We now can see that there is a regularity in the order for the ligands when analogs are compared.

Interpreted in view of the model proposed previously, the negative values of $\Delta(\Delta H)$ and $\Delta(\Delta S)$ would indicate that the α-hydroxy ligands do not disrupt the hydration layer about the lanthanide ion to any greater extent than the analogous simple ligands. Moreover, the increasingly negative trend from glycolate to α-hydroxyisobutyrate is consistent with the postulate in an earlier paper[4] that the increasing basicity of the hydroxyl group due to addition of methyl groups to the α-carbons results in increased stability of the chelate. This could also explain the trend in the $\Delta(\Delta S)$ values since stronger bonding would result in a large decrease in configurational entropy of the chelating ligand.

Grenthe has proposed an alternate explanation for the lower ΔS for the glycolate system compared to the acetate system.[12] He suggests that the chelate may be formed *via* a water molecule between the α-hydroxy group and the cation. Larsson has also offered evidence that a water molecule is present between the hydroxy group and the gadolinium ion in the glycolate chelate.[15] Consequently, the retention of a water molecule in the chelate ring would make the ΔH more exothermic and

the ΔS more negative than might be expected, which is in agreement with the experimental data. The decrease in ΔS, then, between simple and chelate complexing could be due to both the decrease in configurational entropy and the inclusion of a water molecule in the chelate ring. It should be noted that Powell and Farrell report that the lanthanide triglycolates separate from solution as anhydrous complexes from La(III) to Gd(III) and as dihydrates from Gd(III) to Lu(III).[16]

Unfortunately, the values of ΔH_2, ΔH_3, ΔS_2, and ΔS_3 are not sufficiently accurate to permit much discussion of their implications. Generally, ΔH_2 is more exothermic than ΔH_1 while ΔS_2 is smaller than ΔS_1. These orders are also present for the simple carboxylate systems and reflect the decreasing importance of the disruption of hydration layer of the cation to the overall enthalpies and entropies of complexation.[3]

(15) R. Larsson, *Acta Chem. Scand.*, **19**, 783 (1965).

(16) J. E. Powell and J. L. Farrell, "Rare Earth Research," E. V. Kleber, Ed., The Macmillan Co., New York, N. Y., 1961, p 26.

CONTRIBUTION FROM AVERY LABORATORY, DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NEBRASKA, LINCOLN, NEBRASKA

Polarographic Reduction of Copper Chelates of 1,3-Diketones. IV. Chelate Stability and Electron-Transfer Mechanism[1]

BY RICHARD L. LINTVEDT, H. DAVID RUSSELL, AND HENRY F. HOLTZCLAW, JR.

The polarograms of 23 1,3-diketone copper(II) chelates were recorded in aqueous 75% dioxane solution, using potassium nitrate as supporting electrolyte. When the series of chelates is separated into three homogeneous series (aliphatic substituted, aromatic substituted, and chelates in which both aliphatic and aromatic groups are substituted), good correlations between half-wave potentials and stabilities are observed within each of these divisions. The chelates of 1,3-diketones which have aromatic substituents reduce at much more positive potentials than would be expected in view of their stabilities. The relative ease of reduction of the aromatic-substituted chelates, as compared to the aliphatic-substituted chelates, leads to the conclusion that the aromatic groups provide a low-energy path for electron transfer through the π-electron system.

Introduction

Inasmuch as the polarographic reduction of 1,3-diketone copper(II) chelates in dioxane–water mixtures takes place irreversibly, no simple calculation of the stability constants from half-wave potential data can be made. However, the reduction potential should be a function of the electronic density on and around the copper atom. Assuming that the stability of the chelate increases with increasing electron density near the copper ion, the reduction potential ought to become more negative as the chelate becomes more stable.

This relationship presupposes that the mechanism of electron transfer is the same in all chelates for which the half-wave potentials and stability are compared.

Experimental Section

A. Apparatus and Polarographic Procedures.—Each sample solution was 10^{-3} M with respect to chelate, weighed to the nearest 0.1 mg. The solutions were 0.1 M with respect to potassium nitrate as supporting electrolyte. The chelate and supporting electrolyte were dissolved in aqueous 75% dioxane. The resistance of the system, measured through the saturated calomel electrode, a fine frit, and the dropping-mercury electrode (the circuit used in conjunction wih the IR compensator), was about 6000 ohms. The resistance of the system, measured through the mercury pool and the dropping-mercury electrode

(1) For the previous paper in this series see: E. R. Nightingale, Jr., and H. F. Holtzclaw, Jr., *J. Am. Chem. Soc.*, **81**, 3523 (1959).

(the circuit used in conjunction with the mercury pool electrode), was about 4500 ohms. Diffusion currents varied from about 1.0 to 4.0 μa so that the IR drop without compensation is of the order of 0.005–0.024 v. For polarograms in which the IR compensator was employed, the IR drop is of a magnitude which is easily compensated. For polarograms in which the IR compensator was not employed, corrections for IR drop were applied.

Polarograms for the copper chelates were recorded using a Sargent Model XXI polarograph. For the aromatic-substituted chelates the cell consisted of a dropping-mercury cathode, a mercury-pool anode, and an external saturated calomel electrode connected to the cell by means of a salt bridge. The cell arrangement was similar to that described by Lingane and Kolthoff.[2] For the aliphatic copper chelates, the mercury-pool electrode was replaced by a saturated calomel electrode which was used in connection with a Sargent IR compensator to compensate for IR drop in solution. Potentials were measured against a saturated calomel electrode by means of a standard potentiometer circuit. The potentiometer was compared with a standard cell several times during the recording of a polarogram. Cell temperature was maintained at $25.0 \pm 0.1°$ by means of a thermostatically regulated water bath.

Oxygen-free nitrogen was bubbled through each polarographic solution for 30 min to remove dissolved oxygen. The nitrogen was then directed over the surface of the cell solution during the polarographic determination.
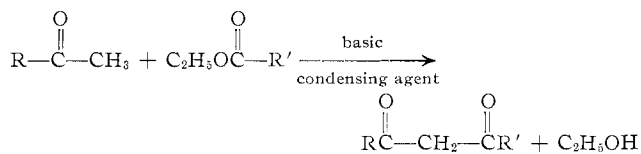
Dioxane used as solvent was reagent grade and freshly distilled over pieces of sodium immediately before use. The fraction collected boiled at 99–100°. When the dioxane solutions were used within 24 hr, no peroxide wave was observed in the polarograms. If the solutions were allowed to stand appreciably longer, a peroxide wave did occur.

Polarographic maxima encountered with these chelates were effectively suppressed by adding a few drops of a solution of rosaniline hydrochloride (140 mg dissolved in 4.0 ml of absolute ethanol). The rosaniline hydrochloride was not polarographically reduced in the potential ranges studied.

The dropping-mercury electrode was calibrated by the usual methods to obtain m and t values.

B. Preparation of Ligands and Copper Chelates.—The copper chelates of 2,4-pentanedione, 1-phenyl-1,3-butanedione, 1,3-diphenyl-1,3-propanedione, 1,1,1-trifluoro-2,4-pentanedione, 1,1,1,5,5,5-hexafluoro-2,4-pentanedione, 1-(2-thienyl)-4,4,4-trifluoro-1,3-butanedione, and 1-(2-furyl)-4,4,4-trifluoro-1,3-butanedione were prepared and analyzed previously in this laboratory.[3-6]

Ligands for the remaining copper chelates were prepared by a general Claisen condensation method in which a methyl ketone is condensed with an ethyl ester in the presence of a basic condensing agent. The following equation indicates the reaction which takes place

$$R-\overset{\overset{O}{\|}}{C}-CH_3 + C_2H_5O\overset{\overset{O}{\|}}{C}-R' \xrightarrow[\text{condensing agent}]{\text{basic}} R\overset{\overset{O}{\|}}{C}-CH_2-\overset{\overset{O}{\|}}{C}R' + C_2H_5OH$$

The copper chelates of these 1,3-diketones were prepared by a modification of the method of Adams and Hauser.[7] To a methanol solution of the ligand was added a hot, filtered solution containing an excess of copper(II) acetate. The mixture was stirred and then allowed to stand until it cooled to room temperature or overnight. After filtering through a Büchner funnel, the chelate was sucked dry in air, washed with 100 ml of ligroin (bp 60–90°),

and again sucked dry. The chelates were recrystallized from ethanol or dioxane. It was necessary to use dioxane for the chelates containing two aromatic rings because of their very limited solubility in ethanol. The aliphatic chelates, with the exception of bis(2,4-pentanedionato)copper(II), were further purified by vacuum sublimation.

Table I summarizes the condensing agents used for ligand preparation, sublimation data for the volatile chelates, and melting points of the chelates.

Results and Discussion

In the series of 23 1,3-diketone copper(II) chelates discussed herein, taken as a whole, little correlation is apparent between the half-wave potentials and the stabilities of the chelates. However, when the series is separated into three homogeneous series (aliphatic substituted, aromatic substituted, and chelates in which both aliphatic and aromatic groups are substituted), good correlations between half-wave potentials and stabilities are observed within each of these divisions.

The copper(II) chelates that comprise the total group are of the general type
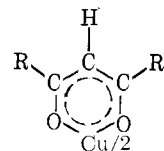
The half-wave potential values for the chelates vary from $+0.038$ to -0.687 v. Table II presents the polarographic data, some dissociation constants for the ligands, and the potentiometrically determined formation constants.

A. The Aliphatic-Substituted Chelates.—The aliphatic-substituted chelates are listed in Table II (compounds 1 through 11) in order of decreasing ease of copper(II) reduction. Relatively little potentiometric formation constant data are available for these chelates. The formation constants given in Table II represent a series of values determined by Van Uitert.[8]

The available data on the formation constants of these chelates do follow the trend of the half-wave potentials, with the most stable chelates being reduced with the most difficulty. Compounds for which no stability data are available might reasonably be expected to have stabilities which increase in order from compound 1 to compound 11 owing to increased electron-releasing power of the substituents. Thus, it would be expected that the stability order should be $10 > 9 > 6$ inasmuch as the electron-releasing power of the substituents decreases in the order $-C(CH_3)_3 > -CH(CH_3)_2 > -CH_2CH_3$. The electronic effect of the substituent group is indicated by the Hammett σ values. In Figure 1, the σ values are plotted vs. half-wave potentials for various chelates. Inasmuch as the substituents on the chelate ring are *meta* with respect to the copper ion, the σ values used are those for *meta*-position substitution.[9] For the unsymmetrically substituted chelates the σ value is taken as the average of the values for the two groups present. The good correla-

(2) J. J. Lingane and I. M. Kolthoff, *J. Am. Chem. Soc.*, **61**, 825 (1939).
(3) H. F. Holtzclaw, Jr., K. W. R. Johnson, and F. W. Hengeveld, *ibid.*, **74**, 3776 (1952).
(4) H. F. Holtzclaw, Jr., A. H. Carlson, and J. P. Collman, *ibid.*, **78**, 1838 (1956).
(5) K. W. R. Johnson, M.S. Thesis, University of Nebraska, July 1950.
(6) J. P. Collman, B.S. Honors Thesis, University of Nebraska, April 1954.
(7) J. T. Adams and C. R. Hauser, *J. Am. Chem. Soc.*, **66**, 1220 (1944).
(8) L. G. Van Uitert, Ph.D. Thesis, The Pennsylvania State College, 1952.
(9) H. H. Jaffé, *Chem. Rev.*, **53**, 222 (1953).

TABLE I

PREPARATION OF LIGANDS AND THEIR COPPER CHELATES

	Basic condensing agent used	Obsd mp, °C	Reported mp, °C.	Ref	Subl temp, °C
1-(2-Thienyl)-1,3-butanedione	NaNH₂	230–232	228–230	*a*	...
1-(2-Furyl)-1,3-butanedione	NaNH₂	224–225	219–222	*b*	...
1,1,1-Trifluoro-4-phenyl-2,4-butanedione	NaOCH₃	241–242	243–244	*c*	...
1-(2-Thienyl)-3-phenyl-1,3-propanedione	NaNH₂	255–256	276–278	*a*	...
1-(2-Furyl)-3-phenyl-1,3-propanedione	NaNH₂	249–251	245–248	*b*	...
1,3-Di(2-thienyl)-1,3-propanedione	NaNH₂	259–264	259–263	*a*	...
1-(2-Thienyl)-3-(2-furyl)-1,3-propanedione	NaNH₂	267–269	272–274	*b*	...
1,3-Di(2-furyl)-1,3-propanedione	NaOCH₃	263–265	...	*d*	...
2,2-Dimethyl-3,5-hexanedione	NaNH₂	200	191–192	*f*	153 (5 mm)
2,4-Hexanedione	NaNH₂	199	197–198	*e*	160 (5 mm)
2,2,6,6-Tetramethyl-3,5-heptanedione	NaNH₂	194	197–198	*f*	125 (5 mm)
2-Methyl-3,5-hexanedione	NaNH₂	172	171–172	*f*	136 (5 mm)
2-Methyl-4,6-heptanedione	NaNH₂	157–158	154–155	*e*	145 (5 mm)
3,5-Heptanedione	NaNH₂	213	209–210	*f*	155 (5 mm)
2,4-Nonanedione	NaNH₂	121–122	...	...	118 (5 mm)
1,1,1-Trifluoro-5,5-dimethyl-2,4-hexanedione	NaOCH₃	106	...	...	90 (0.1 mm)

a S. R. Harris and R. Levine, *J. Am. Chem. Soc.*, **70**, 3360 (1948). *b* S. R. Harris and R. Levine, *ibid.*, **71**, 1120 (1949). *c* J. C. Reid and M. Calvin, *ibid.*, **72**, 2948 (1950). *d* G. S. Hammond and F. S. Schultz, *ibid.*, **74**, 329 (1952). *e* R. Levine, J. A. Conroy, J. T. Adams, and C. R. Hauser, *ibid.*, **67**, 1510 (1945). *f* See ref 7.

TABLE II

POLAROGRAPHIC DATA AND FORMATION CONSTANTS FOR SOME 1,3-DIKETONE COPPER(II) CHELATES AND SOME LIGAND DISSOCIATION CONSTANTS AT 25.0 ± 0.1° IN AQUEOUS 75% DIOXANE

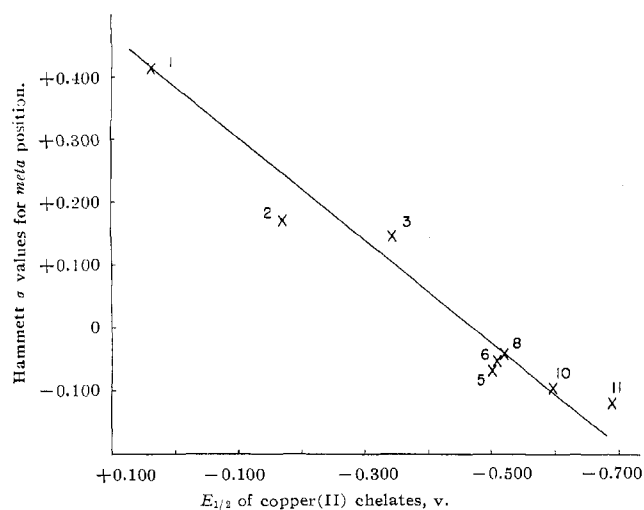| No.	Substituents R	R'	$E_{1/2}$ vs. sce, v.	Cu chelate[8] log $K_{f1}K_{f2}$	Ligand[8] pK_d
		A. Aliphatic			
1	CF₃	CF₃	+0.038	9.0	6.0
2	CH₃	CF₃	−0.169	17.2	8.7
3	C(CH₃)₃	CF₃	−0.345	...	...
4	CH₃	(CH₂)₄CH₃	−0.468	...	...
5	CH₃	CH₃	−0.502	22.6	12.70
6	CH₃	CH₂CH₃	−0.513	...	13.20
7	CH₃	CH₂CH(CH₃)₂	−0.517	...	...
8	CH₂CH₃	CH₂CH₃	−0.524	...	13.75
9	CH₃	CH(CH₃)₂	−0.549	...	13.40
10	CH₃	C(CH₃)₃	−0.600	24.6	14.20
11	C(CH₃)₃	C(CH₃)₃	−0.687	...	...
		B. Aliphatic and Aromatic			
12	CF₃	2-C₄H₃O	−0.130	17.2	
13	CF₃	2-C₄H₃S	−0.137	19.0	
14	CF₃	C₆H₅	−0.150	18.8	
15	CH₃	2-C₄H₃O	−0.341	22.0	
16	CH₃	2-C₄H₃S	−0.317	22.3	
17	CH₃	C₆H₅	−0.381	23.0	
		C. Aromatic			
18	2-C₄H₃O	2-C₄H₃O	−0.288	22.8	
19	2-C₄H₃S	2-C₄H₃O	−0.293	22.9	
20	2-C₄H₃S	2-C₄H₃S	−0.311	23.5	
21	C₆H₅	2-C₄H₃O	−0.323	23.9	
22	C₆H₅	2-C₄H₃S	−0.337	24.4	
23	C₆H₅	C₆H₅	−0.379	25.0	

Figure 1.—Hammett σ values for the substituents at the 1 and 3 positions *vs.* $E_{1/2}$ of the copper(II) chelates. For key to numbers see Table II.

Figure 2.—pK_d of the aliphatic 1,3-diketones *vs.* the $E_{1/2}$ of their copper(II) chelates: $\times$, experimentally determined values; $\odot$, pK_a calculated from resultant values.

tion between the Hammett σ values and half-wave potentials illustrates the importance of the electronic effect of the substituent group on the reduction potential of the chelate.

The dissociation constants for some of the 1,3-diketones which are used in preparing the aliphatic-substituted chelates have been measured by Van Uitert.[8] These values are very important in the determination of chelate formation constants by the method of Calvin and Wilson.[10] The values of the dissociation constants reflect the electronic effect of the groups substituted on the 1 and 3 positions in the 1,3-diketones. Hence, the dissociation constants of the ligands, as well as the Hammett σ values of the substituent groups, ought to be related to the electronic density on the oxygen atoms. Further, whatever will affect the electronic density on the oxygens will thereby affect the reduction potential of the chelate. The correlation between the dissociation constant of the ligand and the reduction potential of the resulting copper chelate is shown in Figure 2. It is evident from Figure 2 that the substituent groups which are capable of increasing the electronic density on the oxygen atoms result in more basic ligands, more negative reduction potentials for the copper chelates, and more stable chelates.

The dissociation constants of some 1,3-diketones which were not measured by Van Uitert have been calculated by assuming that the unmeasured pK_d would be a resultant value determined by the substituent groups present. There is some experimental justification for this assumption. For example, the pK_d for the methyl-substituted ligand (5) is 12.70, while the pK_d of the ethyl-substituted ligand (8) is 13.75. By taking the average of these two values 2,4-hexanedione (6) would have a calculated pK_d of 13.23. The observed value is 13.20. Using the same approach, the calculated pK_d for 1,1,1-trifluoro-2,4-pentanedione (2) is 9.35. The observed value is 8.7. An extension of this method
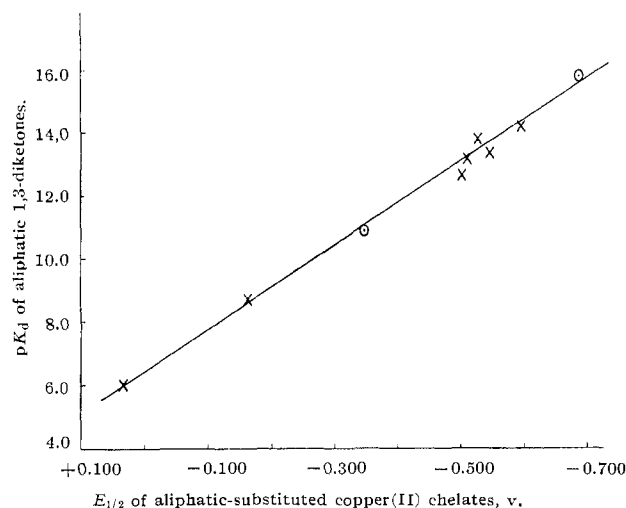
(10) M. Calvin and K. W. Wilson, *J. Am. Chem. Soc.*, **67**, 2003 (1945).

of approximating the dissociation constants would be to calculate the contribution of each substituent group individually and then to combine these to estimate the pK_d values of other ligands. Such calculated contributions are: CF_3, 3.0; CH_3, 6.35; CH_2CH_3, 6.88; CH-$(CH_3)_2$, 7.05; $C(CH_3)_3$, 7.85. Using these values, the following dissociation constants are calculated: 2,2,6,6-tetramethyl-3,5-heptanedione (11), pK_d = 7.85 + 7.85 = 15.70; 1,1,1-trifluoro-5,5-dimethyl-2,4-hexanedione (3), pK_d = 3.0 + 7.85 = 10.85. When these values, together with the reduction potentials of their copper chelates, are plotted in Figure 2 they are in excellent agreement with the other data. Figure 2, like Figure 1, illustrates that the reduction potential of the chelate has a strong correlation to the electronic effects of the substituent groups and hence to the stability of the chelate.

B. The Aromatic-Substituted Chelates.—Compounds **18** through **23** in Table II are the aromatic-substituted chelates. The reduction potentials vary from -0.288 to -0.379 v while the potentiometrically determined formation constants vary from 22.8 to 25.0. There is a good linear relationship between the reduction potentials and the formation constants of these chelates. However, if the reduction potentials and formation constants of these aromatic chelates are compared with those of the aliphatic chelates (**1** through **11**) it is readily apparent that no over-all, simple relationship exists. For example, although the copper(II) chelate of 2,2-dimethyl-3,5-hexanedione (**10**) is slightly less stable than the copper(II) chelate of 1,3-diphenyl-1,3-propanedione (**23**), the reduction of the former is 0.22 v more negative than the reduction of the latter. Other examples of the relative ease of reduction of the aromatic-substituted chelates can be seen by referring to Table II. Thus, two experimentally determined facts are clear: First, within a homogeneous series (*i.e.*, all aliphatic-substituted or all aromatic-substituted chelates), the reduction potential bears a strong relationship to chelate stability. Second,

chelates of the same potentiometric stability, but from different series, vary greatly in their reduction potentials. These facts indicate that a different mechanism of electron transfer is taking place in the aromatic-substituted chelates than in the aliphatic-substituted chelates. A different electron-transfer mechanism would explain the dependence of half-wave potential on chelate stability within a series and the fact that different series cannot be simply compared with each other.

The relative ease of reduction of the aromatic-substituted chelates offers a clue as to the mechanism of electron transfer from the mercury electrode to the chelated copper. Apparently, in the aromatic-substituted chelates, there is a low-energy path for the electrons to move from the electrode to the copper ion that does not exist in the aliphatic-substituted chelates. Since the solvent system is the same for all of the chelates, it can be assumed that solvent interactions have about the same effect on the electron transfer in all cases. Therefore, the great difference in the reduction potentials of aliphatic- and aromatic-substituted copper chelates of similar stability must be due to differences within the molecules. The major apparent difference between the aliphatic- and aromatic-substituted chelates is the π-electron system present in the aromatic-substituted chelates. It has been concluded earlier that resonance in the aromatic substituent and the chelate ring is an important factor in the aromatic-substituted chelates.[11] It is believed that an extensive, delocalized π system exists in these chelates and that this π system may provide a low-energy path for the electron transfer. Other investigators have noted the unusual ease of metal ion reduction when the metal ion is coordinated with a ligand which has a system of conjugated double bonds. Larson and Iwamoto,[12] for example, attribute the relative ease of metal ion reduction in benzonitrile, as opposed to unconjugated nitriles, to the presence of delocalized electrons. They conclude that reduction in nitriles takes place by way of a bridge mechanism, and the transfer of electrons is easier when the nitrile contains a conjugated system.

(11) R. L. Lintvedt and H. F. Holtzclaw, Jr., *Inorg. Chem.*, **5**, 239 (1966).
(12) R. C. Larson and R. T. Iwamoto, *J. Am. Chem. Soc.*, **82**, 3526 (1960).

Taube[13] has suggested much the same type of mechanism for the reaction between Cr^{2+} and $(NH_3)_5Co-(O_2C—CH{=}CH—COOH)^{2+}$. In the case of the aromatic-substituted copper(II) chelates of 1,3-diketones, the electron may enter the system through the π cloud, which may be extensively delocalized. It is believed that the π system of the coordinated ligand acts as a bridge for electron transfer to the copper ion.

C. The Aliphatic- and Aromatic-Substituted Chelates.—Compounds **12** through **17** have one aliphatic group and one aromatic group substituted on each ligand. In this series, the correlation between half-wave potential and the stability of the chelate is lower than in the other two series, as might be expected. However, the trend is still apparent.

The half-wave potentials for these chelates lend additional support to the belief that the aromatic groups act as low-energy bridges for electron transfer. If the theory is reasonable, the chelates with both aliphatic and aromatic substituents should reduce more easily than chelates of comparable stability but possessing only aliphatic substituents. Bis(2,4-pentanedionato)copper(II) is reduced at -0.502 v while the more stable bis(1-phenyl-1,3-butanedionato)copper(II) is reduced approximately 0.1 v more easily at -0.381 v. Also, chelates of this series should reduce with more difficulty than those of comparable stability in the aromatic-substituted series. This is demonstrated by the fact that bis(1-phenyl-1,3-butanedionato)copper-(II) and bis(1-thienyl-3-furyl-1,3-propanedionato)copper(II) have about the same formation constants, but the aromatic-substituted chelate is reduced 0.09 v more easily than the chelate with both aliphatic and aromatic groups. These facts are consistent with the proposed electron-transfer mechanism inasmuch as a decrease in the extent of the delocalized system should bring about a more negative reduction potential.

(13) H. Taube, *Can. J. Chem.*, **37**, 129 (1959).