Cation Complexes of Compounds Containing Carbon–Carbon Double Bonds. III. Cuprous Chloride Complexes of Some Unsaturated Acids[1]

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It has previously been established[2] that cuprous chloride dissolves in aqueous allyl alcohol solutions to form the organo-metallic complexes

$$CH_2=CH-CH_2OH \cdot CuCl \text{ and } CH_2=CH-CH_2OH \cdot Cu^+$$
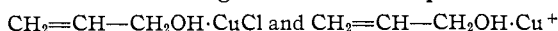
In the preceding paper[3] of this series data concerning the solubility of cuprous chloride in aqueous maleic acid solutions have been interpreted on the assumption that four such complexes ($H_2M \cdot Cu^+$, $H_2M \cdot CuCl$, $HM \cdot CuCl^-$ and $HM \cdot Cu$) are formed.

Further solubility measurements are in progress in this Laboratory to determine the effects of changing the nature of substituents at the carbon–carbon double bond on the tendency for reaction with cuprous chloride. In the present study, which has been concerned with complex formation with certain unsaturated acids, data for fumaric acid have been obtained which illustrate that previous conclusions[4] as to its reaction with cuprous chloride are subject to certain modifications.

Experimental

The Unsaturated Acids.—Crotonic acid obtained from Eastman Kodak Co. was recrystallized from water, m. p. 71.5–72.0°. Samples of fumaric acid prepared as described previously[4] were used. Itaconic, m. p. 163–165°, citraconic, m. p. 87–89°, and mesaconic acids, m. p. 202.5–204.5°, were prepared from citric acid.[5] Tiglic acid furnished through the courtesy of Prof. W. G. Young was recrystallized from water, m. p. 64–65°. Vinylacetic acid, b. p. 60–61° (6 mm.), was prepared from Eastman Kodak Co. vinylacetonitrile.[6] β,β-Dimethylacrylic acid, m. p. 65–67°, was prepared from mesityl oxide[7] supplied through the courtesy of Shell Chemical Corp.

The Solubility Measurements.—Solutions of known concentration of the organic acids in dilute perchloric or hydrochloric acid solutions of ionic strength 0.10 were prepared and were saturated with cuprous chloride at 25°. The detailed method for preparation and analysis of these solutions for cuprous content has been described previously.[2b,3,4] The aqueous solutions

of all the complexes were colorless except those of fumaric, citraconic and mesaconic acids which were yellow (cf. maleic acid[3,4]).

Results

The solubility of cuprous chloride in aqueous solutions of unsaturated acids is given in column 5 of Table I. Since the acids used are weak ($K_a = 10^{-3}$ or less) and the hydrogen ion concentration was fixed at 0.10, the ionization of the acid is small and the concentration of the negative ion or reactions involving the negative ion may be neglected as shown in a previous communication.[4] From Table I it is evident that, at constant concentration of unsaturated acid, the solubility of cuprous chloride decreases as the chloride ion concentration increases although an increase might be expected due to formation of $CuCl_2^-$. The following equations may be shown to account for the solubility of cuprous chloride in the experiments reported in this communication.

$$CuCl = Cu^+ + Cl^- \qquad \text{S. P.} = 1.85 \times 10^{-7} \quad (1)$$

$$Cu^+ + 2Cl^- = CuCl_2^-$$
$$K_2 = (CuCl_2^-)/(Cu^+)(Cl^-)^2 = 3.51 \times 10^5 \quad (2)$$

$$Cu^+ + Un = Un \cdot Cu^+$$
$$K_3 = (Un \cdot Cu^+)/(Un)(Cu^+) \quad (3)$$

$$Cu^+ + Cl^- + Un = Un \cdot CuCl$$
$$K_4 = (Un \cdot CuCl)/(Un)(Cu^+)(Cl^-) \quad (4)$$

The unsaturated acid has been designated as Un and the complexes formed as $Un \cdot Cu^+$ and $Un \cdot CuCl$. Table II gives the unsaturated acids investigated and the values of K_3 and K_4 obtained. In order to calculate K_3 and K_4 the following relations were used

$$(Cu^+_T) = (Cu^+) + (CuCl_2^-) + (Un \cdot Cu^+) + (Un \cdot CuCl) \quad (5)$$
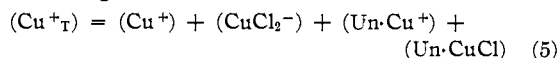
where (Cu^+_T) is the concentration of soluble cuprous species

$$(Cu^+_T) + (Cl^-_i) = 2(CuCl_2^-) + (Un \cdot CuCl) + (Cl^-) \quad (6)$$

where (Cl^-_i) is the concentration of chloride ion in the solution before addition of cuprous chloride and

$$(Un_i) = (Un) + (Un \cdot Cu^+) + (Un \cdot CuCl) \quad (7)$$

where (Un_i) is the concentration of unsaturated acid in solution before addition of cuprous chloride. The method by which K_3 and K_4 were evaluated has been described previously.[2b] To show the adequacy of these constants in explaining the experimental results, values of Cu^+_T were calculated using these constants and are tabulated in column 6 of Table I. It may be

(1) Presented before the Division of Physical and Inorganic Chemistry of the American Chemical Society, Portland, Oregon, Sept., 1948.

(2) (a) Kepner and Andrews, J. Org. Chem., **13**, 208 (1948); (b) Keefer and Andrews, THIS JOURNAL, **71**, 1723 (1949).

(3) Andrews and Keefer, ibid., **71**, 2379 (1949).

(4) Andrews and Keefer, ibid., **70**, 3261 (1948).

(5) Shriner, Ford and Roll, "Organic Syntheses," **11**, 28, 70. 74 (1931).
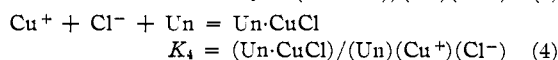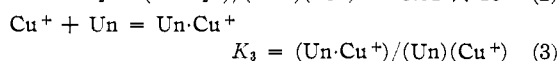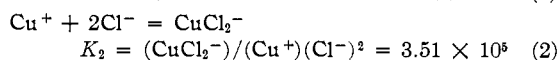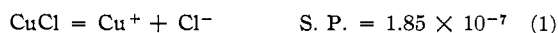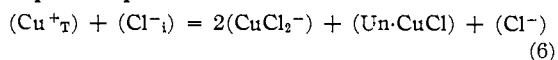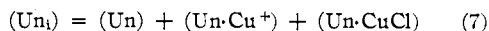
(6) Rietz, ibid., **24**, 96 (1944).

(7) Smith, Prichard and Spillane, ibid., **23**, 27 (1943).

TABLE I
THE SOLUBILITY OF CUPROUS CHLORIDE IN AQUEOUS SOLUTIONS OF UNSATURATED ACIDS AT 25°[a]

(Un_i), mole/ liter	(Cl_i^-), mole/ liter	$(Un\cdot CuCl)$, mole/ liter $\times 10^3$	$(Un\cdot Cu^+)$, mole/ liter $\times 10^3$	(Cu^+_T), mole/liter $\times 10^3$ Meas.	Calcd.
Crotonic Acid					
0.401	0	6.5	10.8	17.2	17.9
.316	0	5.1	9.6	15.2	15.3
.238	0	3.8	8.4	13.1	12.6
.158	0	2.5	6.8	9.7	9.7
.356	0.0938	5.9	1.1	13.0	12.9
.267	.0938	4.5	0.8	11.3	11.1
.178	.0938	3.0	0.6	9.6	9.4
Fumaric Acid					
0.0465	0	3.4	7.9	11.6	11.7
.0399	0	2.9	7.3	9.7	10.7
.0232	0	1.6	5.4	7.2	7.3
.0465	0.0938	4.0	0.1	10.3	9.9
.0399	.0938	3.5	.1	9.0	9.3
.0234	.0938	2.0	.1	8.0	7.8
.0363	.0100	2.8	3.7	7.6	7.3
.0272	.0100	2.1	3.1	6.0	6.0
.0182	.0100	1.4	2.1	4.7	4.3
Vinylacetic Acid					
0.0930	0	14.6	19.7	35.0	35.5
.0465	0	6.7	13.4	20.5	20.9
.0233	0	2.9	8.9	12.3	12.4
.0116	0	1.2	5.7	7.4	7.3
.0930	0.100	17.6	4.5	28.8	28.5
.0465	.100	8.8	2.3	17.5	17.3
.0930	.010	15.4	16.0	32.1	33.0
.0233	.010	3.5	5.8	10.4	10.3
Itaconic Acid					
0.202	0	6.0	9.1	15.0	15.6
.101	0	2.9	6.3	9.9	9.6
.0504	0	1.4	4.5	6.1	6.2
.202	0.100	6.2	0.8	13.0	13.2
.151	.100	4.6	.6	11.5	11.4
.101	.100	3.1	.4	9.8	9.7
.202	.010	6.1	5.4	11.8	12.4
.101	.010	3.0	3.2	7.4	7.1
Tiglic Acid					
0.094	0	0.9	2.0	3.1	3.0
.082	0	.8	1.8	2.6	2.7
.094	0.100	.9	0.0	7.0	7.0
.082	.100	.8	0.0	6.7	6.9
.094	.010	.9	0.4	2.2	1.9
β,β-Dimethylacrylic Acid					
0.136	0	1.1	1.7	2.9	2.9
.136	0.100	1.1	0.0	7.1	7.2
.136	.100	1.1	0.0	7.0	7.2
.136	.010	1.1	0.3	2.0	2.0
Mesaconic Acid					
0.151	0	1.0	3.4	4.5	4.6
.113	0	0.7	3.1	4.1	4.0
.076	0	0.5	2.4	3.0	3.0
.151	0.094	1.0	0.1	6.8	6.8
.113	.094	0.8	0.1	6.6	6.6
Citraconic Acid					
0.345	0	1.5	1.2	2.8	2.8
.459	0.100	2.0	0.0	8.1	8.1

[a] In all cases μ is approximately 0.10.

TABLE II
SUMMARY OF EQUILIBRIUM CONSTANTS FOR THE FORMATION OF $Un\cdot CuCl$ AND $Un\cdot Cu^+$ (25°)

Acid	Formula	K_3 $\times 10^{-2}$	K_4 $\times 10^{-4}$	K_3/K_4 $\times 10^2$
Vinylacetic	$CH_2{=}CH{-}CH_2{-}CO_2H$	340	135	2.5
Fumaric	HO_2C H, C=C, H CO_2H	92	51	1.8
Itaconic	$CH_2{=}C{-}CO_2H$ / $CH_2{-}CO_2H$	22	17	1.3
Maleic (Ref. 3)	HO_2C CO_2H, C=C, H H	11.3	9.7	1.2
Crotonic	CH_3 H, C=C, H CO_2H	16	9.2	1.7
Tiglic	CH_3 CH_3, C=C, H CO_2H	2.1	5.4	0.39
β,β-Dimethylacrylic	CH_3 ⟩C=CH—CO_2H, CH_3	1.1	4.3	.26
Mesaconic	CH_3 CO_2H, C=C, HO_2C H	4.1	3.7	1.1
Citraconic	CH_3 H, C=C, HO_2C CO_2H	0.22	2.3	0.1

seen that the agreement between measured values and calculated values is good.

In cases where only a few measurements are reported work was limited by the solubility of the acid.

The values of K_3 and K_4 may be used to calculate the equilibrium constant for the dissociation of chloride ion from $Un\cdot CuCl$

$$Un\cdot CuCl = Un\cdot Cu^+ + Cl^-$$
$$K_3/K_4 = (Un\cdot Cu^+)(Cl^-)/(Un\cdot CuCl) \quad (8)$$

The values of K_3/K_4 are given in Table II. It is interesting to note that the value of K_3/K_4 for vinylacetic acid is nearly the same as that obtained for allyl alcohol[2b] (2.4×10^{-2}).

The Influence of Structure on the Stability of the Complexes.—It has been postulated previously[2b,3,4] that the following resonance formulas may be used to represent the cupronium chloride (I) and cupronium ion (II).[8,9] One might anticipate that R groups which promote high electron

(8) This nomenclature is consistent with that used for olefin-positive bromine and olefin-mercuric ion complexes. (a) Winstein and Lucas, THIS JOURNAL, **61**, 2845 (1939); (b) Lucas, Hepner and Winstein, ibid., **61**, 3102 (1939).

(9) A less formalized structure in which copper is associated with the π electrons of the double bond might be used. See Price, "Reactions of Carbon-Carbon Double Bonds," Interscience Publishers Inc., New York, N. Y., 1946, p. 39.

$$R_2C=CR_2$$

I

II
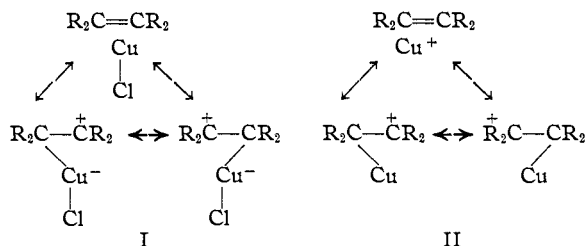
density at the double bond should enhance the stability of I and II. On the other hand large R groups may reduce complex stability through steric hindrance to the approach of copper to the double bond. In any case since the copper–chlorine bond in I is further removed from the influence of R groups than is the copper–carbon bond it is not surprising that K_3 and K_4 show more variation with changing olefin structure than do K_3/K_4 values.

The availability of electrons at the double bond as influenced by the nature of R groups has been illustrated in terms of the rates at which halogen undergoes an electrophilic attack at the double bond in a variety of unsaturated acids.[10] It has been observed that β,β-dimethylacrylic acid chlorinates more rapidly in acetic acid than does crotonic acid. Citraconic and mesaconic acids brominate faster in aqueous acetic acid than do maleic and fumaric acids. That is, methyl substituents increase the electron density at the double bond. Carboxyl groups, however, reduce the rate of halogenation.[11]

From Table II it may be seen that replacement of hydrogen atoms attached to a double bond by either methyl or carboxyl reduces the magnitude of K_3 and K_4. In other words, it appears that stability of the cupronium complex must be more strongly influenced by steric than by electronic effects of R groups, as has been suggested previously in connection with platinum[12] and silver[13] complexes.

(10) Morton and Robertson, J. Chem. Soc., 129 (1945).
(11) Ingold and Ingold, ibid., 2345 (1931).
(12) Anderson, ibid., 1042 (1936).
(13) Winstein and Lucas, This Journal, 60, 836 (1938).

It has been postulated that cis–trans isomerization of maleic acid or its diethyl ester by acidic or Friedel–Crafts catalysts may proceed through formation of an intermediate in which the catalyst is coördinated with the carbonyl oxygen atoms.[14,15] Since maleic acid is not isomerized under the present experimental conditions, such a structure does not seem appropriate for the cuprous complexes of the unsaturated dicarboxylic acids.

The fact cannot be disregarded, however, that the complexes of maleic, fumaric, citraconic and mesaconic acids are yellow while those of the monocarboxylic acids are colorless. This suggests that these dicarboxylic acid complexes contain a bond type which is lacking in the monocarboxylic acid derivatives. For example, fumaric acid cupronium ion may actually best be represented as a chelate structure (III). Such a structure should not necessarily facilitate cis–trans isomerization.

III
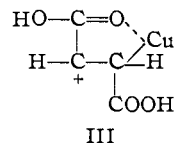
Summary

Measurements of the solubility of cuprous chloride in aqueous solutions of a variety of unsaturated acids have been made. In most cases the results may be interpreted on the assumption that two soluble complexes Un·CuCl and Un·Cu$^+$ are formed. Equilibrium constants for formation of the cupronium complexes have been calculated. The stability of the copper–carbon bond appears to be dependent on steric influences of other groups attached to the double bond.

(14) Gilbert, Turkevich and Wallis, J. Org. Chem., 3, 611 (1939).
(15) Nozaki and Ogg, This Journal, 63, 2583 (1941).