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THERMAL DECOMPOSITION OF METHYLCOPPER AND METHYL(TRICYCLOHEXYLPHOSPHINE)COPPER

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Summary

The thermal decomposition of CH_3Cu and CH_3CuPCy_3 has been studied in the solid state and in solution. Ligand-free methylcopper and its complex with tricyclohexylphosphine gave on thermolysis methane, ethane, ethylene and propane as gaseous products. The solvent does not affect the composition of the gases, and when carried out in benzene-d_6 the thermolysis does not yield deuterated gases. Thermal decomposition of CD_3CuPCy_3 gave CD_3H and CD_4 in a 3 : 2 molar ratio, indicating that the sources of hydrogen for methane formation were tricyclohexylphosphine (60%) and the methyl group of CD_3Cu (40%). Copper–carbon σ-bond scission proceeds via reductive elimination in a bimolecular concerted reaction.

Whitesides et al. [1] have studied the thermolysis of the n-butylcopper (tributylphosphine) complex. During the thermal decomposition, n-butane, 1-butene and small quantities of hydrogen were evolved. Deuterium labelling studies have revealed that the predominant pathway of thermal decomposition is a two-step process consisting of the initial formation of 1-butene by β-elimination of copper hydride, followed by its reaction with a second molecule of n-BuCu(n-Bu_3P) to give n-butane.

Kochi and co-workers [2] examined the decomposition of ethyl- and n-propylcopper compounds in THF solutions. The results obtained were consistent with the investigation of Whitesides et al. The kinetic studies indicated an autocatalytic molecular route for the thermolysis of alkylcopper species. Direct homolytic cleavage of the Cu–C bond occurs when β-elimination is impossible. For instance, Whitesides et al. [3] showed that neophyl(tri-n-butylphosphine)copper in diethyl ether at 30–125°C decomposes mainly by a free radical mechanism. The formation of a neophyl radical after initial homolytic scission of the Cu–C σ-bond was confirmed by the products isolated, derived from 1,2-phenyl migration, coupling and hydrogen abstraction reactions.

Lappert and Pearce [4] have examined the decomposition of tetranuclear trimethylsilylmethylenecopper, $(Me_3SiCH_2)_4Cu_4$, in the solid state as well as in toluene.

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The isolation of Me_4Si (main product), $(Me_3Si)_2CH_2$, $(Me_3SiCH_2)_2$ and $PhCH_2CH_2SiMe_3$, $PhCH_2CH_2Ph$ (in toluene) and of some unidentified minor components was in accord with a free radical decomposition pathway.

The thermal decomposition of *cis*- and *trans*-1-propenylcopper(I) and their complexes with tri-n-butylphosphine yields copper(0) and 2,4-hexadienes with complete retention of the configuration at the olefinic double bonds [5]. Since 1-propenyl radicals have a low configurational stability, this stereochemical result is sufficient to establish that free, long-lived propenyl radicals are not intermediates in these coupling reactions. A bimolecular or concerted mechanism at the surface of multinuclear organocopper cluster species without the participation of free radicals was proposed.

Yamamoto and Miyashita [6] have isolated a series of alkylcopper complexes with various tertiary phosphines. During the thermolysis of alkylcopper with ethyl or a longer alkyl chain, both alkane and alkene are formed, accompanied by the evolution of molecular hydrogen [7]. These observations suggest that the decomposition of alkylcopper (where alkyl = ethyl, propyl or i-butyl) proceeds by β-elimination. In the thermolysis of solid methylcopper complexes, methane, ethane and, in some cases, ethylene are evolved [7,8]. The first-order rate law for the thermolysis of methylcopper complexes suggests that the methyl group liberated from the complex by a unimolecular process will abstract hydrogen from the ligand or couple with the methyl group in another molecule of the CH_3Cu complex, evolving CH_4 and C_2H_6, respectively. Hydrogen abstraction of the methyl group in the methylcopper complex to give CH_4 and carbenoid species may also take place.

From the data presented above it appears that the copper–carbon σ-bond scission for ethyl and higher homologues of alkylcopper compounds proceeds by β-hydrogen elimination and the reaction of copper hydride with alkylcopper. Direct homolytic cleavage of the Cu–C σ-bond involving free radicals cannot be excluded for compounds having no C–H bonds β to the Cu–C bond.

Therefore we decided to examine precisely the thermal decomposition of methylcopper and to establish the most probable mechanistic pathway.

Results and discussion

Thermolysis of methylcopper (CH_3Cu)

Methylcopper was prepared from copper bisacetylacetonate and dimethylaluminium monoethoxide in diethyl ether at −78 to −10°C by the method of Ikariya and Yamamoto [8]. The yellow solid was placed in a Schlenk vessel and connected to a gas burette. No decomposition of methylcopper was observed at 0°C for 2 h. At about 16°C, darkening of the sample was not followed by noticeable gas evolution. At room temperature (20°C), slow decomposition of methylcopper was observed with simultaneous evolution of gases. The distribution of the gases is given in Table 1.

Further warming of methylcopper caused violent explosive thermal decomposition of the compound at 35–40°C. The gas composition after the explosion changed; the amounts of methane, ethylene and propane evolved increased and the molar fraction of ethane decreased. Ikariya and Yamamoto [8] reported that slow decomposition of methylcopper at 0°C for 1 h liberated only ethane. The explosive thermal decomposition of CH_3Cu released methane, ethane, ethylene and hydrogen at molar

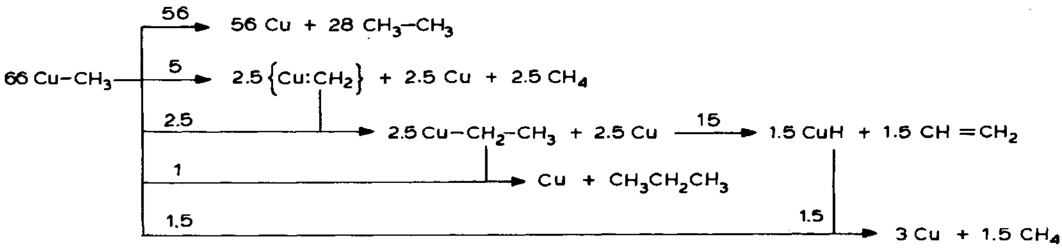
TABLE 1

GASES EVOLVED DURING THE THERMAL DECOMPOSITION OF CH_3Cu

Gases	Decomp. temp. (°C)	
	20	35 (explosion)
Methane	8.2	10.8
Ethane	90.2	81.9
Ethylene	0.8	4.1
Propane	0.8	3.2

ratios of 1 : 9 : 1 : 1. From our studies it appears that the temperatures of the slow thermal decomposition and of the explosion of methylcopper depend strongly on the purity of the compound obtained and the presence of traces of oxygen in the reaction mixture. No evolution of gases was observed on acidolysis of the decomposed methylcopper. Therefore we conclude that complete cleavage of the Cu–C σ-bond took place during the thermolysis.

The course of the thermal decomposition of methylcopper is given in Scheme 1.



	Found (%)	Calcd. (%)
CH_4	10.8	11.6
CH_3CH_3	81.9	81.1
$CH_2{=}CH_2$	4.1	4.3
$CH_3CH_2CH_3$	3.2	2.9

SCHEME 1

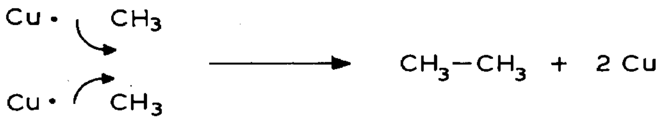
The molar fractions of the gases calculated from the equation are in accordance with those found after thermolysis. The main pathway is the formation of ethane, from 66 mol of CH_3Cu, 56 gave ethane, i.e. 85%. 10% of the total amount of CH_3Cu released methane, 5 mol. Only 5 mol of CH_3Cu gave ethylene and propane.

Ethane is most likely formed during reductive elimination, which may proceed via a concerted reaction and can provide low-energy pathways.

Polymeric structures have been proposed for alkyl-, alkynyl- and arylcopper compounds [9].

Phenylcopper was proposed to have a polymeric structure consisting of a chain of copper atoms with each phenyl group bridging two copper atoms by two-electron–three-centre (2e–3c) bonds [10].

We believe that methylcopper, insoluble in common organic solvents, has a similar polymeric structure. The distance between adjacent methyl groups on the aggregate surface is small enough to facilitate reductive elimination of two methyl groups to give ethane.



It seems very likely that the homolytic cleavage of the Cu–C σ-bond generates short-lived radicals, which immediately form ethane. At low temperatures, below the explosion temperature, the decomposition proceeds on the surface of an aggregate. The reaction is slow and liberates mainly ethane, 90%. Interactions between the transition species formed are hindered and only low yields are obtained; the percentage of ethylene and propane averages 1.6%. At a certain temperature, the pressure inside the CH_3Cu aggregate may increase violently, causing further explosive decomposition. Disintegration of the aggregate facilitates secondary reactions and therefore the yield of ethane decreases by ca. 10% and those of ethylene and propane increase to 8%.

The probable mechanism of methane formation consists of α-hydrogen abstraction in a concerted reaction with the simultaneous formation of carbenoid species $\{Cu{:}CH_2\}$. In a bimolecular reaction with methylcopper the unstable carbenoid form gives propane (Scheme 1). β-Hydrogen elimination of CH_3CH_2Cu liberates ethylene and copper hydride, which reacts with CH_3Cu to give methane.

Thermal decomposition of methyl / tri-cyclohexylphosphine / copper ($CH_3CuP(Cy)_3$)

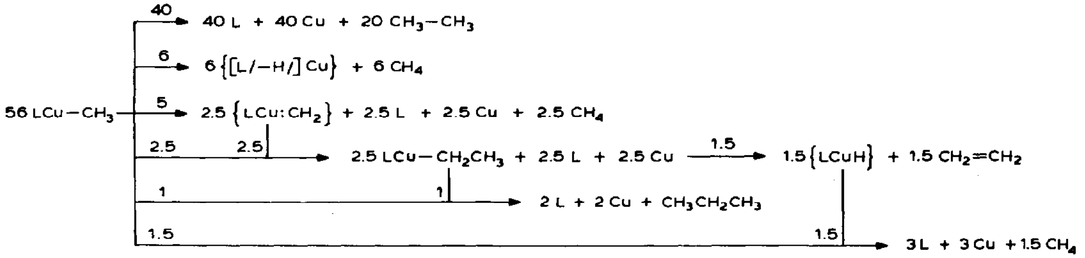
The complex was prepared by the method described by Yamamoto and co-workers [7]. The compound was obtained from the reaction of copper bisacetylacetonate with dimethylaluminium monoethoxide in the presence of tricyclohexylphosphine in diethyl ether at −78 to −5°C.

$CH_3CuP(Cy_3)$ is a white, crystalline solid which dissolves in benzene, toluene, pyridine and diethyl ether. Found: Cu, 17.9; P, 8.58 calcd.: Cu, 17.7; P, 8.65%. The ^1H NMR spectrum of CH_3CuPCy_3 in benzene showed a singlet at τ 9.73 ppm corresponding to the methyl group bonded to copper and an unresolved multiplet at 8.02–8.74 ppm due to the cyclohexyl protons. The ^{13}C NMR spectrum in pyridine-d_5 at +13°C showed a somewhat broadened singlet at −7.93 ppm corresponding to the methyl group bonded to copper. The ^{31}P NMR spectrum of CH_3CuPCy_3 in toluene-d_8 + pyridine showed a signal at 18.1 ppm assigned to the complexed phosphine (free phosphine gives a signal at 8.31 ppm with respect to 85% H_3PO_4).

Thermal decomposition of CH_3CuPCy_3 was carried out in the solid state and in solution at a temperature +60°C to that of the boiling solvent. The gases evolved were collected in a gas burette and analysed by chromatography and mass spectrometry. The compositions of the gases evolved on thermolysis are given in Table 2.

Methane (30%) and ethane (60%) constitute the majority of the gases evolved. Ethylene and propane are also formed (4–7.7%). The volume of the gases is 92–95% of the theoretical value calculated for complete decomposition of the methylcopper complex. The composition of the gases evolved in solution is almost the same as that of gases in the solid state.

The ratio of the yields of methane and ethane formed on thermal decomposition is invariant to the hydrogen-donor ability of the solvent: almost identical ratios are observed in benzene, n-hexane and toluene. The thermolysis of the complex in benzene-d_6 showed a lack of deuterium in the gases evolved, which means that the source of hydrogen for the formation of methane was not the solvent.



	Found (%)				Calcd. (%)
CH_4	30.4	31.4	36.8	37.1	30.8
CH_3-CH_3	60.7	60.9	55.2	55.6	61.5
$CH_2=CH_2$	5.5	4.6	4.6	4.5	4.6
$CH_3CH_2CH_3$	4.4	3.1	3.1	2.8	3.1

SCHEME 2

Scheme 2 gives the proposed decomposition pathway of methyl(tricyclohexylphosphine)copper. The amounts of the gases found and calculated are in accordance. The reactions towards formation of methane (30%) and ethane (60%) proceed with the highest yields.

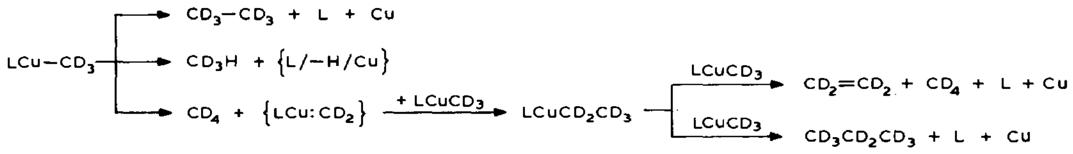
In comparison with the thermal decomposition of methylcopper not complexed with tricyclohexylphosphine, the yield of ethane is lower by 20%, and that of methane is higher by 20%. These differences can be explained by the course of hydrogen abstraction from tricyclohexylphosphine by the methyl group of methylcopper. In order to confirm this proposition, CD_3CuPCy_3 was obtained and its thermal decomposition products were studied. Completely deuterated ethane-d_6, ethylene-d_4 and propane-d_8 as well as CD_3H and CD_4 were found in the gases. The course of the reaction is shown in Scheme 3. A molar ratio of 6/4 found for CD_3H/CD_4 corresponds to the methane molar ratio calculated according to Scheme 2. Hydrogen abstraction from tricyclohexylphosphine by the methyl group in CH_3CuL is confirmed by the formation of CD_3H during the thermolysis of CD_3CuPCy_3 (Table 2, experiment 6) and the absence of deuterated gases during the thermal decomposition of CH_3CuPCy_3 in benzene-d_6 (Table 2, experiment 3). The

TABLE 2

DISTRIBUTION OF THE GASES EVOLVED ON THERMAL DECOMPOSITION OF $CH_3CuP(Cy)_3$

Experiment [a]	1	2	3 [b]	4	5 [c]	6 [c]
Solvent	without solvent	benzene	benzene-d_6	hexane	toluene	toluene
R	CH_3	CH_3	CH_3	CH_3	CH_3	CD_3
Methane	31.4	29.0	34.0	31.2	35.7	38.5
Ethane	60.9	67.0	61.2	62.3	64.3	61.5
Ethylene	4.6	2.0	4.8	3.9		
Propane	3.1	2.0		2.6		

[a] Experiment 1: temperature of thermolysis 100°C; time 1 h; yield 95%. Experiments 2–6: the temperature of thermolysis was increased from 60°C to the b.p. of the solvent; time 4 h. [b] The gases do not contain deuterium. [c] The gases dissolved in toluene were not determined.



	Found (%)
CD_3H	60
CD_4	40

SCHEME 3

hydrogen abstraction increases the yield of methane and decreases that of ethane in the gaseous products obtained after the decomposition of complexed methylcopper.

Tricyclohexylphosphine complexed with methylcopper increases the stability of the complex and increases its decomposition temperature. However, it does not affect the course and composition of the gaseous products of thermolysis to a great extent. The formation of ethylene can be explained by the β-hydrogen elimination of ethylcopper, and the formation of propane by reductive elimination between methyl- and ethylcopper.

The ethylene formation resulting from the reaction of two molecules of $\{Cu:CH_2\}$, as postulated [7], may proceed with a low probability although it cannot be excluded. We were not successful in the isolation of a thermolysis product derived from the abstraction of the hydrogen from the ligand by the methyl group of the methylcopper complex.

Extraction of the thermolysis residue with different solvents gave only tricyclohexylphosphine, as was confirmed by elemental analysis and ^{31}P NMR investigations. The copper sludge after extraction contained from 5 to 10% of phosphorus (from tricyclohexylphosphine bonded to copper).

Experimental

Materials

All the preparations and procedures were carried out under dry, deoxygenated argon. Solvents were purified by usual procedures, dried, distilled, and stored under argon.

Copper bisacetylacetonate was either sublimed in vacuo or recrystallized from $CHCl_3$, washed with diethyl ether, and dried. Dimethylaluminium monoethoxide was prepared by the reaction of trimethylaluminium with ethyl alcohol in hexane, followed by vacuum distillation. Tricyclohexylphosphine (Strem Chemicals Inc., Massachussets) was used without prior purification. Trimethylaluminium-d_9 was prepared by the reaction of CD_3I with powdered aluminium and on Al-Mg alloy. $(CD_3)_3Al$ was distilled off. When the distillate contained iodine, a Na-K dispersion was added and the mixture was warmed for 5 h. The isotopic purity of the methane evolved on acidolysis was determined by mass spectroscopy.

Analytical methods

^1H NMR spectra were recorded on a 100 MHz JEOL spectrometer; ^{13}C NMR and ^{31}P NMR spectra were recorded on a 90 MHz Bruker spectrometer.

The gases evolved were analyzed using a LKB 9000 mass spectrometer and a GID gas chromatograph, using Molecular Sieves 13X column for C_1–C_2 hydrocarbons. A Porapaq Q and Squalan column for C_1–C_4 hydrocarbons and Carbowax 20 M for the solvent were used.

The phosphorus content was determined by a spectrophotometric method [11]. The copper and aluminium contents were determined after digesting the sample with diluted nitric acid [12].

Preparation of the compounds

CH_3Cu

To an ethereal suspension of 0.7016 g (2.68 mmol) of copper bisacetylacetonate, 0.906 g (3.5 *M* equivalent) of dimethylaluminium monoethoxide was added at -78°C under stirring. The mixture was warmed and a gradual change of colour was observed at -10°C. The reaction was completed after 4 h at -15 to -10°C. The yellow powder which precipitated was filtered off and washed with cooled diethyl ether until no aluminium compounds were present in the filtrate.

Methylcopper was carefully dried in vacuo at -10°C for 2 h. Caution! Any operations with dried methylcopper may cause a violent decomposition-explosion reaction.

$CH_3CuP(Cy)_3$

1.03 g (3.94 mmol) of copper bisacetylacetonate, 1.2675 g (4.53 mmol) of tricyclohexylphosphine and 1.2558 g (12.3 mmol) of dimethylaluminium monoethoxide were stirred in diethyl ether at -78°C. The reaction mixture was gradually warmed, and at -30°C the colour of the suspension changed. The white suspension was further stirred for 4 h at -20 to -5°C, then was cooled, filtered, and washed with diethyl ether until no aluminium content could be determined. The crystals were dried in vacuo at -10 to 0°C. The yield of methyl(tricyclohexylphosphine)copper was 70%. The complex is extremely sensitive to air and moisture and microanalysis of C and H is impossible.

$CD_3Cu \cdot P(Cy)_3$ was prepared in the same way as $CH_3CuP(Cy)_3$, using $(CD_3)_2AlOEt$ as the methylating agent.

Thermal decomposition of methylcopper

The Schlenk tube containing the solid methylcopper was placed in a cooling bath at -10°C. The temperature was gradually raised until evolution of the gases was observed. The amount of gases was measured volumetrically. Darkening of the sample followed by gas evolution indicated the decomposition temp., $+20$°C. The composition of the gas mixture was checked during the decomposition reaction and determined by means of chromatography and mass spectrometry. When evolution of the gases had stopped, the bath temperature was raised gradually. Violent decomposition-explosion of the residue took place at 30–35°C. The distribution of the C_1–C_3 hydrocarbons in the gas mixture was determined by GC chromatography.

Thermal decomposition of methylcopper tricyclohexylphosphine complex

The Schlenk tube containing 0.4 g (1.1 mmol) of the solid, crystalline $MeCuP(Cy)_3$ was placed in a thermostated bath, the temperature ($+100$°C) was controlled with an accurancy of ±0.5°C. The system was connected to a burette in order to measure the volume of gases evolved during the decomposition. After 1 h, the reaction was completed, and 18 cm^3 of gases was evolved. The composition of the gases evolved was determined by chromatography and mass spectroscopy (CH_4, C_2H_6, C_2H_4, C_3H_8). The decomposition residue was extracted with pyridine, benzene and diethyl ether and the solvents were distilled off in vacuo.

^1H NMR, ^{13}C NMR and ^{31}P NMR spectra of the benzene solution of the extract were recorded. The copper and phosphorus contents in the residue were determined by analytical methods.

Thermolysis of $CH_3CuP(Cy)_3$ in solvent

0.3 g (0.8 mmol) of $CH_3CuP(Cy)_3$ was dissolved in 2 cm^3 of benzene at +10°C and placed in the vessel connected to the reflux condenser. The temperature was raised gradually from +20° to +60°C and after 1 h to the boiling point of the solvent. Darkening of the solution and slow precipitation of metallic copper were observed at about 50–60°C. At the same time, gases were evolved. When the evolution of gases had stopped, argon was bubbled through the solution to desorb the hydrocarbons dissolved in the solvent, and the mixture was cooled down. The same procedure was applied to the toluene and hexane solutions.

References

1 G.M. Whitesides, E.R. Stredonsky and C.P. Casey, J. Am. Chem. Soc., 92 (1970) 1426.
2 R. Wada, M. Tamura and J. Kochi, J. Am. Chem. Soc., 92 (1970) 6656.
3 G.M. Whitesides, E.J. Panek and E.R. Stredonsky, J. Am. Chem. Soc., 94 (1974) 232.
4 M.F. Lappert and R. Pearce, J. Chem. Soc., Chem. Commun., (1973) 24.
5 G.M. Whitesides, C.P. Casey and J.K. Krieger, J. Am. Chem. Soc., 93 (1971) 1379.
6 A, Yamamoto and A. Miyashita, Bull. Chem. Soc. Jpn., 50 (1977) 402.
7 A. Miyashita, T. Yamamoto and A. Yamamoto, Bull. Chem. Soc. Jpn., 50 (1977) 1109.
8 T. Ikariya and A. Yamamoto, J. Organomet. Chem., 72 (1974) 145.
9 G. van Koten and J.G. Noltes, Comprehensive Organometallic Chemistry, Vol. 2, p. 709, Pergamon Press, Oxford, 1982.
10 G. van Koten, A.J. Leusink and J.G. Noltes, J. Organomet. Chem., 85 (1975) 105.
11 Z. Marczenko, Spectrophotometric Determination of the Elements, PWN, Warszawa, 1979.
12 R. Přibil, Analytical Applications of EDTA and Related Compounds, Pergamon Press, Oxford, 1972.