the same in both cases, and the similarity of catalytic activity is not surprising.

In view of these correlations with stability, one would look for the least stable metal chelate compound in order to obtain maximum catalytic activity. There is a definite limit beyond which this concept cannot be pushed, however, which is defined by the stability necessary to keep the metal ion in solution. Thus the most active catalyst would be the aquo ion itself. Since the aquo ion cannot be obtained in sufficient concentration at a *p*H where the hydroxide ion concentration is also sufficient to carry out the reaction at a reasonable rate, it seems that an important function of the metal chelate compound is to maintain the metal ion at a reasonably high concentration (and activity) in aqueous solution.

Influence of Metal Ion on Catalytic Activity.—Measurements of the catalytic activities of a number of stable aqueous metal chelates of the Fe(III), La(III), Cr(III), Ti(IV) and Sn(IV) ions are listed in Table I. Not listed are a number of additional measurements made on chelates of other common metal ions such as Zn(II), Cd(II), Co(II), Fe(II), Ni(II) and Pb(II). None of the metal chelates, listed and unlisted, showed interesting catalytic activity. The Zn(II) ion was unique in that it was the only third row metal for which no active chelates were found.

On the other hand, a number of metal chelate compounds of oxo- metal ions such as ZrO(IV), UO_2(VI) and MoO_2(VI) showed very high catalytic activity toward the hydrolysis of Sarin, the most active being the ethylenediaminetetraacetato-zirconyl ion ($t_{1/2}$ = 2.2 min.), the dioxomolybdenum(VI) chelate of 3,5-disulfopyrocatechol (~7.0 min.), and the dioxouranium(VI) chelate of 3,6-disulfo-1,8-dihydroxynaphthalene (~3.5 min.), the numbers corresponding to the approximate half times of hydrolysis in the presence of a 0.0010 molar solution of the catalyst. The lack of information on the stabilities of these chelate compounds and the small number of examples of very active chelates make correlation of activity with properties of the ligand impossible. It is noted, however, that all of the active catalysts contain one or more oxo groups bound to the metal ion. Although these chelates are in some instances formed with ligands containing many donor groups, it is possible to state in all cases that oxo- or hydroxy-groups are also present. It seems probable that these basic groups must be involved in the observed catalysis by a push–pull mechanism analogous to that already proposed for the Cu(II) chelates.

Although the uranyl 5-sulfosalicylate chelate has been reported by Ryland, *et al.*,[3] to be catalytically active, studies of systems containing this chelate indicate that it is unstable in aqueous solution at *p*H 7.

General Conclusions.—The catalytic activities of metal chelate compounds listed in Table I are seen to increase with increasing *p*H and increasing concentration of the chelate. The measured rate constants increase with an increase in hydroxide ion and metal chelate concentrations, in accordance with the mechanisms suggested above. The rate constants do not increase with the first power of the concentration of these substances, and possible side reactions or equilibrium with inactive species is indicated. The authors are now engaged in an extensive study of these effects and hope to report their findings in a subsequent publication.

The list of rate constants of DFP hydrolysis in the presence of various metal chelates in Table III is restricted to some of the more active catalysts with interesting structures. The results for these compounds, together with the results reported by Wagner-Jauregg, *et al.*, and by Ryland, *et al.*,[3] indicate that the generalizations made above for the hydrolysis of Sarin also apply to DFP, although the latter compound is more slowly hydrolyzed by all reagents investigated.

As a result of the correlation in this paper of the catalytic activity of metal chelates with structure and other properties of the ligand, the following generalizations may be made concerning the factors which tend to increase catalysis of hydrolysis by a metal chelate compound: 1, the presence of oxo, hydroxy or aquo groups bound directly to the metal; 2, bidentate ligands in the case of Cu(II) (does not hold for metals of higher valence); 3, minimum stability of the metal chelate compound which will still prevent dissociation to the metal ion; 4, high concentration (hence high solubility) of the metal chelate; 5, high *p*H.

The most active catalysts found in this investigation in the order of decreasing activity are

For Sarin: Cu(II)TMEN > Cu(II)DMEN > ZrO(II) EDTA > Cu(II) DAP > UO_2(II) $(DNS)_2$ > Cu(II) DIPY > MoO_2(VI) PDS > Cu(II) N > Cu(II) 2-HEN > Cu(II) HEN > Cu(II) DIEN

For DFP: Cu(II) TMEN > Cu(II) DIPY > Cu(II) EN > Cu(II) DAP > Cu(II) HEN > Cu(II) 2-HEN > Cu(II) 2-HEN >>> Cu(II) DIEN

The tetramethylethylenediamine-Cu(II) chelate is the most active catalyst found up to the present time.

WORCESTER, MASS.

[CONTRIBUTION FROM THE CHEMICAL LABORATORIES, CLARK UNIVERSITY]

Hydrolytic Tendencies of Metal Chelate Compounds. I. Cu(II) Chelates[1]

BY A. E. MARTELL, S. CHABEREK, JR., R. C. COURTNEY, S. WESTERBACK AND H. HYYTIAINEN

RECEIVED MARCH 4, 1957

The hydrolysis of 1:1 chelates of copper with thirty ligands has been studied potentiometrically with a view to determining relative tendencies to form hydroxy complexes. Most of the bidentate chelate compounds investigated were found to undergo hydrolysis in a limited *p*H range, with *pK* values of 7.5 ± 0.3. The number of donor groups in the ligand was found to be more important than stability in determining hydrolytic tendencies. In certain cases the existence of a highly stable 2:1 chelate resulted in disproportionation of the 1:1 chelate with simultaneous precipitation of half of the metal in the form of its hydroxide.

(1) This paper reports work done under contract with the Chemical Corps, U. S. Army, Washington 25, D. C.

Because of the interest in these laboratories in the study of incompletely coördinated metal chelate compounds as catalysts and as enzyme models, it was considered desirable to first investigate the behavior of copper chelates containing one or more uncoördinated positions on the metal ion. A search of the literature reveals very little information on this type of compound. Recently the monohydroxyl complex of dipyridyl-Cu(II) has been reported by Wagner-Jauregg, *et al.*,[2] while the equilibria involving this compound as well as the hydroxides of *o*-phenanthroline-Cu(II) and of ethylenediamine-Cu(II) have been measured quantitatively by Ryland, *et al.*[3]

Experimental

The experimental method consisted of potentiometric titration of the chelating agent in the absence of, and in the presence of, the metal ions being investigated.

Apparatus and Procedure.—A Beckman Model G *p*H meter with extension electrodes was used to record the hydrogen ion concentration. Titrations were carried out in a 200-ml. eight-neck flask designed to accommodate a mercury seal stirrer, microburet delivery tube, nitrogen inlet and outlet tubes, and glass and calomel electrodes. Measurements were made at a temperature of 25 ± 0.1° unless otherwise noted. The ionic strength was maintained relatively constant with a medium containing 0.10 *M* potassium nitrate and relatively low concentrations of ligand and metal ion. Carbonate-free potassium hydroxide prepared by the method of Schwarzenbach and Biedermann[4] was used as a titrant in all cases. In order to prevent absorption of atmospheric carbon dioxide, presaturated nitrogen was bubbled through the experimental solution during the course of the titrations. In all cases reported, titration data were obtained for solutions containing equimolar concentrations of ligand or metal ion.

When thermal equilibrium had been attained, *p*H readings were taken after the addition of small increments of 0.10 *M* potassium hydroxide until the *p*H reached values of 10.5–11.0. The *p*H meter-glass electrode-calomel electrode system was calibrated against standard acetate buffer to determine hydrogen ion concentrations.

Materials.—A solution of reagent grade copper(II) nitrate was standardized by titration with standard Na_2EDTA reagent with murexide as an indicator in ammoniacal solution.[5]

Samples of ethylenediaminetetraacetic acid, N-hydroxyethylethylenediaminetriacetic acid, N,N′-dihydroxyethylethylenediaminediacetic acid, N-hydroxyethyliminodiacetic acid, nitrilotriacetic acid, aspartic acid, N-hydroxyethylaspartic acid and N-aminoethylaspartic acid were obtained through the courtesy of Versenes, Inc., Framingham, Massachusetts. Samples of N-hydroxyethylethylenediamine, N,N′-dihydroxyethylethylenediamine, diethylenetriamine and triethylenetetramine were obtained from Carbide and Carbon Chemical Co., purified by fractional distillation, and converted to the corresponding hydrochlorides. Ethylenediamine, 5-sulfosalicylic acid and 1,8-dihydroxynaphthalene-3,6-disodium sulfonate were purchased from Eastman Kodak Co. The ethylenediamine was dried over potassium hydroxide, redistilled and isolated as the dihydrochloride. Pyrocatechol-3,5-disodium sulfonate was purchased from LaMotte Chemical Products Corp., Baltimore, Maryland. The 1,3-diaminopropane was obtained from the Sharples Chemical Company while the dipicolinic acid (pyridine-2,6-dicarboxylic acid) was donated by Dr. Stanley Chaberek of the Dow Chemical Co., Framingham, Massachusetts. Samples of the dihydrochlorides of N,N′-dimethylethylenediamine and N,N,N′,N′-tetramethylethylenediamine were prepared and recrystallized by conventional methods. The hydrochlorides of *cis*- and *trans*-1,2-diaminocyclohexane and the corresponding cyclohexene derivative were prepared by the stereospecific method described by Craven.[6] N,N′-Dihydroxyethylethylenediaminediacetic acid (HEDDA) was prepared by cation exchange from a solution of the sodium salt in accordance with the method described by Chaberek and Martell[7] for the corresponding monohydroxyethyl compound (HEDTA). Standardization of the aqueous solutions of the above chelating agents was effected by means of potentiometric titration with either standard carbonate-free potassium hydroxide or hydrochloric acid.

Results

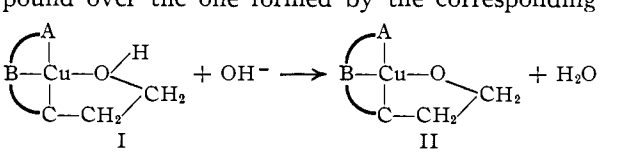
The potentiometric data obtained on the metal chelates outlined above are summarized in Table I. The symbols used to describe the formulas of the metal chelates in Table I involve the notation $H_mA(OH)_i$ for the ligand and the formula $(MAO_j(OH)_{i-j}[OH]_k)^{n-m-j-k}$ for the chelates formed by combination of one mole of ligand with one gram ion of the metal ion M^{+n}. The potentiometric titration curves of the various copper chelate systems investigated are reproduced in Figs. 1 and 2.

Discussion

Potentiometric Titration Curves.—Potentiometric measurements of stabilities of some of the Cu(II) chelates investigated as well as of their hydrolytic tendencies, are indicated in Figs. 1 and 2. Of the compounds listed in Table I, titration curves of metal chelates which have been investigated previously for hydrolytic tendencies have been omitted. Thus potentiometric measurements of the Cu(II) complex of EDTA, as well as those of HEDTA, HIMDA, ASPA, EN, DAP, DIEN, and TRIEN, have been described in sufficient detail by the investigators referred to in Table I.

For the ligands containing four or more strong coördinating groups, there is a single strong inflection in the 1:1 Cu(II) chelate titration curve corresponding to the neutralization of all the displaceable protons (four or less) of the ligand. This behavior is characteristic of EDTA, HEDTA, 2-HEDDA, TRIEN and DIEN. The titration curves of these compounds showed no evidence for the further coördination of the metal with hydroxyl groups derived from the solvent.

Ligands having hydroxyethyl groups in positions favorable for coördination constitute a special case in view of the weak coördinating tendencies of this group. In cases where the number of strong coordinating groups was too small to satisfy the requirements of the Cu(II) ion (*i.e.*, less than four), a step in the titration curve usually is observed. This is true of HASPA (Fig. 1), HEN and 2-HEN (Fig. 2) as well as HIMDA and HxG, titration curves of which have been given previously.[12,13] For these ligands, it is believed that the hydroxyethyl group is coördinated with the Cu(II) ion in view of the enhanced stability of the chelate compound over the one formed by the corresponding



I II

(2) T. Wagner-Jauregg, B. E. Hackley, Jr., T. A. Lies, O. O. Owens and R. Proper, THIS JOURNAL, **77**, 922 (1955).

(3) L. B. Ryland, F. M. Fowkes and G. S. Ronay, Paper No. 108, Division of Physical and Inorganic Chemistry, 128th National Meeting of the American Chemical Society, Minneapolis, Minn., September 11–16, 1955.

(4) G. Schwarzenbach and W. Biedermann, *Helv. Chim. Acta*, **31**, 339 (1948).

(5) G. Schwarzenbach, "Die Komplexometrische Titration," Ferdinand Enke, Stuttgart, 1955, p. 68.

(6) M. Craven, Thesis, Clark University, 1952.

(7) S. Chaberek and A. E. Martell, THIS JOURNAL, **77**, 1477 (1955).

TABLE I

METAL–LIGAND INTERACTIONS AT 25°

Metal ion	Ligand	Formula of initial chelate formed	Log K^c	$pK_a{}^d$	Remarks
Cu(II)	ASPA (H_2A)	$(CuA[OH])^{-1}$	8.4[a]	7.3	.....
Cu(II)	EN (A)	$(CuA[OH])^{+}$	10.5[b]	7.1	Disproportionation above pH 7
Cu(II)	HEN (AOH)	$(CuAOH[OH])^{+}$	10.0	7.3	.....
Cu(II)	2-HEN ($A(OH)_2$)	$(CuA(OH)_2[OH])^{+}$	9.6	7.1	.....
Cu(II)	HEDTA (H_3AOH)	$(CuAOH)^{-1}$	17.4[10]	None	.....
Cu(II)	HEDDA ($H_2A(OH)_2$)	$(CuA(OH)_2)^0$	~16.5[11]	None	.....
Cu(II)	HIMDA (H_2AOH)	$(CuAOH)^0$	~10[12] (30°)	9.1	.....
Cu(II)	2-HxG ($HA(OH)_2$)	$(CuAO(OH))^0$	8.15[13] (30°)	6.8	.....
Cu(II)	HASPA(H_2AOH)	$(CuAOH[OH])^{-1}$	....	7.5	.....
Cu(II)	5-SSA (H_2AOH)	$(CuAO)^{-1}$	....	..	Ppt. above pH 7
Cu(II)	PDS ($A(OH)_2^{-2}$)	$(CuAO_2[OH])^{-3}$	14.57	7.2	.....
Cu(II)	DNS ($A(OH)_2^{-2}$)	$(CuAO_2[OH])^{-3}$	13.80	7.8	.....
Cu(II)	CU (A)	$(CuA[OH])^{+}$	~11.0	7.2	Disproportionation above pH 7
Cu(II)	TU (A)	$(CuA[OH])^{+}$	11.5	7.1	Disproportionation above pH 7
Cu(II)	CS (A)	$(CuA[OH])^{+}$	10.87[14] (20°)	7.1	Disproportionation above pH 7
Cu(II)	TS (A)	$(CuA[OH])^{+}$	11.13[14] (20°)	7.2	Disproportionation above pH 7
Cu(II)	DIEN (A)	$(CuA[OH])$	16.0[15] (20°)	9.2 (25°)	.....
			16.1[16] (30°, μ = 1.0)		.....
Cu(II)	TRIEN (A)	$(CuA)^{+2}$	20.5[17] (20°)	None	.....
Cu(II)	DPA (A)	$(CuA)^0$	....	None	Ppt. of $Cu(OH)_2$ above pH 6
Cu(II)	DMEN	$(CuA[OH])^{+}$	9.69	7.4	.....
Cu(II)	TMEN (A)	$(CuA[OH])^{+}$	7.2	7.2	.....
Cu(II)	PYR (AOH)	$(CuAO)^{+}$	10.2	..	Ppt. above pH 7
Cu(II)	AE-ASPA	$(Cu_2A_2)^0$ Dimer	15.1[11]	None	.....
Cu(II)	GG (H_2A)	$(CuA[OH])^{-1}$	6.6[18]	9.0	.....
Cu(II)	GGG (H_3A)	$(CuA)^{-1}$	5.7[18]	None	.....
Cu(II)	DIPY	$(CuA[OH])^{+}$	....	6.6	.....
Cu(II)	PHEN	$(CuA[OH])^{+}$	....	6.9	.....

[a] Chaberek and Martell[8] report 8.5 at 30°. [b] Ackermann, *et al.*,[9] report log K_{CuEN} = 10.72 at 25°. [c] K is formation constant of normal chelate. [d] K_a is acid dissociation constant of normal chelate.

ligand in the absence of the hydroxyethyl group. The additional step in the titration curve would then be due to the dissociation of a proton from the hydroxyethyl group as shown by I → II. This reaction has no counterpart in the uncoördinated ligand, due to the very weak acidity of hydroxyethyl groups. Since it is not possible to give the stability constant of compound II in terms of the metal ion and ligand, the only other alternative, followed in Table I, is to give a stability constant for I and pK values for the subsequent dissociation steps.

The qualitative comparisons possible in the titration curves of ASPA and HASPA, given in Fig. 1, serve to illustrate the principles involved. The greater pH decrease of HASPA on coördination with Cu(II) ion (observed best between a = 1

TABLE IA

KEY TO LIGAND ABBREVIATIONS

ASPA	Aspartic acid
EN	Ethylenediamine
HEN	N-Hydroxyethylethylenediamine
2-HEN	N,N′-Dihydroxyethylethylenediamine
HEDTA	N-Hydroxyethyl-N,N′-ethylenediaminetriacetic acid
HEDDA	N,N′-Dihydroxyethyl-N,N′-ethylenediaminediacetic acid
HIMDA	N-Hydroxyethyliminodiacetic acid
2-HxG	N,N-Dihydroxyethylglycine
HASPA	N-Hydroxyethylaspartic acid
5-SSA	5-Sulfosalicylic acid
PDS	Disodium 3,5-pyrocatecholdisulfonate
DNS	Disodium 1,8-dihydroxynaphthalene-4,5 disulfonate
CU	*cis*-Δ^4-1,2-Diaminocyclohexene
TU	*trans*-Δ^4-1,2-Diaminocyclohexene
CS	*cis*-1,2-Diaminocyclohexane
TS	*trans*-1,2-Diaminocyclohexane
DIEN	Diethylenetriamine
TRIEN	Triethylenetetramine
DPA	2,6-Dipicolinic acid
DMEN	N,N′-Dimethylethylenediamine
TMEN	N,N,N′,N′-Tetramethylethylenediamine
PYR	Pyridoxamine
AE-ASPA	N-Hydroxyethylaspartic acid
GG	Glycylglycine
GGG	Glycylglycylglycine
DIPY	Dipyridyl
o-PHEN	*o*-Phenanthroline

(8) S. Chaberek, Jr., and A. E. Martell, THIS JOURNAL, **74**, 6021 (1952).

(9) H. Ackermann, J. E. Prue and G. Schwarzenbach, *Nature*, **163**, 723 (1949); *Helv. Chim. Acta*, **33**, 985 (1950).

(10) S. Chaberek and A. E. Martell, THIS JOURNAL, **77**, 1477 (1955).

(11) A. Frost, Dow Chemical Company, private communication.

(12) S. Chaberek, Jr., R. C. Courtney and A. E. Martell, THIS JOURNAL, **74**, 5957 (1952).

(13) S. Chaberek, Jr., R. C. Courtney and A. E. Martell, *ibid.*, **75**, 2185 (1953).

(14) G. Schwarzenbach and R. Bauer, *Helv. Chim. Acta*, **39**, 722 (1956).

(15) J. E. Prue and G. Schwarzenbach, *ibid.*, **33**, 985 (1950).

(16) H. B. Jonassen, R. B. LeBanc and R. M. Rogan, THIS JOURNAL, **72**, 4968 (1950).

(17) G. Schwarzenbach, *Helv. Chim. Acta*, **33**, 995 (1950).

(18) C. B. Murphy and A. E. Martell, *J. Biol. Chem.*, in press (1957).

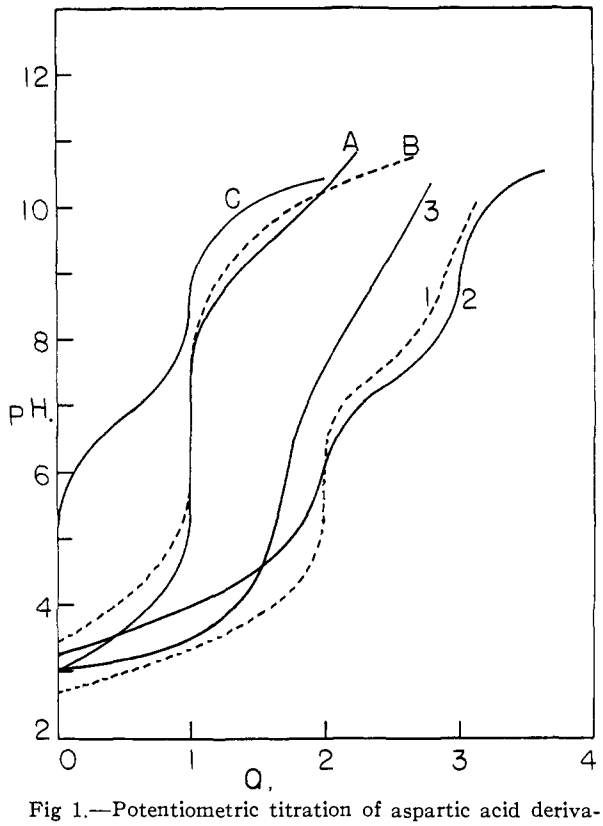
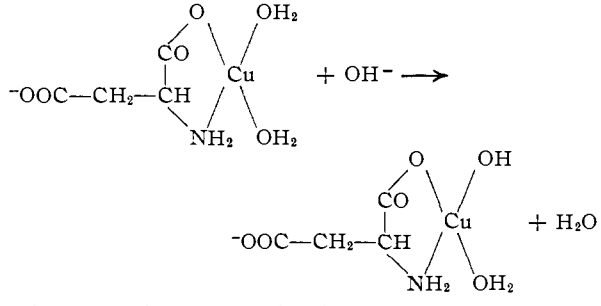


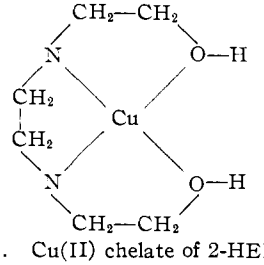
Fig 1.—Potentiometric titration of aspartic acid derivatives in the presence of (indicated by numbers) and in the absence of (indicated by letters) an equivalent molar amount of Cu(II) salt: HASPA, ASPA and AEASPA indicated by A, B, C, and 1, 2 and 3, respectively.

and $a = 2$) is an indication of the greater stability of the Cu-HASPA chelate, even though one would expect the reverse since HASPA is the more acidic ligand. This seems to indicate the participation of the hydroxyethyl group as a weak coördinating partner. For this reason the buffer region in the Cu(II)-HASPA curve is believed to correspond to a reaction similar to that illustrated above. Such a reaction is not possible with the Cu(II) aspartate, and the analogous buffer region must correspond to the dissociation of a coördinated water molecule in accordance with the reaction



It is interesting to note further that the more stable chelate (that of HASPA) shows the lower acidity of the proton attached to a coördinated oxygen. This may be due in part to the greater basicity of oxygen bound to alkyl groups over oxygen in water.

The question of participation of hydroxyalkyl groups in chelation of a metal ion has been considered by a number of investigators[10,13,19,20] with the weight of evidence in favor of direct coördination of the metal ion by the hydroxyalkyl groups. Thus for all of the Cu(II) chelates illustrated in Fig. 2, the coördination of the hydroxyalkyl group is believed to take place when such groups are present, in spite of the similarities of the buffer regions between $a = 2$ and $a = 3$. In the case of HASPA (Fig. 1) and HEN (Fig. 2), it should be pointed out that the hydroxy chelates and the alkoxy chelates would be tautomeric and that the product may actually be an equilibrium mixture of the two. It is noted that a similar interpretation cannot apply to the dihydroxyethyl derivative (III) without implying the displacement of a hydroxyalkyl group, which seems unlikely.



III. Cu(II) chelate of 2-HEN

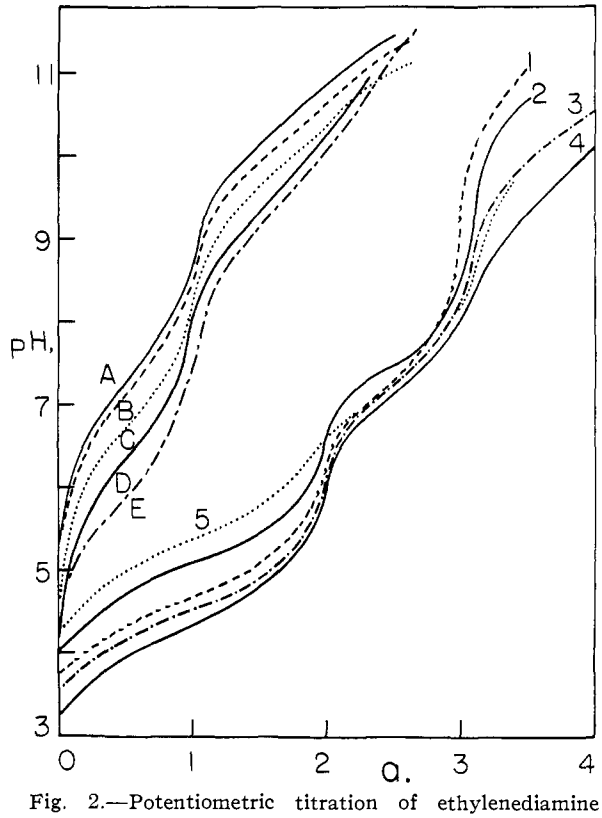


Fig. 2.—Potentiometric titration of ethylenediamine derivatives in the presence of (numbers) and in the absence of (letters) an equivalent amount of Cu(II) salt: EN, DMEN, HEN, 2-HEN and TMEN indicated by A, B, C, D, E, and 1, 2, 3, 4, 5, respectively.

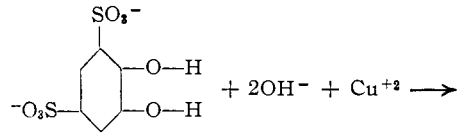
(19) G. Anderegg and G. Schwarzenbach, *Helv. Chim. Acta*, **37**, 1940 (1955).

(20) S. Chaberek, Jr., and A. E. Martell, THIS JOURNAL, **76**, 215 (1954).

The titration curves of *cis*- and *trans*-1,2-diaminocyclohexane and *cis*- and *trans*-1,2-diaminocyclohexene indicate that the Cu(II) chelates are very similar to those of ethylenediamine, with somewhat enhanced stability of the normal chelate, but with little difference in the buffer regions resulting from hydroxy chelate formation. The synthesis and properties of these diamines and of their metal chelates will be given in a subsequent publication.[21]

The potentiometric titrations and related properties of the Cu(II) chelates of glycylglycine and of glycylglycylglycine are being reported elsewhere.[18]

A number of bidentate chelates of Cu(II) with only oxygen donors were also investigated. Thus far only tiron (PDS) and chromotropic salt (DNS) gave stable aqueous systems which did not result in the precipitation of cupric hydroxide as the *p*H of the solution was raised. The titration curve for PDS showed a sharp break after the addition of two moles of base, corresponding to the formation of a bidentate chelate with the displacement of both phenolic protons, in accordance with the reaction



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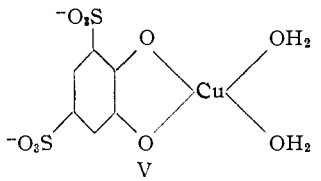
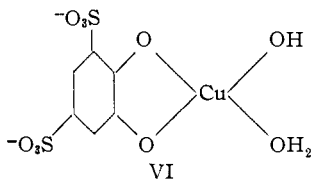


V

↓ +OH-



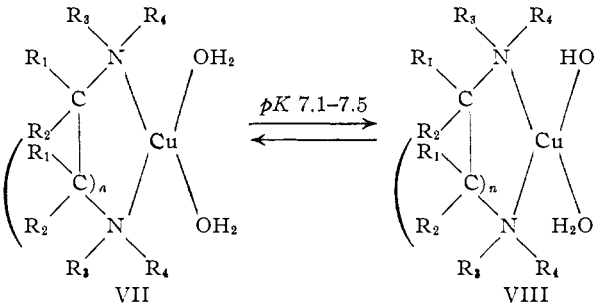
VI

A second step, requiring a third mole of base probably involves the formation of a hydroxy chelate according to the reaction given above.

The titration curve of the 1:1 Cu(II)-DNA chelate is not as clear-cut since there is only a long sloping buffer region in which three moles of base is required per mole of metal ion or ligand. It is probable that the compounds formed are analogous to those indicated above for tiron.

Among the bidentate ligands containing only oxygen donors, which failed to prevent precipitation of the metal at a 1:1 ratio of ligand to metal ion, may be mentioned 5-sulfosalicyclic acid and sodium pyrophosphate.

The majority of the Cu(II) complexes which were found to form soluble hydroxy chelate compounds are diamines with the structure indicated by general formula VII, where the groups R_1 and R_2 may represent a cyclohexane ring or, as in the case of dipyridyl and ortho-phenanthroline described by Ryland, *et al.*,[3] the substituents may represent condensed aromatic rings including the nitrogens. Although the structures of the compounds represented by VII were varied widely, with R_3 and R_4 representing hydrogen, alkyl, hydroxyalkyl, carboxylate (in aminoethylaspartic acid), or part of an aromatic ring system, the hydrolytic tendencies of the bound aquo groups were quite similar, with all *pK* values falling within the narrow range of 7.1–7.5. It would seem, therefore, that the hydrolysis of a bidentate Cu(II) chelate in which the metal is bound to only two basic nitrogen atoms is relatively independent of steric factors and of the stability of the metal chelate compound.



VII VIII

Thus the stabilities of ethylenediamine-Cu(II) and of tetramethylethylenediamine-Cu(II) differ widely, but their hydrolytic tendencies are almost identical. This is also true of the chelates formed from the mono- and dihydroxyethylethylenediamines.

The relative lack of influence of steric factors on the hydrolysis of substituted alkylenediamine-Cu(II) chelates is evidenced by the similarities between such widely different compounds as the Cu(II) chelates of dipyridyl, *o*-phenanthroline, ethylenediamine, and the *cis*- and *trans*-1,2-cyclohexanediamines. A number of Cu(II) chelates with oxygen donors or with oxygen and nitrogen donors show similar hydrolytic tendencies. Thus the Cu(II) chelates of tiron (PDS) and of chromotropic salt (DNS) and of aspartic acid have hydrolytic tendencies which do not differ appreciably from those of the chelates listed above.

The higher hydrolytic constants of the tridentate chelates formed with diethylenetriamine and glycylglycine indicate the importance of the number of bound aquo groups in determining hydrolytic tendencies. In these compounds this effect cannot be separated from the greater electronic influence of tridentate donors over the corresponding bidentate compounds. Hence the distribution of donor groups about the metal as well as the number of free positions available for hydrolysis may determine hydrolytic tendencies. Although one might be tempted to correlate the tendency of Cu(II) chelates toward hydrolysis with the asymmetry of the electronic field about the metal ion, the relative tendencies of stable tridentate and bidentate metal chelates can apparently be explained on much simpler grounds: the greater electron donor effect of the tridentate ligand on the remaining bound

(21) S. Westerback and A. E. Martell, unpublished work.

water molecule and the consequent greater binding of protons (or alternatively lower affinity for the hydroxyl ion). In addition to this, there is probably a stabilization of the monohydroxy form by hydrogen bonding which can occur only when two water molecules (or hydroxylkyl groups) are present.

It is further noted that an important tendency in the Cu(II) chelates which prevents hydroxy chelate formation is the formation of a relatively stable 2:1 chelate compound. Thus, while the 1:1 Cu(II)-ethylenediamine chelate is quite stable and exhibits normal hydrolytic tendencies, the formation of the corresponding monohydroxy chelate above *p*H 7.0 is prevented by the disproportionation reaction

$$2CuA(OH) \longrightarrow CuA_2 + Cu(OH)_2$$

Thus the formation of the 2:1 Cu(II) chelate compound is accompanied by precipitation of half of the copper as the hydroxide. This reaction is favored by the formation of a highly stable 2:1 chelate compound, with the result that the disproportionation reaction of the type given above results in a favorable free energy decrease. Such reactions are prevented in the hydroxyethylethylenediamines by higher stability of the 1:1 chelate as the result of participation of the weak ethanol donors in chelate formation. Disproportionation reactions are also prevented in the N-alkylated ethylenediamines through lowering of the stability of the 2:1 chelate compound as the result of steric repulsions between the alkyl groups.

On the basis of the behavior of the Cu(II) chelates listed in Table I, therefore, the factors favoring the formation of soluble hydroxy chelates are: 1, the formation of a sufficiently stable bidentate chelate to prevent precipitation of the Cu(II) as hydroxide; 2, high stability of the 1:1 chelate over the corresponding compound in which the ratio of ligand to metal ion is 2:1; 3, the absence of more than two strongly coördinating donor groups on the ligand.

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Diacyl Peroxide Reactions. II. The Reaction of δ-Phenylvaleryl Peroxide with Carbon Tetrachloride

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A quantitative study has been made of the products of the thermal decomposition of δ-phenylvaleryl peroxide in carbon tetrachloride over a more than six hundred-fold variation in peroxide concentration and at two temperatures. The product yields are almost independent of concentration and of temperature. It is reasonably certain that induced decomposition of the peroxide is insignificant at concentrations below 0.02 *M* and of only very minor importance even at about 0.6 *M*. It appears that more than 55% of the radicals derived from the peroxide undergo geminate reaction. The results show that under certain conditions aliphatic diacyl peroxides can be used as reliable sources of free alkyl radicals in solution.

The present paper describes a detailed study of the products of the thermal decomposition of δ-phenylvaleryl peroxide in carbon tetrachloride. It is a continuation of work described in the first paper in the series,[2] and is part of a research program directed toward a study of elementary free radical processes in solution.

The decomposition of δ-phenylvaleryl peroxide in carbon tetrachloride was carried out over a range of concentrations from about 0.001 *M* to about 0.6 *M*, a more than 600-fold variation. Two temperatures were used, 55 and 77°. At the higher temperature the analyses of products accounted for 98 ± 1% of the phenylbutyl groups and for 97.5 ± 0.3% of the carboxyl groups. The solvent fragment balance was not quite so good in that the number of CCl_3 groups found in hexachloroethane did not usually agree very well with the number of Cl groups found in 4-phenyl-1-chlorobutane. It is possible that hexachloroethane was lost in the removal of the last traces of the solvent. Enough experiments were carried out to permit a valid estimate of the accuracy and reliability of the results. The details are presented in Tables I and II; a brief examination of the products of the decomposition of the peroxide in the absence of solvent is summarized in Table III.

Except for minor differences, the results are similar to, but more precise than, those reported in the previous paper.[2] One difference is that the phosgene previously reported as a reaction product has been reduced to a negligible factor by a more effective removal of oxygen in the runs at 77° (reported in Table I). The phosgene apparently arises from reaction of trichloromethyl radicals with oxygen.

Phosgene was evolved in small amounts from the 55° runs during distillation of the carbon tetrachloride through the fractionating column. Since free phosgene previously had been removed by sweeping the reaction mixture with nitrogen, it must be surmised that some unstable product was liberating the phosgene. The trichloromethyl ester of δ-phenylvaleric acid is possibly the phosgene precursor. Its decomposition would also yield δ-phenylvaleryl chloride. The increased amount of δ-phenylvaleric acid found in these runs could be accounted for by this hypothesis. However, another potential phosgene source is hexachlorodimethyl peroxide from reaction of trichloromethyl radicals

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(2) D. F. DeTar and C. Weis, THIS JOURNAL, **78**, 4296 (1956).