20% of its room temperature value at 200°. The green decreases much more rapidly and is practically absent at 135°.

5. Alternative explanations of the various phenomena are discussed, and several suggestions concerning mechanism are made. There must be two states of acetone, one with a much shorter life than the other. The biacetyl may be excited by either of two processes: (a) collision of the second kind; (b) radical recombination using biacetyl as the third body. In either case the "active" biacetyl molecules must have a greater probability of decomposition at high temperatures than at low.

ROCHESTER, NEW YORK RECEIVED JUNE 23, 1947

[CONTRIBUTION FROM THE DIVISION OF CHEMISTRY, COLLEGE OF AGRICULUTRE, UNIVERSITY OF CALIFORNIA]

Interaction of Ions and Dipolar Ions. IV. The Solubility of Cupric Iodate in Glycine and in Alanine Solutions

BY R. M. KEEFER

In previous communications[1,2] it was shown that the solubility of certain 1–1 and 2–1 type salts in dipolar ion solutions could be expressed by equations of the type

$$\frac{1}{Z_1Z_2}\log\frac{S}{S_\infty} = 0.506\left(\frac{78.54}{D_s}\right)^{3/2}\frac{\sqrt{\mu}}{1 + A\left(\frac{78.54}{D_s}\right)^{1/2}\sqrt{\mu}} + 0.0625\,\frac{R^2}{a_{id}}[\mathrm{HR}^{\pm}] \quad (1)$$

where Z_1 and Z_2 are the valences of the ions; S_∞ is the theoretical solubility at $\mu = 0$ and $[\mathrm{HR}^{\pm}] = 0$; D_s is the dielectric constant of the solution; A is $0.3288a_i$ where a_i is the distance of closest approach of the ions; R is the dipole distance in the dipolar ion; a_{id} is the distance of closest approach of an ion to a dipolar ion; and $[\mathrm{HR}^{\pm}]$ is the concentration of the dipolar ion. The solubility of silver iodate and lead iodate in glycine and alanine solutions[3] is much higher than would be predicted by eq. (1). The increased solubility was accounted for by assuming complex ions consisting of one negative ion of the amino acid to one silver or lead ion. This investigation was undertaken to obtain information on the stability of a complex between one negative ion of the amino acid[4] and cupric ion.

Experimental

Cupric Iodate.—Equal volumes of 0.2 *M* potassium iodate and 0.1 *M* cupric nitrate were added dropwise with constant stirring to 3 liters of water at 60°. After six hours the precipitate was filtered off and allowed to equilibrate with water overnight. The precipitate was sedimented several times and the smaller particles were discarded. The preparation was air dried before using. After drying for two hours at 250–270° the dried cupric iodate when analyzed iodometrically was 100.1% cupric iodate.

The solubility determinations and general technique have been described in a previous communication.[1] The iodometric determinations were modified for the presence of cupric ion using the method of Foote and Vance.[5] Duplicate solubility determinations agreed to 2 parts in 1000.

The *p*H of the solutions was determined using a Model G Beckman *p*H meter and is accurate to ±0.01 *p*H unit. The definition of *p*H used in this work is the negative logarithm of the hydrogen ion activity.

Results

The solubility (moles/1000 g. H_2O) of cupric iodate in potassium chloride solutions at 25.00° is given in Table I. The solubility of cupric iodate in water is much lower than the value (3.693×10^{-3} *M*) reported by Peterson and Meyers.[6] Column 3 of Table I gives the solubility of cupric iodate calculated by means of equation (2).

$$\log [\mathrm{Cu}^{++}][\mathrm{IO}_3^-]^2 = -7.1353 + \frac{3.036\sqrt{\mu}}{1 + 1.08\sqrt{\mu}} \quad (2)$$

The distance of closest approach of the ions is then 1.08/0.3288 or 3.28 Å.

TABLE I

SOLUBILITY OF CUPRIC IODATE IN POTASSIUM CHLORIDE SOLUTIONS AT 25°

(*M* is Moles/1000 g. H_2O and *S* is *M* of Cupric Iodate)

KCl, *M*	$Cu(IO_3)_2$, $M \times 10^3$	Calcd. $Cu(IO_3)_2$, $M \times 10^3$
0	3.245	3.243
0.00501	3.398	3.396
.01002	3.517	3.521
.02005	3.730	3.730
.03511	3.975	3.969
.05017	4.166	4.166
.07529	4.453	4.454
.1005	4.694	4.697

Table II gives the solubility of cupric iodate in glycine and in alanine solutions together with the *p*H of the resulting solution. Since the *p*H values are all less than the isoelectric point of the amino acids (6.1), it is evident that reactions are taking place which produce hydrogen ion. Assuming

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[1] Keefer, Reiber and Bisson, THIS JOURNAL, **62**, 2951 (1940).

[2] Keefer and Reiber, *ibid.*, **63**, 3504 (1941).

[3] Keefer and Reiber, *ibid.*, **63**, 689 (1941).

[4] Gould and Vosburgh, *ibid.*, **64**, 1630 (1942).

[5] Foote and Vance, *Ind. Eng. Chem., Anal. Ed.*, **8**, 119 (1936).

[6] Peterson and Meyers, *ibid.*, **52**, 4853 (1930).

complex ion formation similar to the case of silver iodate and lead iodate,[3] then

$$Cu^{++} + HR^{\pm} \rightleftarrows CuR^{+} + H^{+} \quad K_1 = \frac{(CuR^{+})(H^{+})}{(Cu^{++})(HR^{\pm})} \tag{3}$$

$$HR^{\pm} + H^{+} \rightleftarrows H_2R^{+} \tag{4}$$

In Fig. 1 the concentration of combined copper (eq. 7) is plotted against the amount of hydrogen ion produced including the hydrogen ion used up in eq. 4. Below 5×10^{-3} *M* combined cupric ion there is more combined cupric ion than there is hydrogen ion produced. This indicates the formation of a complex not liberating hydrogen ion as indicated in the equation.

$$Cu^{++} + HR^{\pm} \rightleftarrows CuHR^{++} \quad K_a = \frac{[CuHR^{++}]}{[Cu^{++}][HR^{\pm}]} \tag{5}$$

Pedersen[7] has shown that cupric ion tends to form complexes with acetate ion. The replacement of a hydrogen by the positively charged NH_3^+ group would tend to decrease the possibility of formation of such a complex.

TABLE II

SOLUBILITY OF CUPRIC IODATE IN GLYCINE AND ALANINE SOLUTIONS AT 25°

(Moles/1000 g. H_2O).

Glycine, *M*	$Cu(IO_3)_2$, $M \times 10^3$	*p*H	Cor. *p*H
0.01253	4.096	3.32	
.02509	4.805	3.31	
.05023	6.17	3.32	3.35
.07542	7.46	3.37	
.1008	8.72	3.38	
.1515	11.16	3.39	
.2025	13.52	3.41	
Alanine			
0.01252	3.98	3.40	
.02508	4.60	3.37	
.05019	5.84	3.40	3.405
.07541	6.98	3.42	3.43
.1008	8.06	3.44	
.1516	10.22	3.48	3.47
.2027	12.30	3.49	

Above 5×10^{-3} *M* combined cupric ion there is more hydrogen ion produced than cupric ion combined, indicating the probable reaction

$$Cu^{++} + 2HR^{\pm} \rightleftarrows CuR_2 + 2H^{+}$$

$$K_2 = \frac{(CuR_2)(H^{+})^2}{(Cu^{++})(HR^{\pm})^2} \tag{6}$$

Attempts to explain the results assuming CuR_2 and $CuHR^{++}$ or CuR_2 and CuR^{+} to be the only complex ions failed to give constant equilibrium constants. The following method was used to evaluate the three equilibrium constants.

The amount of combined cupric ion is given by

$$S - [Cu^{++}] = [CuR_2] + [CuR^{+}] + [CuHR^{++}] \tag{7}$$

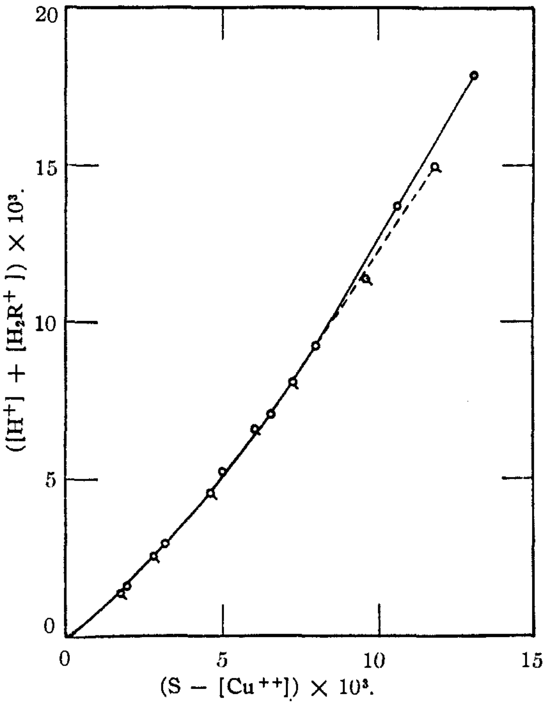

Fig. 1.—Hydrogen ion produced *versus* cupric ion complex formed in glycine and alanine solutions saturated with cupric iodate: O, glycine solutions; ♂, alanine solutions.

The concentration of hydrogen ion produced will be equal to

$$[H^{+}] + [H_2R^{+}] = 2[CuR_2] + [CuR^{+}] \tag{8}$$

$$[HR^{\pm}]_i = [HR^{\pm}] + [H_2R^{+}] + 2[CuR_2] + [CuR^{+}] + [CuHR^{++}] \tag{9}$$

where $[HR^{\pm}]_i$ is the total concentration of dipolar ion used. The ionic strength of the solution is given by

$$\mu = 2([Cu^{++}] + [CuHR^{++}]) + {}^1/_2([CuR^{+}] + [H^{+}] + [H_2R^{+}] + [IO_3^{-}]) \tag{10}$$

or by substituting (7) and (8) in (10)

$$\mu = 2S - [CuR^{+}] - [CuR_2] \tag{11}$$

In the amino acid solutions saturated with cupric iodate there are eight unknowns (exclusive of activity coefficients) as follows: $[Cu^{++}]$, $[CuR^{+}]$, $[CuHR^{++}]$, $[CuR_2]$, $[H_2R^{+}]$, $[HR^{\pm}]$, $[H^{+}]$ and μ. Although individual ion activity coefficients may not be determined, the general calculations are somewhat simplified if they are assumed to be given by equation 1 after substitution of $-1/Z_i^2 \log \gamma_i$ for $1/Z_1Z_2 \log S/S_\infty$. *R* was assumed to be 3.89 Å. for glycine[2] and 3.60 for alanine[2]. For cupric ion a_i was assumed to be the same in solutions containing glycine as in potassium chloride solutions. For CuR^+ and H_2R^+ a_i was assumed to be the radius of the dipolar ion plus one-half the distance of closest approach of cupric ion and iodate ion. At the ionic strengths involved an error of 0.1 Å. in a_i introduces a 1% error in the activity coefficient. The activity coefficients of CuR_2 and

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[7] Pedersen, *Det. Kgl. Danske Videnskab Selskab, Math.-fys. Medd.*, **22**, 1 (1945).

TABLE III

CALCULATED COMPOSITION OF GLYCINE AND ALANINE SOLUTIONS SATURATED WITH CUPRIC IODATE AND THE EQUILIBRIUM CONSTANTS INVOLVED

$[Cu^{++}]$ $M \times 10^3$	γCu^{++}	$[HG^{\pm}]$	$[CuG^+]$ $M \times 10^3$	γCuG^+	$[CuG_2]$ $M \times 10^3$	$[CuHG^{++}]$ $M \times 10^3$	$K_2 \times 10^4$	$K\alpha$
				$K_1 = 0.032$				
2.160	0.634	0.00919	0.940	0.896	0.38	0.87[a]		44
1.670	.608	.01896	1.420	.889	0.72	1.31[a]		41
1.137	.564	.03929	2.06	.874	1.47	1.66[a]	2.97	37
0.867	.524	.05999	2.38	.861	2.34	1.87	2.62	36
.701	.490	.08017	2.50	.849	3.36	2.15	2.66	38
.518	.431	.1222	2.60	.827	5.56	2.46	2.76	39
.423	.383	.1645	2.72	.807	7.58	2.80	2.63	40
				$K_1 = 0.034$				
Alanine		$[HA^{\pm}]$	$[CuA^+]$	γCuA^+	$[CuA_2]$	$[CuHA^{++}]$		
2.265	0.639	0.00967	1.15	0.904	0.18	0.38	..	..
1.800	.614	.01989	1.96	.902	.28	0.56	..	..
1.231	.575	.04065	2.83	.879	.85	1.58	1.12	31
0.945	.541	.06178	3.32	.868	1.51	1.61	1.07	28
.771	.512	.0835	3.64	.858	2.22	1.69	1.04	26
.568	.458	.1272	3.96	.840	3.87	1.93	1.06	27
.455	.414	.1707	4.09	.823	5.46	2.41	1.05	31

[a] Calculated using CuG_2 calculated by assuming $K_2 = 2.65 \times 10^{-4}$.

HR^+ were assumed to be unity. To solve for the above 8 unknowns there are seven equations (1, 4, 7, 8, 9, 11) including the definition of pH. To obtain the eighth equation a value of K_1 was assumed and the equations solved. Then K_2 was calculated. By successive trials a value of K_1 was chosen so that K_2 would be constant for the series of runs. First a value of μ was selected using eq. 11 and then the concentration of cupric ion was calculated using eq. 1. $[H^+]$ and $[H_2R^+]$ were calculated using activity coefficients from eq. 1 and the pK_A of the amino acid (glycine[8] 2.350, alanine[9] 2.348). A value of K_1 was chosen and $[CuR^+]$ calculated. Using eq. 8 $[CuR_2]$ was evaluated. In the final calculations errors in pH measurement were smoothed out by using values from Fig. 1 for the total amount of hydrogen ion produced. The corrections involved are given in column 4 of Table II. With $[CuR_2]$ known, values of K_2 were calculated. The series of calculations was repeated until constant values of K_2 were obtained. Table III gives the concentrations of the ions and the equilibrium constants. Column 7 gives the concentration of $[CuHG^{++}]$ determined from eq. 7 after K_1 and K_2 were evaluated. The concentration equilibrium constant, K_α, for eq. 5 was calculated and appears in column 9 of Table III. $K\alpha$ should show little variation with ionic strength since the effect on Cu^{++} should be practically the same as the effect on $CuHR^{++}$. Equilibrium constants are not included for any case in which the concentration of complex ion falls much below $1 \times 10^{-3}M$.

Pedersen[6] has studied the equilibrium

$$Cu^{++} + Ac^- \rightleftarrows CuAc^+ \quad K_\beta = 146 \qquad (12)$$

The strength of monocarboxylic acids[10] may be calculated from the known constant of acetic acid by introducing corrections for each group replacing a hydrogen as in the equation

$$\log K = \log K_{HAc} + \frac{A\alpha\Sigma I\alpha^{i\alpha}}{1 + B|\Sigma I\alpha^{i\alpha}|} \qquad (13)$$

K is the dissociation constant of the substituted acid. A_α is a constant equal to 0.3. I is the inductive effect for each group replacing a hydrogen. α is the fractional decrease in the inductive effect for each transmission across an atom and is equal to 1/2.8. The number of atoms between the group added and the α carbon atom of the carboxylic acid is i_α. If the complex ion $CuHR^{++}$ involves a linkage between the carboxylate group and the cupric ion, K_α should be given by equation 13 by replacing K by $1/K_\alpha$, K_{HAc} by $1/K_\beta$, and including the inductive effect of the NH_3^+ group (12.3 for the + charge and 1.3 for the N atom). Solving the equation with the above substitutions gives $K_\alpha = 0.2$ which would indicate that the ion would be much less stable than the experimental value of 39 indicates. Thus the linkage is probably between cupric ion and the amine group rather than between cupric ion and the carboxylate group. Values of the concentration dissociation constant[11] for CuG_2 and CuA_2 have been reported. By using the second ionization constants of glycine[8] and alanine[9] (1.67×10^{-11} and 1.36×10^{-10}) and estimating the activity coefficients involved, values of K_2 (eq. 6) may be approximated. The values are 2.2×10^{-4} for glycine and 1.1×10^{-4} for alanine. The agreement is good considering the approximations

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[8] Owen, THIS JOURNAL, **56**, 24 (1934).

[9] Smith, Taylor and Smith, *J. Biol. Chem.*, **122**, 109 (1937).

[10] Branch and Calvin, "The Theory of Organic Chemistry," Prentice-Hall, New York, N. Y., 1941, p. 221.

[11] Keefer, THIS JOURNAL, **68**, 2329 (1946).

involved in estimating the activity coefficients.

Summary

The solubility of cupric iodate in glycine and in alanine solutions has been determined. The solubility results may be explained by assuming three complex ions, namely, $CuHR^{++}$, CuR^{+} and CuR_2. The equilibrium constants for the reaction of cupric ion and the amino acids to form the above complex ions have been evaluated.

DAVIS, CALIFORNIA RECEIVED JUNE 30, 1947

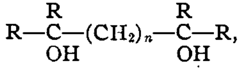
[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF EMORY UNIVERSITY]

A Study of Organic Parachors. IX. The Additive Nature of Structural Units in the Parachors of Ditertiary Glycols and Chlorides[1,2]

BY THOMAS P. JOHNSTON[3] AND OSBORNE R. QUAYLE

Parachor, first considered primarily an additive property, has been shown to be highly susceptible to minor differences in structure, as, for example, those existing between two isomeric tertiary alcohols. This sensitivity would at first seem to decrease its usefulness as a method of correlating the physical properties of organic compounds with their structure. If such differences are capable of evaluation, however, the parachor immediately becomes a more delicate tool. Results have been obtained with series of tertiary alcohols[4,5] and chlorides[6,7] evaluating the inherent constitutive variations so that the parachor of any tertiary alcohol or chloride having normal alkyl groups may be predicted with reasonable accuracy. These results have been published in the form of tables[5,7] from which reliable theoretical values for such types may be conveniently calculated. It is to be emphasized that the actual value of CH_2 in all cases is considered essentially a constant, 40.0,[8,9] and that constitutive variations are attributed to the alteration of valence forces around the tertiary carbon atom and the attached chlorine or hydroxyl.

The neglect of minor structural effects in the calculation of parachor values is a common cause of considerable deviation between theoretical and calculated values. If structural groups exhibiting constitutive variations can be evaluated, they should in turn be primarily additive in more complex molecules. To test this assumption the parachors of a number of symmetrical ditertiary glycols and chlorides were measured and compared with calculated theoretical values. Parachors for the structural units of each molecule, divided as nearly as possible at the center of symmetry, were calculated and added to obtain the theoretical parachor for the whole molecule. The validity of treating structural units of a complex molecule in an additive manner once the constitutive divergence has been evaluated is upheld by the experimental data presented in this paper.

Ditertiary glycols (Table I) of the general formula,  $R-\underset{OH}{\overset{R}{C}}-(CH_2)_n-\underset{OH}{\overset{R}{C}}-R$, in which R is methyl, ethyl and propyl and n is 2, 4, 7 and 8, were prepared by the standard method of adding the appropriate dibasic ester to the Grignard reagent.[10] The 2,10-, 3,11- and 4,13-diols have not been previously reported in the literature. The yield in the preparation of the 4,13-diol from dimethyl sebacate was least satisfactory; a yield of less than 5% of purified crystals was separated from the predominant viscous non-crystallizable oil. The Grignard addition complexes were hydrolyzed with either saturated aqueous ammonium chloride or cold dilute sulfuric acid, preferably the former. Toluene was the usual solvent for crystallization. These glycols are somewhat more stable than the simple tertiary alcohols in that they all withstand the temperature of boiling toluene and subjection to temperature up to 80° *in vacuo* and at least one, the 3,11-diol, may be distilled without decomposition at a relatively high temperature, about 140° at less than 1 mm. Parachors of only the lower melting glycols were measured, since solid compounds do not lend themselves to ready parachor measurement with the apparatus presently installed in this Laboratory.

The dichlorides (Table I) corresponding to the above ditertiary glycols were in general made by passing dry hydrogen chloride into an anhydrous ether solution of the glycol at a low temperature. A small amount of methanol was added to increase the solubility. After standing twenty-four hours the solvent was removed under reduced pressure

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(1) Presented in part before the Division of Organic Chemistry of the American Chemical Society at the Atlantic City meeting, April 17, 1947.

(2) The authors wish to express their gratitude to Prof. E. Emmet Reid, research consultant to the department, for his continued interest in the problem and for his several suggestions.

(3) From material to be presented by Thomas P. Johnston to the graduate faculty of Emory University in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(4) Owen, Quayle and Beavers, THIS JOURNAL, **61**, 900 (1939).

(5) Quayle and Smart, *ibid.*, **66**, 935 (1944).

(6) Quayle, Owen and Beavers, *ibid.*, **61**, 3107 (1939).

(7) Smart and Quayle, *ibid.*, **67**, 21 (1945).

(8) Mumford and Phillips, *J. Chem. Soc.*, 2112 (1929).

(9) Quayle, Day and Brown, THIS JOURNAL, **66**, 938 (1944).

(10) The glycol in which R is propyl and *n* is 7 was not isolated; the only attempt to prepare it from dimethyl azelate gave a non-crystallizable oil.