compounds generate the aquo complexes, which in turn can probably be substituted with appropriate ligands by anation. We are investigating the extent to which other diamines and triamines will form chromium(IV) diperoxo compounds and the products that form on addition of these to acids.

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Crystalline Complex of Acrolein with Copper(I) Chloride

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Yellow crystalline complex of acrolein with copper(I) chloride, $(CH_2CHCHO)CuCl$, was synthesized through the direct reaction of acrolein with copper(I) chloride at room temperature in a vacuum system. The equilibrium vapor pressure data at various temperatures and the electronic and infrared absorption spectra were determined. The frequency of C=C stretching is shifted about 90 cm^{-1} to the lower frequency side by the ligation, but that of the C=O stretching shows only a small decrease, indicating that acrolein coordinates to copper(I) mainly with the double bond.

Introduction

Acrolein seems to be a very interesting substrate in catalytic reactions since the molecule is composed of two reactive parts, formyl and vinyl groups. With the object of searching for fundamental aspects concerning the prospective homogeneous catalytic reactions, we are trying to synthesize the acrolein complexes of various metals.

Schrauzer[1] obtained bis(acrolein)nickel(0), $(C_3H_4O)_2Ni$, by the reaction of acrolein with nickel carbonyl. Acroleiniron(0) tetracarbonyl,[2] $(C_3H_4O)Fe(CO)_4$, and bis(acrolein)molybdenum(0) dicarbonyl,[3] $(C_3H_4O)_2Mo(CO)_2$, have also been synthesized by the reactions of acrolein with diiron enneacarbonyl and tris(acetonitrile)molybdenum(0) tricarbonyl, respectively. This paper reports the preparation of copper(I) chloride complex of acrolein by the direct combination of both components. The reduction of copper(II) in the presence of appropriate ligands is frequently effective in preparing copper(I) complexes, and Haight, *et al.*,[4] obtained crystalline copper(I) complexes of various cyclic olefins by this means. In the present case, acrolein can dissolve copper(I) chloride and reacts easily, depositing a crystalline compound. The yellow solution is very sensitive to air, and the whole procedure of synthesis was performed in a vacuum system.

Experimental Section

Starting Materials.—Copper(I) chloride was prepared by reducing copper(II) sulfate solution containing sodium chloride with sulfur dioxide. The fine, white, crystalline product thus obtained was filtered, then washed with water containing sulfur dioxide and with acetic acid without exposing to air. Copper(I) chloride was dried and kept *in vacuo*. The specimen for the spectroscopic study was specially purified by the distillation *in vacuo*.

Acrolein was purchased from Wakamatsu Chemicals Co. and purified by the fractional distillation through a 30-cm Widmer column after drying with Molecular Sieves, Type 3A, Linde Co. In each experiment the freshly distilled sample was used.

Synthesis of Acrolein–Copper(I) Chloride Complex.—The ampoule system employed for the synthesis and analysis of the complex is illustrated in Figure 1. A freshly distilled sample of acrolein was charged in ampoule C, deaerated completely, and distilled into ampoule B containing copper(I) chloride. The apparatus was sealed off at E from the vacuum line. Acrolein readily reacts with copper(I) chloride forming yellow crystals, which dissolve in acrolein itself (to about 10^{-2} *M*) yielding a yellow solution. The yellow solid might contain unreacted copper(I) chloride as the nucleus. To obtain a pure product, the yellow solution was passed through a glass filter D into an empty ampoule A. The solvent was distilled back to B by keeping A at 10° and B at 0°. The saturated solution was again transferred into A, and the solvent was distilled back to B. This procedure was repeated until the desired amount of crystalline product was accumulated in A. Finally, the solvent acrolein was distilled from B into A to wash the solid product, and the solution was transferred back to B through D. The solid complex was then kept at 5° and the ampoule B at 0° for more than 30 hr. As will be shown by the vapor pressure data, the complex can be dried safely without any accompanying decomposition at this temperature difference.

Analysis of the Complex.—The crystalline complex, which had been prepared and dried in ampoule A as described in the preceding section, was kept at 0°, and the empty vessel A′ was cooled to −78° after ampoule B was sealed off at F. The complex was decomposed at this temperature difference, and finally A was heated up to 50° to make sure of the complete decomposition. The volatile material gathered in the cold vessel A′ was identified as acrolein by means of the infrared assay in another experiment. After ampoule A′ was sealed off and weighed, the quantity of acrolein was determined by brominating with the bromide–bromate reagent and then titrating the excess bromine iodometrically.[5] Nonvolatile copper(I) chloride left in ampoule A was added with aqueous ammonia after weighing the sealed vessel. After copper (I) was oxidized completely to copper (II),

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[1] G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5310 (1959); **82**, 1008 (1960); *Chem. Ber.*, **94**, 642 (1961).

[2] E. Weiss, K. Stark, J. E. Lancaster, and H. D. Murdoch, *Helv. Chim. Acta*, **46**, 288 (1963).

[3] D. P. Tate, A. A. Buss, J. M. Augl, B. L. Ross, J. G. Grasselli, W. M. Ritchey, and F. J. Knoll, *Inorg. Chem.*, **4**, 1323 (1965).

[4] H. L. Haight, J. R. Doyle, N. C. Baenziger, and G. F. Richards, *ibid.*, **2**, 1301 (1963).

[5] C. W. Smith, Ed., "Acrolein," John Wiley and Sons, Inc., New York, N. Y., 1962, p 244.

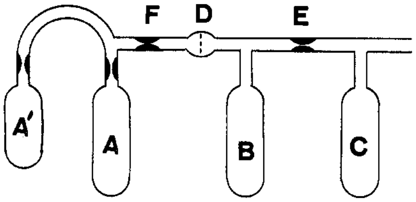

Figure 1.—The ampoule system for the synthesis and analysis of the complex.

the solution was added with a small amount of sodium hydroxide and heated to repel ammonia. Copper(II) oxide precipitated was submitted to the electrolytic analysis of copper. Chloride ion in the filtrate was determined gravimetrically as silver chloride. The total amount of complex analyzed was calculated as the sum of weights of the solid in ampoule A and the liquid in A'.

Anal. Calcd for $CuCl(C_3H_4O)$: Cu, 41.0; Cl, 22.9; C_3H_4O, 36.1. Found: Cu, 39.9; Cl, 22.7; C_3H_4O, 35.8.

Vapor Pressure Measurement.—A U-type mercury manometer was equipped in place of ampoule A' in Figure 1. The dried pure crystalline compound was prepared in A. Equilibrium vapor pressure values were measured at various temperatures by keeping vessel A in appropriate thermostat baths.

Absorption Spectra.—Electronic spectra of the complex were measured in acrolein and aqueous solutions by means of a Hitachi spectrophotometer, Model EPS-2. The desired solution was prepared *in vacuo* and was allowed to flow into a quartz cell 1 cm in width, which was then sealed off. Reflection spectra of the crystalline complex were observed with a Hitachi Perkin-Elmer spectrophotometer, Model 139.

Infrared Spectra.—A Hitachi infrared spectrophotometer, EPI-2, was used. The acrolein complex decomposes in the open atmosphere on account of its high vapor pressure. The crystalline specimen was mixed with Nujol and ground down quickly. After a spectrum was recorded, the specimen was kept standing for about 20 min, and then another scanning was performed. The change in the absorption curve discriminates the true absorption bands because of the complex among other bands of the decomposition product (acrolein).

Magnetic Measurement.—The diamagnetism of the complex was observed by the Gouy method.

Results and Discussion

The copper(I) chloride complex of acrolein is obtained easily by the direct reaction of the two components in a vacuum system. The crystalline complex is remarkably stable *in vacuo* and shows no change although it has been kept more than 1 year at room temperature. Acrolein itself is very reactive and polymerizes easily. Even after it was distilled into a carefully cleaned vessel *in vacuo*, acrolein becomes turbid by the polymer deposition in several days at 0°. However, if a small amount of copper(I) chloride is dissolved in it, acrolein is surprisingly stabilized. The copper(I) chloride complex is an excellent stabilizer for acrolein far better than hydroquinone and other conventional stabilizers. It may serve as a scavenger for oxygen and other radicals.

The Vapor Pressure.—The composition of the complex was ascertained to be one to one for copper(I) chloride and acrolein by the elemental analysis as shown in the Experimental Section. The vapor pressure of the complex, *i.e.*, the equilibrium pressure of the heterogeneous reaction

$$CuCl(s) + CH_2CHCHO(g) \longrightarrow CuCl(CH_2CHCHO)(s) \quad (1)$$

was measured at several temperatures. The results are shown in Table I and represented by

$$\log P(\text{mm}) = 10.8751 - 2.570 \times 10^3/T \quad (2)$$

The enthalpy of formation of the compound according to eq 1 was thus calculated to be −11.76 kcal/mole.

TABLE I

THE VAPOR PRESSURE DATA OF CRYSTALLINE COPPER(I) CHLORIDE COMPLEX OF ACROLEIN AT SEVERAL TEMPERATURES

T, °C	−20.1	−15.0	−10.5	0.0	5.4	13.4
P, mm	5.21	8.17	12.03	29.16	44.46	83.57

The vapor pressure of acrolein itself, which had been purified by the formation and decomposition of the copper(I) chloride complex, was also determined and found to obey the equation

$$\log P(\text{mm}) = 8.012 - 1.668 \times 10^3/T \quad (3)$$

These values are slightly higher than the literature data,[6] but the heat of vaporization calculated from eq 3, $\Delta H_{\text{vap}} = 7.63$ kcal/mole, almost coincides with the value, 7.61 kcal/mole, which is obtained as ΔH_{vap} at 0° from the Antoine equation[6] (t is in degrees centigrade)

$$\log P(\text{mm}) = 7.22570 - 1262.635/(t + 237.912) \quad (4)$$

Thus, we obtain $\Delta H = -4.13$ kcal/mole as the heat of formation of the complex from solid copper(I) chloride and liquid acrolein.

By equating (2) and (3) we can see that the vapor pressure of the complex becomes equal to that of acrolein at 41.9°. This suggests that the copper(I) chloride–acrolein complex cannot exist above this temperature. In fact, the complex breaks down to the white powder of copper(I) chloride when heated to more than 40° in a sealed tube.

In preparing the pure crystalline complex, excess acrolein was driven off by keeping the product at 5° and another vessel at 0°. The vapor pressure of acrolein is 100 and 80 mm, respectively, at these temperatures, while that of the complex is 40 mm at 5°. Therefore, excess liquid is distilled off completely from the complex, but the latter does not decompose at all under these circumstances.

Electronic Spectra.—The absorption spectrum was examined in the range of wavelength from 350 through 900 mμ, and only one sharp band at 396 mμ (ϵ 160) was observed (Figure 2). The assignment of this absorption band is not certain. The absorption maximum of acrolein itself is observed at 320 mμ ($\epsilon \approx 10$) in an aqueous solution and at 340 mμ in hexane; this band is attributed to the $n \rightarrow \pi^*$ transition.[7] (Thus, the absorption spectrum of the complex in the wavelength region shorter than 350 mμ cannot be observed in acrolein as a solvent.)

Solid copper(I) chloride shows a strong absorption peak at 387 mμ, but this is characteristic only of the

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(6) See ref 5, p 13.

(7) K. Inuzuka, *Bull. Chem. Soc. Japan*, **33**, 678 (1960).

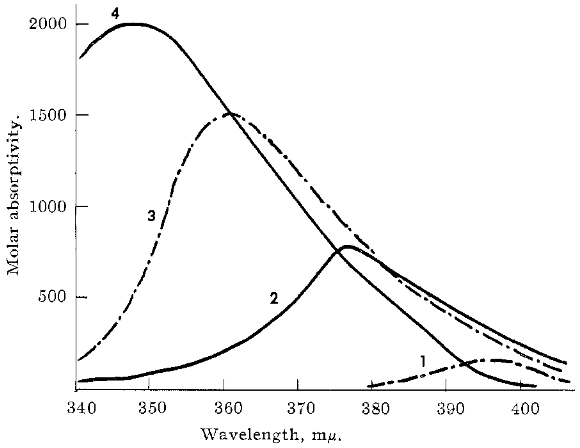

Figure 2.—The absorption spectra of the copper(I) chloride–acrolein–water system. The weight per cent of acrolein is 0.59 (curve 1), 2.3 (curve 2), 13.9 (curve 3), and 18.2 (curve 4), respectively.

crystalline state[8] and disappears when copper(I) chloride is dissolved in water containing the chloride anion or ammonia. For instance, copper(I) chloride solution containing the chloride ion exhibits an absorption maximum at 272 mμ (ε 4300) as the lowest frequency band.[9] The 396-mμ band of the complex solution in acrolein might be due to the charge-transfer type of transition.[10]

Copper(I) chloride dissolves in water containing acrolein resulting in a yellow solution. The absorption spectra of this system were measured and are presented in Table II and Figure 2. It should be noticed that, as the concentration of acrolein decreases, the absorption maximum shifts to shorter wavelength and the extinction coefficient becomes larger. This interesting behavior of the copper(I) chloride–acrolein–water system cannot be well explained at present, and further study is awaited.

TABLE II
THE ABSORPTION SPECTRAL DATA OF THE COPPER(I) CHLORIDE—ACROLEIN—WATER SYSTEM

Acrolein, wt %	Mole ratio of acrolein to CuCl	Abs max, mμ	Apparent ϵ_{max}
100		396	160
18.2	4.12×10^3	376	790
13.9	3.14×10^3	374	860
4.4	1.0×10^3	365	1100
2.3	5.2×10^2	360	1500
0.59	1.3×10^2	347	2000

The reflection spectrum of the crystalline complex was also examined. Solid copper(I) chloride shows a reflection maximum at 385 mμ (log R_d = 0.87) and the complex at 410 mμ (log R_d = 1.01).

Infrared Spectra.—The infrared spectrum of the complex in Nujol was observed clearly in the region of 800 to 2500 cm^{-1}, but a good spectrum was not obtained for the high-frequency region beyond 2500 cm^{-1}. This may be due to the fact that the fine powder specimen was not prepared by the quick grinding of the complex in Nujol. Frequencies of principal bands and their assignments are listed in Table III. The assignments of infrared absorption bands of acrolein have been reported by several authors,[7,11–14] but the complete agreement has not yet been attained. In Table III we adopted the assignments by Brand and Williamson.[13] The descriptions in parentheses are due to Harris.[14]

TABLE III
INFRARED ABSORPTION DATA FOR FREE ACROLEIN AND ITS COPPER(I) CHLORIDE COMPLEX (NUJOL MULL)

Acrolein	Complex	Assignment
920 s	915 s	C—C stretching (CH_2 rocking)
975 s	960 s	CH_2 wagging
990 s	970 s	C=C torsion
1030 vw	1010 w	
1160 s	1150 s	CH_2 rocking (C—C stretching)
1275 m	1240 w	CH (vinyl) rocking
1365 s	1355 s	CH (formyl) rocking
1425 m	1430 m	CH_2 bending
1620 m	1530 s	C=C stretching
1700 vs	1665 vs	C=O stretching
	1685 vs	

The absorption bands of the coordinated acrolein resemble those of the free compound and shift a little to the lower frequency side in general. The most remarkable change is shown by the C=C stretching, which is shifted by 90 cm^{-1} to the lower frequency side by the ligation. This suggests that acrolein coordinates to copper mainly *via* the double bond. The torsion frequency of C=C also decreases by 20 cm^{-1} indicating the lowering of the bond order of the C=C linkage.

The C=O stretching band of acrolein vapor at 1700 cm^{-1} also shifts and splits to two peaks at 1665 and 1685 cm^{-1}. The C=O stretching band of the liquid ketone or aldehyde appears generally in the lower frequency side by 20 to 30 cm^{-1} than in the vapor state, and it further shifts by 20 to 40 cm^{-1} if the intramolecular hydrogen bonding exists. In the iron complex,[2] a strong band was observed at 1680 cm^{-1} which coincides with the pure liquid, suggesting little involvement of the aldehydic carbonyl in the complex formation. However, in nickel[1] and molybdenum[3] complexes, peaks at 1518 and 1550 cm^{-1} were assigned to the carbonyl stretching, and a strong participation of the carbonyl group was considered. In the present case the situation is similar as in the iron complex, and the participation of carbonyl group in the complex formation is considered to be minor even if it does exist. Further information concerning the structure of this diamagnetic copper(I) chloride–acrolein complex will be offered by the X-ray analysis now in progress.

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(9) H. Fromherz and W. Menschick, *Z. Physik. Chem.*, **B3**, 1 (1929).
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