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

Polarographic Reduction of Copper Chelates of 1,3-Diketones. II[1,2]

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Half-wave potentials and diffusion current constants are reported for copper chelates of several 1,3-diketones in aqueous solutions of dioxane, methylcellosolve and ethanol. The half-wave potentials are discussed in relation to stabilities of the chelates and extent of covalent and ionic bonding in the copper–oxygen linkage. From the half-wave potentials, effects on stability caused by substituting various groups on the 2,4-pentanedione ligand are deduced. The half-wave potentials of the copper chelates in 75% dioxane–25% water solution become increasingly negative, indicating increasing stability, in the ligand order hexafluoroacetylacetone, 2-furoyltrifluoroacetone, 2-thenoyltrifluoroacetone, trifluoroacetylacetone, 1,3-diphenyl-1,3-propanedione, 1-phenyl-1,3-butanedione, 2,4-pentanedione, 3-phenyl-2,4-pentanedione, 3-benzyl-2,4-pentanedione, 3-*n*-propyl-2,4-pentanedione, 3-methyl-2,4-pentanedione and 3-ethyl-2,4-pentanedione. No over-all trend is apparent in the diffusion current constants.

Introduction

A previous article from this Laboratory[2] discussed the polarographic reduction of the copper chelates of several 1,3-diketones in the solvent systems (1) water, (2) 50% ethanol–50% water, (3) 75% ethanol–25% water, (4) 75% 2-methoxyethanol (methylcellosolve)–25% water, (5) 50% dioxane–50% water, and (6) 75% dioxane–25% water. The purpose of the present article is to extend the discussion to additional compounds of special interest in establishing trends in half-wave potentials, to relate the half-wave potentials to stabilities of the metal chelates, and to deduce the effect upon chelate stability caused by substituting various groups upon the ligand.

Experimental

Apparatus.—Sargent Model XII and XXI Polarographs were used with a cell employing a dropping mercury cathode, a mercury pool anode and an external saturated calomel electrode connected to the cell by means of a salt bridge.[3] Potentials were measured against the saturated calomel electrode by means of a standard potentiometer circuit. Oxygen-free nitrogen was used to remove oxygen. Cell temperature was maintained at 25.0 ± 0.1° by means of a water thermostat. A plot of log $i/(i_d - i)$ *versus* potential was used to determine half-wave potentials and as a test for reversibility.

Preparation of Materials. (1) **3-Benzyl-2,4-pentanedione.**—The method, a modification of that described by Morgan and Taylor,[4] involved refluxing the sodium salt of 2,4-pentanedione with benzyl chloride. The product was obtained by fractional distillation under reduced pressure.

(2) **3-Phenyl-2,4-pentanedione.**—The method employed was a modification of that of Hauser and Adams,[5] involving reaction of phenylacetone with acetic anhydride in the presence of boron trifluoride. Steam distillation yielded the product, which was recrystallized three times from petroleum ether.

(3) **2-Thenoyltrifluoroacetone and 2-Furoyltrifluoroacetone.**—These diketones were purchased from the Midcontinent Chemicals Corporation, Chicago.

(4) **Copper Chelates.**—The general method involved adding an ammoniacal solution of copper(II) nitrate or copper(II) acetate to an alcoholic solution of a solid 1,3-diketone or directly to a liquid 1,3-diketone. The precipitated chelates were filtered and recrystallized. Analyses for each chelate were made by standard methods.[6]

Results and Discussion

For the copper chelates of various 1,3-diketones, the stability of a particular chelate is probably largely dependent upon three factors: (1) basic strength of the oxygen donor atoms, (2) the resonance of the chelate ring, and (3) steric hindrance.[7] In general, more basic donor atoms should exhibit a stronger covalent bond with the metallic ion, by virtue of a higher electron density about them. This basic effect is the same factor responsible for the bonding of the hydrogen in the chelate ring of the enolic form of the ketone. The postulated resonance effect in the chelate ring, of greater importance in the stability of a metal–oxygen bond than of a hydrogen–oxygen bond, represents the chelate ring as a conjugated six-membered ring somewhat analogous to benzene. A group upon the ligand which will interfere with the resonance of this ring will probably lower the stability of the chelate. Calvin and Bailes[8] have presented convincing evidence of the resonance effect. Steric hindrance affects chelate stability through distortion of the planar chelate ring.

Table I shows half-wave potentials for several copper chelates in three solvents. The data are arranged in order of increasingly negative half-wave potentials as measured in aqueous dioxane solution. The plots of log $i/(i_d - i)$ *versus* potential indicate irreversible reduction for all chelates. The half-wave potential, although not a quantitative measure of chelate stability under conditions of irreversible reduction, provides a reasonable basis for qualitative comparisons between the various compounds. Considering the ligand 2,4-pentanedione as a standard for comparison, the data in Table I may be used to deduce the effect upon the stability of the chelate caused by substitution of various groups on the ligand. A more negative half-wave potential, or more accurately a greater difference in half-wave potential between the solvated copper ion and the copper chelate, may be considered as an indication of a more stable chelate, or one in which the copper–oxygen bond is more covalent in character. A chelate which is comparatively less stable will have a less negative half-wave potential and will be considered to have a more ionic copper–oxygen bond. It is of interest to note, in this connection, that stability constants for seven copper chelates and dissociation constants

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[1] Abstracted from the M.S. Thesis of Alan H. Carlson, July, 1952, and the B.S. Honors Thesis of James P. Collman, April, 1954, University of Nebraska.

[2] For previous article, see H. F. Holtzclaw, Jr., K. W. R. Johnson and F. W. Hengeveld, THIS JOURNAL, **74**, 3776 (1952).

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

[4] G. T. Morgan and C. J. A. Taylor, *J. Chem. Soc.*, **127**, 797 (1925).

[5] C. R. Hauser and J. T. Adams, THIS JOURNAL, **66**, 345 (1944).

[6] The authors are indebted to Professor A. L. Henne, Ohio State University, for samples of bis-(hexafluoroacetylacetone)-copper(II) and bis-(trifluoroacetylacetone)-copper(II).

[7] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice–Hall, Inc., New York, N. Y., 1952, Ch. 4.

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

for the corresponding 1,3-diketone ligands,[9] as calculated by Van Uitert from *p*H measurements in aqueous solution,[10] follow the same order as the half-wave potentials reported in Table I.

TABLE I

HALF-WAVE POTENTIALS OF COPPER CHELATES (ARRANGED IN ORDER OF INCREASINGLY NEGATIVE HALF-WAVE POTENTIAL IN AQUEOUS DIOXANE)

0.1 *M* potassium nitrate as supporting electrolyte; $n = 2$, $Cu(II) \rightarrow Cu(O)$.

	$E_{1/2}$, v. *vs.* S.C.E.		
Chelating agent	In 75% dioxane–25% water	In 75% Methylcellosolve–25% water	In 75% ethanol–25% water
(Copper(II) nitrate)[a]	+0.059	+0.072	+0.074
Hexafluoroacetylacetone	+ .040	.....	>+ .16
2-Furoyltrifluoroacetone	− .146	.....	.....
2-Thenoyltrifluoroacetone	− .155	.....	.....
Trifluoroacetylacetone	− .173	− .070	− .095
1,3-Diphenyl-1,3-propanedione	− .376	.....	.....
1-Phenyl-1,3-butanedione[a]	− .384	.....	.....
2,4-Pentanedione[a]	− .487	− .336	− .306
3-Phenyl-2,4-pentanedione	− .497	− .437	− .398
3-Benzyl-2,4-pentanedione	− .555	− .385	− .360
3-*n*-Propyl-2,4-pentanedione[a]	− .557	− .428	− .407
3-Methyl-2,4-pentanedione[a]	− .559	− .438	− .423
3-Ethyl-2,4-pentanedione[a]	− .564	− .440	− .422

[a] See ref. 2.

The following discussion will be chiefly for the solvent dioxane. As may be noted from Table I, the trends in ethanol and methylcellosolve are similar. Deviations in trend between solvents will be considered.

The chelate exhibiting the most positive half-wave potential of the 12 reported in Table I is that of hexafluoroacetylacetone. The great ease of reduction, indicating a large proportion of ionic character in the copper–oxygen bonds, is to be expected from the basic strength of the oxygen donor atoms. The fluorine atoms impart to the trifluoromethyl groups a powerful attraction for electrons, thereby making the oxygen donor atoms in hexafluoroacetylacetone less basic than in 2,4-pentanedione. The half-wave potential of the hexafluoroacetylacetone is, indeed, nearly the same as that of the ionic copper(II) nitrate. The trifluoromethyl group should not inhibit resonance of the chelate ring; neither should steric hindrance be a significant contributing factor.

The chelate of trifluoroacetylacetone should and does exhibit an intermediate stability between those of 2,4-pentanedione and hexafluoroacetylacetone.

If the methyl group in the trifluoroacetylacetone is replaced by a heterocyclic five-membered ring, as in 2-furoyltrifluoroacetone, the resulting chelate would be expected to be less stable than that of trifluoroacetylacetone. The half-wave potentials in Table I support this expectation. All three factors—basic strength, resonance and steric hindrance—might be of significance with the first two predominating. The five-membered ring probably attracts electrons to some extent and, in addition, could set up an interfering resonance with the chelate ring. The chelate of 2-thenoyltrifluoroacetone, in which the oxygen in the five-membered ring is replaced by a sulfur atom, should be somewhat more stable than that of 2-furoyltrifluoroacetone, in view of the lower electronegativity of the sulfur. The half-wave potential in dioxane is, as expected, slightly more negative for 2-thenoyltrifluoroacetone.

The 2-thenoyltrifluoroacetone should, however, have a less stable copper chelate than trifluoroacetylacetone, since the five-membered ring should have a greater attraction for electrons than a methyl group, which in fact should repel electrons. The five-membered ring may, furthermore, enter into interfering resonance with the chelate ring, whereas the methyl group probably does not. Half-wave potentials support this trend.

The chelates of 1-phenyl-1,3-butanedione and 1,3-diphenyl-1,3-propanedione are shown by the half-wave potentials in Table I to be intermediate in stability between the chelates discussed above and bis-(2,4-pentanediono)-copper(II). Although it is difficult to determine whether the phenyl groups substituted for the end methyls of 2,4-pentanedione would repel or withdraw electrons from the chelate ring, it seems relatively certain that in either case methyl groups should produce a stronger inductive effect (electron repelling, as used throughout the manuscript) than phenyl groups. This would establish the chelate of 2,4-pentanedione as more stable than those of 1-phenyl-1,3-butanedione and 1,3-diphenyl-1,3-propanedione, in agreement with the half-wave potentials in Table I.

It should be noted that when first a methyl and then a phenyl group is substituted on the number three carbon of 2,4-pentanedione, the copper chelate of 3-methyl-2,4-pentanedione is more stable than that of 3-phenyl-2,4-pentanedione. However, the chelate of 3-phenyl-2,4-pentanedione is more stable than that of 2,4-pentanedione, itself. This suggests that, if the inductive effect is the principal determining factor, the phenyl group in the number three position is repelling electrons to a greater extent than a hydrogen does in the same position but to a lesser extent than a methyl group. Possible steric effects must, however, be considered before such a statement can be made with certainty and before a valid conclusion can be reached with respect to any analogy in substitution of a phenyl group in the number three position as compared to an end position of 2,4-pentanedione.

Fisher–Taylor–Hirschfelder models indicate that a phenyl group substituted on the number three carbon of 2,4-pentanedione cannot become coplanar with the heterocyclic ring of the chelate molecule. Thus, the main effect exhibited by a phenyl group in this position is that of inductive interaction. However, if one of the two terminal methyls of 2,4-pentanedione is replaced by phenyl, the model shows that the phenyl group can become coplanar with the heterocyclic ring with slight strain and thereby might withdraw electrons from the heterocyclic ring and interfere with the resonance of the ring by setting up a competing

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[9] Hexafluoroacetylacetone, 2-furoyltrifluoroacetone, 2-thenoyltrifluoroacetone, trifluoroacetylacetone, 1,3-diphenyl-1,3-propanedione, 1-phenyl-1,3-butanedione and 12,4-pentanedione.

[10] Ref. 7, see pp. 549–555.

resonance through quinoidation. An important difference is thus indicated in the behavior of the metal chelate when a phenyl group is substituted in the number three position and in the end position of the ligand.

The rather striking decrease in stability, therefore, for the chelates of 2,4-pentanedione, 1-phenyl-1,3-butanedione and 1,3-diphenyl-1,3-propanedione, in that order, may not mean that the phenyl groups are repelling electrons to a lesser extent than methyl groups but rather that through the postulated competing resonance the phenyl groups may be in fact withdrawing electrons from the ring. The rather large difference in stability between the chelates of 2,4-pentanedione and the two phenyl derivatives as contrasted to the rather small difference in stability between the 1-phenyl and 1,3-diphenyl chelates may lend credence to this concept.

A benzyl group, substituted in the number three position of 2,4-pentanedione, should release electrons more readily than a phenyl group, indicating that the copper chelate of 3-benzyl-2,4-pentanedione should be more stable than that of 3-phenyl-2,4-pentanedione and should have a more negative half-wave potential. The half-wave potentials in dioxane support this idea; in the solvents ethanol and methylcellosolve the behavior seems anomalous in that the trend is reversed.

The substitution of other electron repelling groups upon the number three carbon of 2,4-pentanedione should increase the electron density about the oxygens and increase the stability of the corresponding chelates. The half-wave potentials of the chelates of 2,4-pentanedione, 3-methyl-2,4-pentanedione and 3-ethyl-2,4-pentanedione show increasing stability in that order, in agreement with the increase in inductive effect in the order hydrogen, methyl and ethyl. The chelate of 3-*n*-propyl-2,4-pentanedione has a little more positive half-wave potential than the others, exhibiting a reversal of trend sometimes characteristic of the *n*-propyl group. In this particular instance, steric crowding between the *n*-propyl group and the end methyls may be a factor contributing to the decreased stability. A model of the chelate supports this proposal by showing considerable crowding between the groups.

It might be expected that if a phenyl group is more electron repelling than a hydrogen in the number three position of 2,4-pentanedione, as suggested above, a benzyl group in the same position should have a greater inductive effect than a methyl group. From inductive effects alone, a greater electron density would be postulated on the oxygen donor atoms and stronger covalent bonding in bis-(3-benzyl-2,4-pentanediono)-copper(II) than in bis-(3-methyl-2,4-pentanediono)-copper(II). The half-wave potentials, however, indicate greater stability for the chelate of 3-methyl-2,4-pentanedione in each of the three solvent systems. This may indicate that steric crowding between the benzyl group and the end methyl groups, analogous to that postulated for bis-(3-*n*-propyl-2,4-pentanediono)-copper(II), decreases the stability of the 3-benzyl compound below that predicted on the basis of over-all electrical effects alone. Models of the two chelates show considerably more tendency toward crowding for the 3-benzyl compound than for the 3-methyl compound, in agreement with this line of reasoning.

The same trends in half-wave potential are exhibited generally in aqueous ethanol and methylcellosolve solutions as in aqueous dioxane, by those compounds which have been tested, the only significant deviation being the aforementioned exception with the chelates of 3-benzyl-2,4-pentanedione and 3-phenyl-2,4-pentanedione. Comparing the three solvents, corresponding half-wave potentials tend to be increasingly negative in the solvent order ethanol, methylcellosolve, dioxane.

Diffusion current constants are reported in Table II. The constants reported usually represent values obtained in at least two different solutions, separately prepared and individually checked polarographically. No trend is apparent in the values as a whole, although trends which might seem to be of some significance can be noted by comparing small groups of chelates with similar ligands. It is fair to say, however, that with the data now available, no predominant over-all trends are evident in diffusion current constants in a given solvent nor in a comparison between solvents. This is in contrast to the half-wave potential data, which show logical trends. Among the factors which influence diffusion current constants may be listed weight and bulk of the reducible compound, dipole moments, solvation effects, and solution viscosity. Such factors are singularly difficult to separate and evaluate. With additional data, trends in diffusion current constants may become evident.

TABLE II

DIFFUSION CURRENT CONSTANTS OF COPPER CHELATES

0.1 *M* potassium nitrate as supporting electrolyte; $n = 2$.

	$i_d/(Cm^{2/3}t^{1/6})$		
Chelating agent	In 75% dioxane–25% water	In 75% methylcellosolve–25% water	In 75% ethanol–25% water
(Copper(II) nitrate)[a]	1.77	1.72	2.20
2,4-Pentanedione[a]	2.64	1.80	2.46
3-Methyl-2,4-pentanedione[a]	1.96	1.27	1.63
3-Ethyl-2,4-pentanedione[a]	1.92	1.13	1.49
3-Benzyl-2,4-pentanedione	1.64	0.95	..
3-Phenyl-2,4-pentanedione	1.40	1.48	1.66
2-Thenoyltrifluoroacetone	1.81	..	..
2-Furoyltrifluoroacetone	1.68	..	..
Trifluoroacetylacetone	1.84	1.37	1.95
Hexafluoroacetylacetone	0.80	..	..
1-Phenyl-1,3-butanedione[a]	1.93	..	..
1,3-Diphenyl-1,3-propanedione[a]	1.05	..	..

[a] See ref. 2.

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