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COMPLEX FORMATION BETWEEN ALLYL ALCOHOL AND CUPROUS CHLORIDE

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The tendency for certain olefins to form coordination complexes with cuprous salts has been amply demonstrated. In the cases of butadiene, isoprene, and piperylene the formulas of the complexes with cuprous chloride have actually been established as diene·2CuCl (1, 2).

Cuprous chloride is known to promote the conversion of allyl alcohol to allyl chloride in concentrated hydrochloric acid solution (3, 4). The catalytic effect of $CuCl_2^-$ in promoting the hydrolysis of allyl chloride and other allylic halides has also been described (5, 6). It has been presumed that the catalytic effect of cuprous salts in these reactions results from the formation of complexes with the allylic compounds (6, 7).

With these facts in mind an investigation of the tendency for complex formation between cuprous chloride or $CuCl_2^-$ with allyl alcohol in aqueous solution has been undertaken. It has been demonstrated that an equilibrium exists between the alcohol, the cuprous salts and $CH_2{=}CHCH_2OH \cdot CuCl$.

Qualitative experiment showed that cuprous chloride is soluble in allyl alcohol to a considerable extent. The resulting solution is water-soluble but when treated with ether or carbon tetrachloride reprecipitates cuprous chloride. These observations suggested that a water-soluble olefin-cuprous complex had formed.

A procedure similar to that used for studying complex formation between olefins and silver ion (8) was adopted for investigating the reaction between allyl alcohol and $CuCl_2^-$. In experiments in which allyl alcohol was distributed between carbon tetrachloride and aqueous solutions of hydrochloric acid containing dissolved cuprous chloride it was observed that the total olefin content of the aqueous layer increased with increasing concentration of cuprous salts. From two series of runs (at 1.1 and 2.2 *M* hydrochloric acid concentration in the aqueous layer) data were obtained and interpreted on the assumption that the equilibrium (I) was established in the aqueous phase.

(I) $CH_2{=}CHCH_2OH + CuCl_2^- \rightarrow CH_2{=}CH{-}CH_2OH \cdot CuCl + Cl^-$

Equilibrium constants, K_I, for this reaction were calculated from the expressions

$$K_I = \frac{(A_w - A')(Cl^-)}{(A')(CuCl_2^-)} = \frac{(A_w - A')(Cl^-)}{(A')\dfrac{(Cu_t - A_w + A')}{1 + K_c(Cl^-)}}$$

in which

A' = K_0A_0 = the concentration of uncomplexed allyl alcohol in the aqueous phase in moles per liter

K_0 = the distribution coefficient of allyl alcohol between carbon tetrachloride and aqueous hydrochloric acid

A_c = the concentration of allyl alcohol in the carbon tetrachloride phase in moles per liter
A_w = the total allyl alcohol concentration in the aqueous phase in moles per liter
Cu_t = the original cuprous salt concentration in the aqueous phase in moles per liter
$K_c = \frac{(CuCl_3^=)}{(CuCl_2^-)(Cl^-)} = 0.31$

Since hydrochloric acid solutions of cuprous chloride contain $CuCl_3^=$ in addition to $CuCl_2^-$, the term K_c is introduced to determine the $CuCl_2^-$ concentration at equilibrium. The value for K_c was calculated from the known constants K_a and K_b (9, 10).

$$CuCl + Cl^- \rightarrow CuCl_2^- \quad K_a = 6.5 \times 10^{-2}$$

$$CuCl + 2\,Cl^- \rightarrow CuCl_3^= \quad K_b = 2.0 \times 10^{-2}$$

TABLE I

DISTRIBUTION RATIO OF ALLYL ALCOHOL BETWEEN CARBON TETRACHLORIDE AND AQUEOUS SOLUTIONS AT 25°

ELECTROLYTE IN AQUEOUS PHASE	MAGNITUDE OF A_0 MOLE/LITER	K_0
1.14 *M* HCl	0.01–0.035	14.8
2.28 *M* HCl	.01	14.2
none	.01	15.9
0.10 *M* NaCl 2.28 *M* HCl	.01	13.9

Values of K_0, the distribution coefficient of allyl alcohol between carbon tetrachloride and aqueous hydrochloric acid at 25°, are listed in Table I. The coefficient obtained for the run in which sodium chloride was added to the aqueous layer demonstrates the salting out of allyl alcohol from the aqueous phase by other than a cuprous halide.

The equilibrium data for the distribution experiments in the presence of dissolved cuprous chloride are listed in Table II. In actual practice the hydrochloric acid concentrations in the aqueous phase, neglecting the dissolved cuprous salt, were 1.14 *M* or 2.28 *M*. To account for the consumption of chloride ion in forming complexes with cuprous chloride the values 1.1 *M* or 2.2 *M* were used as close approximations for chloride ion concentration in calculating K_I values.

The several K_I values obtained are in reasonable agreement with each other. Since the approximations as to chloride ion concentration and the assumptions that the activity coefficients of anions are all unity are undoubtedly in error, the expected accuracy of K_I values is not too great. Other errors result from the limited accuracy of K_a and K_b values and from inclusion of traces of oxygen in the reaction vessel.

As a check on the validity of the assumption that the distribution data could be explained on the basis of formation of $CH_2{=}CHCH_2OH \cdot CuCl$, a series of solubility measurements of solid cuprous chloride in aqueous allyl alcohol solutions was made. The solutions were analyzed for cuprous compounds after the solid and liquid phases had reached equilibrium. Equilibrium constants for reaction (II) were calculated.

TABLE II

Distribution of Allyl Alcohol between Carbon Tetrachloride and Aqueous Hydrochloric Acid Solutions of Cuprous Chloride at 25°

A_c mole/liter	A_w mole/liter	Cu_t mole/liter	K_I
$(Cl^-) = 1.1\ M$			
0.01056	0.1814	0.0411	15.1
.01040	.1830	.0460	16.3
.00966	.1904	.0788	15.5
.01014	.1856	.0627	12.8
.00936	.1934	.0929	15.3
.01364	.2654	.0893	17.9
Av.			15.5
$(Cl^-) = 2.2\ M$			
.01088	.1846	.0797	15.0
.01086	.1848	.0736	17.3
.01142	.1792	.0402	17.1
.01022	.1912	.1093	18.7
Av.			17.0

$$\text{(II)}\ CH_2{=}CHCH_2OH + CuCl \rightarrow CH_2{=}CH{-}CH_2OH \cdot CuCl$$

from the expression

$$K_{II} = \frac{(Cu^+)}{(A - Cu^+)}$$

in which

Cu^+ = concentration of soluble cuprous compounds in moles per liter

A = original allyl alcohol concentration of aqueous solution in moles per liter

All determined cuprous concentrations were corrected on the basis of blank runs on the solubility of cuprous chloride in the alcohol free solvent.

Three series of solubility measurements were made. In the first series using neutral aqueous solutions of allyl alcohol considerable hydrolysis of cuprous chloride occurred as evidenced by development of a brick red color in the solid phase. In the other two series, run in solutions originally 0.01 *M* with respect to hydrochloric acid, no hydrolysis was observed. The data for the several runs are summarized in Table III. The small amount of $CuCl_2^-$ introduced in the acidic media should be insufficient to affect the results within the limits of error. The discrepancy in values for K_{II} in Series II and Series I and III may result from errors in determining the solubility of cuprous chloride in the solvent. The agreement between the three series is reasonably good and indicates that the solubility expression II holds over a wide range of alcohol concentrations.

TABLE III

Solubility of Cuprous Chloride in Aqueous Allyl Alcohol Solutions at 25°

A MOLE/LITER	Cu^+ FOUND MOLE/LITER	Cu^+ CORRECTED MOLE/LITER	K_{II}
SERIES I (HCl) ORIG. = 0.000 *M*			
0.0145	0.00778	0.00540	(0.59)
.0290	.0137	.0113	.64
.0580	.0256	.0232	.67
.0724	.0300	.0276	.62
.1086	.0459	.0435	.67
.0000	.00238	—	—
Av.			0.65
SERIES II (HCl) ORIG. = 0.0094 *M*			
0.0132	0.00782	0.00684	(1.07)
.0264	.0125	.0115	0.77
.0527	.0246	.0236	.81
.0658	.0298	.0288	.78
.0986	.0438	.0428	.77
.0000	.00098	—	—
Av.			0.78
SERIES III (HCl) ORIG. = 0.0094 *M*			
0.9923	0.406	0.404	0.69
.5954	.234	.232	.64
.3969	.153	.151	.61
.0000	.0022	—	—
Av.			0.65

Choosing 0.7 as an average value for K_{II} one can calculate the value for K_I by use of the data of Noyes and Chow (9).

$$K_I = \frac{K_{II}}{K_a} = \frac{0.7}{0.065} = 11$$

This figure checks those obtained from the distribution experiments reasonably well considering the limitations of the methods as previously mentioned.

Inconclusive evidence was obtained for the formation of $2CH_2{=}CHCH_2OH \cdot CuCl$. It was noted in a few distribution runs in which A′ values ranged as high as 0.4–0.6 *M* that slightly more alcohol appeared to be complexed in the aqueous layer than there were moles of cuprous ion in solution. A similar observation was made in a series of runs in which the chloride ion concentration of the aqueous phase was varied and the ionic strength maintained constant throughout the series by using varying amounts of potassium chloride and potassium nitrate. At high nitrate ion concentration the amount of complexed alcohol again exceeded the total moles of cuprous compounds in solution. No satisfactory quantitative treatment for these results has been found. The possibility of higher complex formation of this type does not seem too remote in view of the evidence existing for the formation of $2CH_2{=}CHCH_2OH \cdot Ag^+$ (8).

The possibility that some $CH_2{=}CHCH_2OH \cdot CuCl_2^-$ might have formed in the distribution runs was considered. No positive evidence for its existence was found. Attempts to discover this complex by the series of experiments run at varying chloride ion concentrations as noted above were unsuccessful.

EXPERIMENTAL

Cuprous chloride. This material was prepared in 5-g. batches according to the procedure of Keller and Wycoff (11). Each batch was stored in a tightly stoppered container and used within two days after preparation.

Allyl alcohol. A sample of Paragon Testing Laboratories allyl alcohol was fractionated through a silvered vacuum jacketed, 1.5 x 120 cm. glass helix (3 mm. turns) packed column and a cut collected at 97.1°/761 mm.

Carbon tetrachloride. C. P. carbon tetrachloride was fractionated through the column described above and material boiling at 76.0°/761 mm. collected.

Solubility of cuprous chloride in pure allyl alcohol. One gram of cuprous chloride was almost completely dissolved in twenty ml. of allyl alcohol by a few minutes shaking at room temperature. The clear brown solution was decanted and investigated as follows: One sample was diluted with water to give a colorless solution. This aqueous solution after treatment with ammonium hydroxide slowly developed the color of cupric ammonia complex ion. Other samples of the allyl alcohol solution of cuprous chloride were treated with ether and with carbon tetrachloride. In both cases cuprous chloride was precipitated. This was verified by analyzing a portion of this precipitate which had been washed thoroughly with ether. A weighed sample was dissolved in hydrochloric acid and analyzed volumetrically for cuprous content in the usual manner.

Anal. Calc'd for CuCl: Cu, 64.2. Found: Cu, 62.7.

Absolute ethanol gave no evidence of acting as a solvent for cuprous chloride.

Distribution experiments. Solutions of allyl alcohol in carbon tetrachloride were brought to 25° in a constant temperature bath and standardized against bromide-bromate solution by the following modification of the procedure of Francis (12): A sample of the bromide-bromate solution (0.05 *M* available bromine) was pipetted into 25 ml. of water in a glass-stoppered Erlenmeyer flask; the flask was flushed with nitrogen and a 5-ml. sample of the allyl alcohol solution to be analyzed was introduced. Ten ml. of 6 *N* sulfuric acid was added and the tightly stoppered flask shaken mechanically for five minutes. One gram of potassium iodide was then added and the liberated iodine titrated with 0.025 *N* sodium thiosulfate solution.

One hundred-ml. samples of the standardized carbon tetrachloride solutions were placed in a standard taper three-neck flask equipped with a mercury sealed stirrer and a device for flushing the system with nitrogen. The flask was immersed in a constant temperature bath at 25°. A sample of cuprous chloride was weighed into a nitrogen filled volumetric flask and dissolved by the addition of a measured volume of concentrated hydrochloric acid of known concentration. The volumetric flask was filled to the mark with freshly-boiled distilled water, (cooled to 25°) and a 10-ml. sample of this solution was immediately added to the three-neck flask against a counter current stream of nitrogen. The nitrogen stream was discontinued. The flask was closed to the atmosphere and the contents stirred vigorously for forty-five minutes. After a ten-minute interval to allow phase separation, samples of the carbon tetrachloride layer were removed for allyl alcohol analysis by the bromide-bromate procedure. Owing to the small volume of the aqueous phase, the allyl alcohol content of this layer was calculated from the initial and final concentrations of allyl alcohol in the carbon tetrachloride phase. No cuprous salts appeared to accumulate in the carbon tetrachloride layer, as shown by the complete lack of any blue copper ammonia complex formation on shaking this phase with concentrated ammonium hydroxide.

Samples of the aqueous cuprous solution were also taken immediately after its preparation for volumetric determination of the cuprous content according to the procedure of Hatch and Estes (6). It was found that the volumetric analyses agreed to within 1–1.5% of those calculated from the weight of cuprous chloride used.

Solubility of cuprous chloride in aqueous solutions of allyl alcohol. Solutions of allyl alcohol in freshly boiled distilled water were prepared and standardized by the bromide-bromate procedure. In some cases the solutions also contained dilute hydrochloric acid. To 50 ml. of each solution in a nitrogen filled glass-stoppered Erlenmeyer flask was added excess (0.5–2.5 g.) cuprous chloride. The flasks were tightly sealed and shaken mechanically for four hours at 25°. Preliminary experiments indicated that equilibrium was established after about two hours of shaking. The excess solid cuprous chloride was allowed to settle, and samples of the aqueous solution were carefully removed under a nitrogen atmosphere and analyzed immediately for cuprous content.

SUMMARY

Evidence based on distribution experiments and solubility measurements supports the conclusion that in aqueous solution allyl alcohol forms a complex of the type $CH_2{=}CHCH_2OH \cdot CuCl$ on treatment with cuprous chloride or $CuCl_2^-$. Equilibrium data for the complex formation are presented.

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