperature range 16 to 25°, are $\Delta H_1^* = 24.6$ kcal./mole, $\Delta H_2^* = 21.7$ kcal./mole, $\Delta S_1^* = 16$ e.u. and $\Delta S_2^* = 7$ e.u. The effect of ionic strength and the specific effects of various anions and cations on the rate were examined. The results suggest, but do not demonstrate conclusively that the reaction occurs through a single two-equivalent step rather than through successive one-electron changes.

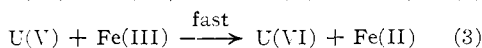
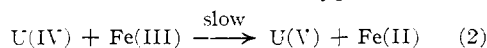
Introduction

This work forms part of a program of investigations being conducted in this Laboratory² on the kinetics and mechanisms of simple inorganic oxidation-reduction reactions between two-equivalent oxidants and two-equivalent reductants. The present reaction

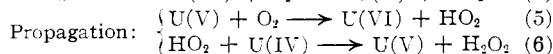
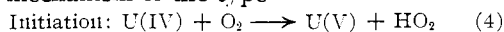


is of this type. One objective of these studies is to determine whether reactions of this type occur in a single step or through successive one-electron changes.

Of immediate interest in connection with the present study are earlier kinetic investigations of the oxidation of U(IV) to U(VI) by other oxidants including Fe(III),³ Ce(IV),⁴ Pu(VI)⁵ and O₂.⁶ In each of these systems the evidence suggests that the over-all reaction involves two successive one-equivalent changes, U(V) being formed as an intermediate. It is probable that the mechanisms of the first three of these reactions, involving one-equivalent oxidants, are all of the type



On the other hand the reaction of U(IV) with O₂, a multi-equivalent oxidant, proceeds through a chain mechanism of the type



(1) Support of this work through a grant from the National Research Council of Canada and through a Fellowship (to A.C.H.) from the Consolidated Mining and Smelting Co. of Canada Ltd. is gratefully acknowledged.

(2) Related studies are described in (a) J. Halpern, *Can. J. Chem.*, **37**, 148 (1959); (b) A. M. Armstrong, J. Halpern and W. C. E. Higginson, *J. Phys. Chem.*, **60**, 1661 (1956); A. M. Armstrong and J. Halpern, *Can. J. Chem.*, **35**, 1020 (1957); (c) H. N. Halvorson and J. Halpern, *This Journal*, **78**, 5562 (1956).

(3) R. H. Betts, *Can. J. Chem.*, **33**, 1780 (1955).

(4) F. B. Baker and T. W. Newton, private communication.

(5) T. W. Newton, *J. Phys. Chem.*, **62**, 943 (1958).

(6) J. Halpern and J. G. Smith, *Can. J. Chem.*, **34**, 1419 (1956).

In the light of this it seemed of interest to examine the oxidation of U(IV) by a two-equivalent metal ion oxidant, and Tl(III) whose reactions with other reducing agents have been extensively investigated from related standpoints was considered a logical choice for this purpose. Some measurements also were attempted on the oxidation of U(IV) by the isoelectronic ion, Hg(II), and it is of interest that this reaction, although also thermodynamically favorable, was found to be too slow for convenient kinetic study.

Experimental

Stock solutions of thallium(III), thallium(I), uranium(IV) and uranium(VI) perchlorates and of sodium perchlorate were prepared as described earlier.^{2b,6} Silver perchlorate, obtained from G. F. Smith Co., was purified by recrystallization from perchloric acid. All other chemicals were of reagent grade. Water was purified by redistillation from alkaline permanganate in a Pyrex still.

The kinetic measurements were made by measuring the U(IV) concentration with a Beckman DU spectrophotometer using the 6500 Å. absorption peak; at this wave length interference from U(VI) and other ions was found to be negligible. To minimize zero-time errors, the reaction was started by mixing suitable aliquots of solutions of the separate reactants, which previously had been brought to the reaction temperature. In most of the experiments the readings were made on the same sample of solution which remained in the spectrophotometer cell compartment (thermostated to $\pm 0.1^\circ$) throughout the reaction. Identical results were obtained when the reacting solution was kept in a thermostated water-bath and sampled periodically for analysis.

Results and Discussion

It was established that the stoichiometry of the reaction conforms, within experimental error, to equation 1. At constant HClO₄ and NaClO₄ concentrations, the kinetics were found to be consistently of second order (first order each with respect to U(IV) and to Tl(III)), as shown by the linear second-order kinetic plots in Fig. 1. The apparent second-order rate constants, k' , determined from the slopes of these plots were unaffected by variation of the initial U(IV) concentration between 0.0035 and 0.011 M and of the initial Tl(III) concentration between 0.005 and