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Crystalline Complex of Allyl Alcohol with Copper(I) Chloride

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A colorless crystalline complex of allyl alcohol with copper(I) chloride, $(CH_2{=}CHCH_2OH)$-CuCl, was synthesized at room temperature in a vacuum system. A similar complex with calcium chloride was also prepared for the sake of comparison. The equilibrium vapor pressure of the copper(I) chloride complex was determined at vairous temperatures, and $\Delta H = -12.0$ kcal/mol was obtained as the heat of formation from solid copper(I) chloride and gaseous allyl alcohol. The C=C stretching frequency of allyl alcohol is shifted by 95 cm^{-1} to the lower frequency side by ligation to copper(I). The C–O stretching band shows a very minor shift of 15 cm^{-1}. This value is almost the same as in the calcium chloride complex. Thus, in the copper(I) chloride complex, allyl alcohol coordinates to the metal mainly through the double bond, but the OH group also participates in the coordination. By measuring the decrease in vapor pressure, copper(I) chloride was found to exist as a dimer in allyl alcohol at 23—43°C, but as a monomer at 97°C.

The reaction of allyl alcohol with hydrogen chloride gas to produce allyl chloride is very much enhanced by the addition of copper(I) chloride, although it does not proceed appreciably in the absence of a catalyst.[1] The reverse reaction, *i. e.*, the acid hydrolysis of allyl chloride, is also catalyzed by copper(I) chloride;[2] the formation of the addition compound of $CuCl_2^-$ with allyl chloride was assumed to precede the rate-determining step.[3] The formation of a complex between copper(I) and allyl alcohol was also assumed to explain the solubility of copper(I) chloride in an aqueous allyl alcohol solution.[4] The formation constants of CuCl(alc) and $Cu(alc)^+$ have been reported to be 2.2×10^6 and 5.2×10^4 respectively;[5] the latter value was reconfirmed recently by a polarographic study.[6]

However, no crystalline complex of copper(I) chloride with allyl alcohol has yet been isolated, possibly because of the high decomposition pressure of the compound. We previously reported the preparation of a crystalline complex of copper(I) chloride with acrolein in a vacuum system[7]; we have now applied the same technique to the preparation of the copper(I) chloride - allyl alcohol complex.

Experimental

Materials. Copper(I) chloride was prepared by reducing a copper(II) sulfate solution containing sodium chloride with sulfur dioxide; the product was then purified by sublimation *in vacuo* at around 400°C. Calcium chloride dihydrate (extra pure grade), supplied by Kishida Chemicals & Co., was used without further treatment. Allyl alcohol was purchased from Wako Pure Chemical Industry, Ltd., and was purified by fractional distillation through a 30-cm Widmer column after having been dried with molecular sieves, Type 3A (Linde Co.); it was then stored over the molecular sieves. In each experiment a freshly-distilled sample was used.

Synthesis of the Allyl Alcohol-Copper(I) Chloride Complex. The complex was synthesized in an evacuated ampoule system identical with that described previously.[7] Copper(I) chloride was dissolved in allyl alcohol to a concentration of about 1.5 mol/*l*. The solution was colorless and transparent. The excess alcohol was distilled into another, empty ampoule between 5°C and 0°C different in temperature. When the crystallization was difficult, however, the complex solution became supersaturated and very viscous, and sometimes it took a very long time, for instance, more than 100 hr, to remove the excess solvent completely. Crystals of the allyl alcohol complex of copper(I) chloride thus obtained were colorless and transparent, but crystals synthesized with an undistilled sample of copper(I) chloride were pale brown in color.

Synthesis of the Allyl Alcohol - Calcium Chloride Complex. Calcium chloride dihydrate was kept at 250°C *in vacuo* for more than 3 hr until no water vapor was detected in the vacuum line by means of a discharge test in a Geisller tube. Allyl alcohol was then distilled into the ampoule containing anhydrous calcium chloride. The complex was dried by distilling the excess solvent into another vessel between 20°C and 0°C different in temperature. First colorless and transparent crystals appeared; they might be $CaCl_2(C_3H_6O)_n$ $(n>2)$, but

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1) A. Dewael, *Bull. Soc. Chim. Belg.*, **39**, 40 (1930); *Chem. Abstr.*, **24**, 2717 (1930).

2) L. F. Hatch and R. R. Estes, *J. Am. Chem. Soc.*, **67**, 1730 (1945).

3) L. F. Hatch and G. B. Roberts, *ibid.*, **68**, 1196 (1946).

4) R. E. Kepner and L. J. Andrews, *J. Org. Chem.*, **13**, 208 (1948); R. M. Keefer and L. J. Andrews, *J. Am. Chem. Soc.*, **71**, 1723 (1949).

5) R. M. Keefer, L. J. Andrews and R. E. Kepner, *ibid.*, **71**, 3906 (1949).

6) S. E. Manahan, *Inorg. Chem.*, **5**, 482 (1966).

7) S. Kawaguchi and T. Ogura, *ibid.*, **5**, 844 (1966).

they were not investigated further.[8] By prolonged drying a more stable species was obtained as a white fine powder, the properties of which were investigated in detail.

Analysis of the Complexes. The copper(I) chloride complex was decomposed at 50°C *in vacuo*, and the volatile species was collected in an ampoule kept at −78°C. In the case of the calcium chloride complex, a higher temperature of about 250°C was needed to complete the decomposition. The volatile decomposition product was identified as allyl alcohol by means of the IR assay in another experiment. The quantity of allyl alcohol collected was determined by brominating with the bromide-bromate reagent and then titrating the excess bromine iodometrically. The nonvolatile material left in the initial ampoule was essentially copper(I) chloride or calcium chloride. Copper(I) chloride was analyzed according to the method reported in a previous paper.[7] The calcium ion was determined gravimetrically as the oxalate monohydrate, and the chloride ion, as silver chloride.

Found: Cu, 40.0; Cl, 22.4; C_3H_6O, 37.1%. Calcd for $CuCl(C_3H_6O)$: Cu, 40.4; Cl, 22.6; C_3H_6O, 37.0%.

Found: Ca, 17.9; Cl, 31.0; C_3H_6O, 50.4%. Calcd for $CaCl_2(C_3H_6O)_2$: Ca, 17.7; Cl, 31.2; C_3H_6O, 51.1%.

Vapor Pressure Measurement. The dried pure crystalline compound was prepared in an ampoule connected with a U-type mercury manometer. Equilibrium vapor pressure values were measured at various temperatures by keeping the sample tube in appropriate thermostat baths.

Molecular Weight Measurement. The allyl alcohol - copper(I) chloride complex is not so stable as to permit the determination of molecular weight in another solvent, and so the state of the aggregation of copper(I) chloride in allyl alcohol was studied. To determine the relatively small value of the decrease in vapor pressure, allyl alcohol itself was used as the manometer liquid. The apparatus employed is shown in Fig. 1. Pure copper(I) chloride was placed into the vessel, A. Allyl alcohol was distilled into both ampoules, A and B, *via* the vacuum line, and then the apparatus was sealed off at D. The U-type manometer, C, was cooled with dry ice, and then an adequate amount of alcohol was collected from A and B. The whole system was then kept in a thermostat bath, and the difference between the equilibrium vapor pressures of the solvent in B and of the solution in A was measured with the manometer, C.

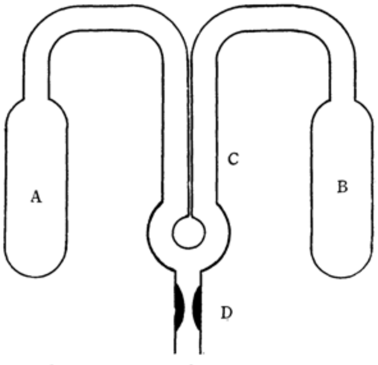

Fig. 1. The apparatus for the measurement of vapor pressure depression.

The validity of this method of vapor pressure measurement was checked by another experiment. A, B and C were charged with pure allyl alcohol. The part including A and C was kept in a thermostat at 25°C, while the B ampoule was held at temperatures 0.1—0.5°C lower. In each case the manometer reading coincided, within an error of 5%, with the difference in vapor pressures calculated according to Eq. (3).

The elevation of the boiling point was also measured by method identical with that of Cottrell[9] except for the necessary modification of the apparatus to exclude air.

Infrared Spectra. The crystalline specimen was mixed with Nujol and ground down quickly, whereupon its absorption spectrum was measured with a Hitachi Infrared Spectrophotometer, EPI-2. No absorption bands due to free allyl alcohol were detected, indicating that no serious decomposition of the complex had occurred in such a process.

Results and Discussion

The Vapor Pressure of the Copper(I) Chloride Complex. The equilibrium vapor pressure of the heterogeneous reaction system,

$$CuCl(s) + CH_2{=}CHCH_2OH(g) \rightleftarrows CuCl(CH_2{=}CHCH_2OH)(s), \qquad (1)$$

was measured at several temperatures. The results obtained are listed in Table 1 and are reproduced by Eq. (2),

$$\log P \text{ (mmHg)} = -2.631\times10^3/T + 9.065, \qquad (2)$$

which was derived by the least-squares method. The vapor pressure of allyl alcohol was determined by the same apparatus. The results in Table 1 are reproduced by Eq. (3),

$$\log P \text{ (mmHg)} = -2.217\times10^3/T + 7.871, \qquad (3)$$

which is in good agreement with the data in the literature.[10]

The enthalpy of formation of the copper(I) chloride complex in Eq. (1) was calculated to be −12.0 kcal/mol from Eq. (2). By employing the ΔH_{vap} value of 10.1 kcal/mol obtained from Eq. (3) for the heat of vaporization of allyl alcohol, the heat of formation of the complex from solid copper(I) chloride and liquid allyl alcohol was calculated as $\Delta H = -1.9$ kcal/mol.

Infrared Spectra. The frequencies of the main infrared absorption bands of free allyl alcohol and its copper(I) chloride and calcium chloride complexes are listed in Table 2. The absorption bands of coordinated allyl alcohol closely resemble

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[8] For instance, $CaCl_2(C_3H_7OH)_3$ was reported in the following paper: E. Lloyd, C. B. Brown, D. G. R. Bonnell and W. J. Jones, *J. Chem. Soc.*, **1928**, 658.

[9] F. G. Cottrell, *J. Am. Chem. Soc.*, **41**, 721 (1919).

[10] D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

TABLE 1. THE VAPOR PRESSURE DATA OF ALLYL ALCOHOL AND ITS COPPER(I) CHLORIDE COMPLEX AT SEVERAL TEMPERATURES

t, °C	11.4	20.1	30.0	40.1	50.0
P, mmHg ($CuCl\cdot C_3H_6O$)	5.63	10.89	29.99	46.97	86.02
P, mmHg (C_3H_6O)	9.93	18.28	33.23	59.89	100.99

TABLE 2. INFRARED ABSORPTION BANDS OF ALLYL ALCOHOL AND ITS COPPER(I) CHLORIDE AND CALCIUM CHLORIDE COMPLEXES (IN NUJOL)

Allyl alcohol	$CuCl(C_3H_6O)$	$CaCl_2(C_3H_6O)_2$	Assignment
3340 vs, br	3340 vs, br	3320 vs, br	ν(OH)
3080 w	3070 w	3080 w	ν_{as}(vinyl CH)
3010 w	3000 w	3010 w	ν(CH)
2990 w	2980 w	2970 w	ν_s(vinyl CH)
1645 w	1550 w	1645 w	ν(C=C)
		1615 w	
1425 m	1420 m	1425 m	δ(vinyl CH)
1235 w	1255 w	1235 w	
	1230 w		
1115 m	1107 m	1105 m	
1030 s	1015 s	1015 s	ν(CO)
995 s	995 s	995 s	δ(vinyl CH)
920 s	925 m	925 s	δ(vinyl CH)

those of the free ligand, except for the C=C and C–O stretching bands. This suggests that the molecular structure of the bound alcohol is not seriously deformed by ligation in these complexes.

The C=C stretching band of the copper(I) chloride complex, however, shifts by 95 cm^{-1} to the lower frequency side. This lowering nearly coincides with the value of 90 cm^{-1} observed in the case of the acrolein complex of copper(I) chloride.7) The C=C band remains unchanged in the calcium chloride complex, but a new band appears at 1615 cm^{-1}. This could be identified as a C=C stretching band, but it is not clear whether the shift is to be attributed to the symmetry alteration or to the coordination of the double bond.

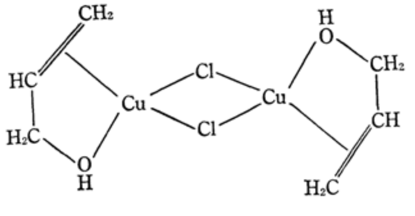
The C–O stretching band shows a shift of 15 cm^{-1} to the lower frequency side in either complex. In the calcium chloride complex, the alcohol must be coordinated to the metal mainly through oxygen, resulting in a lowering of the bond order of the C–O linkage. The fact that the copper(I) chloride complex also shows the same amount of the shifting of C–O stretching band indicates that the oxygen atom of the alcohol has an interaction with copper(I) similar to that with calcium. Thus, allyl alcohol may here be assumed to act as a bidentate ligand in the copper(I) chloride complex.

TABLE 3. MOLECULAR WEIGHT OF COPPER(I) CHLORIDE IN THE ALLYL ALCOHOL SOLUTION

Concn. of CuCl wt%	Temp. °C	Relative lowering of vapor pressure, %	Molecular weight*
5.329	23.8	1.87	171
3.469	23.8	1.04	198
1.540	24.2	0.438	206
0.4268	43.3	0.142	175

* Calcd for CuCl : 98.99

Molecular Weight of Copper(I) Chloride in Allyl Alcohol. As has been described in the Experimental Section, the molecular weight of copper(I) chloride in the allyl alcohol solution was determined by means of a U-type allyl alcohol manometer. The results are shown in Table 3. The observed values of the molecular weight of copper(I) chloride in the concentration region of 0.04—0.5 M are rather divergent, but they all lie in the vicinity of 198, the calculated value as a dimer. The number of the coordinated alcohol molecule can not, however, be obtained by this method. If allyl alcohol is still functioning as a bidentate ligand in the solution, the copper(I) complex may assume the following tetrahedral dimeric configuration I:



If they are extrapolated to the higher temperature region, the two straight lines of the log P *vs.* $1/T$ plot according to Eqs. (2) and (3) intersect with each other at a point corresponding to 73°C. This suggests that the vapor pressure of the copper(I) chloride complex is larger than that of the free ligand at temperatures higher than 73°C, and that the complex can not exist there.

When a copper(I) chloride solution in allyl alcohol, say 2 mol/*l*, is heated, some copper(I) chloride suddenly deposits around 70°C. The decrease in solubility at higher temperatures suggests a change in the state of copper(I) chloride in allyl alcohol, that is, decomposition of the dimeric complex **I**. In fact the ebulliometric measurement in allyl alcohol indicated that copper(I) chloride exists as a monomer at 97°C. Copper(I) must be weakly surrounded by more than one allyl alcohol molecules. The equilibrium between the monomer and the dimer of copper(I) chloride has not been measured.