Copper(I) Perchlorate Complexes of Allyl, 2-Methylallyl and *cis*- and *trans*-2-Butenyl Alcohols[1]

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[Cu(allyl alcohol)(H_2O)]ClO_4 (abb. Cu(all)(H_2O)ClO_4), [Cu(allyl alcohol)$_2$(H_2O)]ClO_4 (abb. Cu(all)$_2$(H_2O)ClO_4), [Cu(2-methylallyl alcohol)(H_2O)]ClO_4 (abb. Cu(meth)(H_2O)ClO_4) and [Cu(*cis*- and *trans*-2-butenyl alcohol)$_2$ (H_2O)]ClO_4 (abb. Cu(*cis*-and *trans*- but$_2$ (H_2O)ClO_4) were synthesized. It was shown by means of equivalent conductance that Cu(all)(H_2O)ClO_4 is a strong electrolyte of uni-uni valent in acetone. The molecular weight of Cu(all)(H_2O)ClO_4 obtained from measurements of the direct vapor-pressure depression of acetone showed that the complex is monomeric. The C=C stretching band of the allylic alcohol shifts by about 100 cm^{-1} to the lower frequency side upon coordination. The chemical shifts of the vinyl protons in these complexes shift by about 0.5—1 ppm to the higher frequency side than those of free alcohols. It was concluded that the allylic alcohol coordinates to the copper atom through both the double bond and the oxygen atom. The equilibrium constant corresponding to Cu(*trans*-but)$^+_2$(H_2O)ClO_4+2*cis*-2-butenyl alcohol=Cu(*cis*-but)$^+_2$(H_2O)ClO_4+2*trans*-2-butenyl alcohol in 2-butenyl alcohol was estimated to be 9.82 at 25°C and the enthalpy change was estimated to be -3.13 kcal/mol.

Manahan[3] found that two potentials corresponding to Cu(II)=Cu(I)+e and Cu(I)=Cu(0)+e are observed in aqueous solutions containing allyl alcohol. However only one potential corresponding to Cu(II)=Cu(0)+2e is observed in the absence of allyl alcohol. Further data concerning the dependence of the reduction potential on the concentrations of copper(II) and allyl alcohol were explained on the basis of the formation of the copper(I)-allyl alcohol complex with a mole ratio of one to one and with a formation constant of 5.02×10^4mol^{-1} *l*. The isolation of the complex, however, has not been successful.

Previously we synthesized crystalline complexes of allyl alcohol[4] and some related compounds[5,6] with copper(I) chloride. It was then established that allyl alcohol coordinates to the copper(I) atom with both the double bond and the oxygen atom, and that this complex is a dimer with a double chloro bridge. However, the dissociation vapor pressures of these complexes are fairly large and they easily decompose to the original unsaturated ligands and copper(I) chloride. From the fact that one of the decomposition products, copper(I) chloride, is stabilized by the chloro bridges with the formation of a tetrahedral configuration, this instability is presumably enhanced by the high donating power and by the bridging potential of the chloride ligand. Now we have synthesized the copper(I) perchlorate-allylic alcohol complexes with molar ratios of one to one and one to two with expectation of obtaining stable complexes, but the former was rather explosive.

Experimental

Materials. The copper(II) perchlorate hexahydrate was prepared from copper(II) hydroxide and a 60% aqueous solution of perchloric acid and was recrystallized from ethyl acetate. The allyl alcohol, 2-methylallyl alcohol and 2-butenyl alcohol were used after distillation. The acetone used for the measurements of the molecular weight and the electric conductance was purified in the usual manner[7] and distilled *in vacuo*.

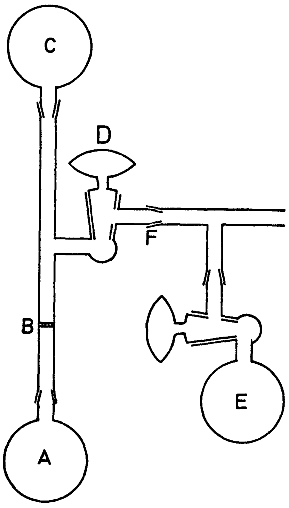

Fig. 1. The ampoule system for the synthesis of the copper(I) perchlorate complexes with allylic alcohols.

Synthesis of Cu(all)(H_2O)ClO_4. The ampoule system employed for the synthesis of the complex is illustrated in Fig. 1. Copper(II) perchlorate hexahydrate (100—200 mg), copper metal and a stirring bar were placed in an ampoule A. Allyl alcohol was then transferred from another ampoule E and the stopcock D was closed. The solution was stirred magnetically till the blue color of copper(II) faded and it became colorless. Then the apparatus was inverted at the taper joint F so that the solution could be filtered through the

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[3] S. E. Manahan, *Inorg. Chem.*, **5**, 482 (1966).

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

[5] S. Kawaguchi and T. Ogura, *Inorg. Chem.*, **5**, 944 (1966).

[6] T. Ogura, T. Hamachi, and S. Kawaguchi, This Bulletin, **41**, 892 (1968).

[7] A. Weissberger and E. S. Proskauer; J. A. Riddick and E. E. Toops, Jr., "Organic Solvents," 2nd ed., Interscience Publishers, New York (1955), p. 379.

sintered glass B into yet another ampoule C. The solvent was then transferred into E by vacuum distillation. In the course of the transfer of the alcohol, colorless crystals were formed. The complex was obtained as a white powder by further drying.

After the complex was weighed, the ligand was freed by the addition of aqueous ammonium chloride. All the allyl alcohols were collected together with the water by the vacuum distillation of the aqueous solution. It was determined by means of gas chromatographic and IR assay that the volatile materials were composed of water and allyl alcohol. The quantity of allyl alcohol was determined by bromination as has been described previously.[4] The nonvolatile material was dissolved in aqueous ammonia and analyzed for copper electrolytically and for the perchlorate ion as a nitron adduct.

Found: Cu, 26.1; C_3H_6O, 24.7; ClO_4, 41.7%. Calcd for $Cu(C_3H_6O)(H_2O)ClO_4$: Cu, 26.6; C_3H_6O, 24.7; ClO_4, 41.7%. Further, the water was detected in the IR spectra and the mole ratio of water to allyl alcohol was estimated to be unity on the basis of the NMR assay.

Synthesis of $Cu(all)_2(H_2O)ClO_4$. A small quantity of allyl alcohol was distilled into the ampoule C containing $Cu(all)(H_2O)ClO_4$, and then the complex was dissolved completely (Fig. 1). The excess of alcohol was distilled back to the E ampoule by means of a difference of temperature of between 20.5°C (the mp of acetophenone) and 0°C, the complex was thus obtained as colorless and transparent crystals. When the temperature of the ampoule C was higher by several degrees, the complex was decomposed to $Cu(all)(H_2O)ClO_4$; when it was lower by several degrees, the complex was not dried because of its high solubility in allyl alcohol. The complex was analyzed as has been described above.

Found: Cu, 21.5; C_3H_6O, 40.0; ClO_4, 34.8%. Calcd for $Cu(C_3H_6O)_2(H_2O)ClO_4$: Cu, 21.4; C_3H_6O, 39.2; ClO_4, 33.4%.

Synthesis of $Cu(meth)(H_2O)ClO_4$ *and* $Cu(but)_2(H_2O)ClO_4$. $Cu(meth)(H_2O)ClO_4$ was synthesized and analyzed much as in case of $Cu(all)(H_2O)ClO_4$.

Found: Cu, 25.3; C_4H_8O, 28.5; ClO_4, 40.6%. Calcd for $Cu(C_4H_8O)(H_2O)ClO_4$: Cu, 25.3; C_4H_8O, 28.5; ClO_4; 39.3%. The presence of the 1:2 complex of 2-methylallyl alcohol was suggested on the basis of the IR spectra, but its isolation was difficult.

$Cu(but)_2(H_2O)ClO_4$ was obtained and analyzed much as in the case of $Cu(all)(H_2O)ClO_4$.

Found: Cu, 20.5; C_4H_8O, 44.3; ClO_4, 31.2%. Calcd for $Cu(C_4H_8O)_2(H_2O)ClO_4$: Cu, 19.0; C_4H_8O, 44.4; ClO_4, 30.6%. We failed to obtained the one to one 2-butenyl alcohol complex.

Equivalent Conductance. The equivalent conductance of $Cu(all)(H_2O)ClO_4$ in acetone was measured at 25.0°C with a cell modified only enough to make it possible to operate it in a vacuum using the Yanagimoto conductivity outfit, Model MY-7. The results are listed in Table 1.

TABLE 1. EQUIVALENT CONDUCTANCES OF $Cu(all)(H_2O)ClO_4$ IN ACETONE (at 25.0°C)

Concn. $\left(\frac{\text{formal}}{\text{kg acetone}}\right)$	Equivalent conductance
0.1055	39.6
0.05174	71.6
0.02745	107.9
0.02003	118.3

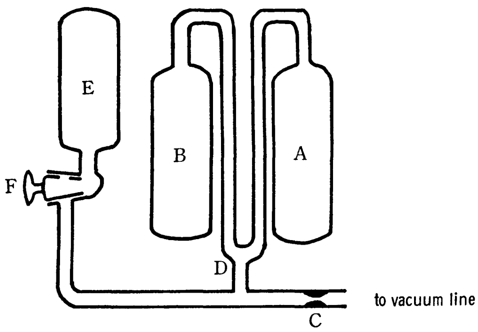

Fig. 2. The apparatus used for the direct measurements of depressions of vapor pressures.

Molecular Weight Measurement. The molecular weight of $Cu(all)(H_2O)ClO_4$ was determined by direct measurements of the vapor-pressure depressions of acetone. The apparatus used is illustrated in Fig. 2. The complex was prepared and dried completely in the A ampoule. Carefully degassed acetone was transferred from the vacuum line to A and B at the same time and the apparatus was sealed off at C. Mercury charged in E was transferred to D through the stopcock F. The difference in the vapor pressure between the pure solvent and the acetone solution of the complex was measured at a constant temperature by the U-type mercury manometer formed at D. The value of Dreisbach[8] was referred to be estimating the vapor pressures of acetone in this study. The estimated values are in good agreement with our measurement; for instance, the 263 mmHg measured at 28.5°C agrees with the 263 mmHg evaluated from Ref. 8. The results are listed in Table 2.

TABLE 2. THE DATA TO OBTAIN THE MOLECULAR WEIGHT OF $Cu(all)(H_2O)ClO_4$ IN ACETONE

	Sample 1	Sample 2	
Concn. (wt. %)	2.92	3.01	
Temp. (°C)	28.8	25.7	30.0
Depression of vapor press. (mmHg)	3.05	2.60	3.29
Vapor press. of acetone (mmHg)[a]	266	209	279
Mol. wt.	151	145	153
	average 150		

a) Evaluated from $\log P = 7.19038 - 1233.4/(t - 230)$

Gas Chromatography. The *cis*- and *trans*-isomers of 2-butenyl alcohol were separated by the use of gas chromatography under the following conditions: PEG 1500/siliconized Celite; temperature, 110°C; column, 4.5 mm in od×3.5 m; carrier gas, hydrogen, 30 m*l*/min. The ratio of the isomers was evaluated from the average value of five measurements.

IR Spectra. The infrared absorption spectra were measured with a Hitachi infrared spectrophotometer EPI-2. The sprctra of $Cu(all)_2(H_2O)ClO_4$ and $Cu(but)_2(H_2O)ClO_4$ were measured by the use of both a sodium chloride cell and a polyethylene film, since these complexes easily exchange the anion. All the samples were prepared in nitrogen atmospheres.

NMR Spectra. The samples for NMR measurements were prepared in the vacuum system and the spectra were measured with a 60 MHz spectrometer, model JNM 3H60 of the Japan Electron Optics Laboratory, Ltd.

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[8] R. R. Dreisbach and R. A. Martin, *Ind. Eng. Chem.*, **41**, 2875 (1949).

Results and Discussion

The present investigation has been undertaken to synthesize stable complexes of allylic alcohols with copper(I) perchlorate; however the complexes obtained were slightly unstable. For instance, when a methanol solution of Cu(all)$(H_2O)ClO_4$ was kept standing at room temperature it became turbid forming copper(I) oxide within a few days. The decomposition rate of the complex increased markedly upon heating. The solid complex heated under a vacuum exploded at around 200°C. A further accidental explosion occurred when it was treated with a spatula of stainless steel in a nitrogen atmosphere.

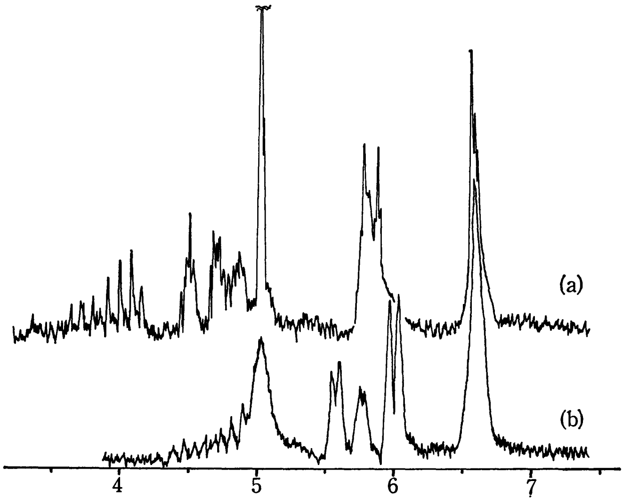


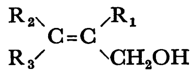
Fig. 3. The NMR spectra of allyl alcohol (a) and Cu(all)ClO_4 (b) in CD_3OD. The quintet lines around 6.6 τ are signals of CHD_2OD.

TABLE 3. THE NMR SPECTRA OF ALLYLIC ALCOHOLS AND THEIR COMPLEXES WITH COPPER(I) PERCHLORATE[a)] (τ value in CD_3OD)

	R_1	R_2	R_3	CH_2	OH
Allyl alcohol	4.1m	(4.53 4.90	4.73)	5.85d	5.05
Cu(all)$(H_2O)ClO_4$	4.9m	(5.59 5.83m	5.64)	6.03d	5.07
2-Methylallyl alchohol	8.28	(5.02	5.46)	6.02	5.10
Cu(meth)$(H_2O)ClO_4$	8.25	(5.46	5.59)	6.04	5.05
cis-2-Butenyl alcohol			8.30m	5.81	5.10
Cu(*cis*-but)$_2$-$(H_2O)ClO_4$			8.29m	5.91d	5.10
trans-2-Butenyl alcohol	4.3m	8.30m	4.3m	6.04	5.10
Cu(*trans*-but)$_2$-$(H_2O)ClO_4$	4.8m	8.33d	4.8m	6.06	5.06

d; doublet, m; multiplet.

a) R_n's are based on



Cu(all)$(H_2O)ClO_4$ and Cu(meth)$(H_2O)ClO_4$. The NMR spectra of allyl alcohol and its complex are shown in Fig. 3. Table 3 shows the data of the NMR spectra of allylic alcohols and their complexes.

The spectra of allyl groups are very complex.[9)] The NMR spectra of the complex of allylic alcohol are also so complex that the chemical shifts and coupling constants of the vinyl protons were difficult to determine. However, it is clear that the chemical shifts of the protons attached to the saturated carbons are affected little by coordination, and that the chemical shifts of the vinyl protons shifted by 0.5—1 ppm to a higher field. These shifts can be explained as being mostly due to a decrease in the double bond character upon coordination, and the small shift of methylene protons to a higher field is consistent with the decrease in the electron density of the double bond.

It is found that the intensity ratio of $(OH+R_1)$: (R_2+R_3): CH_3 of Cu(all)$(H_2O)ClO_4$ is 4:2:2; this is consistent with the composition obtained from elementary analysis, $Cu(CH_2=CHCH_2OH)(H_2O)ClO_4$. A similar intensity ratio was observed in the case of the 2-methylallyl alcohol complex.

The NMR spectra of neat 2-methylallyl alcohol are essentially the same as those of 2-methylallyl alcohol in deuterated methanol solutions. Because the OH proton signal overlaps with one of the vinyl proton signals, the NMR spectra of 2-methylallyl alcohol was used to distinguish between the absorptions of the OH group and the vinyl proton.

TABLE 4. THE C=C STRETCHING BANDS OF ALLYLIC ALCOHOLS AND THEIR COMPLEXES WITH COPPER(I) PERCHLORATE

	ν(C=C) cm^{-1}
Allyl alcohol	1646
Cu(all)$(H_2O)ClO_4$	1538
Cu(all)$_2(H_2O)ClO_4$	1537
2-Methylallyl alcohol	1657
Cu(meth)$(H_2O)ClO_4$	1579
trans-2-Butenyl alcohol	1673
Cu(*trans*-but)$_2(H_2O)ClO_4$	1558
cis-Butenyl alcohol	1654
Cu(*cis*-but)$_2(H_2O)ClO_4$	1540

The frequencies of the C=C stretching bands of both the free and the coordinated allylic alcohols are listed in Table 4. The IR spectra of the complexes with allylic alcohols closely resemble those of copper(II) perchlorate and free alcohols except for the C=C stretching bands. The C=C stretching bands of the ligands are shifted by about 110 cm^{-1} to the lower frequency side by coordination. This shift indicates a decrease in the electron density of the double bond and is consistent with the decrease in shielding observed in the NMR spectra. The shift in the copper(I) perchlorate complex is considerably larger than that in the copper(I) chloride complex (95 cm^{-1}) and suggests a stronger coordination as expected.

It has been reported[10)] that the Cl-O stretching

[9)] L. M. Jackman, "Application of Nuclear Magnetic Rsonance Spectroscopy in Organic Chemistry," Pergamon Press, London (1959).

[10)] B. J. Hathaway and A. E. Underhill. *J. Chem. Soc.*, **1961**, 3091.

absorption of the perchlorate ion at around 1100 cm^{-1} is split into three or four peaks and is shifted to the lower frequency side by coordination. No absorption bands of the complexes in this region split and differ from those of copper(II) perchlorate hexahydrate.

The equivalent conductances of the one to one complex of allyl alcohol listed in Table 1 were plotted against the roots of the concentrations and the conductance at an infinite dilution, 195, was obtained by extrapolation. This value is close to those of lithium halides and potassium iodide in acetone[11] suggesting that the complex is a strong electrolyte of uni-uni valent.

The equivalent conductance at 25.7°C of a 30.1% solution of Cu(all)$(H_2O)ClO_4$ in acetone was found to be 40. This value is quite small as compared with the conductance at an infinite dilution, showing a small activity coefficient together with the presence of nondissociated species at this concentration. As Table 2 shows, the molecular weight of the complex in acetone is about 150. Because the formula weight of the complex in acetone is 237, the molecular weight of the completely dissociated complex is 119. From this fact, it can be concluded that the complex is monomeric and that the somewhat large molecular weight may be due to the presence of the undissociated complex in acetone.

It is difficult to obtain direct evidence showing the coordination of the oxygen atom of allylic alcohols to the copper atom. We failed to isolate similar complexes with alkene such as ethylene, propene and butenes. This failure suggests that the coordination ability of simple monoolefins is too weak for them to form stable complexes and that the allylic alcohol chelates to copper(I) *via* both the double bond and oxygen atom.

There is some evidence of coordination of the water to the copper(I) ion. Firstly, as has been described above, Cu(all)$(H_2O)ClO_4$ dissolved in alcohols or ketones forms Cu(I) oxide slowly. This implies that the dissociation constant of the proton of the water molecule coordinated to the copper(I) ion is larger than that of free water. Secondly, at room temperature the water molecule can not be removed under a vacuum of 10^{-3} mmHg. Furthermore, the complex does not lose its water molecule on treatment with 2,2-dimethoxypropane. It seems that the water is removed before an explosion.

Cu(all)$_2$(H$_2$O)ClO$_4$ and Cu(but)$_2$(H$_2$O)ClO$_4$. The NMR spectrum of Cu(all)$_2(H_2O)ClO_4$ could not be measured because it dissociates rapidly into the one to one complex and allyl alcohol in solution.

The NMR data of the complex of 2-butenyl alcohol are listed in Table 3. As Fig. 4 shows, commercial 2-butenyl alcohol is composed of *cis*- and *trans*-isomers in a ratio of about one to three. The complex prepared from the commercial alcohol, however, had nearly the same amounts of the *cis*- and *trans*-isomers. The vinyl protons of both isomers shift to the lower frequency side by about 0.5 ppm from the parent vinyl proton upon coordination; the intensity ratio of the protons is consistent with the $[Cu(C_4H_8O)_2(H_2O)]ClO_4$ composition (Fig. 4 and Table 3).

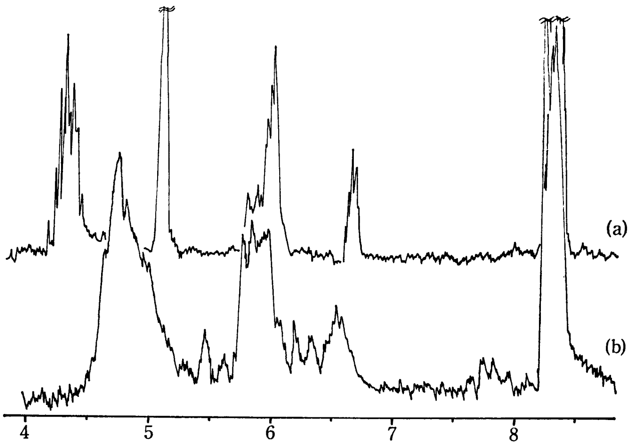


Fig. 4. The NMR spectra of commercial 2-butenyl alcohol and Cu(but)$_2$ClO$_4$ (b) in CD_3OD.

The IR spectra of the one to two complexes are similar to those of the one to one complexes (Table 4), and they show no absorption due to the free double bond. Therefore, both double bonds may coordinate to copper(I). The oxygen atoms of alcohols may coordinate to copper(I) just as in Cu(all)$(H_2O)ClO_4$. It is not clear from the present data whether the water molecule coordinates or not.

*The Equilibrium between the Cu(*cis*-but)$_2$(H$_2$O)ClO$_4$ and Cu(*trans*-but)$_2$(H$_2$O)ClO$_4$.* As has been described above, the mole ratio of *cis*-isomers to *trans*-isomers in the complex is greater than that in the original alcohol. Copper(I) chloride is soluble in 2-butenyl alcohol, suggesting the formation of a copper(I) chloride-2-butenyl alcohol complex similar to the copper(I) chloride-allyl alcohol complex.[4] When 2-butenyl alcohol was added to an excess of powdered copper(I) chloride and was then collected by vacuum distillation, it was found that the early fractions were rich in the *trans*-isomer while the later fractions were rich in the *cis*-isomer. These facts show that the *cis*-2-butenyl alcohol coordinates more easily to copper(I) chloride than does the *trans*-alcohol. On the basis of these findings, we tried to evaluate the difference in the stabilities of the complexes of these isomers.

It is known that the vapor pressure of *trans*-butene is rather close to that of the *cis*-isomer. For instance, the vapor pressures of the former and the latter at 0°C are 660 and 730 mmHg respectively.[12] The smallness of the difference may reflect the isomers of 2-butenyl alcohol. In fact, when 2-butenyl alcohol was collected by vacuum distillation, no difference in the composition of the isomers was found between the early and the final fractions. It was confirmed that the complex does not catalyze the isomerization of 2-butenyl alcohol.

Now the following equilibrium and equilibrium constant can be assumed:

$$2C + CuT_2(H_2O)^+ = 2T + CuC_2(H_2O)^+ \qquad (1)$$

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[11] L. G. Savedoff, *J. Amer. Chem. Soc.*, **88**, 664 (1966).

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

$$K = \frac{[\mathrm{T}]^2[\mathrm{CuC_2(H_2O)^+}]}{[\mathrm{C}]^2[\mathrm{CuT_2(H_2O)^+}]} \tag{2}$$

where C and T represent *cis*- and *trans*-2-butenyl alcohol respectively. It was ascertained that all the copper(II) used is reduced to the copper(I) complexes. The α_0 and α fraction are defined by:

$$\alpha_0 = [\mathrm{T}]_0/[\mathrm{C}]_0 \tag{3}$$

$$\alpha = [\mathrm{T}]/[\mathrm{C}] \tag{4}$$

where $[\mathrm{T}]_0$ and $[\mathrm{C}]_0$ are the concentrations of *trans*- and *cis*-2-butenyl alcohol respectively before the preparation of the complex, while [T] and [C] are those of *trans*- and *cis*-2-butenyl alcohol after the preparation of the complex. The following relations are obtained:

$$[\mathrm{C}]_t = [\mathrm{C}] + 2[\mathrm{CuC_2(H_2O)^+}] \tag{5}$$

$$[\mathrm{T}]_t = [\mathrm{T}] + 2[\mathrm{CuT_2(H_2O)^+}] \tag{6}$$

$$[\mathrm{Cu}]_t = [\mathrm{CuC_2(H_2O)^+}] + [\mathrm{CuT_2(H_2O)^+}] \tag{7}$$

where the subcript "t" represents the total concentration of each species. The β fraction is defined by Eq. (8). Equation (9) then results, since no isomerization occurs.

$$\beta = [\mathrm{C}]_t/[\mathrm{C}]_0 \tag{8}$$

$$[\mathrm{T}]_t/[\mathrm{T}]_0 = \beta \tag{9}$$

The following relations are derived from Eqs. (3)—(9):

$$[\mathrm{CuC_2(H_2O)^+}] = \{2[\mathrm{Cu}]_t + (\alpha-\alpha_0)\beta[\mathrm{C}]_0\}/2(\alpha+1) \tag{10}$$

$$[\mathrm{CuT_2(H_2O)^+}] = \{2\alpha[\mathrm{Cu}]_t + (\alpha-\alpha_0)\beta[\mathrm{C}]_0\}/2(\alpha+1) \tag{11}$$

Substitution in Eq. (2) results in:

$$K = \alpha^2\{2[\mathrm{Cu}]_t + (\alpha-\alpha_0)\beta[\mathrm{C}]_0\}/\{2\alpha[\mathrm{Cu}]_t - (\alpha-\alpha_0)\beta[\mathrm{C}]_0\} \tag{12}$$

If the ratio of *cis*-2-butenyl alcohol to the *trans*-isomer in the vapor phase is equal to that in the liquid phase, α and α_0 should be the ratio of the isomers of the starting 2-butenyl alcohol measured in the vapor phase and after the preparation of the complex respectively.[13]

In this experiment, we prepared the copper(I) complex in pure 2-butenyl alcohol and collected small portions of the solvent (~10 μl) by vacuum distillation in order to determine α_0 and α. The results are listed in Table 5.

The temperature dependence of the equilibrium constant was determined. Figure 5 shows the plot of log$K$ *versus* $1/T$. The enthalpy change corresponding to Eq. (1) was evaluated as −3.13 kcal/mol from the gradient.

Table 5. The equilibrium constant for the reaction of Eq.(1)[a] (at 30.1°C)

Concn. (mol/kg sol)		$\frac{trans\text{-Isomer}}{cis\text{-Isomer}}$ at vapor phase	Equilibrium constant, K
2-Butenyl alcohol	Cu(I)		
6.13	2.44	4.25	8.00
7.67	1.94	3.85	8.27
8.69	1.61	3.53	7.95
9.40	1.39	3.38	8.03
			av. 8.06

a) The ratio of *trans*- to *cis*-isomer of starting 2-butenyl alcohol is 2.53.

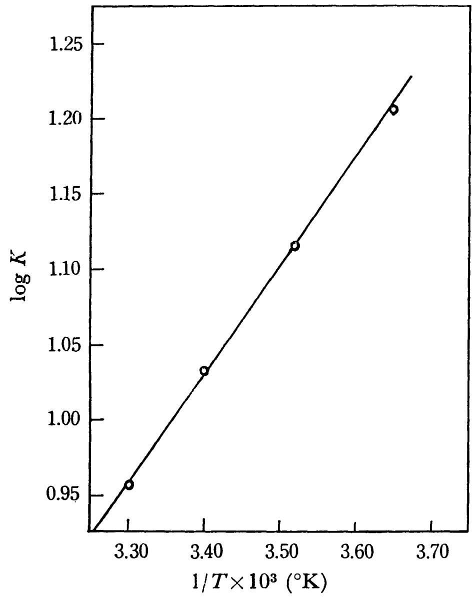

Fig. 5. The temperature dependencies of the formation constant, K.

Muhs and Weiss[14] determined the equilibrium constants of silver-olefin complexes by the use of ethylene glycol solutions of silver nitrate as the liquid phase of gas chromatographic column. These reactions are expressed by:

$$\text{olefin} + \mathrm{AgNO_3} = \text{olefin}\cdot\mathrm{AgNO_3}$$

In the case of 2-butene, the ratio of the equilibrium constants of *cis*- and *trans*- is 3.9 at 40°C. The ratios of most olefins fall around 4. These values must be squared in order to be compared with the present data. The value of K at 40°C is estimated to be 7.1 by the extrapolation of the straight line in Fig. 5. The value for copper(I) is rather similar to that of silver(I) though the former is smaller. The stability of *cis*-2-butenyl alcohol compared to that of the *trans*-isomer may be attributed to the relief of the inner strain of the *cis*-isomer by coordination.

The authors wish to thank Professor Shinichi Kawaguchi of Osaka City University for his valuable advice and encouragement.

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[13] Here we assumed that the fractions, α_0 and α, in liquid phase are equal to those of gas phase. However, if the *trans*- and *cis*-2-butenyl alcohol have their vapor pressures, Pt and Pc, respectively, and obey Raoult's law, then α_0 and α in Eq. (12) are represented as $(Pt/Pc)\alpha_0$(gas) and $(Pt/Pc)\alpha$(gas), respectively, where α_0(gas) and α(gas) are the fractions in gas phase corresponding to them in liquid phase.

[14] M. A. Muhs and F. T. Weiss, *J. Amer. Chem. Soc.*, **84**, 4697 (1962).