[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA]

Stability of Chelate Compounds. II. Polarographic Reduction of Copper Chelates

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Introduction

In a previous paper[2] we have reported the effects of some structural variations of the chelating group upon the stability of the chelate compounds formed with cupric ion, as evidenced by a more or less directly measured equilibrium constant for the reactions

$$Cu^{++} + Ke^{-} \rightleftarrows CuKe^{+}$$
$$CuKe^{+} + Ke^{-} \rightleftarrows CuKe_2$$

In our search for a more generally applicable method for estimating the effects of structural changes on the nature of the chelate compound, we have tried the polarographic reduction[3] of the copper chelate. The present paper contains a report of an initial broad survey of a fairly large number of compounds from which certain definite conclusions may be drawn, together with an indication of the moot questions which remain to be answered.

Experimental

The selection of a solvent was based upon a balance of two requirements, namely, the solubility of the compounds and the dielectric constant or electrolytic properties of the solvent. This was most generally achieved with a 50% by volume mixture of pyridine and water. It was not a completely satisfactory solvent but fulfilled most of the required conditions for most of the compounds. The supporting electrolyte was either 0.1 *M* potassium nitrate or 0.1 *M* potassium chloride. The nitrate was the better one, especially for the easily reducible substances, since with it the range is extended somewhat on the positive side; in the chloride the dissolution of mercury is not stopped until a potential of the order of -0.1 volt against the saturated calomel electrode is reached (Fig. 1). The difference between chloride and nitrate in this solvent is, however, not as large as it is in aqueous solutions.[3]

The apparatus used was a manually operated instrument. An "H" cell was used, the reference electrode being a saturated calomel electrode, and the whole cell being thermostated at 25 ± 0.1°. Pure dried mercury was used throughout. C. P. chemicals were used in all cases. Solvents were given special purification as needed and as indicated. Some lots of Baker C. P. pyridine were pure enough for use, but others had to be distilled over ferrous sulfate, or fractionally crystallized before satisfactory blanks were obtained.

At first tank nitrogen was bubbled through the samples to remove dissolved oxygen. However, oxygen is so much more soluble in the pyridine water solutions than in pure water, and since the nitrogen contains a small percentage of oxygen, discernible waves for this gas were present in many of the potential curves (Fig. 1). Very pure electrolytic hydrogen was substituted for the nitrogen and bubbled through the solution for thirty minutes. The hydrogen was first passed through an alkaline pyrogallol solution to further remove any oxygen.

The sample to be measured was dissolved in 15 ml. of pyridine, then diluted with 3 ml. of 1.0 *M* potassium chloride or potassium nitrate solution and then the total volume made to 30 ml. with distilled water. The sample was then placed in the dried cell, and pure hydrogen bubbled through for thirty minutes. The hydrogen was then shut off and the electrolysis begun, with the sample out of contact with air. The first run was usually completed within fifteen minutes and a repeat run was then made on the same solution. The concentration of the chelate compound was never over 10^{-3} *M* since higher concentrations always induced the formation of maxima in the polarograms. No maximum suppressors were used, partly because no satisfactory one was found and partly because the nature of suppressor compounds is such that they might form complexes with the chelates.

The compounds were made by the general methods described by Pfeiffer.[4]

A number of new compounds of this type are included. They were prepared and analyzed by the usual methods.

Results

The reduction of the cupric and cuprous ions (from cupric nitrate and cuprous chloride) is shown in Figs. 1 and 2, respectively. It is apparent that cupric ion is reduced in two one-electron stages[5] and that the $Cu^{+} \rightarrow Cu^{0}$ stage, at least, is reversible (the slope of the $\log i/(i_d - i)$ *vs.* E line is the theoretical 0.06). The wave having the half-wave potential of -0.52 to -0.53[6] represents the reaction

$$Cu^{+}(py)_m + e^{-}(Hg) \rightleftarrows Cu^{0}(Hg) + m\,py \quad (1)$$

where py = pyridine and m represents the number of pyridine molecules coördinated to the cuprous ion. The first wave at $+0.05$ volt represents the reaction

$$Cu^{++}(py)_x + e^{-}(Hg) \longrightarrow Cu^{+}(py)_m + (x - m)py \quad (2)$$

This reaction also appears to be reversible but it cannot be ascertained because of the interference of the mercury solution reaction. Figs. 2 and 3 are polarograms typical of the simple open chelates of salicylaldehyde and its derivatives. It is apparent that the process here is much the same but that the first wave seems to occur at a hardly significant more negative potential while the second ($Cu^{+} \rightarrow Cu^{0}$) is identical with that obtained with simple cupric and cuprous ions in this

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[1] Abstracted from the thesis presented by R. H. Bailes to the University of California in partial fulfillment of the requirements for the Ph.D. degree in 1942.

[2] Calvin and Wilson, THIS JOURNAL, **67**, 2003 (1945).

[3] Heyrovsky, "Polarographie," Julius Springer, Vienna, 1941; Kolthoff and Lingane, "Polarography," Interscience Publishing Co., New York, 1941. A discussion of the use of the polarograph in cases involving metal ammines, cyanides, oxalates, etc., in aqueous solutions is to be found in a review by Lingane, *Chem. Rev.*, **29**, 1 (1941).

[4] Pfeiffer, *et al.*, *Ann.*, **503**, 84 (1933); *J. prakt. Chem.*, **129**, 163 (1931); **151**, 313 (1938); **153**, 265 (1939); **153**, 300 (1939); **155**, 77 (1940); **157**, 97 (1941); **162**, 279 (1943). For a summary and bibliography see P. Pfeiffer, *Angew. Chem.*, **53**, 93 (1940).

[5] Lingane and Kerlinger [*Ind. Eng. Chem.*, *Anal. Ed.*, **13**, 77 (1941)] have already reported this separation of the steps in the cupric ion reduction in aqueous solutions containing up to 1 *M* pyridine. A similar phenomenon in ammoniacal solutions has been studied in some detail by Stackelberg and Freyhold, *Z. Elektrochem.*, **46**, 120 (1940).

[6] Lingane and Kerlinger (ref. 5) report this wave at -0.25 v. in 1 *M* pyridine.

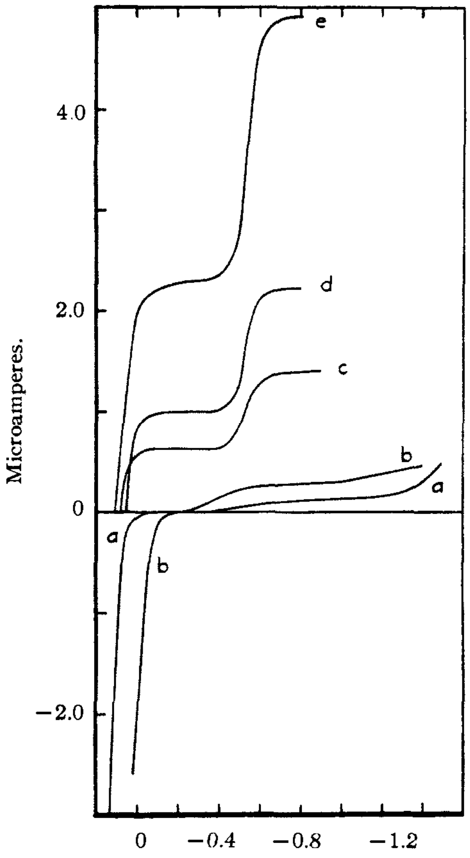

Fig. 1.—(a) Blank 0.1 M potassium nitrate; (b) blank 0.1 M potassium chloride; (c) 0.001 M cupric acetate monohydrate, 0.1 N $HClO_4$; (d) 0.0005 M cupric nitrate, 0.1 M KNO_3; (e) 0.001 M cupric nitrate, 0.1 M KNO_3. All are in 50% by volume aqueous pyridine.

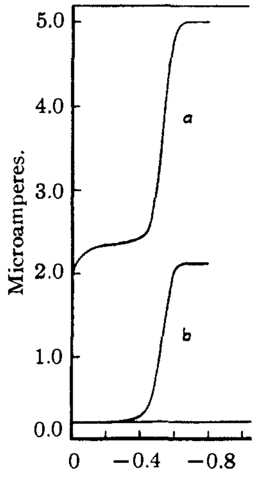

Fig. 2.—(a) 0.001 M cupric salicylaldehyde in 50% by volume aqueous pyridine and 0.1 M potassium nitrate at 25°; (b) 0.001 M cuprous chloride in 50% by volume aqueous pyridine and 0.1 M potassium chloride at 25°.

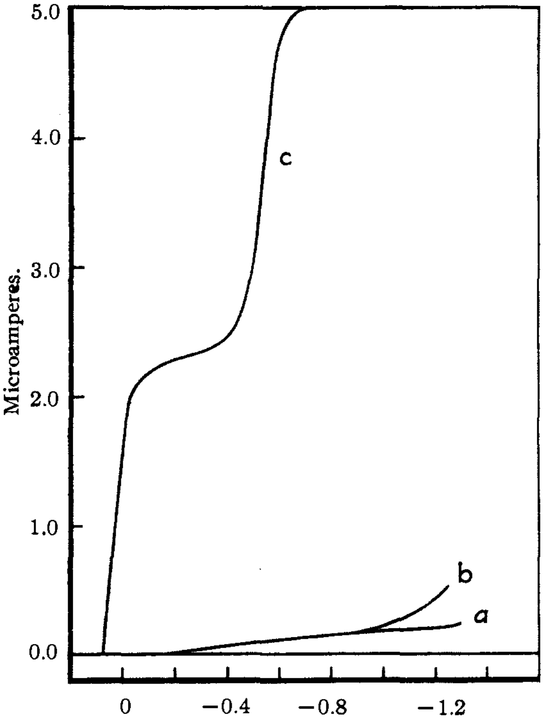

Fig. 3.—(a) Blank; (b) 0.0024 M resorcylaldehyde; (c) 0.001 M cupric resorcylaldehyde. All are in 50% by volume aqueous pyridine and 0.1 M KNO_3 at 25°.

solvent. In Fig. 3 there is also recorded a blank run and one of the parent chelating substances itself. These show no reduction below −1.0

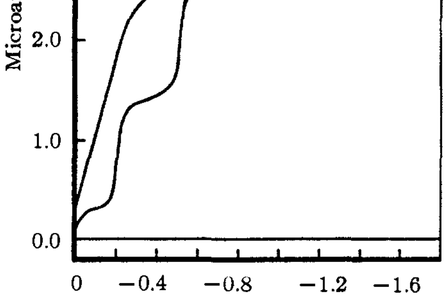

Fig. 4.—(a) 0.001 M cupric salicylaldehyde anil; (b) 0.001 M cupric salicylaldehyde-p-methoxyanil. All are in 50% by volume aqueous pyridine and 0.1 M potassium nitrate at 25°.

volt.[7] In Fig. 4a there is shown a case in which the first ($Cu^{II} \rightarrow Cu^+$) wave is clearly not reversible. This type is characteristic of the various salicylaldehydeanil chelates; and an extreme case, in which the first, and possibly even the second, wave is broken into two distinct parts, is shown in Fig. 4b.

The sum of the heights of the first pair is equal to that of the second pair, so that one may almost certainly ascribe them to $Cu^{II} \rightarrow Cu^I$ and $Cu^I \rightarrow Cu^0$ reductions, respectively. Furthermore, there seems to be a correlation between the parts as well, the first wave of the first pair corresponding to the second wave of the second pair. The explanation of this splitting is not yet clear. One fairly probable explanation would be the existence of a pair of isomers (either *cis* and *trans*, if the molecule is planar, or planar and tetrahedral forms) the equilibrium between which is slow compared to the rate of reduction at the drop. This awaits further investigation.

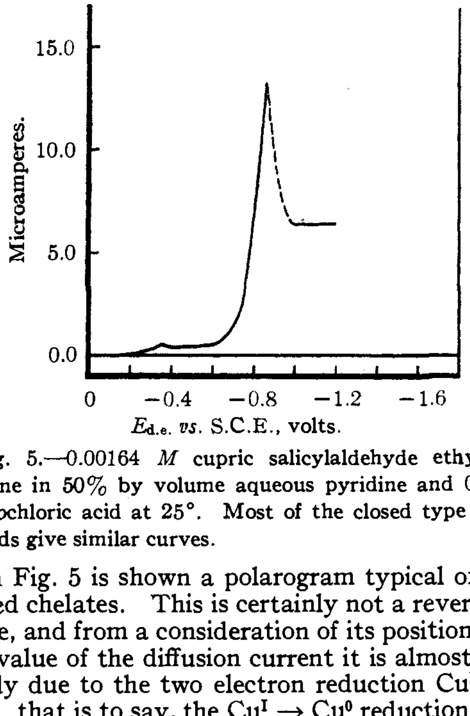

Fig. 5.—0.00164 *M* cupric salicylaldehyde ethylenediimine in 50% by volume aqueous pyridine and 0.1 *N* hydrochloric acid at 25°. Most of the closed type compounds give similar curves.

In Fig. 5 is shown a polarogram typical of the closed chelates. This is certainly not a reversible wave, and from a consideration of its position and the value of the diffusion current it is almost certainly due to the two electron reduction $Cu^{II} \rightarrow Cu^0$; that is to say, the $Cu^I \rightarrow Cu^0$ reduction is as easy, or easier, than the $Cu^{II} \rightarrow Cu^I$ reduction. Figure 6 is a polarogram showing the single case among these closed chelates which departs from the above type; that is, it actually shows two waves whose positions and magnitudes indicate that they correspond to the stepwise reduction of $Cu^{II} \rightarrow Cu^I \rightarrow Cu^0$. The results of measurements on 41 compounds which gave clearly definable waves are summarized in Table I.

Discussion

From the fact that the second wave ($Cu^I \rightarrow Cu^0$) for all of the open compounds (Nos. 1–26, 38–41, Table I), and at least one of the closed type (No. 34, Table I), occurs at the same potential, and that potential is identical with the reversible one obtained for a simple cuprous salt in this solvent (No. 1, Table I), one must assume that the same species is being reduced in all cases. The only alternative would appear to be that each of these 31 different compounds happened to have the same reduction potential, and this does not seem likely. This then leads to the formulation of the electrode process as follows:

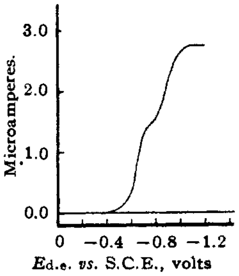

Fig. 6.—0.005 *M* cupric resorcylaldehyde ethylenediimine in 50% by volume aqueous pyridine and 0.1 *M* potassium nitrate at 25°.

A reaction characteristic and different for each compound

$$Cu^{II}\,Ke_2(py)_n + e^-(Hg) \xrightarrow{\epsilon^{(1)}_{1/2}} Cu^I\,(py)_m + 2Ke^- + (n - m)py \quad (3)$$

followed by the reaction common to all of them (having $\epsilon^{(2)}_{1/2} \cong -0.53$)

$$Cu^I\,(py)_m + e^-(Hg) \xrightarrow{\epsilon^{(2)}_{1/2}} Cu^0\,(Hg) + m\,py \quad (4)$$

Here Ke^- represents one equivalent of the chelating compound which fills two coördination positions, *i. e.*, the anion of salicylaldehyde or the enolate ion of acetyl acetone; py represents a pyridine molecule and *n*, *m*, *x*, represent the number of pyridines bound to each species.

Since the product of the reduction in the first wave is the same for all cases under consideration, one can set up the first reaction in terms of two steps: (a) a dissociation into the unchelated Cu^{++} and the chelating ions; and (b) the reduction of the unchelated Cu^{++}. In actual fact, of course, the reduction does not proceed by this path since the dissociation is slow compared to the direct reduction of the chelate at the drop.[8]

$$\begin{tikzcd}
Cu^{II}\,Ke_2(py)_n + e^-(Hg) \arrow[dr, "\epsilon^{(1)}_{1/2}"] \arrow[dd, "\Delta\epsilon^{(1)}_{1/2}"] & \\
 & Cu^+(py)_m + 2Ke^- + (n - m)py \\
Cu^{++}(py)_x + 2Ke^- + (n - x)py + e^-(Hg) \arrow[ur, "\epsilon^{(1)}_{1/2}(0)"'] &
\end{tikzcd}$$

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[7] Salicylaldehyde and some of its organic derivatives have been examined polarographically in aqueous solutions by G. Scaramelli, *Atti accad. Italia*, [7] 1, 764 (1940).

[8] The evidence for this lies in the fact that the color (absorption spectrum) of the chelate solutions is not that of the unchelated cupric ion, indicating an extremely small degree of dissociation at equilibrium and the apparent reversibility of the first half-wave potential which in all cases is at least as negative as that of unchelated cupric ion.

TABLE I

SUMMARY OF HALF-WAVE POTENTIALS

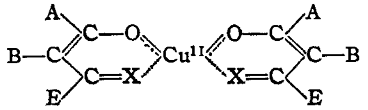
The solvent for all these determinations is 50% pyridine to 50% water by volume and 0.1 *M* potassium nitrate unless otherwise specified. The temperature is 25°.

	Complex	Concn., *M*	$\epsilon^{(1)}_{1/2}$	$\epsilon^{(2)}_{1/2}$	Remarks
1	CuCl	0.001		−0.52	0.1 *M* KCl
2	$CuCl_2$	.001	0.06[a]	− .52	.1 *M* KCl
3	$Cu(NO_3)_2$	.0005	.03[a]	− .52	
4	$Cu(Ac)_2 \cdot H_2O$	.001	.06[a]	− .52	.1 *M* KCl
5	$Cu(C_6H_5{-}\ddot{N}{=}\ddot{N}{-}\underset{\cdot\cdot}{\ddot{N}}{-}C_6H_5)$	.001		− .52	.1 *M* KCl
6	$Cu(C_6H_5{-}\ddot{N}{=}\underset{\cdot}{\ddot{N}}{-}\underset{\cdot\cdot}{\ddot{N}}{-}C_6H_5)_2$	.001	− .16	− .54	
7	Copper salicylaldehyde	.0005	.01	− .53	
		.001	.01	− .53	
		.002	.00	− .53	
8	Copper-5-methyl-salicylaldehyde	.001	.00	− .52	
9	Copper-4-hydroxy-salicylaldehyde	.001	.01	− .53	
10	Copper-5-chlorosalicylaldehyde	.001	.04[a]	− .53	
11	Copper-5-nitrosalicylaldehyde	.001	.04[a]	− .53	
12	Copper-3-nitrosalicylaldehyde	.001	.03[a]	− .53	
13	Copper-resacetophenone	.001	.04[a]	− .53	
14	Copper salicylaldoxime	.00107	− .12	− .53	
15	Copper salicylaldimine	.00108	− .20	− .53	
16	Copper salicylaldehyde methylimine	.001	.02[a]	− .52	
17	Copper salicylaldehyde *n*-heptylamine	Satd. sol.	− .40	− .52	
18	Copper salicylaldehyde 2-hydroxyethylimine	.001	− .18	− .52	
19	Copper salicylaldehyde benzylimine	Satd. sol.	− .31	− .52	
20	Copper salicylaldehyde anil	.001	− .12	− .52	.1 *M* KCl
21	Copper salicylaldehyde *p*-hydroxy-anil	.001	− .17	− .52	.1 *M* KCl
		.001	− .17	− .52	
22	Copper salicylaldehyde *p*-phenyl-anil	Satd. sol.	− .10	− .51	.1 *M* KCl
23	Copper salicylaldehyde *p*-methyl-anil	.001	− .12	− .50	.1 *M* KCl
		.001	− .04 − .20	− .53	
24	Copper salicylaldehyde *p*-methoxy-anil	.001	− .21	− .52	
		.001	− .21	− .53	
25	Copper salicylaldehyde *p*-nitro-anil	Satd. sol.	.03[a]	− .52	
26	Copper salicylaldehyde *p*-SO_3Na-anil	.001	− .09	− .54	
27	Copper salicylaldehyde ethylenediamine	.001	−0.75		
28	Cu-5-chloro-sal[b]-en[c]	.0005	− .68		
29	Cu-5-methyl-sal[b]-en[c]	.005	− .73		
30	Cu-4-hydroxy-sal[b]-en[c]	.0005	− .63	− .89	
31	Cu-5-methoxy-sal[b]-en[c]	.0005	− .74		
32	Copper resacetophenone ethylenediamine	.001	− .64		
33	Copper *o*-aminobenzaldehyde-ethylenediamine	.001	− .55		
34	Copper salicylaldehyde tetra-methylenediamine	.0001	− .17	− .52	
35	Copper salicylaldehyde penta-methylenediamine	.001	− .64		
		.0005	− .66		
36	Copper salicylaldehyde *o*-phenylenediamine	.0005	− .76		
37	Copper salicylaldehyde 1,8-diaminonaphthalene	.001	− .55		
38	Copper acetoacetic ester	.001	− .09	− .53	
39	Copper acetylacetone	.001	− .13	− .54	
40	Copper benzoylacetone	.0005	− .11	− .53	
41	Copper dibenzoylmethane	Satd. sol.	− .06	− .52	

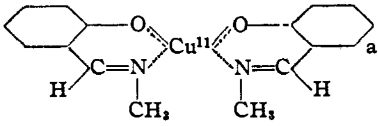
[a] At this potential, as shown by the blank, mercury is going into solution, and giving a mixed potential. Consequently the $Cu^{II} \rightarrow Cu^{I}$ reduction of aldehydes (10 to 13) cannot be distinguished from cupric ion. [b] Sal. = Salicylaldehyde. [c] En = Ethylenediamine.

where $\epsilon^{(1)}_{1/2}(0)$ represents the reduction potential of the unchelated cupric ion as obtained with cupric nitrate or cupric acetate. Thus, the difference, $\Delta\epsilon^{(1)}_{1/2}$, between the first half-wave potential for the chelate $\epsilon^{(1)}_{1/2}$ and that for the unchelated cupric ion, $\epsilon^{(1)}_{1/2}(0)$, should be a measure of the stability of the Cu^{II} chelate. Since our present purpose is a comparison of the effects of changes in structure of the chelating residue on the nature of the chelate, it is unnecessary to know the actual value of $\epsilon_{1/2}^{(1)}(0)$. The relative stabilities in the series of compounds will be given directly by the relative values of $\epsilon_{1/2}^{(1)}$ for each of the compounds; the more negative the potential, the greater the stability of the chelate. The complexity of the solvent and the accuracy of the measurements do not warrant any quantitative interpretation other than the observation of orders of magnitude; only the qualitative order of the compounds in the stability scale can be deemed to have unequivocal significance.[9]

Most of the chelates in the present study can be formulated as compounds of the general type

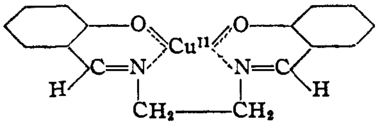


The first and most pronounced effect to be observed is the great increase in stability accompanying the binding together of the two halves of the chelate through the groups at X. This is observed for both aliphatic and aromatic binding chains. Thus we have the pair



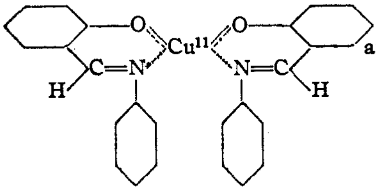
and

$\epsilon_{1/2}^{(1)} = +0.02$



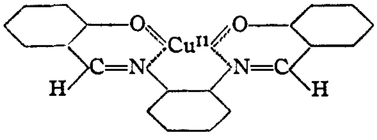
$\epsilon_{1/2}^{(1)} = -0.75$

and the pair



and

$\epsilon_{1/2}^{(1)} = -0.12$



$\epsilon_{1/2}^{(1)} = -0.76$

The precise source of this great increase in stability is as yet impossible to identify. The purely steric factors influencing the ΔH of the reaction no doubt affect the bond energies themselves to some extent by changing the steric repulsions of the groups and enforcing the *cis* position of the N atoms. In the case of the aliphatic binding there can hardly be any great increase of resonance,[2] and it is unlikely that very much of this effect appears in the aromatic case. It is almost certain that a large part of this change in ΔF (some 10 to 15 kcal. per mole) will be found in the ΔS of the reaction. Some indication of this may be found in a comparison of the two reactions upon which preliminary measurements have been made in this laboratory, extending those of Bjerrum[10]:

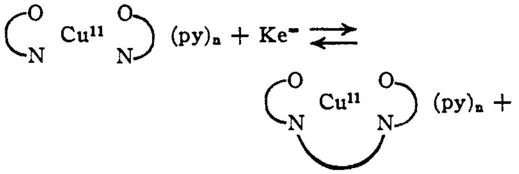
$$\mathrm{Ni^{++}(H_2O)_x + 6NH_3(aq.)} \rightleftarrows \mathrm{Ni(NH_3)_6^{++} + \mathit{x}H_2O} \quad \Delta H \cong -19 \text{ kcal.} \quad \Delta S \cong -22 \text{ cal./deg.}$$

$$\mathrm{Ni^{++}(H_2O)_x + 3\,en(aq.)} \rightleftarrows \mathrm{Ni(en)_3^{++} + \mathit{x}H_2O} \quad \Delta H \cong -25 \text{ kcal.} \quad \Delta S \cong +2 \text{ cal./deg.}$$

By combination of these two reactions we can compare the results directly

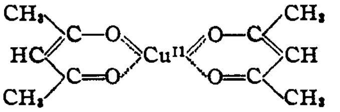
$$\mathrm{Ni(NH_3)_6^{++} + 3\,en(aq.)} \rightleftarrows \mathrm{Ni(en)_3^{++} + 6(NH_3)_{aq.}} \quad \Delta H \cong -6 \text{ kcal.} \quad \Delta S \cong +24 \text{ cal./deg.}$$

The $\mathrm{Ni(en)_3^{++}}$ ion probably has a somewhat greater entropy than $\mathrm{Ni(NH_3)^{++}}$ because of its greater size, but the major increase must be attributed to the other species involved and especially to the fact that there are three more particles on the right side of the reaction than there are on the left. An analogous reaction may be written for the chelates we are here discussing



Crystallization experiments seem to indicate that *n* is near one for both compounds so that here again one may expect to find a considerable increase in entropy favoring the right-hand side of the reaction. Because of the importance of the combination of poly-functional species, in biological systems especially, we are pursuing these measurements and those on the simpler systems mentioned above in order to fix precisely the entropy changes.

Another very interesting series is



$\epsilon_{1/2}^{(1)} = -0.13$

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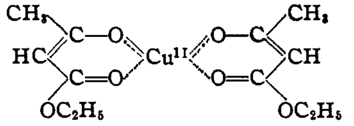
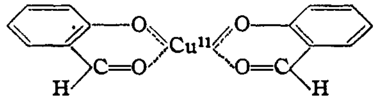
(9) Although the values of $\epsilon_{1/2}^{(1)}$ have not been shown in all cases to be reversible values, they are at least upper limits to the reversible potentials. Furthermore, since we are concerned only with the differences, and since all the compounds are of similar type, the following treatment will assume that the differences in $\epsilon_{1/2}^{(1)}$ are very close to the differences in the reversible potentials.

(10) J. Bjerrum, "Metal Ammine Formation in Aqueous Solution," P. Haase and Son, Copenhagen, 1941.



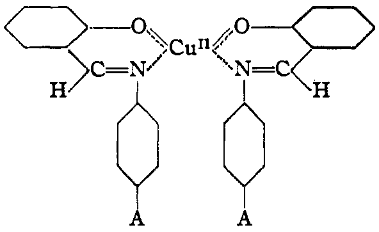
$\epsilon^{(1)}_{1/2} = -0.09$

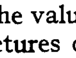


$\epsilon^{(1)}_{1/2} = +0.01$

Here the result exactly parallels that reported in an earlier paper[2] in which the relative stabilities of these compounds were measured by a different method in another solvent. It is due in part to the contribution of a benzenoid resonance involving the copper atom and the interference with it by the ester resonance in the acetoacetic ester chelate and by the benzene resonance in the salicylaldehyde chelate.

The last series from which a definite conclusion may be drawn as yet is formed by the substituted anils of salicylaldehyde giving chelates of the type



where A may be varied. The values of $\epsilon^{(1)}_{1/2}$ for the series for the various structures of A are: NO_2, +0.03; SO_3Na, −0.09; , −0.10; H, −0.12; CH_3, −0.15; OH, −0.17; OCH_3, −0.21. This is just the order of increasing base strength of the corresponding aniline except for the inversion of the last two of the series, which inversion may be real or more likely is due to uncertainties in these measurements or inaccuracies in the base strength determination. Thus we are again[2] led to the conclusion that the more available the coördinating electron pair the stronger the coördination bond which it may form with a metal.

Summary

1. The reduction of 41 compounds, 37 of which are chelate compounds, at the dropping mercury electrode has been studied in 50% by volume aqueous pyridine.

2. It has been shown that the cuprous compounds of most of the chelating groups studied are unstable under these solvent conditions and that they dissociate, giving a cuprous pyridine ion.

3. Certain trends have been pointed out in the effect of the structure of the chelating group upon the relative stability of the copper chelates; among these, the effect of tieing together the coördinating groups is by far the largest and most important.

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[CONTRIBUTION FROM THE RESEARCH LABORATORY, GENERAL ELECTRIC COMPANY]

Group and Bond Refractions in Organosilicon Liquids

BY ROBERT O. SAUER

Introduction

The use of the atomic refraction values computed by Eisenlohr[1] for a number of atoms frequently present in organic liquids has proved a convenient tool for confirming the identity and structure of new organic compounds.[2] This paper deals with the establishment and application of refractometric constants for organosilicon liquids.

Bygdén[3] has measured and discussed the refraction of silicon compounds. He concluded that the simple concept of additivity of atomic refractions did not give satisfactory results when applied to a wide variety of silicon compounds[3e,4] and states[5]: "It is therefore of interest to investigate whether (or not) the introduction of specific refraction values for the various types of silicon bonding permit at least an approximate calculation of the atom refraction of silicon in compounds where its valences are occupied by dissimilar radicals." From the refractions of the symmetrical molecules SiY_4, where Y was chlorine, bromine, ethoxyl or alkyl, Bygdén subtracted the sum of the Eisenlohr values for the four Y groups and the difference was then divided by four to give the (artificial) refraction of the Si–Y bonds. These figures when applied to the

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(1) Eisenlohr, *Z. physik. Chem.*, **75**, 585 (1911).

(2) See, for example, Shriner and Fuson, "The Systematic Identification of Organic Compounds," 2nd ed., John Wiley and Sons, Inc., New York, 1940, p. 107.

(3) (a) Bygdén, *Ber.*, **44**, 2640 (1911); (b) *ibid.*, **45**, 707 (1912); (c) *ibid.*, **48**, 1236 (1915); (d) *Z. physik. Chem.*, **90**, 243 (1915); (e) Dissertation, Uppsala, 1916.

(4) This conclusion was aptly illustrated in our experience by attempting to calculate the atomic refraction of the oxygen atom in hexamethyldisiloxane. By subtracting the Eisenlohr atomic refractions for carbon and hydrogen from the observed molar refraction (30.33 mls.) of silicon tetramethyl we obtained the value 7.45 mls. for the atomic refraction of silicon. Using this value (and again the Eisenlohr values for carbon and hydrogen) we next calculated the refraction of two trimethylsilyl groups and found that this computed figure (49.22 mls.) was actually *larger* than the molar refraction of hexamethyldisiloxane (48.90 mls.). Thus, by the concept of atomic refractions the oxygen atom in hexamethyldisiloxane would have a *negative value*.

(5) Ref. 3e, p. 171.