BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 643—650 (1969)

The Etherification Reactions of Allyl Alcohol Catalyzed by the Copper(I) Chloride Complex[*1]

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(Received July 17, 1968)

Diallyl ether was produced exclusively when an allyl alcohol solution containing copper(I) chloride and ammonium chloride was heated in the absence of air. A mixture of allyl and ethyl alcohols gave diallyl and ethyl allyl ethers, but no trace of diethyl ether. The tracer experiment employing ^{18}O-enriched allyl alcohol showed that the C–O bond in allyl alcohol was ruptured in the ethyl allyl ether formation. The kinetic study of these etherification reactions showed that the rate determining step would include the nucleophilic attack of an allyl or ethyl alcohol molecule on the catalyst-substrate complex. A novel allyl alcohol complex, $(NH_4)_2Cu_2Cl_4(C_3H_6O)_2$, was isolated and characterized, but the active catalyst species was assumed to be $(NH_4)_2Cu_4Cl_6$. Methyl derivatives of allyl alcohol were also allowed to react in the presence of the same catalyst and the possible mechanism of etherification was discussed.

Copper(I) chloride was found by Berthelot[1] to enhance the solubilities of olefins such as ethylene and propylene in aqueous solutions. This fact suggests the specific interaction between copper(I) and the olefinic double bond. Gilliland *et al.*[2] succeeded later in synthesizing these complexes under pressure of olefins.

In our laboratory syntheses and reactions of metal complexes of substituted olefins have been studied, and crystalline complexes of copper(I) chloride with acrolein,[3] allyl alcohol[4] and allylamine[5] were prepared by direct reactions. This paper reports the catalytic action of copper(I) chloride complex for the etherification reactions of allyl alcohol, and a possible reaction mechanism is presented based on the kinetic and tracer experiments.

Experimental

Materials. Copper(II) chloride dihydrate was mixed with excess copper powder and heated to 110°C under reduced pressure. After the dehydration, the mixture was heated to 500°C resulting in liquid copper(I) chloride, which was cooled to room temperature. The crude product was crushed and purified by distillation at 500°C *in vacuo*. The highly pure specimens of copper(I) chloride for the kinetic experiments were prepared by distilling more than three times. Ammonium chloride of analytical grade was further purified by sublimation. Allyl alcohol was dried with molecular sieves, Type 3A (Linde Co.) and distilled through a 30 cm Widmer column. Commercial methylallyl alcohols were used

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[*1] Presented at the 17th Symposium on the Chemistry of Metal Coordination Compounds of the Chemical Society of Japan, Hiroshima, December, 1967.

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1) M. P. E. Berthelot, *Ann. chim. phys.*, **23**, 32 (1901).

2) E. R. Gilliland, J. E. Seebold, J. R. Fitz Hugh and P. S. Morgan, *J. Am. Chem. Soc.*, **61**, 1960 (1939); E. R. Gilliland, H. L. Bliss and C. E. Kip, *ibid.*, **63**, 2088 (1941).

3) S. Kawaguchi and T. Ogura, *Inorg. Chem.*, **5**, 844 (1966).

4) T. Ogura, N. Furuno and S. Kawaguchi, This Bulletin, **40**, 1171 (1967).

5) T. Ogura, T. Hamachi and S. Kawaguchi, *ibid.*, **41**, 892 (1968).

without further purification. Ethyl alcohol was dried employing magnesium ribbon.

Stoichiometry Determination of the Etherification Reactions. Into an ampoule containing 0.1—1 g of copper(I) chloride and 0.05—0.5 g of ammonium chloride was distilled 5 g of allyl alcohol or a mixture of allyl and ethyl alcohols *in vacuo*. The ampoule was sealed off, put into an autoclave together with water whose vapor pressure is very similar to that of allyl alcohol, and heated to 160—180°C.

Volatile reaction products were collected in a trap by vacuum distillation and separated by vapor phase chromatography (abbreviated as VPC) using a 1 m column packed with 30% triethanolamine on Chamelite CS of Kishida Chemicals, Ltd. (60°C, H_2 flow of 80 m*l*/min). The water content was determined by the Karl Fischer method.

Preparation and Reaction of Allyl Alcohol Enriched with ^{18}O. Twenty five grams of silver perchlorate was dissolved in 20 m*l* of ^{18}O-enriched (2%) water, to which 8 g of allyl chloride was added gradually under vigorous agitation in an ice bath. An exothermic reaction occurred separating out silver chloride. In order to neutralize perchloric acid produced, sodium hydrogen carbonate was added occasionally until yellow silver carbonate began to appear. The reaction mixture was kept standing for two days at room temperature. Volatile products were collected by distillation under reduced pressure and dried with anhydrous copper(II) sulfate. Allyl alcohol was separated from the by-product, diallyl ether, by means of VPC.

A mixture of labeled allyl alcohol (0.4 g), unlabeled ethyl alcohol (1.6 g), copper(I) chloride (0.05 g) and ammonium chloride (0.02 g) was allowed to react in an ampoule at 160—180°C. Calcium chloride was added to the product mixture to separate the ether layer. Ethyl allyl ether was fractionated through the VPC column and submitted to the mass spectrometric analysis.

Kinetic Studies. Since the reaction system containing copper(I) chloride is very sensitive to air, the whole procedure was performed under rigorous exclusion of air. A desired number of ampoules containing a reaction mixture of the same composition were prepared using the apparatus depicted in Fig. 1. The reaction mixture (30—40 m*l*) was made up by vacuum distillation of allyl alcohol into a large ampoule (A) containing a mixture of copper(I) chloride and ammonium chloride. The ampoule (A) was attached to the vacuum line in an inverse fashion. A small portion (about 2 m*l*) of the solution was transfered to each small ampoule (C) evacuated in advance through the tap (B). The ampoule (C) was then fused off at D. Many ampoules thus prepared were immersed in a liquid paraffin bath and maintained at a constant temperature between 120—180°C. Each ampoule was picked up at appropriate time intervals and quenched. The extent of reaction was determined by measuring the water content by means of the Karl Fischer method.

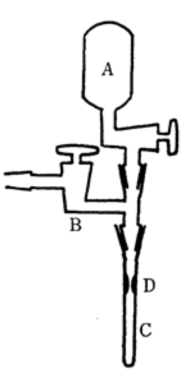

Fig. 1. The apparatus for preparing ampoules containing the reaction mixture of the same composition.

When a mixture of allyl and ethyl alcohols was allowed to react in the presence of copper(I) chloride and ammonium chloride, the produced ethers were separated through the VPC column. Diallyl and ethyl allyl ethers were identified, but no trace of diethyl ether was found. Preliminary calibration experiments revealed that the mole ratios of diallyl ether to allyl alcohol and ethyl allyl ether to ethyl alcohol in their mixture are proportional in the region below 0.05 to the respective peak height ratios on a vapor phase chromatogram (Fig. 2.) Many ampoules containing allyl and ethyl alcohols in various ratios together with copper(I) chloride and ammonium chloride were kept at a constant temperature of 148.1°C. The reaction was quenched at 0.01—2% conversion in either case, and amounts of diallyl and ethyl allyl ethers were determined by means of Fig. 2.

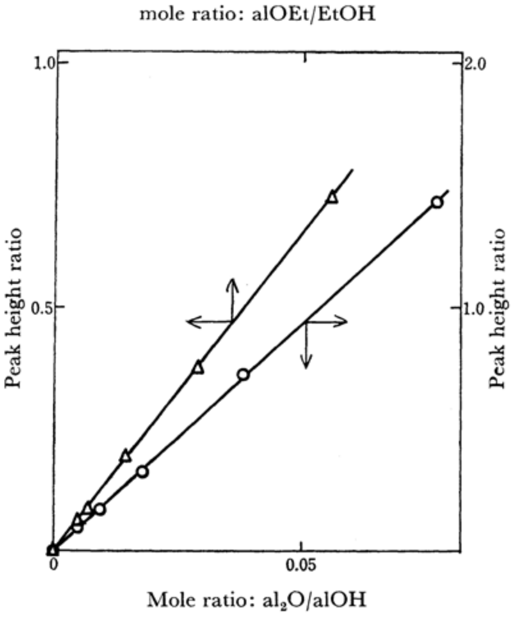

Fig. 2. Calibration lines between the mole ratio and the peak height ratio on a gas chromatogram of diallyl ether to allyl alcohol and ethyl allyl ether to ethyl alcohol.

Etherification of α-, β- and γ-Methylallyl Alcohols. To promote the elucidation of the reaction mechanism, the etherification reaction of substituted allyl alcohols were performed and the products distribution was measured in each case. In 3 m*l* of a methylallyl alcohol, 30 mg of copper(I) chloride and 10 mg of ammonium chloride were dissolved and allowed to react at 92°C for 2.5—16 hr to attain 1—7% conversion. Reaction products were fractionated through a VPC column containing polyethylene glycol (1 m) and triethanolamine (1 m) at 96°C using hydrogen gas flow of 40 m*l*/min. The nature of each fraction was identified by means of its infrared and proton magnetic resonance spectra. Table 1 summarizes reaction products from each methylallyl alcohol and their relative rates of formation.

TABLE 1. REACTION PRODUCTS FROM METHYL-SUBSTITUTED ALLYL ALCOHOLS IN THE PRESENCE OF COPPER(I) CHLORIDE CATALYST*

Substrate	Products	Relative rates of formation
α OH	γ OH	<0.1
	α_2O	1.2
	α O γ	1
β OH	β_2O	1
γ OH	α OH	1
	α O γ	1
	γ_2O	~ 0.03

* α, β and γ denote α-methylallyl (CH_2=CH–CH(CH_3)–), β-methylallyl (CH_2=C(CH_3)–CH_2–) and γ-methylallyl (CH(CH_3)=CH–CH_2–) radicals, raspectively.

Synthesis of the Crystalline Complex $(NH_4)_2Cu_2Cl_4(C_3H_6O)_2$. An allyl alcohol solution (30 m*l*) containing copper(I) chloride (0.531 g, 5.36 mmol) and ammonium chloride (0.287 g, 5.37 mmol) was heated at 80°C for 3 hr, and most of excess alcohol was distilled off. White crystals resulted were dried completely by distillation of the remaining solvent *in vacuo* at the temperature difference between 5 and 0°C for 3 days.

Found: Cu, 29.9; Cl, 33.4; C_3H_6O, 28.2%; Calcd for $(NH_4)_2Cu_2Cl_4(C_3H_6O)_2$: Cu, 30.1; Cl, 33.6; C_3H_6O, 27.6%.

Measurements. Copper was determined by the electrolysis, chloride gravimetrically as the silver salt, and allyl alcohol by the brominating method.[4] The infrared spectra were measured in Nujol with a Hitachi infrared spectrophotometer EPI-2, and NMR spectra with a 60 MC spectrophotometer, model JNM 3H60 of Japan Electron Optics Laboratory, Ltd. The mass analysis was performed with a Hitachi mass spectrometer RMU-6.

Results

The Stoichiometry of Diallyl Ether Formation. When allyl alcohol containing copper(I) chloride and ammonium chloride was heated for several hours at 160–180°C, the mixture separated into two liquid layers. The upper layer consisted of dially ether containing a small amount of copper(I) chloride, and the lower aqueous layer included copper(I) chloride, ammonium chloride and remaining allyl alcohol. In an experiment at 180°C for 24 hr, 93% of allyl alcohol employed (90.2 mmol) was converted to diallyl ether (42.1 mmol) and water (42.0 mmol), and no side reaction occurred. The mass balance can thus be represented by Eq. (1).

$$2CH_2{=}CH{-}CH_2OH \longrightarrow (CH_2{=}CH{-}CH_2)_2O + H_2O \qquad (1)$$

When allyl alcohol containing highly pure copper(I) chloride alone was heated under the same conditions, no allyl ether was produced. Ammonium chloride alone does not work either. The effective catalyst must be composed of copper(I) chloride and a certain amount of chloride ions since calcium chloride works as well as ammonium chloride and lithium chloride is also effective though to a lesser extent. Silver perchlorate and nitrate were examined. Diallyl ether was produced in these cases, too, but some side reactions also proceeded depositing metallic silver.

Kinetics of the Diallyl Ether Formation. With any catalyst composition a first order linear plot was obtained before the extent of reaction attained to 25% (Fig. 3). The reaction rate is thus represented by Eq. (2). At a higher extent of the reaction the mixture separated into two layers

$$\frac{d[H_2O]}{dt} = -\frac{1}{2}\frac{d[C_3H_5OH]}{dt} = k_1[C_3H_5OH] \quad (2)$$

and the first order rate law did not hold any more.

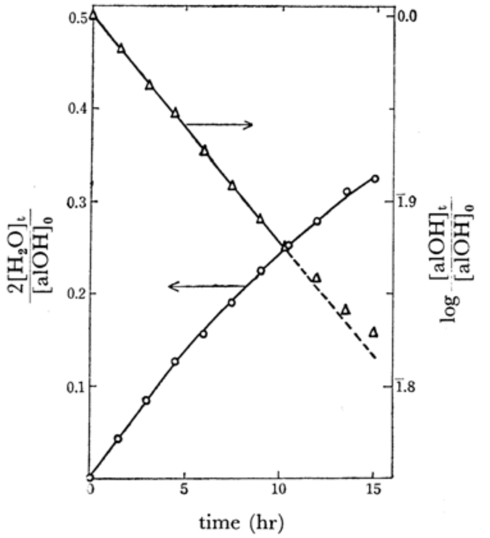

Fig. 3. The pseudo first order plot of the etherification reaction of allyl alcohol at 144.8°C. $[Cu_2Cl_2]_0=0.0630$, $[NH_4Cl]_0=0.0581$ mol/kg solvent

The pseudo first order rate constant k_1 changed with concentrations of both copper(I) chloride and ammonium chloride. When the concentration of ammonium chloride was kept constant and that of copper(I) chloride increased, the recation rate increased linearly as shown in Fig. 4. It should be noticed that the straight line intersects the abscissa. On the other hand the dependence of k_1 upon the concentration of ammonium chloride was rather complicated as illustrated in Fig. 5. A maximum appeared at a concentration of ammonium chloride about half that of copper(I) chloride in the monomer unit.

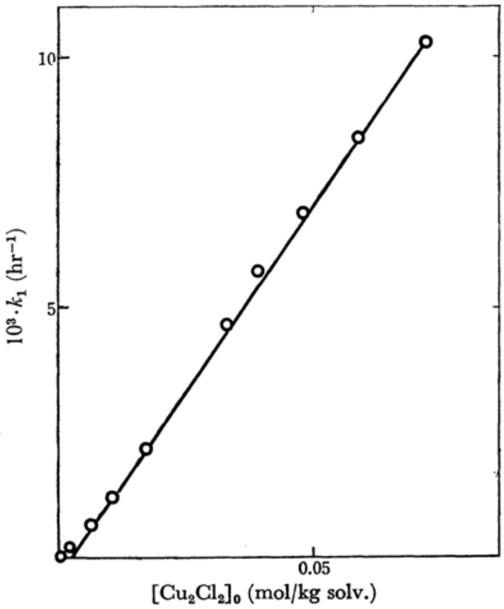

Fig. 4. Dependence of the pseudo first order rate constant (Eq. (1)) upon the concentration of copper(I) chloride at 148.6°C.
[NH_4Cl]$_0$=0.00916 mol/kg solvent

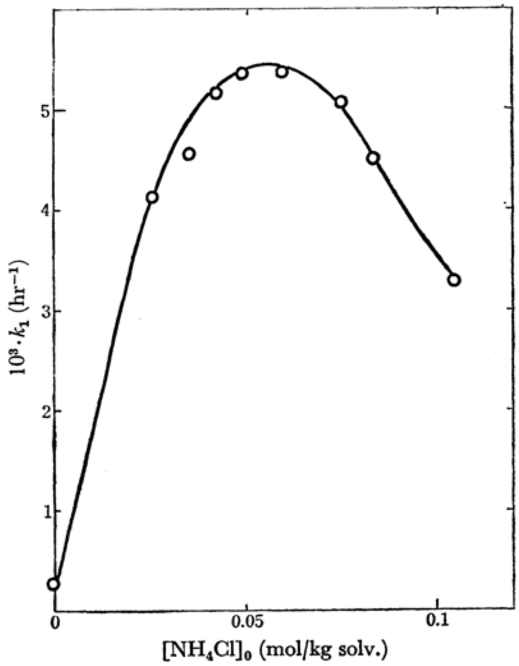

Fig. 5. Dependence of the pseudo first order rate constant (Eq. (1)) upon the concentration of ammonium chloride at 135.0°C.
[Cu_2Cl_2]$_0$=0.0546 mol/kg solvent

Adduct Formation of Copper(I) Chloride with Ammonium Chloride in Allyl Alcohol. The solubility of copper(I) chloride in water is very low, but is much enhanced by the coexistence of ammonium chloride and the formation of adducts, $CuCl \cdot NH_4Cl$ and $2CuCl \cdot NH_4Cl$ was reported.[6] On the other hand the solubility of ammonium chloride in allyl alcohol is very low (0.246 g in 100 g solvent at 20°C), but is enhanced by the presence of copper(I) chloride. For instance 0.685 g of ammonium chloride dissolves in 100 g of allyl alcohol at 10°C containing 1.26 g of copper(I) chloride. The mole ratio of the two solutes is close to unity suggesting the formation of 1 : 1 adduct in allyl alcohol.

The state of aggregation of copper(I) chloride by itself and also in the coexistence of ammonium chloride was investigated by measuring the boiling point elevation of allyl alcohol in nitrogen atmosphere with the modified Cotrell apparatus.[7] The molal elevation constant of boiling point of allyl alcohol was determined to be 1.615°C employing naphthalene as a reference solute. (Value of the constant calculated using 10.1 kcal/mol as the molar heat of vaporization[8] is 1.57°C.) Table 2 summarizes the results obtained. In each case the molality of solution found is nearly half of that employed, revealing that copper(I) chloride exists as a dimer in boiling allyl alcohol.[9] It should be noticed that

TABLE 2. DEGREE OF DIMERIZATION OF COPPER(I) CHLORIDE IN ALLYL ALCOHOL IN THE ABSENCE AND PRESENCE OF AMMONIUM CHLORIDE DETERMINED BY THE BOILING POINT ELEVATION

Molality employed $\times 10^3$		Molality found $\times 10^3$	Degree of dimerization
CuCl	NH_4Cl		
5.48	0	2.71	1.01
3.94	0	2.17	0.90
3.44	0	1.84	0.93
3.19	0	1.66	0.96
5.06	2.67	2.66	0.95
2.71	2.18	1.37	0.99
			Mean 0.96

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6) I. S. Morozov and G. V. Ustavschikova, *Bull. acad. sci. USSR, Classe sci. chim.*, **1944**, 451; *Chem. Abst.*, **39**, 3199 (1945).

7) F. G. Cotrell, *J. Am. Chem. Soc.*, **41**, 721 (1919).

8) D. R. Stull, *Ind. Eng. Chem.*, **39**, 517 (1947).

9) The report in a previous paper (Ref. 4) that copper(I) chloride exists as a monomer in boiling allyl alcohol was in error.

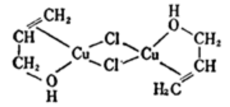
the degree of dimerization of copper(I) chloride is not affected by the presence of ammonium chloride up to the equimolar amount. This fact indicates that the equilibrium constant of the adduct formation (Eq. (3)) is very large and also that this adduct is not ionized appreciably in boiling allyl alcohol.

$$Cu_2Cl_2 \cdot xC_3H_6O + 2NH_4Cl \rightleftarrows (NH_4)_2Cu_2Cl_4 \cdot xC_3H_6O \qquad (3)$$

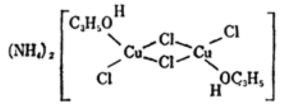
The crystalline adduct $(NH_4)_2Cu_2Cl_4 \cdot (C_3H_6O)_2$ was in fact isolated as described in the Experimental Section. The characteristic infrared absorption bands of this complex are listed in Table 3 together with those for dimeric copper(I) chloride complex with allyl alcohol.[4] In the latter complex coordination of the double bond of allyl alcohol is evidenced by the large shift of C=C stretching frequency to the lower frequency side. The coordination of OH group was also concluded by a slight shift of C–O stretching frequency in comparison with the allyl alcohol complex of calcium chloride,[4] and the dimeric structure of I was assigned to this complex. On the other hand the infrared absorption data in Table 3 indicate that in the present complex containing ammonium chloride, allyl alcohol is linked to copper as a unidentate ligand solely *via* the oxygen atom as shown by II.

Table 3. Characteristic infrared absorption bands in Nujol (cm^{-1})

$(NH_4)_2Cu_2Cl_4 \cdot (C_3H_6O)_2$	1630	1010	~3400	1700
$Cu_2Cl_2 \cdot (C_3H_6O)_2$	1550	1015	3340	—
C_3H_6O	1645	1030	3340	—
Assignment	ν(C=C)	ν(C–O)	ν(O–H)	$\delta(NH_4)$



I



II

In the aqueous solution of copper(I) chloride together with ammonium chloride, the water molecule may take the position of allyl alcohol, and the reported complex[10] $KCuCl_2 \cdot H_2O$ may be considered to have a dimeric structure like II.

Etherification Reactions in the Mixture of Allyl and Ethyl Alcohols. The rates of formation of diallyl and ethyl allyl ethers were calculated assuming the pseudo first order kinetics, and data thus obtained were plotted against each alcohol concentration. Straight lines were obtained as shown in Fig. 6 indicating that these reactions obey the following rate equations:

$$\frac{d[al_2O]}{dt} = k_1[alOH] = (k_a'[Cu_2Cl_2]_0[NH_4Cl]_0)\,[alOH] \qquad (4)$$

$$\frac{d[EtOal]}{dt} = k_2[EtOH] = (k_e'[Cu_2Cl_2]_0[NH_4Cl]_0)\,[EtOH] \qquad (5)$$

Here alOH denotes allyl alcohol. Figure 6 also indicates that the rate of formation of ethyl allyl ether is somewhat larger than that of diallyl ether: $k'_a = 17.9$, $k'_e = 29.2$ (kg·solvent)^2/mol^2·hr.

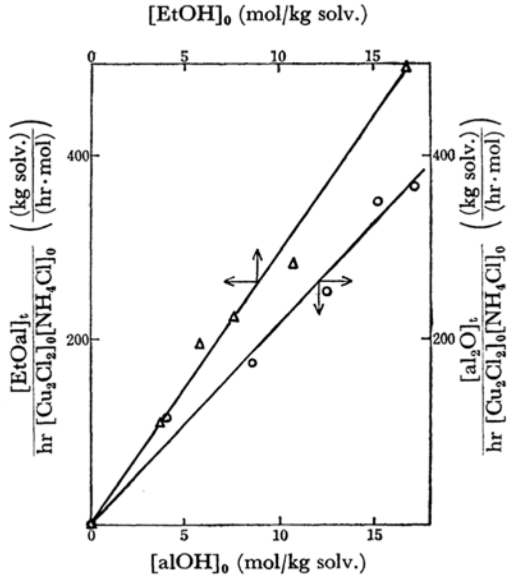


Fig. 6. Dependences of rates of diallyl and ethyl allyl ether formations upon the composition of mixtures of allyl and ethyl alcohols at 148.1°C.

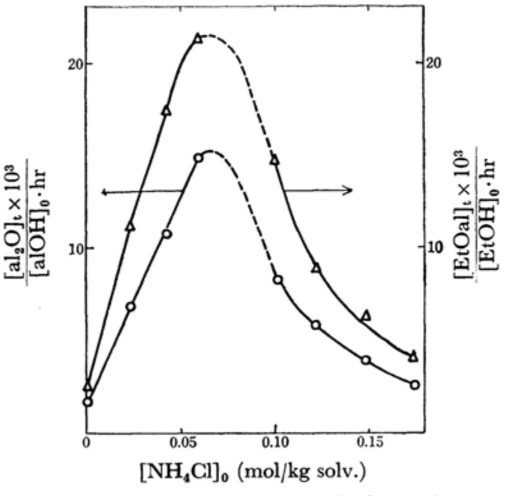


Fig. 7. Dependences of the pseudo first order rate constants of diallyl and ethyl allyl ether formations upon the concentration of ammonium chloride at 148.1°C.

$[Cu_2Cl_2]_0 = 0.0654$ mol/kg solvent

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[10] J. J. P. Valeton and W. Frömel, *Z. anorg. u. allg. Chem.*, **137**, 91 (1924).

Data plotted in Fig. 6 were obtained in the region of low concentrations of ammonium chloride, and Eqs. (4) and (5) hold only at these conditions. If the concentration of copper(I) chloride is kept constant and that of ammonium chloride is changed, the pseudo first order rate constants k_1 and k_2 change in the fashion shown in Fig. 7. Again, maximum rates are attained when the concentration of ammonium chloride is about half as large as that of copper(I) chloride in the monomer unit. These are the same features as that observed in the case of allyl alcohol alone (Fig. 5).

Tracer Experiments. In the etherification reaction between allyl and ethyl alcohols one molecule of water is eliminated. In order to elucidate the reaction mechanism, it is very important to find out from which alcohol the oxygen atom of water molecule originates. Allyl alcohol containing 1.83 atom % of ^{18}O was allowed to react with natural ethyl alcohol and ethyl allyl ether produced was submitted to the mass analysis. If the ether molecule has oxygen atom from allyl alcohol, the peak height ratio of mass 88 to mass 86 should be 18.8×10^{-3}. On the other hand if the oxygen atom in the ether molecule originated from ethyl alcohol, the ratio is expected to be 4.5×10^{-3}. Natural isotopic abundances of carbon, hydrogen and oxygen were taken into account in these calculations. Ethyl allyl ether produced in the reaction between natural allyl and ethyl alcohols showed the value of 4.4×10^{-3} as this ratio. The reaction product from the ^{18}O-enriched allyl alcohol and natural ethyl alcohol gave the ratio value of 4.6×10^{-3}, clearly indicating the following reaction.

$$C_3H_5{}^{18}OH + C_2H_5OH = C_3H_5OC_2H_5 + H_2{}^{18}O \quad (6)$$

Discussion

Effective Catalyst Species. It should be concluded that the complex I does not catalyze the reaction since highly pure copper(I) chloride alone was found to be ineffective. The points lying on the ordinates in Figs. 5 and 7 were brought about by copper(I) chloride which had been exposed to air for a while. Partial oxidation of copper(I) might have occurred resulting in a a mixture of copper(II) chloride and oxide playing a role of the chloride source. Figures 5 and 7 suggest that the most effective catalyst may have the composition of $Cu_2Cl_2 \cdot NH_4Cl$. In Fig. 5 an appreciable activity is observed at the catalyst composition of $Cu_2Cl_2 \cdot 2NH_4Cl$. This may be due either to the true activity of the complex II, or to a small amount of the above catalyst $Cu_2Cl_2 \cdot NH_4Cl$ existing in equilibrium with the ineffective complex II. The rate profiles of diallyl ether formation in Figs. 5 and 7 were determined at different conditions, but calculations utilizing the dependences of rate upon temperature and the catalyst composition show that the maximum rates are nearly equal in both cases, indicating absence of the appreciable solvent effect upon the rate process. On the other hand, the rate of diallyl ether formation at the catalyst composition of $Cu_2Cl_2 \cdot 2NH_4Cl$ in a mixture of allyl and ethyl alcohols (Fig. 7) is much lower than that at the corresponding conditions in allyl alcohol alone (Fig. 5). This fact might suggest that the complex II may not be appreciably effective, but the equilibrium forming the true catalyst $Cu_2Cl_2 \cdot NH_4Cl$ may be unfavorable in the mixed solvent.

Now we assume that the following two equilibria are attained in allyl alcohol or in a mixture of allyl and ethyl alcohols.

$$Cu_2Cl_2 + 2NH_4Cl \xrightleftharpoons{K_1} (NH_4)_2Cu_2Cl_4 \quad (7)$$

$$(NH_4)_2Cu_2Cl_4 + Cu_2Cl_2 \xrightleftharpoons{K_2} (NH_4)_2Cu_4Cl_6 \quad (8)$$

Allyl alcohol molecules in the coordination sphere of copper(I) are omitted in these formulas. Equilibrium quotients are represented by

$$K_1 = \frac{y}{(a-2x-y)(b-2x-2y)^2} \quad (9)$$

$$K_2 = \frac{x}{y(a-2x-y)} \quad (10)$$

where $a=[Cu_2Cl_2]_0$, $b=[NH_4Cl]_0$, $x=[(NH_4)_2Cu_4Cl_6]$, and $y=[(NH_4)_2Cu_2Cl_4]$. If the active catalyst species is presumed to be $(NH_4)_2Cu_4Cl_6$, that is

$$k_1 = k_a x \quad (11)$$

the optimum activity should be shown when the maximum value of x is attained at appropriate b. Differentiating Eq. (10) with b,

$$\left(\frac{1}{K_2}+2y\right)\frac{dx}{db} = (a-2x-2y)\frac{dy}{db}$$

Here $dy/db \neq 0$ and the maximum of x is realized when

$$a - 2x - 2y = 0 \quad (12)$$

From Eqs. (9) and (12)

$$|\, a - b \,| = \frac{1}{\sqrt{K_1}} \quad (13)$$

As is evidenced by the data in Table 2 and the fact that the complex $(NH_4)_2Cu_2Cl_4(C_3H_6O)_2$ was isolated as crystals, K_1 must be very large and hence Eq. (13) indicates that the maximum rate will be observed at $[NH_4Cl]_0$ near $[Cu_2Cl_2]_0$. This feature was in fact observed in Figs. 5 and 7.

From Eqs. (10) and (11)

$$k_1 = k_a K_2 y(a-2x-y)$$

If $K_1 \gg 1$, then $y \fallingdotseq b/2$ and if $K_2 \ll 1$, then $a-y \gg 2x$, and hence

$$k_1 \fallingdotseq k_a K_2 \frac{b}{2}\left(a-\frac{b}{2}\right)$$

$$= k_a K_2([NH_4Cl]_0/2)([Cu_2Cl_2]_0-[NH_4Cl]_0/2) \quad (14)$$

This relation is reconciled with the observed results in Fig. 4. The straight line really intersects the abscissa at $[Cu_2Cl_2]_0 \fallingdotseq [NH_4Cl]_0/2$. When $[Cu_2Cl_2]_0 \gg [NH_4Cl]_0/2$ Eq. (14) may be approximated by Eq. (4). The facts that the formation of ethyl allyl ether shows a similar rate profile with respect to the ammonium chloride concentration (Fig. 7) and obeys a similar rate law (Eq. (5)) suggest that this reaction also is promoted by the same catalyst species and goes through the same pathways as the diallyl ether formation.

The temperature dependence of $k_a K_2$ was measured and the apparent activation energy of 19.9 kcal/mol was obtained from the Arrhenius plot in Fig. 8. However the activation energy referring to k_a can not be determined since the heat of formation of the catalyst-substrate complex is unknown.

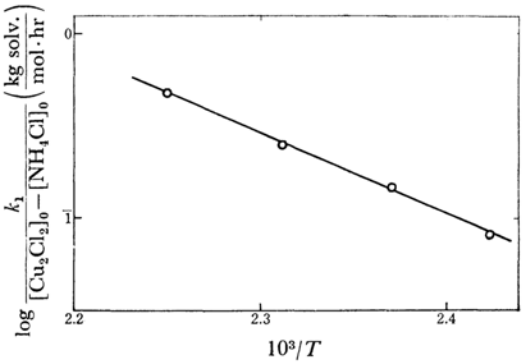


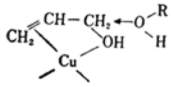
Fig. 8. The Arrhenius plot of the composite rate constant $k_a K_2$ (Eq. (14)) at a fixed concentration of ammonium chloride, 0.00916 mol/kg solvent.

The effective substrate-catalyst complex here assumed, $(NH_4)_2Cu_4Cl_6 \cdot x(C_3H_6O)$ looks like a tetrameric species. Unfortunately this complex has not been isolated due to its low stability, or may be due to far larger stability of $(NH_4)_2Cu_2Cl_4(C_3H_6O)_2$. However, several examples of tetrameric copper(I) chloride complexes have been reported so far. Wilkins and Burkin[11] synthesized copper(I) halide complexes with long-chain aliphatic amines such as n-$C_{18}H_{37}NH_2$, n-$C_{12}H_{25}NH_2$ and n-$C_8H_{17}NH_2$. Monoamine complexes $CuX(RNH_2)$, where X=Cl, Br, I, were all tetrameric and substituted by pyridine to form $[CuXpy]_4$. The molecular weight of copper(I) chloride in diethylamine was determined by Clifton and Yoke to be tetrameric.[12] Furthermore the molecular structure of tetrameric copper(I) chloride complex of norbornadiene was determined with X-ray by Baenziger, Haight and Doyle to contain an eight-membered ring composed of copper and chlorine atoms.[13]

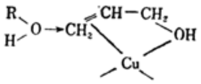
The reason is not clear at present why copper(I) chloride alone is not effective, but a little excess amount of chloride (Cu : Cl=2 : 3) is needed to realize the highest activity, and more excess amount of chloride is retarding. Chloride ions coordinated to copper(I) atom might modify the electronic state of the metal very delicately. Further comparative studies using fluoride, bromide or other ligands are needed.

Reaction Pathways. The etherification of alcohols is usually catalyzed by protonic acids and is believed to proceed *via* carbonium ions.[14] This view is supported by the fact that other Lewis acids such as zinc chloride, boron trifluoride and aluminum chloride also convert alcohols to ethers. However it is quite certain that the present copper(I) chloride catalyst is not playing the same role as these simple Lewis acids, but is activating the double bond mainly since diethyl ether was not produced at all. Tracer experiments employing ^{18}O-enriched allyl alcohol clarified that the C–O bond in allyl alcohol was ruptured in the etherification with ethyl alcohol. Furthermore the observed kinetics was interpreted to be first order with respect to the copper(I) complex of allyl alcohol and also first order concerning allyl or ethyl alcohol.

There still remain two possibilities whether the alkoxy group adds to the α-carbon III, or attacks the γ-carbon from the back side IV. In order to obtain a clue to this question allyl alcohol derivatives containing a methyl substituent at each carbon atom were used as substrates.



III



IV

In the etherification of γ-methylallyl alcohol, α-methylallyl γ-methylallyl ether was produced exclusively, bis(γ-methylallyl) ether being a very minor product (Table 1). This result strongly supports the supposition that the nucleophilic attack of the alcohol molecule occurred on the γ-carbon accompanying migration of the double bond (SN2′) and cleavage of the C–O bond. On the contrary α-methylallyl alcohol produced both bis(α-allylmethyl) ether and α-methylallyl γ-methylallyl ether in nearly equal amounts.

The solvolysis reactions of allylic chlorides have

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[11] R. G. Wilkins and A. R. Burkin, *J. Chem. Soc.*, **1950**, 127, 132.

[12] J. R. Clifton and J. T. Yoke III, *Inorg. Chem.*, **5**, 1630 (1966).

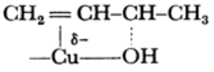
[13] N. C. Baenziger, H. L. Haight and J. R. Doyle, *ibid.*, **3**, 1535 (1964).

[14] E. R. Alexander, "Principles of Ionic Organic Reactions," Wiley, New York, N. Y. (1950), p. 214.

[15] R. H. DeWolfe and W. G. Young, "The Chemistry of Alkenes," ed. by S. Patai, Interscience Publishers, New York, N. Y. (1964), p. 681.

been studied very extensively.[15] The data on solvent effects indicate that the solvolysis of allyl chloride is closest to the bimolecular end of the mechanistic range, and that the mechanism shifts toward limiting S_N1 in the sequence $CH_2{=}CHCH_2Cl$, $CH_2{=}C(CH_3)CH_2Cl$, $CH_3CH{=}CHCH_2Cl$, $CH_3CHClCH{=}CH_2$, ––––––$(CH_3)_2CClCH{=}CH_2$. Thus, γ-methylallyl chloride is solvolyzed mainly *via* S_N2 path in ethanol resulting in γ-methylallyl alcohol in 91% yield. The electronic effect of γ-substituent is interpreted to greatly favor the normal S_N2 pathway. It is very interesting that quite the opposite result was obtained in the present etherification reaction. The ligation of the double bond to copper atom might decrease the electron density around γ-carbon so much as to favor the S_N2' pathway. The fact that the etherification of either methylallyl alcohol is about a hundred times faster than that of allyl alcohol suggests the specific character of the copper(I) catalysis.

In the case of allyl alcohol itself almost extreme S_N2' mechanism might be realized. The partial labeling of hydrogen atoms in allyl alcohol and NMR assays of the product ether will answer this question. On the other hand α-methylallyl chloride lies at the righthand side than γ-methylallyl chloride in the above mechanistic sequence from S_N2 to S_N1, and the products composition in Table 1 suggests that α-methylallyl alcohol may follow an intermediate mechanism between S_N2' and S_N1 and the polarized structure V of the copper complex may accept the nucleophilic atttack of the alcohol molecule on both α-and γ-carbon atoms.



$$\underset{\underset{\textstyle -Cu}{|\,\delta-}}{CH_2}=CH-\underset{\underset{\textstyle OH}{\vdots}}{CH}-CH_3$$

V

The isomerization of methylallyl alcohol proceeds remarkably in the case of γ-methylallyl alcohol. The mechanism is not yet certain at all, but the trend agrees with the previous finding[15] that α-, β- and γ-methyl substituents on the allylic system increase the rate of isomerization of allylic alcohols by factors of 10^2, 10^1 and 10^3, respectively.

The authors are grateful to Professor Nobukazu Okazaki of the Nara Women's University for his kind gift of ^{18}O-enriched water. They also wish to thank Dr. Yoshio Hirose, Director of the Institute of Food Chemistry, for the mass spectrometric measurements.