Thermal Stability of Alkylcopper(I) Complexes Coordinated with Tertiary Phosphines

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(Received November 12, 1976)

Thermolysis of isolated alkylcopper(I) complexes having tertiary phosphine ligand(s) $RCuL_n$ ($R=CH_3$, C_2H_5, n-C_3H_7, i-C_4H_9) in the solid state and in toluene has been studied in order to clarify the role of the tertiary phosphine ligand in stabilizing the alkylcopper(I) complexes. The distribution of the thermolysis products shows that the thermolysis of the alkylcopper complexes having ethyl or longer alkyl chain proceeds through a β-elimination mechanism. The rate of the thermolysis obeys the first order rate law, $-d[RCuL_n]/dt=k[RCuL_n]$. The activation parameters of the thermolysis were obtained from the temperature dependence of k and a compensation effect between ΔH^* and ΔS^* was demonstrated. The activation energy E_a of the thermolysis of $RCu(PPh_3)_2$ increases in the order of $R=C_2H_5<n\text{-}C_3H_7<i\text{-}C_4H_9$. Coordination of electron-donating tertiary phosphine decreases E_a and a linear relationship between $\nu(Cu\text{–}CH_3)$ frequencies and E_a for thermolysis of the methylcopper complexes was observed. Addition of PPh_3 into the toluene solutions of $CH_3Cu(PPh_3)_2(\text{diethyl ether})_{0.5}$ and C_2H_5-$Cu(PPh_3)_2$ causes some retardation of the thermolysis. The major role of the tertiary phosphine ligand in stabilizing the alkylcopper complexes is proposed to strengthen the Cu–C bond by changing the electronic state of copper atom. An energetic consideration based on Chatt and Shaw's theory is given in order to account for the results concerning the stabilities of the alkylcopper complexes. Photolysis of the alkylcopper complexes takes a quite different decomposition pathway producing mainly RH from $RCuL_n$.

The problem of the stability of transition metal to carbon bond is of fundamental importance in organotransition metal chemistry. Information regarding the stability of trasition metal-carbon σ bond and how to stabilize or activate the σ bond is quite desirable for theoretical discussion of the nature of the metal-carbon σ bond as well as in accounting for the mechanisms of organic syntheses promoted by transition metal compounds.$^{1)}$ However, because of the scarcity of the isolated alkyltransition metal compounds possessing considerable thermal stabilities, the discussions have remained empirical and often have been based on the relative ease for the preparation of an alkyltransition metal compound. Two lines of theories have been proposed concerning the factors determining the stability of a transition metal-carbon bond. The first one, originally proposed by Chatt and Shaw,$^{2)}$ relates the stability with the energy gap required to promote an electron from predominantly non-bonding d-orbitals to antibonding metal-carbon orbitals (σ^*_{M-C}) or from bonding metal-carbon orbitals (σ_{M-C}) to vacant or half-filled d-orbitals, and the role of the stabilizing ligand was accounted for in terms of the increase in the energy gap. A partially modified scheme of this model was proposed by us to account for the stability of dialkyl(2,2′-bipyridine)nickel and activation of the Ni–C bonds in the presence of electronegative olefins.$^{3)}$ The other theory stresses the importance of low energy decomposition pathway, particularly a β-elimination process$^{4,5)}$ and accounts for the role of the "stabilizing ligand" mainly as blocking the site required for the β-elimination process to proceed. On the basis of the latter theory some "elimination stabilized alkyls" such as trimethylsilylmethyl have been successfully prepared.$^{4,5c,5d)}$

Although the number of isolated alkyltransition metal complexes is rapidly increasing in recent years, works reporting the kinetics of the decomposition process and dealing with the analysis of the decomposition products are relatively limited.$^{3,5,6,12,15)}$ Thermolysis of alkylcopper complexes have been studied by Whitesides$^{5a,5e)}$ and Kochi.$^{7)}$ Unfortunately, however, the studies have been made on the complexes prepared *in situ* from copper salts and alkylating agents and the systems studied may well contain some impurities, albeit in small quantities. Since the presence of a Lewis acid is known to affect the stability and decomposition course of an alkyl- or hydridotransition metal complex,$^{8,9)}$ results obtained in somewhat impure systems are not quite unequivocal.

We have isolated series of alkylcopper complexes containing various tertiary phosphines and observed the pronounced effect of the tertary phosphine ligands on stabilization of the alkylcopper compounds.$^{10)}$ In contrast to the extremely unstable ligand-free methylcopper which decomposes violently at room temperature, the phosphine-stabilized alkylcopper complexes are considerably stable and provide a suitable probe for testing the validity of the existing theories. We report here the kinetic study of thermolysis of the alkylcopper complexes and analysis of the gaseous products generated in the thermolysis with a hope to provide pertinent data relevant to the discussion of the thermal stability of alkylcopper complexes.

Results and Discussion

Thermolysis of Alkylcopper Complexes in Solid State. Decomposition Temperature and Thermolysis Products: The isolated alkylcopper complexes containing tertiary phosphine ligands were thermolyzed in solid state in vacuum and the composition of the evolved gases was analyzed. Table 1 summarizes the decomposition points of various alkylcopper complexes with teriary phosphine ligands and the compositions of the evolved gases. Table 1 also includes the sum of the amounts of gaseous products generated per copper atom ($\sum$R).

The results in Table 1 indicate almost quantitative

TABLE 1. DECOMPOSITION POINTS (dp) OF ALKYLCOPPER COMPLEXES AND THEIR PYROLYSIS PRODUCTS

Compound[a]	Dp (°C)	Composition of the gas evolved[b]				ΣR(%)[j]
		H_2	R(−H)	RH	R-R	
$CH_3Cu(PPh_3)_2(ether)_{0.5}$	75—76	0	3[g]	7	90	108
$CH_3Cu(PPh_3)_3(toluene)$	70—75	0	0	25	75	98
$C_2H_5Cu(PPh_3)_2$	56—58	14	55	29	2	97
$C_2H_5CuPPh_3$	55—58	11	54	32	3	87
n-$C_3H_7Cu(PPh_3)_2$	61—62	22	60	18	0	96
i-$C_4H_9Cu(PPh_3)_2$	60—63	29	60[h]	11[i]	0	102
CH_3CuPCy_3	105—110	0	0	0	100	71
$C_2H_5CuPCy_3$	75—80	17	67	17	0	88
$C_3H_7CuPCy_3$	85—90	26	70	4	0	77
i-$C_4H_9CuPCy_3$	100—102	29	65[h]	7[i]	0	98
$(CH_3)_4CuAl_2(dpe)_2(OC_2H_5)_2$	230[c]	0	0	37	63	—
$(CH_3Cu)_2(dpe)_3$	149—150	0	9[g]	48	43	95
$(C_2H_5Cu)_2(dpe)_3$	124—127	2	53	45	0	81
(*n*-$C_3H_7Cu)_2(dpe)_3$	130—150	4	41	55	0	96
(*i*-$C_4H_9Cu)_2(dpe)_3$	102—105	5	45[h]	50[i]	0	95
$CH_3Cu(P(C_6H_5)_2(CH_3))_3$	95—98	0	0	2	98	100
$CH_3Cu(P(C_6H_5)(CH_3)_2)$	50—90[d]	0	0	62	38	110
$CH_3Cu(P(n\text{-}C_4H_9)_3)$	90—130[e]	0	0	61	39	112
$CH_3Cu(P(C_2H_5)_3)$	60—90[f]	0	0	85	15	93

a) PPh_3 = triphenylphosphine, PCy_3 = tricyclohexylphosphine, dpe = 1,2-bis(diphenylphosphino)ethane, ether = diethyl ether. b) Mol%. c) At 136—139 °C it melted turning to black and decomposed at 230 °C. d) Mp, 50—51 °C. e) Mp, 57—60 °C. f) Mp, 40—45 °C. g) C_2H_4. h) 2-Methylpropene. i) 2-Methylpropane. j) The mol percent of the alkyl group decomposed was determined by measuring the volume of the gas evolved. The amount of R-R was doubled in calculation.

liberation of the alkyl groups as gaseous products on the thermolysis. Decomposition points in Table 1 refer to the temperature at which smooth evolution of gas started on heating the complexes in vacuum. Most complexes decompose with melting but some complexes evolve gas at much higher temperature than their melting points. The dpe-coordinated complexes (dpe = 1,2-bis(diphenylphosphino)ethane) showed the highest decomposition points and particularly the methylcopper complex containing an aluminum component was so stable as it was not decomposed up to 230 °C. A similar enhancement of the thermal stability was observed in a manganese hydride complex containing an alkylaluminum component.[9] The decomposition points of the tricyclohexylphosphine (PCy_3)-coordinated complexes ranked next to the dpe-containing complexes to be followed by PPh_3-coordinated (PPh_3=triphenylphosphine) complexes. The dpe- and PCy_3-coordinated complexes showed some variation in decomposition points depending on the alkyl group bonded to copper, whereas the difference in decomposition points of the PPh_3-coordinated complexes was not so marked.

In the thermolysis of solid methylcopper complexes coordinated with $P(C_6H_5)(CH_3)_2$, $P(C_2H_5)_3$, and $P(C_4H_9)_3$ ligands, considerable amounts of methane were evolved in addition to ethane. Since the value of ΣR is about 100%, the source of hydrogen for methane formation should be the phosphine ligands and this fact together with the absence of ethylene in the thermolysis products excludes the possibility of α-elimination which was observed for thermolysis of $(CH_3)_2Fe(dpe)_2$[11] and $CH_3CrCl_2L_n$.[12] On the other hand, evolution of ethylene was observed in thermolysis of $CH_3Cu(PPh_3)_2$(diethyl ether)$_{0.5}$ and $(CH_3Cu)_2(dpe)_3$ which may partly decompose by the α-elimination.

In the thermolysis of the alkylcopper complex with ethyl or longer alkyl chain, both alkane and alkene are formed, the latter being more predominant, accompanied by evolution of molecular hydrogen. Examination of the distributions of alkanes, alkenes and H_2 evolved from PPh_3- and PCy_3-coordinated complexes revealed that the amounts of H_2 evolved correspond to about half of the difference between the amounts of alkanes and alkenes.

These observations suggest that the thermolysis of the alkylcopper complexes having ethyl or longer alkyl chain proceeds by the following scheme comprising β-elimination (Eq. 1), coupling of the alkyl and hydrido ligands (Eq. 2), and evolution of H_2 from the copper hydride (Eq. 3). The participation of all molecules of the copper hydride in either the reaction (2) or (3) was confirmed by the absence of hydrogen evolution on treatment of the thermolysis residue with H_2SO_4.

$$RCuL_n \rightarrow CuHL_n + R(-H) \qquad (1)$$

$$HCuL_n + RCuL_n \rightarrow RH + 2CuL_n \qquad (2)$$

$$HCuL_n \rightarrow 1/2H_2 + CuL_n \qquad (3)$$

Whitesides and coworkers have proposed a similar mechanism for the thermolysis of butyl-1,1-d_2-(tributylphosphine)copper(I) prepared *in situ* by analyzing the composition of the gases evolved.[5a]

Kinetics of the Thermolysis of Solid Alkylcopper Complexes: The thermolysis of the alkylcopper complexes

Table 2. The first-order rate constants of pyrolysis of alkylcopper(I) complexes

Compound[a]	Rate constant[b]
$CH_3Cu(PPh_3)_2(ether)_{0.5}$	0.91(69.5), 3.56(74.6), 5.08(76.8), 9.28(79.0)
$CH_3Cu(PPh_3)_3(toluene)$	0.79(59.6), 1.60(62.6), 3.53(66.2), 8.45(71.8)
$C_2H_5Cu(PPh_3)$	1.23(34.0), 3.69(37.3), 12.0(41.2), 39.1(44.6)
$C_2H_5Cu(PPh_3)_2$	1.14(40.8), 2.45(45.2), 8.36(50.5), 20.8(53.0)
$n\text{-}C_3H_7Cu(PPh_3)_2$	0.65(40.6), 1.12(45.2), 5.61(48.0), 8.40(50.4), 20.3(53.2), 90.8(57.5)
$i\text{-}C_4H_9Cu(PPh_3)_2$	1.31(34.5), 2.30(39.0), 5.67(41.5), 12.8(43.3), 26.1(45.5)
$CH_3Cu(P(C_6H_5)_2(CH_3))_3$	1.23(87.5), 3.71(93.0), 16.4(102.5), 42.0(107.5)
CH_3CuPCy_3	3.82(76.5), 5.68(80.0), 6.49(82.6), 10.4(86.0), 14.6(89.2)
$i\text{-}C_4H_9CuPCy_3$	3.44(75.4), 8.52(80.0), 21.4(85.0), 41.9(89.0)
$(CH_3Cu)_2(dpe)_3$	2.04(120.0), 2.49(129.0), 12.2(134.5), 31.0(139.0)
$(i\text{-}C_4H_9Cu)_2(dpe)_3$	0.88(78.2), 3.24(84.2), 4.47(88.5), 13.3(94.5)

a) For abbreviations, see Table 1. b) $10^4\ k\ s^{-1}$. The numbers in the parentheses refer to the thermolysis temperatures in °C.

in solid state was followed by measuring the gas evolved at fixed temperatures.

Figure 1 shows the results of typical thermolysis experiments. The volume of gas evolved on heating a solid sample at certain temperature was measured and plotted *versus* time. Since the composition of the gas evolved during the course of thermolysis did not vary significantly, the value of $(V_\infty - V_t)$, where V_∞ and V_t refer to the gas volumes evolved at infinite time and time t, corresponds to the amount of the alkylcopper complex remaining undecomposed. Plots of $\log(V_\infty - V_t)$ *versus* time t give straight lines with some curvatures in the initial stages as shown in Fig. 2. In most cases the portion of the straight line covers a range corresponding to decomposition of about 80% of the alkylcopper complex. In this paper we are concerned with the region where the linear relationship holds between $\log(V_\infty - V_t)$ and time. The rate constants in the first-order expression

$$-d[RCuL_n]/dt = k[RCuL_n]$$

are given in Table 2. From Arrhenius plots of the rate constants in Table 2 activation energies and kinetic parameters were computed and are summarized in Table 3.

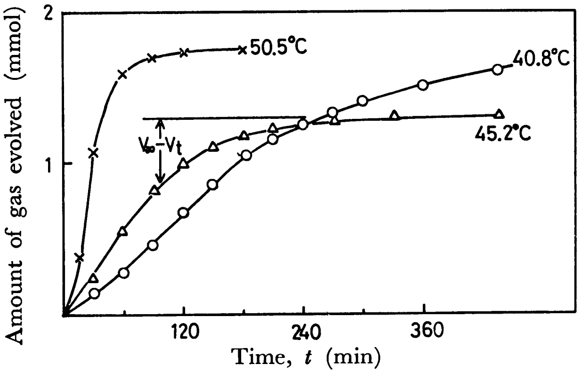


Fig 1. Time curves of the amount of gas evolved in the thermolyses of $C_2H_5Cu(PPh_3)_2$ at fixed temperatures. Amount of $C_2H_5Cu(PPh_3)_2$: 50.5 °C, 920 mg; 45.2 °C, 690 mg; 40.8 °C, 950 mg.

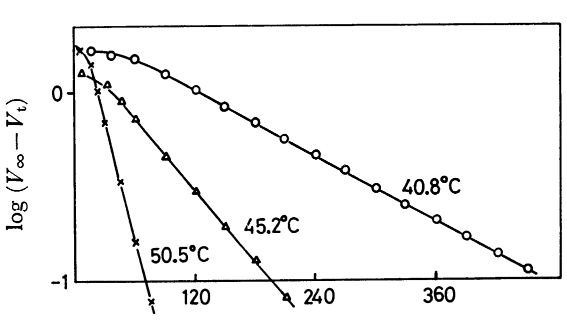


Fig. 2. The first-order plots of the data in Fig. 1.

That the first-order rate law holds in the thermolysis of the alkylcopper complexes having ethyl or longer alkyl chain indicates that the formation of the copper hydride by the β-elimination (Eq. 1) is rapidly followed by the process (2) or (3). This is consistent with Whitesides and coworker's observation[13] that the copper hydride prepared *in situ* decomposed even at −20 °C to evolve H_2 and in the presence of an alkylcopper(I) complex it underwent a facile coupling reaction to produce RH at −20 °C to −30 °C.

Furthermore, the first-order rate law for the thermolysis of the methylcopper complexes suggests that the methyl group ("CH_3") liberated from the methylcopper complex by a spontaneous unimolecular process

Table 3. Activation energies and kinetic parameters for thermolysis of alkylcopper compounds

Compound[a]	E_a (kcal·mol^{-1})	ΔH^* (kcal·mol^{-1})	ΔS^* (e.u.)	ΔF^* (kcal·mol^{-1})
$CH_3Cu(PPh_3)_3(toluene)$	50	50	72	26
$CH_3Cu(PPh_3)_2(ether)_{0.5}$	57	57	85	27
$C_2H_5Cu(PPh_3)$	62	61	123	22
$C_2H_5Cu(PPh_3)_2$	48	47	74	24
$n\text{-}C_3H_7Cu(PPh_3)_2$	63	63	119	25
$i\text{-}C_4H_9Cu(PPh_3)_2$	71	70	151	23
$CH_3Cu(P(C_6H_5)_2(CH_3))_3$	46	45	49	28
CH_3CuPCy_3	27	26	0.3	26
$i\text{-}C_4H_9CuPCy_3$	47	46	57	26
$(CH_3Cu)_2(dpe)_3$	50	50	50	30
$(i\text{-}C_4H_9Cu)_2(dpe)_3$	43	42	43	27

a) For abbreviations see Table 1.

(Eq. 4) will rapidly abstract hydrogen from the phosphine ligand (Eq. 5) or couple with the CH_3 group in another molecule of the methylcopper complex (Eq. 6) to evolve CH_4 and C_2H_6, respectively. Abstraction of hydrogen of CH_3 group in the methylcopper complex by "CH_3" to produce CH_4 and a carbenoid species (Eq. 7) may also take place,

$$CH_3CuL_n \rightarrow \text{“}CuL_n\text{”} + \text{“}CH_3\text{”} \tag{4}$$

$$\text{“}CuL_n\text{”} + \text{“}CH_3\text{”} \rightarrow CH_4 + CuL_{n-1}(L(-H)) \tag{5}$$

$$\text{“}CH_3\text{”} + CH_3CuL_n - \begin{cases} \longrightarrow C_2H_6 + CuL_n & (6) \\ \longrightarrow CH_4 + CH_2{=}CuL_n & (7) \end{cases}$$

$$CH_2{=}CuL_n \rightarrow 1/2C_2H_4 \tag{8}$$

where L(—H) represents a ligand from which a hydrogen atom was taken away by the methyl group.

The course of the thermolysis of $CH_3Cu(PPh_3)_2$ (diethyl ether)$_{0.5}$ consists of two stages. The gas evolved at the earlier stage was composed mainly of diethyl ether and scission of the Cu–CH_3 bond started after the quantitative evolution of diethyl ether. The rate constants in Table 2 and the activation energy in Table 3 are referred to the latter stage.

A Compensation Effect between the Enthalpy of Activation and the Entropy of Activation: Examination of the results in Tables 1, 2 and 3 reveals several interesting features of the thermolysis. Although it may be expected that a complex having higher activation energy for the thermolysis has a higher decomposition temperature, it is seen from the tables that there exists no correlation between the decomposition point of an alkylcopper complex and its activation energy for thermolysis. We consider that the activation energy for thermolysis more directly reflects the intrinsic strength of the Cu–C bond than the decomposition temperature. The present observation suggests that it is not always justified to discuss the strength of the alkyl-transition metal bond referring only to the decomposition points of the complexes, although they may be often used as practical criteria of the strength of the alkyl-transition metal bond.

A plot of the enthalpy of activation ΔH^* against the entropy of activation ΔS^* for the thermolysis of the alkylcopper complexes gave a straight line with a slope $\Delta H^*/\Delta S^*=270$ deg (Fig. 3) which corresponds to a value of about one for $\Delta H^*/T\Delta S^*$ under the experimental conditions indicating that the increase in ΔH^* does not cause a direct increase in ΔF^* but is almost completely cancelled by the decrease in $-T\Delta S^*$.

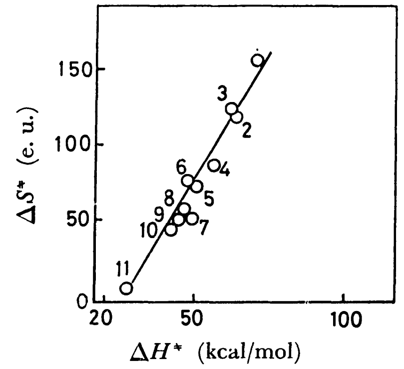


Fig. 3. The compensation effect between ΔH^* and ΔS^*. 1: i-$C_4H_9Cu(PPh_3)_2$, 2: n-$C_3H_7Cu(PPh_3)_2$, 3: $C_2H_5CuPPh_3$, 4: $CH_3Cu(PPh_3)_2$(diethyl ether)$_{0.5}$, 5: $CH_3Cu(PPh_3)_3$(toluene), 6: $C_2H_5Cu(PPh_3)_2$, 7: $(CH_3Cu)_2(dpe)_3$, 8: i-$C_4H_9CuPCy_3$, 9: $CH_3Cu(P(C_6H_5)_2CH_3)_3$, 10: $(i$-$C_4H_9Cu)_2(dpe)_3$, 11: $CH_3Cu(PCy_3)$.

These results explain the lack of correlation between the decomposition points of alkylcopper complexes and their activation energies for thermolysis. The compensation effect is particularly well demonstrated in a series of $RCu(PPh_3)_2$ complexes. In contrast to the steady and significant increase of the activation energy for thermolysis from the ethyl (47 kcal/mol) through the propyl (63) to the isobutyl (70) the decomposition points vary only slightly (Table 1).

We have observed a compensation effect between ΔH^* and ΔS^* for the splitting of nickel-alkyl bonds induced by olefin coordination.[14)]

Thermolysis of Alkylcopper Complexes in Solution.

The alkylcopper complexes have lower stability in solution than in the solid state. The decomposition of the complexes in solution set in at the lower temperature by 40—50 °C than that in the solid state. One mol of $C_2H_5Cu(PPh_3)_2$ evolved 0.59 mol of ethylene, 0.33 mol of ethane and 0.15 mol of H_2 on the thermolysis in toluene at 10 °C. The distribution of the gases evolved in toluene is essentially the same as that of gases evolved in solid state. The results indicate that the thermolysis of the ethylcopper complex in toluene proceeds through the same processes as those proposed for the thermolysis in the solid state (Eqs. 1, 2 and 3). The thermolysis in toluene obeyed

TABLE 4. THE FIRST-ORDER RATE CONSTANTS OF THE THERMOLYSIS OF $C_2H_5Cu(PPh_3)_2$ AND $CH_3Cu(PPh_3)_2$(DIETHYL ETHER)$_{0.5}$ IN TOLUENE

Compound[a)]	$\frac{[PPh_3\ added]}{[Cu\ complex]}$	Rate constant[b)] (s^{-1})
$C_2H_5Cu(PPh_3)_2$	0	4.8(−2.1), 7.1(0.3), 18(4.7), 34(7.8)
$C_2H_5Cu(PPh_3)_2$	1.0	13(4.7)
$C_2H_5Cu(PPh_3)_2$	2.0	9.4(4.7)
$C_2H_5Cu(PPh_3)_2$	4.1	1.3(−3.3), 3.0(0.2), 8.9(4.7)
$CH_3Cu(PPh_3)_2(Et_2O)_{0.5}$	0	1.3(22.6), 3.4(27.1), 7.7(30.0)
$CH_3Cu(PPh_3)_2(Et_2O)_{0.5}$	1.9	3.0(27.0)
$CH_3Cu(PPh_3)_2(Et_2O)_{0.5}$	4.0	0.52(17.0), 1.2(21.6), 2.7(27.0), 7.1(30.3)

a) Et_2O=diethyl ether. b) $10^4\ k$. The numbers in the parentheses show the thermolysis temperatures in °C.

the first-order rate law and the first-order rate constants are listed in Table 4.

The activation energy for the thermolysis of $C_2H_5Cu(PPh_3)_2$ in toluene calculated from an Arrhenius polt of the rate constants was 32 kcal/mol, being considerably smaller than that in the solid state (48 kcal/mol) The heat of fusion of the ethylcopper complex required in the thermolysis in the solid phase accounts for a part of the difference between the two activation energies. However, in order to account for whole of such a great difference, it will be necessary to consider other unrevealed factors such as ease of intramolecular rearrangement of the copper complex in forming the so-called activated complex and the coordination of solvent.

On addition of PPh_3 into the toluene solution of $C_2H_5Cu(PPh_3)_2$ the first-order rate constant decreased approaching a limiting value. The effect of the addition of PPh_3 on the rate constant can be accounted for by assuming the formation of a stabler ethylcopper complex having three PPh_3 ligands $C_2H_5Cu(PPh_3)_3$. In fact the methyl analog of $C_2H_5Cu(PPh_3)_3$ is isolable from toluene containing sufficient amount of PPh_3.[10c)] An alternative explanation that there exists a dissociation equilibrium in the solution to form a less stable complex $C_2H_5Cu(PPh_3)$ by an equilibrium, $C_2H_5Cu(PPh_3)_2 \rightleftharpoons C_2H_5Cu(PPh_3)+PPh_3$, and addition of PPh_3 suppresses the dissociation seems less probable, since the molecular weight determination of $C_2H_5Cu(PPh_3)_2$ in benzene showed a negligible dissociation of PPh_3 from the complex.[10c)]

Thermolysis of $CH_3Cu(PPh_3)_2(\text{diethyl ether})_{0.5}$ in toluene also obeyed the first-order rate law and the rate constants are included in Table 4. Addition of PPh_3 into the solution influences the rate of the thermolysis. However, this is not so marked as that observed in the thermolysis of $C_2H_5Cu(PPh_3)_2$ and the result suggests that the methylcopper complex having three PPh_3 ligands which is formed in solution on addition of PPh_3 is thermolyzed at almost the same rate as the methylcopper complex having two PPh_3 ligands.

Thermolysis of $CH_3Cu(P(n\text{-}C_4H_9)_3)_3$ in toluene did not obey the first-order rate law. $(RCu)_2(dpe)_3$ in solutions underwent a quite different reaction, a selective hydrogen abstraction reaction from the methylene group of the dpe ligand by the alkyl group.[10c)]

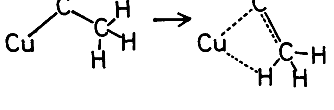
Consideration of the Effect of the Tertiary Phosphine Ligands on the Thermal Stability of the Cu–R Bond.

The Role of the Tertiary Phosphine Ligands in Stabilizing the Alkylcopper Complexes: If addition of ligand L to the solution of an alkyltransition metal complex R_mML_n causes complete inhibition of the thermolysis of the alkyltransition metal complex as observed in the thermolysis of alkylplatinum,[5b)] -iron[6d,15a)] and -cobalt[15b)] complexes in solutions, the major role of the ligand in stabilizing the alkyltransition metal complex may be the blocking the site to hinder the β-elimination to proceed.[4,5)] However, this is not the case for the thermolysis of the present alkylcopper complexes, since addition of PPh_3 into a toluene solution of $C_2H_5Cu(PPh_3)_2$ did not cause complete inhibition of the thermolysis of the ethylcopper complex though it caused a change in the rate of the thermolysis which may be accounted for by assuming a change in the strength of the Cu–C bond by the coordination of the third PPh_3(see above). Furthermore, ^{31}P-NMR spectra of mixtures of the alkylcopper complex ($C_2H_5Cu(PPh_3)_2$ or $CH_3Cu(PPh_3)_2(\text{diethyl ether})_{0.5}$) and PPh_3 in toluene showed that a rapid exchange between the coordinated PPh_3 and free PPh_3 occurs even at −60 °C. This observation is not compatible with the assumption that the dissociation of a ligand from copper constitutes the rate determining step in the thermolysis.

The following three observations also are not consistent with the assumption that the predominant role of the tertiary phosphines in stabilizing the Cu–R bond is the blocking of the site for β-elimination. (1) Comparison of the activation energies of $C_2H_5Cu(PPh_3)$ and $C_2H_5Cu(PPh_3)_2$ (Table 3) reveals that the ethylcopper complex containing one triphenylphosphine ligand has a *higher* activation energy than the ethylcopper complex with two PPh_3 ligands. As far as one compares the stability of an alkylcopper complex in terms of the activation energy for the thermolysis, this is not compatible with the theory to explain the role of the stabilizing ligand as blocking the site to hinder the β-elimination.

(2) The alkylcopper complexes generally have a monomeric structure in benzene as revealed by the cryoscopic molecular weight measurements of the complexes in benzene.[10c)] This indicates that the copper complexes, especially those having one or two tertiary phosphines are not fully coordinated and have vacant site(s) at least in benzene. Thereupon the dissociation of the tertiary phosphine ligand seems not to be required for the β-elimination to proceed.

(3) The presence of the compensation effect between ΔH^* and ΔS^* (Fig. 3) for both the methylcopper complexes and the other copper complexes having ethyl or longer alkyl chain implies that the same factor which control the thermal stability of the methylcopper complexes dominates the thermal stability of the copper complexes having ethyl or longer alkyl chains. Since the thermal stability of the methylcopper complexes seems to be controlled only by the strength of the Cu–C bond, the observation concerning the compensation effect implies that even the thermolysis of the copper complexes having ethyl or longer alkyl chain is controlled by the intrinsic strength of the Cu–C bond. We assume that the loosening of the Cu–C bond as shown below is necessary to allow the copper atom to approach the β-hydrogen and thus to allow the β-elimination to proceed. If the β-elimination does not require the loosening of the Cu–C bond, we may anticipate that the activation energy for the thermolysis of copper complexes having ethyl or longer chain is much smaller than that for the



thermolysis of the methylcopper complexes. However, this is not the case in the thermolysis of the alkylcopper complexes.

From the above described reasons we conclude that the prime role of the tertiary phosphine ligand in stabilizing the present alkylcopper complexes is not simply to block the site but rather to strengthen the Cu–C bond by changing the electronic state of the complexes.

Effect of the Tertiary Phosphine Ligands on the Strength of the Cu–C Bond: Figure 4 shows a correlation between the activation energies for thermolysis and $\nu(\mathrm{Cu-CH_3})$ frequencies of the methylcopper complexes. The correlation supports our assumption that the activation energy for thermolysis corresponds to the energy required for loosening the Cu–C bond. Figure 5 shows the relationship between $\nu(\mathrm{Cu-CH_3})$ frequencies and pK_a of the conjugate acid of the tertiary phosphine ligand $[\mathrm{HPR'_3}]^+$, and Fig. 6 shows the correlation between the activation energy and the pK_a value. It is seen that the complex with less basic ligands exibits the $\nu(\mathrm{Cu-CH_3})$ band at higher frequency and has a higher activation energy.

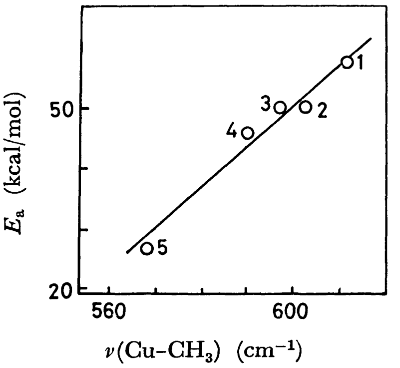


Fig. 4. Relationship between activation energy for thermolysis of methylcopper complexes and $\nu(\mathrm{Cu-CH_3})$. 1: $\mathrm{CH_3Cu(PPh_3)_2(diethyl\ ether)_{0.5}}$, 2: $\mathrm{CH_3Cu(PPh_3)_3(toluene)}$, 3: $\mathrm{(CH_3Cu)_2(dpe)_3}$, 4: $\mathrm{CH_3Cu(P(C_6H_5)_2CH_3)_3}$, 5: $\mathrm{CH_3Cu(PCy_3)}$.

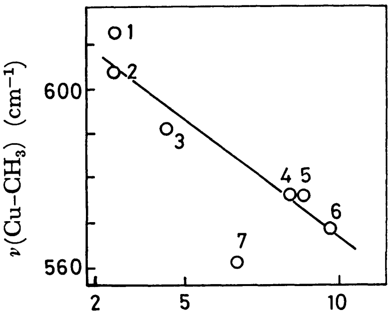


Fig. 5. Relationship between $\nu(\mathrm{Cu-CH_3})$ frequencies of methylcopper complexes and pK_a value of the conjugate acid of the tertiary phosphine ligand. 1: $\mathrm{CH_3Cu(PPh_3)_2(diethyl\ ether)_{0.5}}$, 2. $\mathrm{CH_3Cu(PPh_3)_3(toluene)}$, 3: $\mathrm{CH_3Cu(P(C_6H_5)_2CH_3)_3}$, 4: $\mathrm{CH_3Cu(P(\mathit{n}-C_4H_9)_3)}$, 5: $\mathrm{CH_3Cu(P(C_2H_5)_3)}$, 6: $\mathrm{CH_3Cu(PCy_3)}$, 7: $\mathrm{CH_3Cu(P(C_6H_5)(CH_3)_2)}$.

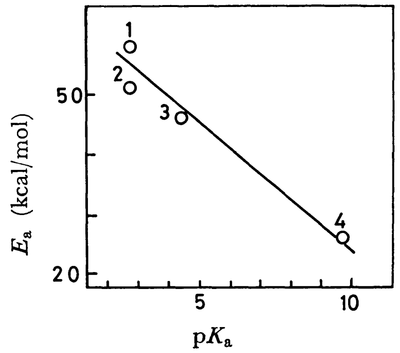


Fig. 6. Relationship between activation energy for thermolysis of methylcopper complexes and pK_a value of the conjugated acid of the tertiary phosphine ligand. 1: $\mathrm{CH_3Cu(PPh_3)_2(diethyl\ ether)_{0.5}}$, 2: $\mathrm{CH_3Cu(PPh_3)_3(toluene)}$, 3: $\mathrm{CH_3Cu(P(C_6H_5)_2CH_3)_3}$, 4: $\mathrm{CH_3Cu(PCy_3)}$.

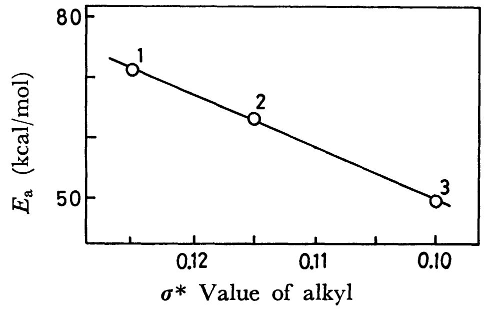


Fig. 7. Relationship between Taft's σ^* value of alkyl and activation energy for thermolysis of $\mathrm{RCu(PPh_3)_2}$. 1: $\mathrm{R}=i\text{-}\mathrm{C_4H_9}$, 2: $n\text{-}\mathrm{C_3H_7}$, 3: $\mathrm{C_2H_5}$.

In order to see the effect of the alkyl group bonded to copper on the activation energy for thermolysis, the activation energies were plotted *versus* Taft's σ^* values[16] of the alkyl groups in Fig. 7.

The theory originally proposed by Chatt and Shaw,[2] upon some modification by Yamamoto and coworkers,[3] is consistent in accounting for the strength of the alkyl-copper bond which may be evaluated from the activation energy.

Since alkylcopper(I) complex has completely filled d-orbitals it is not necessary in terms of Chatt-shaw's theory[2] to consider the electronic promotion from bonding Cu–R orbital to vacant d-orbitals ($\sigma_{\mathrm{M-R}}\rightarrow\mathrm{d}$) and consideration of only the promotion from the filled d-orbital to anti-bonding Cu–R orbital ($\mathrm{d}\rightarrow\sigma^*_{\mathrm{Cu-R}}$) is required. If we assume that the order of energy of anti-bonding Cu–R orbitals ($\sigma^*_{\mathrm{Cu-R}}$) is related to the order of electron affinities (E.A.) of alkyl radicals (E. A. in kcal/mol: $\mathrm{CH_3}$, 32.2; $\mathrm{C_2H_5}$, 21.6; $\mathrm{C_3H_7}$, 15.9; $\mathrm{C_4H_9}$, 15.0),[17] the anti-bonding Cu-methyl orbital ($\sigma^*_{\mathrm{Cu-CH_3}}$) is expected to have the lowest energy and the energy level of $\sigma^*_{\mathrm{Cu-R}}$ is expected to increase in the order of $\mathrm{R}=\mathrm{CH_3}<\mathrm{C_2H_5}<n\text{-}\mathrm{C_3H_7}<i\text{-}\mathrm{C_4H_9}$. The energy gap required for an electronic promotion from the metal d-orbitals to the $\sigma^*_{\mathrm{Cu-R}}$ orbital may be related to the activation energy for thermolysis of the alkyl-copper complex (Fig. 8). The agreement between the order of the increasing activation energy of the thermolysis of $\mathrm{RCu(PPh_3)_2}$ by changing

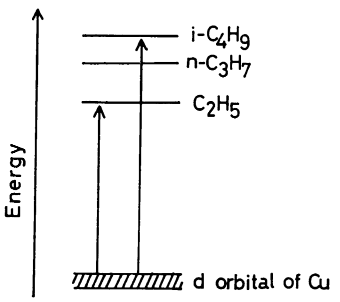


Fig. 8. Tentative energy level relation diagram in activation of Cu–R bond.

R,R=C_2H_5<n-C_3H_7<i-C_4H_9, and the order of the increasing energy gap in Fig. 8, R=C_2H_5<n-C_3H_7<i-C_4H_9, can be seen. The effect of the tertiary phosphine on the stability of the alkylcopper complexes can also be accounted for by assuming the scheme represented in Fig. 8. The fact that the methylcopper complex having phosphines with the larger Lewis basicity shows the smaller thermolysis activation energy may arise from raise in the energy of the d-orbital by coordination of phosphines with the larger Lewis basicity thus causing the decrease in the energy required for promotion. If this interpretation is valid the pronounced stabilizing effect of the tertiary phosphine ligand may be related with its ability of accepting d-electron by back-donation from the metal to phosphorus orbital, the consequence being the lowering of the energy of d-orbitals and higher stability for alkylcopper complexes with phosphine ligands having greater π-accepting ability.

One serious argument against this type of energetic consideration is that the concept of such a direct electronic exitation as depicted in Fig. 8 may not be related to thermolysis. We agree that in the thermolysis the simple electronic exitation may not be involved, but the energy gap for the excitation may still provide a measure for the stability to a first approximation. In lack of the knowledge about the potential energy curves for the bonding and anti-bonding orbitals a discussion based on energetic consideration admittedly remain speculative. However, the scheme depicted in Fig. 9 seems to be fairly consistent with the experimental facts obtained in this work. When an electron is directly promoted to the anti-bonding orbital shown as the upper curve in Fig. 9a, the splitting of Cu–C bond will take place. In the thermal reaction, if the potential curve of the anti-bonding orbital is crossed with that of d-orbital (Fig. 9a), on loosening of the Cu–C bonding to a certain extent a crossing over to the anti-bonding potential curve may take place, thus splitting of the Cu–C bond will result. The effects of the alkyl group and of the basicity of the tertiary phosphine ligands are explained similarly in this model as in Fig. 8. The crossing over to the anti-bonding orbital curve would take place at lower energy when the energy of the $\sigma^*_{\mathrm{Cu-R}}$ orbital lies lower (Fig. 9b), and the raise in the d-orbital by coordination of more electron-donating phosphines would lead to the crossing-over at smaller ΔE (Fig. 9c).

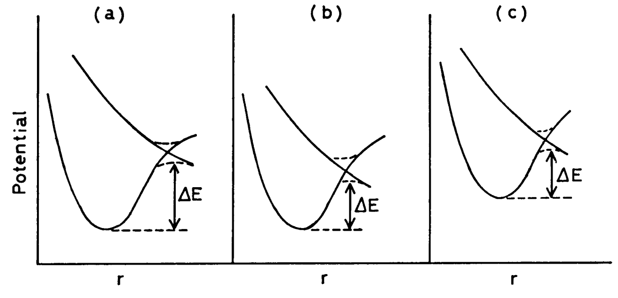


Fig. 9. Tentative potential energy curves for the splitting of Cu–R bond. Upper curve, $\sigma^*_{\mathrm{Cu-R}}$; lower curve, d-orbital. For (a), (b), and (c) see the text. r=distance between Cu and C.

Previously Yamamoto *et al.* discussed the stability of alkylnickel[3)] and alkylchromium[12b)] complexes by taking into account similar energetic consideration. In contrast to the alkylcopper(I) complexes, these alkyltransition metal complexes have vacant d-orbital(s) and the stability of the transition metal-alkyl (M–R) bond in the series of the alkyltrasition metal complexes increased in a reverse order compared with the stability of the Cu–R bond, R=n-C_3H_7<C_2H_5<CH_3. Furthermore, the effect of the basicity of ligand in stabilizing the M–R bond in these alkyltransition metal complexes is reversed to that observed in the alkylcopper complexes; coordination of electron-donating ligand enhanced the stability of the M–R bond, whereas that acidic ligand destabilized the M–R bond. The stability of these alkyltransition metal complexes with vacant d-orbitals was explained by considering the electronic promotion from the low-lying bonding M–R orbital to the vacant d-orbital(s) ($\sigma_{\mathrm{M-R}}\rightarrow$d) instead of that from the d-orbital to $\sigma^*_{\mathrm{M-R}}$ bond(d$\rightarrow\sigma^*_{\mathrm{M-R}}$). Therefore, the postulate considered here is consistent with previously proposed scheme to explain the order of the stability in the series of the alkylnickel and alkylchromium complexes, although the order of the stability of these alkyltransition metal complexes is reversed to that of alkylcopper complexes.

We are concerned here with the loosening of the copper-alkyl bond in the thermolysis, but it should be stressed that we do not imply the formation of a free radical of any significant life time. The experimental results concerning the thermolysis do not indicate the formation of the free radicals. As described above the alkyl group will be subject to the further reaction, such as β-elimination reaction (Eq.1) at the instant when the copper-carbon bond in the alkylcopper complex become loose.

Photolysis of the Alkylcopper(I) Complexes. In order to get further information concerning the stability of the alkylcopper complexes we studied the photolysis of the alkylcopper complexes. The alkylcopper complexes are quite light-sensitive[10)]and decompose even below −20 °C upon illumination by light. Comparison of the gaseous products in the thermolysis (Table 1) with those in the photolysis (Table 5) indicates a considerable difference in the decomposition pathways. In contrast to the thermolysis of $CH_3Cu(PPh_3)_3$(toluene) which gave ethane as the main product, the photolysis of the complex gave methane exclusively. Since the use of dueterated PPh_3 ligand and solvent did not

TABLE 5. PRODUCTS IN THE PHOTOLYSIS OF THE ALKYLCOPPER(I) COMPLEXES

Complex[a]	Solvent[a]	Temp (°C)	Time (h)	Products (Yield[b])			
				CH_4	CH_3D	C_2H_4	C_2H_6
$CH_3Cu(PPh_3)_3(C_7D_8)$	None	−30	48	31	0	0	0
$CH_3Cu(PPh_3)_3(C_7D_8)$	C_7D_8	−30	48	41	0	0	0
$CH_3Cu(PPh_3\text{-}d_6)_3(C_7D_8)$	None	−30	48	26	0	0	0
$CH_3Cu(PPh_3\text{-}d_3)_3(C_7D_8)$	None	80	5	21	2	6	31
$CH_3Cu(PPh_3\text{-}d_3)_3(C_7D_8)$	C_7D_8	−30	48	42	1	0	0
				H_2	C_2H_6	C_2H_4	C_4H_{10}
$C_2H_5Cu(PPh_3)_2$	None	−30	24	0	33	4	0
$C_2H_5Cu(PPh_3)_2$	C_7D_8	−30	24	0	55	37	0

a) C_7D_8 = toluene-d_8, $PPh_3\text{-}d_6$ = triphenylphosphine-2,6,2′,6′,2″,6″-d_6. b) Mol per 1 mol of the complexes.

cause the deuterium incorporation into methane, abstraction of a hydrogen of CH_3 group by another CH_3 group may consitute an important decomposition pathway in the photolysis of the methylcopper complex. Evolution of considerable amount of ethylene on irradiation of the methyl copper complex at 80 °C also suggest the hydrogen abstraction from the methyl group which will yield a carbenoid species. Formation of carbenoid species during thermolysis[11,12,18] and photolysis[19] of methyltrasition metal complexes has been proposed, and isolation of an alkylcarbene complex of tantalum has been reported.[20]

Photolysis of $C_2H_5Cu(PPh_3)_2$ produced ethane as the main gaseous product and ethylene as the minor product. This result is in contrast with thermolysis which generated ethylene as the major decomposition product.

Experimental

General Procedures and Preparation of Alkylcopper(I) Complexes. All experiments were carried out under deoxygenated argon or nitrogen atmosphere, or in vacuum. IR spectra were recorded on a Hitachi Model EPI-G3 spectrometer, and ^{31}P-NMR and ^1H-NMR spectra were recorded with a Japan Electron Optics Lab. JNM-PS-100 spectrometer. Evolved gas was analyzed with a Hitachi RMU-5B mass spectrometer and with a Shimadzu GC-5B gas chromatograph, using an active carbon column for C_1 and C_2 hydrocarbons, a VZ-7 column for C_1–C_4 hydrocarbons and a column with 20% TCP on 40/60 Uniport B for diethyl ether. A series of alkylcopper(I) complexes having various tertiary phosphines were prepared as previously reported.[10]

Preparation of $CH_3Cu(PPh_3\text{-}d_6)_3$(toluene-$d_8$). Triphenylphosphine-2,6,2′,6′,2″,6″-d_6 ($PPh_3\text{-}d_6$) was prepared by exchange reaction of PPh_3 with excess deuterium gas catalyzed by $RuH_2(PPh_3)_4$[21] and had 98.0% isotopic purity as determined by ^1H-NMR spectroscopy. To an etheral suspension of copper(II) acetylacetonate (2.0 g.) and $PPh_3\text{-}d_6$ (4.0 g.), 4 ml of dimethylaluminum monoethoxide was added slowly at −40 °C. The light yellow complex $CH_3Cu(PPh_3\text{-}d_6)_2$(diethyl ether)$_{0.5}$ precipitated after sufficient reaction time at −10 °C was separated by filtation, washed with dry ether and then dried *in vacuo*. From toluene-d_8 (isotopic purity, 98.8%) solution containing $CH_3Cu(PPh_3\text{-}d_6)_2$(diethyl ether)$_{0.5}$ (3.0 g) and $PPh_3\text{-}d_6$ (1.0 g), yellow crystals of $CH_3Cu(PPh_3\text{-}d_6)_3$(toluene-$d_8$) was isolated.

Kinetic Studies for the Thermal Decomposition of Alkylcopper(I) Complexes. A 20 ml Schlenk tube containing 0.10—0.20 g of the solid alkylcopper(I) complex or a toluene solution (3 ml) of the alkylcopper(I) complex (0.13—0.35 g) and PPh_3 (0—400 mg) was connected to a vacuum line equipped with a mercury manometer and the system was evacuated. The Schlenk tube was placed in a thermostatted bath controlled to ±0.5 °C. The rate constant for the thermal decomposition of the complex was obtained by measuring the volume of the gas evolved with time.

Photolysis of Alkylcopper(I) Complexes. A 10 ml quartz Schlenk tube containing 0.3 g of the alkylcopper(I) complex in the solid state or its solution in 2 ml of toluene-d_8 was irradiated by a 100-Watt Toshiba super high-pressure mercury lamp in a thermostatted aqueous ethylalcohol bath controlled to −30±0.5 °C. The sample tubes were positioned in the region of maximum luminosity. Evolved gas was collected with a Toepler pump and analyzed by mass spectrometry.

The sample in toluene-d_8 solution was immediately decomposed on irradiation turning to dark brown.

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