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II. REDUCTION OF COPPER(II) BY TETRAETHYLLEAD. EVIDENCE FOR ETHYL RADICALS IN ACETIC ACID

NYE A. CLINTON and JAY K. KOCHI
Chemistry Department, Indiana University, Bloomington, Indiana 47401 (U.S.A)

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SUMMARY

Cupric acetate, triflate and chloride are readily reduced to the cuprous salts by tetraethyllead in acetic acid solutions. Cuprous salts are subsequently involved in the catalytic process described previously, to produce ethane by the acetolysis of more tetraethyllead. The stoichiometry of the reduction step requires the consumption of two Cu^{II} for each triethyllead acetate produced. The ethyl group which is liberated in the process can be quantitatively accounted for as ethylene, ethyl acetate or ethyl chloride. The latter are identical to the products obtained from the oxidation of independently generated ethyl radicals by the same Cu^{II} complexes. The reduction of Cu^{II} is suggested to proceed by alkyl transfer from tetraethyllead to form a metastable ethylcopper(II) intermediate, which subsequently undergoes rapid homolysis. The liberated ethyl radicals are efficiently scavenged by Cu^{II}. The relationship of these organocopper(II) intermediates to those previously generated by the alkylation of Cu^{II} by a variety of other alkylating agents in aprotic media is discussed.

INTRODUCTION

Tetraalkyllead compounds readily reduce a variety of copper(II) salts to copper(I) species which are involved in further reactions with the organolead reactant[1]. The non-stoichiometric relationship among the products has been partially resolved by the mechanistic study of the catalytic decomposition of tetraethyllead by copper(I) described in the previous paper[2].

The initial step involving the reduction of Cu^{II} by tetraalkyllead is still unclear, although there is evidence that alkyl radicals are intermediates. Thus, Bawn and coworkers showed that vinyl monomers are polymerized in the presence of Cu^{II} and tetraalkyllead, and that alkylcopper(I) can be isolated if the reaction is carried out at −30° in alcohol[1]. They suggested that alkyl radicals are formed in reaction (1) together with cuprous salts, which are involved in a further dealkylation of tetra-

$$Cu^{2+} + PbR_4 \rightarrow Cu^{+} + PbR_3^{+} + R\cdot \qquad (1)$$

$$PbR_4 + Cu^{+} \rightarrow PbR_3^{+} + RCu, \text{ etc.} \qquad (2)$$

alkyllead [eqn. (2)]. It was assumed that the alkyl radicals underwent subsequent dimerization and/or disproportionation. However, these results are ambiguous since the decomposition of the organocopper(I) intermediate under these conditions also affords similar products[1-5]. Their proposal, however, merits further attention since the formation so readily of alkyl radicals by a redox reaction such as (1) would be highly unusual. Furthermore, since alkyl radicals are not involved in the subsequent catalytic reactions of the Cu^I species, it is necessary to distinguish between Cu^{II} and Cu^I species in their reaction with tetraalkyllead compounds*.

The difficulties encountered in the study of this system heretofore are largely associated with the simultaneity of a number of similar competing processes. The clean delineation of the mechanism of the Cu^I catalyzed reaction[2] now allows us to consider separately the reduction of Cu^{II} by tetraethyllead. Furthermore, other earlier studies[6] showed that alkyl radicals are scavenged very efficiently by Cu^{II} under these conditions. Such redox reactions proceed with second order rate constants in excess of 10^7 $l \cdot mol^{-1} \cdot sec^{-1}$ to afford products which are characteristic of the particular Cu^{II} oxidant employed. We hope to show that they can be employed as probes for the presence of alkyl radicals in this system.

RESULTS AND DISCUSSION

Stoichiometry and rate of reduction of Cu^{II} acetate by tetraethyllead

The reaction between Cu^{II} acetate and tetraethyllead (in excess) produces triethyllead acetate, ethane and ethylene in non-stoichiometric amounts in acetic acid solutions. Careful examination shows, however, that the combined yields of ethane and ethylene are equal to that of triethyllead acetate. In other words, the mono-dealkylation of tetraethyllead leads only to ethane and ethylene. Furthermore,

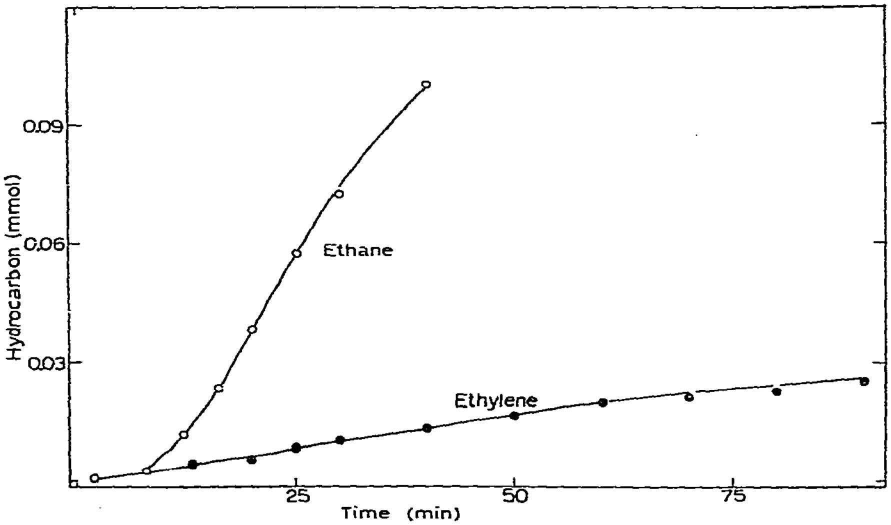

Fig. 1. Decomposition of tetraethyllead in acetic acid by copper(II) acetate (0.051 mmol): ● ethylene, ○ ethane.

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* Formal oxidation states of copper are only used for convenience in order to keep account of the equivalency changes and are not meant to convey structural connotations. The alkyl ligand is considered anionic in this context.

$$C_2H_6 + C_2H_4 \approx (C_2H_5)_3PbOAc$$

the yield of ethylene formed in Table 1 is equal to just one-half of the amount of Cu^{II} acetate employed, *i.e.*,

$$2\ Cu^{II}(OAc)_2 \approx C_2H_4\,.$$

No butane is formed under these conditions.

TABLE I

FORMATION OF ETHYLENE FROM TETRAETHYLLEAD AND Cu^{II} ACETATE[a]

$Cu(OAc)_2$ (10^2 *mmol*)	C_2H_4 (10^2 *mmol*)	$2\ C_2H_4/Cu^{II}$
0.323	0.17	1.06
5.12	2.5	0.98
0.323[b]	0.15	0.92

[a] In acetic acid solutions (3.0 ml) of 0.15 *M* Et_4Pb at 20°. [b] Also contains 1.47 mmol LiOAc.

The *rates* of formation of ethane and ethylene clearly show (Fig. 1) that they are arising from two different paths. The appearance of ethylene follows a pseudo first order dependence to at least 50% completion, and the kinetics can be described by:

$$\frac{d(C_2H_4)}{dt} = \tfrac{1}{2}k_{II}\cdot[Et_4Pb]\cdot[Cu^{II}(OAc)_2] \tag{3}$$

at the concentrations of Cu^{II} acetate (0.017 *M*) and tetraethyllead (0.17 *M*) employed. The rate constant k_{II} is approximately $1\times10^{-3}\ l\cdot mol^{-1}\cdot sec^{-1}$ at 20°.

There is an induction period, on the other hand, before ethane is generated. Significantly, the rate of formation of ethane is independent of the concentration of Cu^{II} acetate, provided the latter is in excess of 10^{-2} *M*. Under these conditions the rate of ethane formation is given by,

$$\frac{d(C_2H_6)}{dt} = k_I\cdot[Et_4Pb] \tag{4}$$

The value of k_I is $4.2\times10^{-5}\ sec^{-1}$ at 20°, which is the same as the catalytic constant k_c ($0.033\ l\cdot mol^{-1}\cdot sec^{-1}$) obtained previously for the Cu^I acetate catalyzed decomposition of tetraethyllead[2] after the solubility of Cu^I acetate (1.27×10^{-3} *M*) is taken into account, *i.e.*,

$$k_I = k_c\cdot(Cu^IOAc)_s\,, \tag{5}$$

where $(Cu^IOAc)_s$ represents the solubility of Cu^I acetate in acetic acid.

The results show that ethylene is derived from the *stoichiometric* reaction of Cu^{II} acetate with tetraethyllead. On the other hand, ethane is formed from the *catalytic*

$$2\ Cu^{II}(OAc)_2 + Et_4Pb \longrightarrow 2\ Cu^IOAc + Et_3PbOAc + C_2H_4 \tag{6}$$

decomposition of tetraethyllead described previously[2]. With the exception that Cu^I acetate is generated from Cu^{II} acetate, these processes are largely independent of one another.

$$Et_4Pb + HOAc \xrightarrow{Cu^IOAc} Et_3PbOAc + C_2H_6 \qquad (7)$$

The simplification of the kinetics for these simultaneous reactions results largely from the limited solubility of Cu^I acetate and the high value of the catalytic constant k_c. In fact, the onset of the liberation of ethane in Fig. 1 corresponds roughly to the solubility of Cu^I acetate formed from the independent reduction of Cu^{II} acetate. Beyond this point the accumulation of Cu^I soon results in the precipitation of crystalline Cu^I acetate. The latter is identical to that synthesized independently from cuprous oxide[7]. The reduction of Cu^{II} acetate can also be followed visually due to its relatively intense color. There is a direct relationship between the Cu^{II} acetate reduced and the ethylene generated, the liberation of which terminates with the decoloration of the solution.

Copper in the resulting mixture is present only as Cu^I acetate, which can be readily re-oxidized to Cu^{II} quantitatively by molecular oxygen. Under these conditions the formation of ethane is inhibited until Cu^{II} is re-reduced by tetraethyllead. During this inhibition period ethylene is produced in amounts equivalent to the oxygen added. For example, the addition of 1.86×10^{-2} mmol oxygen produced 1.96×10^{-2} mmol of ethylene. Since two Cu^{II} are required for each ethylene we deduce that two Cu^I are oxidized by each oxygen, *e.g.*,

$$2\,Cu^IOAc + 2\,HOAc + O_2 \rightarrow 2\,Cu^{II}(OAc)_2 + H_2O_2 \qquad (8)$$

The stoichiometry given in eqn. (8), however, must be accepted with certain reservations since the reaction of oxygen with other species (produced) in the reaction was not examined.

Reduction of Cu^{II} triflate by tetraethyllead

The reduction of Cu^{II} triflate (trifluoromethanesulfonate) differs from that of Cu^{II} acetate in two ways. First, the reduction of Cu^{II} triflate by tetraethyllead at 20° is essentially complete within a few seconds of mixing as seen by the immediate discharge of the blue color. All of the ethylene (in Table 2) is liberated within this period,

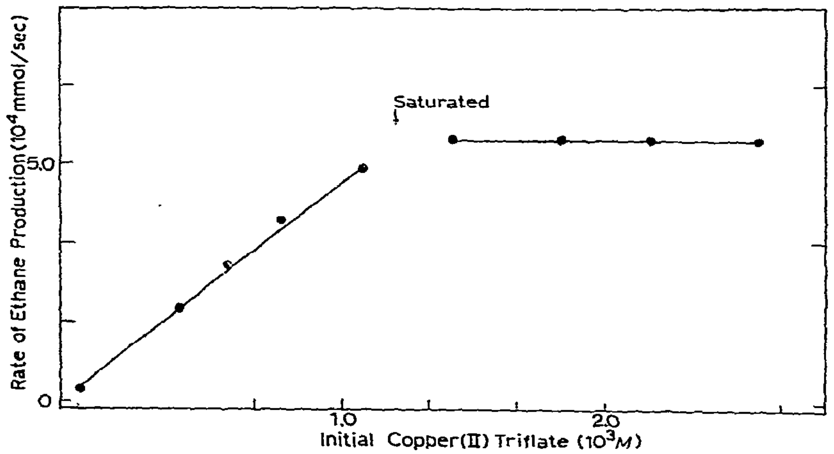


Fig. 2. Rate of ethane production during the reduction of copper(II) triflate and tetraethyllead in acetic acid at 20°.

and no significant amount is generated on further standing. Meanwhile, the formation of ethane follows the pseudo first order kinetics given by[2];

$$\frac{d(C_2H_6)}{dt} = k_c \cdot [Cu] \cdot [Et_4Pb] \tag{9}$$

The rate is linearly dependent on the copper added up to 1.27×10^{-3} M as shown in Fig. 2, whereupon the rate is unaffected by the further addition of copper. It is clear that the ethane is generated from the Cu^I catalyzed process[2], and the ultimate rate is bound to the solubility limit of Cu^I acetate. That is, [Cu] in eqn. (9) represents the amount of Cu^I acetate in solution. That formed in excess of the solubility appears as a crystalline precipitate. The acetate complex no doubt results from the rapid exchange of ligands with the highly substitution-labile triethyllead acetate.

$$Et_3PbOAc + Cu^IT \rightarrow Et_3PbT + Cu^IOAc \tag{10}$$

The slower rate of reduction of Cu^{II} acetate compared to triflate is clearly reflected in the rate of *ethane* formation. In Fig. 3 the limiting rate (after the induction period) is defined by the solubility of Cu^I acetate, and is the same for both the triflate and acetate salts due to the rapid metathesis given in eqn. (10). The triflate salt shows no induction period. In fact, the initial rate is *faster* than the limiting catalytic rate and may be due to supersaturation of Cu^I acetate. It is more likely, however, that Cu^I triflate is incompletely metathesized [see eqn. (10)], and the faster rate is due to the alkyl transfer step, in which X = triflate is more effective than acetate[8]. The latter explanation is in accord with the increasing initial rates observed with increasing Cu^{II} triflate, despite the low solubility of Cu^I acetate.

$$Et_4Pb + Cu^IX \rightarrow Et_3PbX + EtCu, \text{ etc.} \tag{11}$$

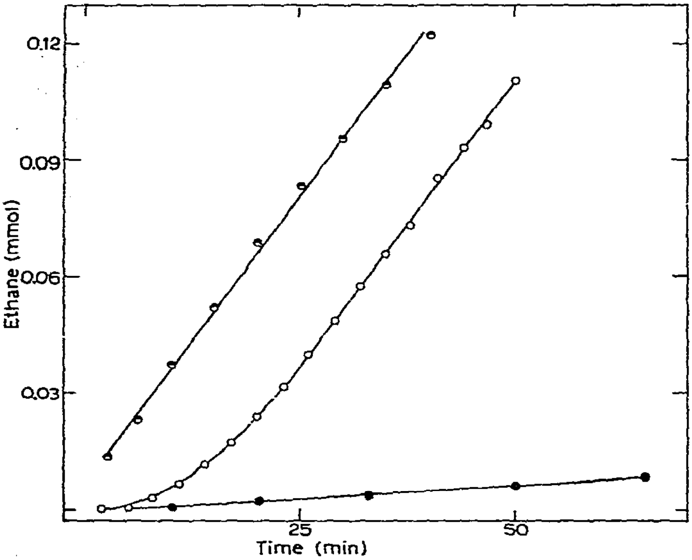


Fig. 3. Ethane production during the reduction of copper(II) triflate ◒ or copper(II) acetate ○, by tetraethyllead in acetic acid; ● no copper(II).

TABLE 2

REDUCTION OF Cu^{II} TRIFLATE BY TETRAETHYLLEAD[a]

CuT_2 (10^2 *mmol*)	C_2H_4 (10^2 *mmol*)	C_2H_5OAc (10^2 *mmol*)	$2C_2H_4/Cu^{II}$	$2\Sigma Et_{ox}{}^{b}/Cu^{II}$
0.337	0.08	[c]	0.47	
2.20	0.62	[c,e]	0.56	
4.90	1.1	[c,e]	0.44	
2.77	0.46	0.76[d]	0.34	0.92

[a] In 0.17 *M* Et_4Pb solutions (3.0 ml) of acetic acid at 20°. [b] Material balance. [c] Not determined. [d] $\approx 3 \times 10^{-4}$ mmol of butane also formed. [e] $\approx 5 \times 10^{-4}$ mmol of butane also formed.

Triethyllead acetate is formed from tetraethyllead and Cu^{II} triflate by the same stoichiometry as that given in eqns. (6) and (7) for Cu^{II} acetate. Ethylene is produced in 40–50% yield and the remainder of the ethyl groups is accounted for as ethyl acetate (Table 2), *i.e.*,

$$2\ Cu^{II}T_2 \approx C_2H_4 + C_2H_5OAc$$

A small but discrete amount ($\approx$2%) of the ethyl groups always appears as n-butane when Cu^{II} triflate is used but not with Cu^{II} acetate. Furthermore, if tetraethyllead is carefully added to a solution of Cu^{II} triflate without stirring a transient purple color which has been attributed to a mixed valence complex $[Cu^{I}Cu^{II}(OAc)_3]$[9] can be seen.

The reduction of Cu^{II} chloride by tetraethyllead

Copper(II) chloride is only partially soluble in acetic acid, but can be readily solubilized as the chlorocuprate by the addition of lithium chloride.

$$Cu^{II}Cl_2 + n\ LiCl \rightleftarrows Li_nCu^{II}Cl_{2+n} \qquad n = 1, 2 \tag{12}$$

Tetraethyllead (in excess) reacts rapidly with either Cu^{II} chloride present as a suspension or chlorocuprate in solution to produce one-half mole of ethyl chloride for each mole of Cu^{II} chloride. The reactions given in Table 3 are essentially complete in 5 min

TABLE 3

REDUCTION OF Cu^{II} HALIDE BY TETRAETHYLLEAD[a]

CuX_2 (10^2 *mmol*)	*Solvent*	*EtX* (10^2 *mmol*)	$2EtX/Cu^{II}$[b]
Cl 9.24[c]	HOAc	4.59	0.99
Cl 4.50[d]	HOAc	2.11	0.95
Cl 9.29[c]	THF	4.45[e]	0.96
Br 9.49[c]	THF	4.04[e]	0.85
Cl 46.0[c]	THF	20.1[e]	0.88
Cl 6.77[c]	THF	3.16[e]	0.94

[a] In solutions (3.0 ml) of 0.15 *M* Et_4Pb in acetic acid at 20°C. [b] Deviation from 1.0 may be attributed to incomplete reaction due to heterogeneity. [c] Suspension. [d] Also contains 0.439 mmol LiCl, homogeneous solution. [e] Traces of ethylene also observed.

$$\mathrm{Et_4Pb + 2\,Cu^{II}Cl_2 \rightarrow Et_3PbCl + EtCl + 2\,CuCl} \tag{13}$$

at 20°, and no more ethyl chloride is produced on further standing. The same reaction (13) also occurs rapidly when $\mathrm{Cu^{II}}$ chloride is employed in two-fold excess. In the latter case, additional ethyl chloride is formed only in a much slower reaction probably due to a further dealkylation reaction [eqn. (14)].

$$\mathrm{Et_3PbCl + 2\,Cu^{II}Cl_2 \rightarrow Et_2PbCl_2 + EtCl + 2\,Cu^{I}Cl} \tag{14}$$

Copper(I) chloride is also insoluble in acetic acid except when complexed with additional chloride[10]. Thus, the suspension of the brown $\mathrm{Cu^{II}}$ chloride is replaced by

$$\mathrm{Cu^{I}Cl} + n\,\mathrm{LiCl} \rightleftharpoons \mathrm{Li}_n\mathrm{CuCl}_{1+n} \tag{15}$$

$\mathrm{Cu^{I}}$ chloride and merely becomes colorless on reduction with tetraethyllead. The copper(I)-catalyzed formation of ethane under these conditions is not much faster than the uncatalyzed acetolysis of tetraethyllead (Fig. 3), no doubt due to the low concentration of $\mathrm{Cu^{I}}$ in solution.

The reduction of a solution of chlorocuprate(II), on the other hand, leads to a colorless solution of chlorocopper(I) species. The latter is a catalyst for the production of ethane by a pseudo first order decomposition of tetraethyllead. The catalytic constant k_c' in eqn. (16), however, is a composite of at least two others since lithium

$$\frac{\mathrm{d(C_2H_6)}}{\mathrm{d}t} = k_c' \cdot [\mathrm{LiCu^{I}Cl}_x] \cdot [\mathrm{Et_4Pb}] \tag{16}$$

chloride itself is also capable of inducing the formation of ethane from tetraethyllead as shown in Fig. 4. The magnitude of the effect by LiCl is larger than that induced by the neutral salt $\mathrm{LiClO_4}$[2], and may be due to the more favorable equilibrium in eqn. (17) to generate the strong acid (HCl). Be that as it may, the quantitative separation

$$\mathrm{LiCl + HOAc \rightleftharpoons HCl + LiOAc} \tag{17}$$

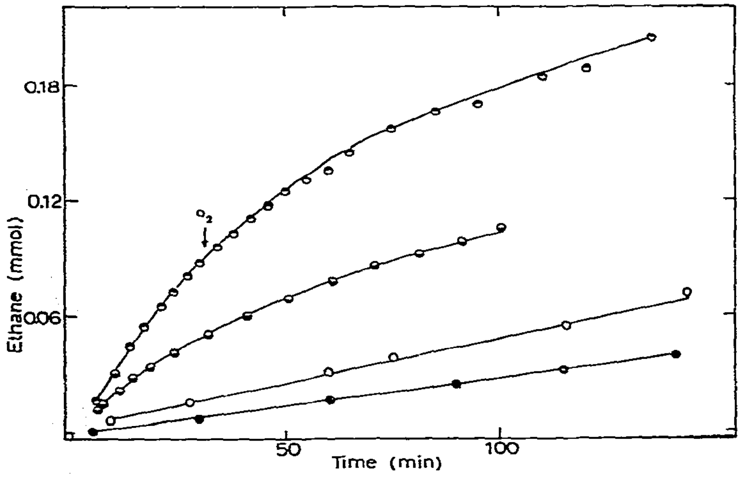


Fig. 4. Salt effects in the formation of ethane during the decomposition of tetraethyllead in acetic acid; ● none, ○ 2.6×10^{-2} *M* cupric chloride, ◒ 1.5 *M* lithium chloride, ◓ 1.5 *M* lithium chloride plus 3.1×10^{-3} *M* cupric chloride. Oxygen (0.02 mmol) added at arrow.

of the catalytic constant k'_c into that associated with the chlorocopper(I) species and that due to LiCl is not yet possible since the equilibrium constants in eqn. (15) are unknown. If we assume that the formation constant(s) of chlorocopper(I) species

$$\frac{d(C_2H_6)}{dt} = k_{Cu}\cdot[CuCl_x]\cdot[Et_4Pb] + k_{Li}\cdot[LiCl]\cdot[Et_4Pb] \tag{18}$$

are high[6], we can simply equate $[CuCl_x]$ and [LiCl] in eqn. (18) to the added copper halide and LiCl, respectively. The values of k_{Cu} and k_{Li} based on this approximation are 1.6×10^{-2} and 4.5×10^{-5} $l\cdot mol^{-1}\cdot sec^{-1}$.

The addition of molecular oxygen does not inhibit the copper(I)-catalyzed formation of ethane as shown in Fig. 5, and is consistent with the relatively slow autoxidation of chloro-Cu^I species previously observed in aqueous solutions[11]. It is clear, moreover, that chloro-Cu^I species are oxidized by oxygen, since additional ethyl

$$2\,LiCu^ICl_2 + O_2 \longrightarrow (LiCu^{II}Cl_2)_2O_2 \text{ etc.} \tag{19}$$

chloride is generated after the addition of oxygen. The relatively slow rate of formation of ethyl chloride under these circumstances must directly reflect the rate of autoxidation of chloro-Cu^I, since the reduction of chloro-Cu^{II} by tetraethyllead is fast.

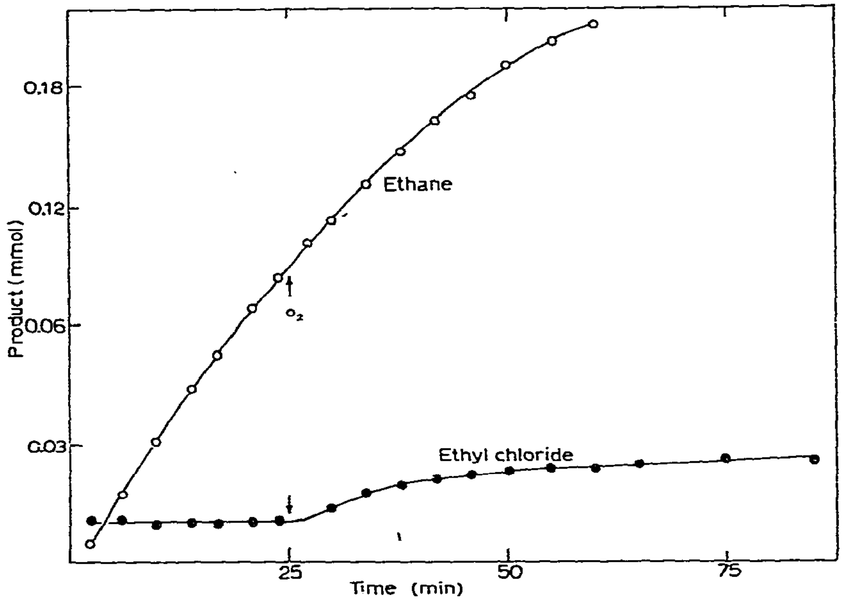


Fig. 5. Ethane ○ and ethyl chloride ● from the decomposition of tetraethyllead in acetic acid by copper(II) chloride (0.03 mmol). Oxygen (0.02 mmol) added at arrow.

Cu^{II} chloride and bromide, which are insoluble in tetrahydrofuran (THF), are readily reduced to Cu^I chloride and bromide by tetraethyllead. Two Cu^{II} are required for each ethyl halide produced as shown in Table 3. The stoichiometry is thus the same as that obtained [eqn. (13)] in acetic acid. The subsequent Cu^I-catalyzed reaction, however, does not obtain in this aprotic medium.

Ethyl radicals from the reduction of Cu^{II} complexes with tetraethyllead.

The reductions of Cu^{II} acetate, triflate and chloride by tetraethyllead proceed at widely different rates in acetic acid. In all cases, however, the ethyl group suffers a two-equivalent oxidation such that two Cu^{II} are required, *i.e.*,

$$Et_4Pb + 2\,Cu^{II}X_2 \rightarrow Et_3PbX + 2\,Cu^{I}X + Et_{ox} \tag{20}$$

where $Et_{ox} = (C_2H_4 + HOAc), C_2H_5OAc, C_2H_5Cl$

It is noteworthy that the products (Et_{ox}) given in Tables 1–3 are *identical* to those obtained from the reduction of the same Cu^{II} complexes by ethyl radicals generated by independent methods.

$$Et\cdot + Cu^{II}X_2 \rightarrow Et_{ox} + Cu^{I}X \tag{21}$$

Thus, alkyl radicals generated from the decarboxylation of acyl peroxides or carboxylic acids by a variety of methods[12] undergo characteristic oxidations with Cu^{II} complexes. Extensive studies show that the products are uniquely defined by the nature of the ligands associated with the Cu^{II} nucleus and the medium in which the oxidation is carried out[6]. It is highly unlikely that the broad spectrum of products obtained from the divers sources of the ethyl group shown in Table 4 should be the same unless they are all derived from the ethyl radical.

We conclude that ethyl radicals are the prime intermediates formed in the reduction of Cu^{II} by tetraethyllead and are further oxidized by a second Cu^{II}. The formation of ethyl radical in eqn. (22) is the same as that previously postulated by

$$Et_4Pb + Cu^{II}X_2 \rightarrow Et_3PbX + Cu^{I}X + Et\cdot \tag{22}$$

$$Et\cdot + Cu^{II}X_2 \xrightarrow{\text{fast}} Et_{ox} + Cu^{I}X \tag{23}$$

TABLE 4

OXIDATION OF ETHYL RADICALS BY Cu^{II} COMPLEXES IN ACETIC ACID

Source of ethyl radicals	*Cu^{II} oxidant*	*Products (mol % × 2)*			
		$CH_2{=}CH_2$	*$CH_3CH_2(X)$*	*n-C_4H_{10}*	*Ref.*
Et_4Pb	$Cu(OAc)_2$	100	0	0	This work
$(EtCO_2)_2$	$Cu(OAc)_2$	100	0	0	[a]
$EtCO_2H$	$Cu(OAc)_2$	100	0	0	[b]
Et_4Pb	CuT_2	43	55 (OAc)	2	This work
$(EtCO_2)_2$	CuT_2	45	55(OAc)	0	[c]
Et_4Pb	$CuCl_2$	Trace	99 (Cl)	0	This work
$(EtCO_2)_2$	$CuCl_2$	0	100 (Cl)	0	[d]
$EtCO_2H$	$CuCl_2$	0	100 (Cl)	0	[e]
Et_4Pb	$CuBr_2$	Trace	100 (Br)	0	This work
$(EtCO_2)_2$	$CuBr_2$	0	100 (Br)	0	[d]

[a] Cu-catalyzed decomposition of peroxide see ref. 31. [b] Oxidative decarboxylation of acids with lead tetraacetate see ref. 32. [c] See ref. 33. [d] Halodecarboxylation of peroxides see ref. 34. [e] Halodecarboxylation of acids see ref. 35.

Bawn and co-workers and is in accord with their polymerization results[1]. The second order rate constant for the subsequent oxidation of ethyl radical by Cu^{II} in eqn. (23) is generally in excess of $10^7\ \text{l}\cdot\text{mol}^{-1}\cdot\text{sec}^{-1}$[13], and it readily accounts for the excellent material balance obtained for Et_{ox} based on the further oxidation of ethyl radicals.

Alternative methods for the detection of ethyl radicals as intermediates are not readily adaptable to this system. Thus, conventional radical traps such as oxygen, halogens, *N*,*N*-diphenyl-*N'*-picrylhydrazyl, galvinoxyl or quinones are inadequate in this circumstance due to the presence of Cu^{I} and Cu^{II}. Pending the development of such probes, we believe that reactions with various Cu^{II} complexes themselves represent the best proof for the intermediacy of ethyl radicals.

Alkylation of Cu^{II} by tetraethyllead

There are essentially two possible mechanisms by which Cu^{II} may be reduced by tetraethyllead. An outer-sphere electron transfer given in eqn. (24) would involve fragmentation of the cation-radical. Such a process is unlikely in view of the high ionization potential of tetraethyllead (12.5 eV in the gas phase)[14] relative to the reduction potential of Cu^{II} complexes ($\approx$1.2 eV at most)[15]. Studies are in progress to determine if outer-sphere oxidants[16] such as hexachloroiridate(IV), tris-phenanthrolineiron(III) and ferricyanide will react with tetraethyllead by a similar process.

SCHEME 1

$$\text{Et}_4\text{Pb}+\text{Cu}^{\text{II}}\text{X}_2 \rightarrow \text{Et}_4\text{Pb}^{+}\cdot+\text{Cu}^{\text{I}}\text{X}_2^{-} \tag{24}$$

$$\text{Et}_4\text{Pb}^{+}\cdot \xrightarrow{\text{fast}} \text{Et}_3\text{Pb}^{+}+\text{Et}\cdot \tag{25}$$

Alkyl transfer from tetraethyllead to Cu^{II} represented in eqn. (26) is an alternative pathway for reduction. The alkyl radical is formed in this mechanism by *homolysis* of a metastable alkylcopper(II) intermediate [eqn. (27)]. We favor alkylation of Cu^{II} as a viable mechanism since it fits into the general pattern established with other metal complexes[17]. This pathway would require, however, that the subsequent homolysis of the alkylcopper intermediate takes place exceedingly rapidly since the reduction occurs spontaneously even at −35°. Furthermore, such an intermediate does not even have an opportunity to undergo acetolysis since we find no evidence of a copper(II)-catalyzed process for the generation of ethane.

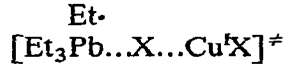
SCHEME 2:

$$\text{Et}_4\text{Pb}+\text{Cu}^{\text{II}}\text{X}_2 \rightarrow \text{Et}_3\text{PbX}+\text{EtCu}^{\text{II}}\text{X} \tag{26}$$

$$\text{EtCu}^{\text{II}}\text{X} \xrightarrow{\text{fast}} \text{Et}\cdot+\text{Cu}^{\text{I}}\text{X} \tag{27}$$

$$\text{EtCuX}+\text{HOAc} \nrightarrow \text{Et–H}+\text{Cu}^{\text{II}}\text{X(OAc), etc.} \tag{28}$$

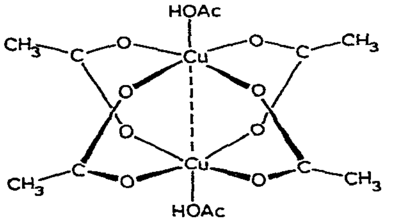
Alternative formulations involving the simultaneous loss of an alkyl radical and reduction of Cu^{II} via a transition state such as



$$[\text{Et}_3\overset{\text{Et}\cdot}{\text{Pb}}..\text{X}...\text{Cu}^{\text{I}}\text{X}]^{\neq}$$

obviates this difficulty*, but they all lack mechanistic appeal since they present no obvious driving force for such a facile process.

Scheme 2 is consistent with the relative rates of reduction of various Cu^{II} complexes with tetraethyllead. For example, Cu^{II} acetate is reduced so slowly that the disappearance of Cu^{II} can be readily followed by conventional techniques. In glacial acetic acid, Cu^{II} acetate exists as a highly complexed binuclear species[19],



and alkylation is only possible by loss of the axial ligands or dissociation into monomeric species. On the other hand, the highly reactive Cu^{II} triflate is not only monomeric but it is also highly dissociated into Cu^{II} cations or ion-pairs**[,20]. Alkylation of such cationic species by tetraethyllead is at least 100 times faster than it is with Cu^{II} acetate.

Reduction of Cu^{II} by alkylating agents in aprotic media

The reduction of Cu^{II} triflate by tetraethyllead also proceeds readily at 20° in tetrahydrofuran (THF) solutions. The reaction is homogeneous initially. Butane is a major product, and Cu^{II} under these conditions is completely reduced to a metallic mirror. Furthermore, the aprotic nature of this medium precludes the further *catalytic* reaction of Cu^{I} such as that found in acetic acid. Non-stoichiometric amounts of ethane, ethylene and n-butane are formed as shown in Table 5. Unfortunately, the reaction is difficult to study quantitatively in THF since the ethyl groups cannot be

TABLE 5

REDUCTION OF Cu^{II} TRIFLATE BY TETRAETHYLLEAD IN TETRAHYDROFURAN SOLUTIONS[a]

CuT_2 (10^2 mmol)	*Additive (mmol)*	*Products (10^2 mmol)*			*ΣEt^b (%)*
		C_2H_4	*C_2H_6*	*C_4H_{10}*	
7.42		< 0.01	4.4	2.0	57
8.07	H_2O (15)	0.25	9.4	0.6	67
8.8	$C_3H_6(1.86 \times 10^{-2})$	[c]	6.0		

[a] In solutions of 0.050 *M* Et_4Pb in (4.9 ml) THF at 20°. [b] Ethyl groups accounted for as C_2H_4, C_2H_6 and C_4H_{10} assuming 2 Et liberated by each Cu^{II}. [c] Propylene not recovered ($< 5 \times 10^{-4}$ mmol) at the end of reaction.

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* A similar transition state has been proposed for trialkylboron and Cu^{II} but is not appropriate for Group IVB metals (ref. 18).

** Salts are poorly dissociated in acetic acid (ref. 20b).

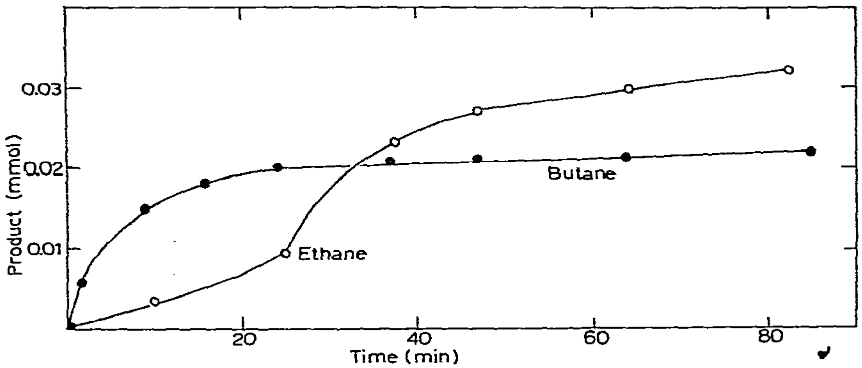


Fig. 6. Butane ● and ethane ○ from the decomposition of tetraethyllead (0.24 mmol) by copper(II) triflate (0.067 mmol) in tetrahydrofuran (5 ml) at 0°.

completely accounted for among these products (last column, Table 5). The poor yield of ethylene may be due to its consumption under reaction conditions, since propylene deliberately added at the commencement of reaction cannot be totally recovered. Addition of small amounts of water to THF promotes the formation of ethane and some ethylene at the expense of butane as shown in Table 5.

The results in THF clearly show that dimerization is an important fate of the ethyl fragment generated during the reduction of $\mathrm{Cu^{II}}$ triflate by tetraethyllead. In strong contrast, the reaction carried out in acetic acid produces only minor amounts of butane. The reaction in THF also involves several steps, since the rates of formation of butane and ethane can be clearly distinguished as shown in Fig. 6. In studies carried out at 0°, there is a rapid reaction to produce butane, followed by a slower process to liberate ethane which apparently shows autocatalytic behavior. The latter is similar to that observed previously in the decomposition of ethylcopper(I) produced from ethylmagnesium bromide in THF[21]. The production of n-butane is also qualitatively

$$2\mathrm{EtCu} \xrightarrow[\mathrm{THF}]{0^\circ} \mathrm{C_2H_4 + C_2H_6 + 2Cu} \tag{29}$$

similar to that produced in the reaction between ethylmagnesium bromide and cupric halides in THF[4].

$$\mathrm{EtMgBr + Cu^{II}Cl_2} \xrightarrow[\mathrm{THF}]{-78^\circ} \tfrac{1}{2}\mathrm{C_4H_{10} + EtCu^{I} + 2\,MgBrCl} \tag{30}$$

Ethylcopper(II) species are likely intermediates in reaction (30) and appear to be as labile as they are when generated from tetraethyllead in the same medium. On the other hand, ethylcopper(II) species generated from tetraethyllead in acetic acid produce no or little butane and afford only monomeric products ($\mathrm{Et_{ox}}$) of oxidation. The solvent is the principal difference between these dramatically divergent results. We tentatively suggest the following mechanism as a working hypothesis for further elaboration:

$$\mathrm{Et_4Pb + Cu^{II}X_2 \rightarrow Et_3PbX + EtCuX} \tag{26}$$

$$\mathrm{EtCuX \rightleftarrows Cu^{I}X + Et\cdot}, \text{ etc.} \tag{27'}$$

$$\mathrm{2\,EtCuX \rightleftarrows (EtCuX)_2 \rightarrow Et_2 + 2\,Cu^{I}X} \tag{31}$$

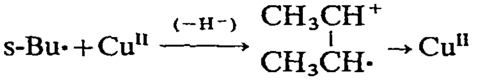
$$Et_4Pb + Cu^{I}X \rightarrow Et_3PbX + EtCu, \text{ etc.} \quad (32)$$

In this scheme, Et_2 and Et_{ox} arise from a competition between dimerization* [eqn. (31)] and homolysis [eqn. (27′)]. The former would be favored by high instantaneous concentrations of the ethylcopper(II) species promoted by a reactive alkylating agent such as ethylmagnesium bromide or an electrophilic form of Cu^{II} such as the triflate salt. Ethereal solvents are also less strongly coordinating than acetic acid and would favor association.

Cu^{II} salts have been alkylated by a variety of other reagents including organomagnesium, organolithium, organozinc, organoboron and organoaluminum compounds[2,18,22]. Even when the reaction is carried out at very low temperatures there is no direct indication of an alkylcopper(II) species under conditions in which alkylcopper(I) intermediates are readily obtained. Reduction to Cu^{I} invariably occurs, often accompanied by the formation of a dialkyl (R_2). There is evidence that the latter does not arise via dimerization of free alkyl radicals since the oxidative coupling of *trans*-propenyllithium with Cu^{II} chloride to 2,4-hexadiene occurs with complete retention despite the rapid inversion of the propenyl radical[23]. Furthermore, alkenes $R(-H)$ and alkanes RH expected from the disproportionation of alkyl radicals are absent although they invariably accompany the dimerization of alkyl radicals formed in the gas phase[24] or in solution[25]. Similarly, the high yields of dialkyl obtained from the *oxidation* of alkylcopper(I)[26] and dialkylcuprate(I)[27] by a variety of oxidants, belie the formation of significant amounts of disproportionation products. The unimportance of long-lived free alkyl radicals during oxidation of organocopper(I) species has been stressed[27].

The presence of stable radicals under similar conditions, however, has been shown recently[28]. Thus, an electron spin resonance spectrum exhibiting interesting hyperfine structure has been obtained when a benzene solution of either Cu^{II} acetylacetonate or 2,4-diisopropyl salicylate is mixed with sec-butyllithium in pentane. The following process was suggested[28]:

$$\text{s-BuLi} + Cu^{II} \rightarrow \text{s-Bu}\cdot + Cu^{I} + Li^{+} \quad (33)$$



$$\text{s-Bu}\cdot + Cu^{II} \xrightarrow{(-H^-)} \begin{array}{c} CH_3CH^{+} \\ | \\ CH_3CH\cdot \end{array} \rightarrow Cu^{II} \quad (34)$$

However, the proposed structure of the Cu^{II} radical-cation complex is highly unlikely since (*a*) the presence of Cu^{II} would greatly broaden the ESR spectrum and (*b*) the hyperfine splittings are at wide variance with those of similar radical-cations[29]. The absence of detectable hyperfine splitting from a Cu nucleus and the *g*-factor of the paramagnetic species indicate, however, that the unpaired electron is largely associated with a hydrocarbon molecular orbital. Further characterization of this radical species is desirable.

We have attempted in this section to reconcile our results and to relate them to the interesting but somewhat contradictory information in the extant literature regarding the role of alkyl radicals in the formation and reactions of organocopper(II) transients. It is abundantly clear that this question(s) merits further scrutiny and no doubt will yield novel insight into organometallic mechanisms.

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* Higher aggregates are also possible.

EXPERIMENTAL SECTION

Materials

Anhydrous Cu^{II} chloride was prepared from the dihydrate by desiccation in a vacuum oven at 100°. Cu^{II} acetate monohydrate was Baker reagent grade and used as received. Cu^{II} bromide was anhydrous Baker reagent grade. Lithium chloride was anhydrous reagent grade obtained from Lithium Corporation of America. THF was refluxed with lithium aluminium hydride and distilled under a nitrogen atmosphere immediately before use. The other materials were the same as in the previous study[2].

Procedure and analysis

The procedure and analysis of the products used in this study were described earlier[2] for the reactions of Cu^{I} complexes with tetraethyllead.

Analysis of ethyl acetate was complicated by the thermal decomposition of triethyllead acetate and tetraethyllead in the chromatographic injector. The following procedure was used to effect this analysis quantitatively. A solution of 0.0277 mmol Cu^{II} triflate in 3 ml acetic acid was deaerated with a stream of argon and the gaseous internal standards added. The flask was placed in a constant temperature bath and 0.51 mmol of tetraethyllead added with a microliter hypodermic syringe. After the initial reaction was complete, ethylene was analyzed and the reaction mixture allowed to sit until all the tetraethyllead had reacted. A known weight of n-propyl acetate was added and the vaporizable components quantitatively transferred on a vacuum line. The distillate was analyzed for ethyl acetate on a 10 ft. 15% carbowax 20M/chromosorb P column at 70°.

Copper-catalyzed decomposition of dipropionyl peroxide

A weighed amount of dipropionyl peroxide was placed in a 125 ml round bottom flask and 25 ml dry acetic acid added. A weighed sample of the Cu^{II} salt was added and the flask sealed with a gas-tight rubber serum cap. The vessel was placed in a thermostated bath and deaerated with a stream of nitrogen. Measured amounts of methane and isobutane were added as internal standards. The reaction was initiated by adding with a hypodermic syringe the Cu^{I} initiator to the magnetically stirred solution as described previously[30]. Typical results are given in Table 6.

TABLE 6

CU-CATALYZED DECOMPOSITION OF DI-PROPIONYL PEROXIDE IN ACETIC ACID

CuX_2	CO_2	C_2H_4	C_2H_5OAc	C_2H_4/CO_2	C_2H_5OAc/CO_2
$Cu(OAc)_2^a$	0.515	0.504	0	0.98	0
CuT_2^b	0.503	0.227	0.277	0.45	0.55

[a] Acetic acid (25 ml) solution of 0.022 *M* Cu^{II} acetate and 0.02 *M* dipropionyl peroxide (0.54 mmol) initiated with 1 ml of 0.0424 *M* Cu^{I} acetate in 80 vol% $HOAc/CH_3CN$. [b] Acetic acid solution (25 ml) of 0.021 *M* Cu^{II} triflate and 0.020 *M* dipropionyl peroxide (0.51 mmol) initiated with 1 ml of a solution of 0.02 *M* Cu^{I} triflate in acetic acid at 20°.

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