Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

I. THE CATALYTIC DECOMPOSITION OF TETRAETHYLLEAD BY COPPER(I). ACETOLYSIS OF ALKYLCOPPER(I) INTERMEDIATES

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

(Received February 7th, 1972)

SUMMARY

The decomposition of tetraethyllead is strongly catalyzed by copper(I) species in acetic acid. Ethane and triethyllead acetate are formed in stoichiometric amounts. The kinetics are first order in tetraethyllead and Cu^I but reach limiting values of the latter due to the partial solubility of Cu^I acetate. The different kinetic isotope effects for the uncatalyzed and the copper-catalyzed acetolysis indicates that the latter occurs via a metastable intermediate. A mechanism is proposed in which alkyl transfer from tetraalkylead to Cu^I is rate-limiting. The subsequent rapid protonolysis of the alkylcopper intermediate is discussed.

INTRODUCTION

Tetraalkyllead compounds, among organometallic compounds are desirable candidates for study as alkylating agents because they are readily prepared, thermally and aerially stable and are well-behaved in solution[1]. The alkylation of various metal complexes mainly from the main group elements has been studied. For example, alkyl transfer from tetraethyllead to aluminum chloride occurs readily at room temperature in a stepwise manner[2]:

$$Et_4Pb + AlCl_3 \rightarrow Et_3PbCl + EtAlCl_2$$

$$Et_3PbCl + EtAlCl_2 \rightarrow Et_2PbCl_2 + Et_2AlCl, \text{ etc.}$$

Alkyl transfer to transition metal complexes is of particular interest since the resultant alkylmetal species are often metastable and oxidation–reduction as well as other reactions are a possibility. Thus, tetraalkyllead compounds undergo facile reaction with copper, silver and gold salts even at −30° [3–9] and in certain cases some alkylsilver and alkylcopper species have been isolated[4–9]. The reaction between tetramethyl- or tetraethyl-lead with Cu^{II} nitrate in ethanol was postulated to proceed by initial reduction to Cu^I followed by subsequent decomposition of the alkylcopper intermediate[4–8].

$$R_4Pb + Cu^{II} \rightarrow R_3Pb^+ + Cu^I + R\cdot \quad (1)$$

$$R_4Pb + Cu^I \rightarrow R_3Pb^+ + RCu \quad (2)$$

$$RCu \rightarrow Cu + [R_2, RH, R(-H)] \quad (3)$$

The simultaneity of at least three competing processes, involving metathetical as well as oxidation–reduced reactions, makes an understanding of the chemistry difficult. For example, the role of alkyl radicals is obscure since there is ambiguity as to whether reaction (1), (2) or (3), or perhaps all three, involves homolysis[10].

We chose to investigate this interesting system by first dissecting it into a Cu^{I} and then into a Cu^{II} induced pathway. In this paper we describe the mechanism of the efficient catalytic decomposition of tetraethyllead by Cu^{I} species. In the following paper we examine the reduction of tetraethyllead by Cu^{II} salts.

RESULTS AND DISCUSSION

The stoichiometry and kinetics of decomposition in acetic acid

Tetraethyllead is relatively stable in acetic acid solutions, but undergoes protonolysis slowly according to eqn. (4) with a pseudo first order rate constant k_0 of 4.9×10^{-6} sec^{-1} at 20°.

$$Et_4Pb + HOAc \rightarrow Et_3PbOAc + Et\text{–}H \qquad (4)$$

The liberation of ethane is markedly accelerated in the presence of a catalytic amount of Cu^{I} acetate as shown in Fig. 1. One mole of ethane is liberated from each mole of tetraethyllead; and the formation of a mole of triethyllead acetate indicates that the copper(I) catalyzed reaction also follows the stoichiometry given in eqn. (4). Furthermore, the reaction essentially stops after one ethyl group is transferred. The subsequent loss of an ethyl group from triethyllead acetate is much slower and is consistent with other dealkylation studies of tetralkyllead compounds[11]. The unambiguous stoichiometry can also be deduced indirectly from the rate of liberation of ethane which follows first order kinetics to well beyond 90% (Fig. 1) by equating the intitial concentration of tetraethyllead to the infinity point. The same results are obtained by using the Guggenheim method which does not depend on the latter.

The rate of ethane liberation is linearly dependent on the concentration of Cu^{I} acetate as shown in Fig. 2. However, beyond 1.27×10^{-3} M the rate becomes in-

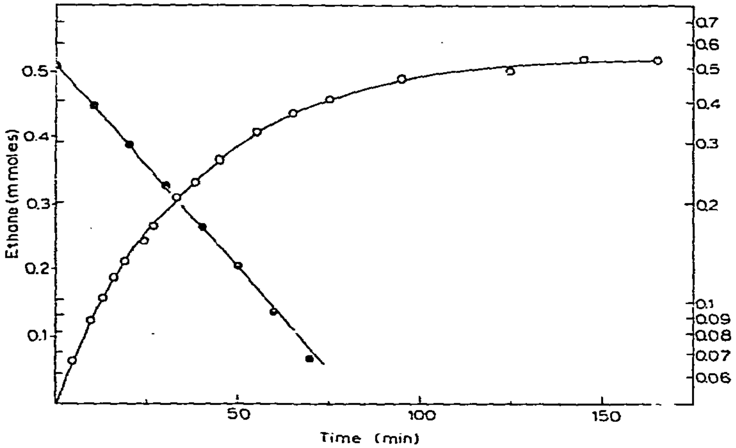


Fig. 1. Copper catalyzed decomposition of tetraethyllead in glacial acetic acid at 20°. ○ liberation of ethane (linear scale); ● Disappearance of tetraethyllead (log scale).

dependent of added Cu^I acetate. This limiting value corresponds to the solubility of Cu^I acetate in glacial acetic acid, since it coincides with the saturation concentration of Cu^I acetate determined independently. The latter studies are carried out by adding excess Cu^I acetate to a carefully degassed solution of pure acetic acid. After equilibration, the mixture is filtered and the clear solution of Cu^I acetate oxidized to Cu^{II}.

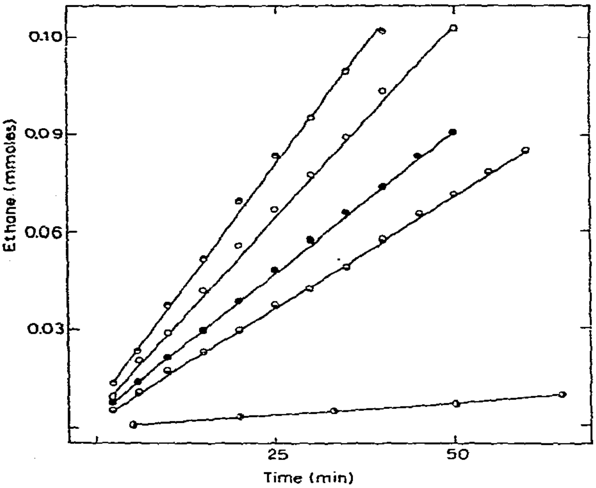


Fig. 2. Copper(I) catalysis in the decomposition of tetraethyllead in acetic acid. ◐ no Cu^I; ◒ 3.8×10^{-4} M Cu^I; ● 5.6×10^{-4} M Cu^I; ○ 7.5×10^{-4} M Cu^I; ◓ 1.1×10^{-3} M Cu^I.

The concentration of the latter is determined spectroscopically. The accuracy of the solubility of Cu^I acetate in glacial acetic acid ($1.19 \pm 0.1 \times 10^{-3}$ M) determined in this manner, however, is somewhat limited by the extreme sensitivity of these solutions to air.

The kinetics of the copper catalyzed decomposition of tetraethyllead in acetic acid can, thus, be described by eqn. (5),

$$\frac{\mathrm{d\,EtH}}{\mathrm{d}t} = k_0 \cdot [Et_4Pb] + k_c \cdot [CuOAc] \cdot [Et_4Pb] \tag{5}$$

where k_0 and k_c represent the pseudo first order rate constant for acetolysis and the second order rate constant for the copper-catalyzed process, respectively. The value of the catalytic constant k_c is 0.033 $l \cdot mol^{-1} \cdot sec^{-1}$ at 20°.

Copper(II) acetate has a rather intense absorption band in the visible region of the spectrum (λ_{max} 680 nm; ε 176)[12] and can be readily detected even in small amounts. Since the copper-catalyzed decomposition of tetraethyllead in acetic acid remains homogeneous and colorless, the value of k_c in eqn. (5) is indeed representative of catalysis by Cu^I acetate. The steady state concentration of Cu^{II} acetate under these conditions must be less than 10^{-6} M, and no doubt maintained at this level (or lower) by the ready oxidation of tetraethyllead (see accompanying paper)[13]. Only after the tetraethyllead in solution is depleted, does the Cu^I acetate undergo slow disproportionation.

$$2\,CuOAc \rightarrow Cu + Cu(OAc)_2 \tag{6}$$

Inhibition of the copper catalysis

The rapid decomposition of tetraethyllead in the presence of Cu^I acetate is efficiently quenched by the addition of small amounts of molecular oxygen as shown in Fig. 3. The oxidation of Cu^I acetate is immediately apparent by the appearance of the intense blue-green color characteristic of Cu^{II} acetate. Analysis indicates that Cu^I is quantitatively oxidized to Cu^{II} under these conditions. Previous studies in aqueous acetonitrile solutions[14] were consistent with the stoichiometry:

$$2\,Cu^I + 2\,H^+ + O_2 \rightarrow 2\,Cu^{II} + H_2O_2 \tag{7}$$

but the catalytic decomposition of hydrogen peroxide by Cu^I under our conditions complicates this analysis.

The catalytic decomposition of tetraethyllead by Cu^I acetate may also be interrupted by the addition of molecular chlorine (Fig. 4), which is an efficient oxidant for Cu^I.

$$2\,Cu^I + Cl_2 \rightarrow 2\,Cu^{II}Cl_2 \tag{8}$$

The rate of decomposition of tetraethyllead after the introduction of either oxygen

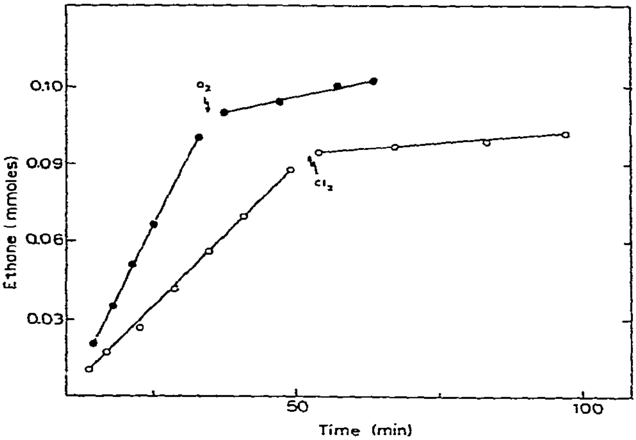


Fig. 3. Inhibition by 1.86×10^{-2} mmole oxygen ● or chlorine ○ added at the arrow to the copper(I) catalyzed decomposition of tetraethyllead in acetic acid.

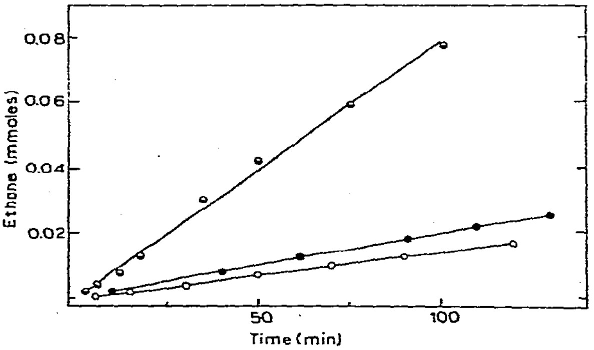


Fig. 4. Salt effect on the uncatalyzed decomposition of tetraethylead in acetic acid at 20° ○ no salt, ● 1.0 *M* lithium acetate, ◒ 0.75 *M* lithium perchlorate.

or chlorine is essentially that of the uncatalyzed acetolysis. However, the rate increases again with time due to the slow regeneration of Cu^I by the reduction of Cu^{II} in the presence of tetraethyllead[13]. The length of the inhibition period is dependent on the amount of oxygen or chlorine added. The reduction of Cu^I can easily be followed visually by the fading of the color due to Cu^{II}, and when the mixture becomes colorless the rate resumes at that value observed before the interruption. These studies clearly show that catalysis is effected by a Cu^I species.

Kinetic isotope effect of acetolysis

The uncatalyzed decomposition of tetraethyllead in deuterio-acetic acid affords only ethane-d_1:

$$Et_4Pb + DOAc \rightarrow Et{-}D + Et_3PbOAc \tag{9}$$

The pseudo first order rate of formation of ethane-d_1 under these conditions is 9 times slower than that in protio-acetic acid as given in Table 1. The ratio of Et–H to Et–D formed during the acetolysis of tetraethyllead in mixtures of HOAc and DOAc reflect a fractionation factor of 9, which is the direct measure of the primary kinetic isotope effect in the proton transfer step. The value of 1.0 derived for the solvent (secondary) isotope effect is in line with those obtained in the study of other systems[15].

The copper catalyzed decomposition of tetraethyllead in deuterio-acetic acid also affords ethane-d_1 according to the stoichiometry given in eqn. (9). However, the rate of liberation of ethane given in Table 2 is *independent* of whether the reaction is

TABLE 1

KINETIC ISOTOPE EEFECTS IN THE ACETOLYSIS OF TETRAETHYLLEAD[a]

Solvent[b] *DOAc (mol %)*	*Rate constant* $10^6 k_0$ *(sec*$^{-1}$*)*	C_2H_6/C_2H_5D[c]	$k_0(H)/k_0(D)$
0	4.9		
45.8	2.0	8.9±0.4	2.41
62.8	1.1	9.1±0.5	4.27
88.4	0.61		8.1

[a] Solutions of 0.15 *M* Et_4Pb at 20°. [b] Remainder is protio-acetic acid. [c] Normalized to the solvent composition.

TABLE 2

COPPER-CATALYZED DECOMPOSITION OF TETRAETHYLLEAD IN DEUTERIO-ACETIC ACID[a]

Solvent[b] *DOAc (mol %)*	*Rate constant* k_c $(l \cdot mol^{-1} \cdot sec^{-1})$	C_2H_6/C_2H_5D[c]	$k_c(H)/k_c(D)$
0	0.033±0.001		
46.7	0.035±0.001	6.2±0.3	0.95
61.4	0.033±0.001	6.0±0.3	1.0
93.5	0.026±0.005		1.3

[a] In solution of 0.15 *M* Et_4Pb and 1.0×10^{-3} *M* CuOAc at 20°. [b] Remainder is protioacetic acid. [c] Normalized to the solvent composition.

carried out in deuterio- or protio-acetic acid or mixtures thereof. In the latter experiments, the isotopic analysis of the ethane indicates that the fractionation factor for Et–H/Et–D is 6, that is, Et–H is formed 6 times faster than Et–D.

The mechanism of the catalyzed acetolysis of tetraethyllead

The studies presented above clearly show that the rate-determining step in the copper-catalyzed reaction is separate from and precedes the product (ethane) forming step. The formation of a metastable intermediate is indicated, and we propose the following catalytic mechanism:

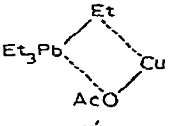
$$Et_4Pb + Cu^IOAc \xrightarrow{\text{slow}} Et_3PbOAc + EtCu \qquad (10)$$

$$EtCu + HOAc \xrightarrow{\text{fast}} Et\text{–}H + Cu^IOAc, \text{ etc.} \qquad (11)$$

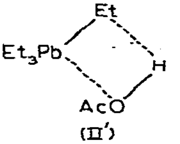
The first step [eqn. (10)] represents the rate-limiting alkylation of Cu^I acetate, and it is consistent with the isolation of alkylcopper species when the reaction is carried out in less acidic media[4–9]. The catalysis by Cu^I acetate is associated with the preferential transfer of an ethyl group to Cu^I relative to acetic acid. Possible transition states are represented as (I) and (II), respectively.

$$\underset{\text{(I)}}{[Et_3Pb\text{–}Et\text{–}CuOAc]^{\ddagger}} \qquad \underset{\text{(II)}}{[Et_3Pb\text{–}Et\text{–}H\text{–}OAc]^{\ddagger}}$$

Alternatively, a four-centered process may be envisioned as in the cleavage of organomercurials[16].



(I′)



(II′)

The metastability of the alkylcopper intermediate in acetic acid is due to its rapid protonolysis given in eqn. (11). The latter is also consistent with the relatively low value of the primary kinetic isotope effect observed in the catalyzed reaction. The magnitude of the kinetic isotope effect generally varies with the symmetry of the transition state. It is a maximum when the hydrogen is symmetrically bonded to the atoms between which it is being transferred[17]. The uncatalyzed acetolysis of tetraethyllead represents such an example. The value of the kinetic isotope effect in the acetolysis of the alkylcopper species ($k_H/k_D = 6$) is intermediate between a maximum value and that obtained for a number of the organometals of the main Groups I and II[18]. The low values of k_H/k_D (≈ 1) often obtained for the latter are consistent with their lability and indicate that proton transfer has not proceeded very far in the transition state. Alkylcopper[19] species, on this basis, are less labile than organozinc compounds toward protonolysis of the alkyl–metal bond.

An homolytic mechanism has been presented for the copper-catalyzed decomposition of tetramethyllead in methanol[20].

$$(CH_3)_4Pb + Cu^IOCH_3 \rightarrow (CH_3)_3PbOCH_3 + CuCH_3 \qquad (12)$$

$$CuCH_3 \rightarrow Cu + CH_3^{\bullet} \qquad (13)$$

$$CH_3^{\bullet}+CH_3OH(D) \rightarrow CH_3\text{-}H(D)+CH_3O^{\bullet} \tag{14}$$

$$Cu+{}^{\bullet}OCH_3 \rightarrow Cu^{I}OCH_3, \text{ etc.}$$

Methyl radicals according to this mechanism must abstract the hydroxylic hydrogen [eqn. (14)] to account for the formation of monodeuteriomethane from reactions carried out in methanol-*d*. There is, however, no evidence for either the ready homolysis of alkylcopper species[21] or the thermodynamically unfavored abstraction from a hydroxylic group by an alkyl radical[22]. A mechanism involving protonolysis of the alkylcopper intermediate by alcohol [eqn. (16)] obviates these difficulties [eqns. (13)–(15)], and is consistent with our studies in acetic acid. Homolytic attack on the

$$CuCH_3+CH_3OH \rightarrow CuOCH_3+CH_3\text{-}H \tag{16}$$

latter is rigorously discounted by the absence of carbon dioxide, since the decarboxylation of acetoxy radicals is exceedingly rapid[23,24].

$$CH_3CO_2H \xrightarrow{(-H\cdot)} CH_3CO_2^{\bullet} \xrightarrow{>10^9\,sec^{-1}} CH_3^{\bullet}+CO_2 \tag{17}$$

The alkylation of Cu^{I} species by tetraethyllead

The rate of alkyl transfer from tetraethyllead is highly dependent on the nature of the Cu^{I} species. For example, Cu^{I} which is coordinated by acetonitrile[25,26] is not significantly better than acetic acid itself. Furthermore, bis(triphenylphosphine)-copper(I) acetate [$(PH_3P)_2CuOAc$][27] possesses no catalytic activity.

$$Cu^{I}OAc+CH_3CN \rightleftarrows Cu^{I}(NCCH_3)_4(OAc) \tag{18}$$

Earlier studies have also shown[4,5] that the copper-catalyzed decomposition of tetramethyllead in an alcoholic solution is many orders of magnitude slower than we observe in acetic acid. For example, in methanol the turnover of Cu^{I} to produce methane occurs on the average only 12 times within 161 h; and another reaction was only two-thirds complete after 500 h at room temperature. The rate-limiting step under these conditions appeared to be the very slow alkyl transfer from lead to Cu^{I} alkoxide[5]. However, the subsequent protonolysis of the intermediate by alcohol also could not have been very rapid since an alkylcopper species could be isolated when the reaction was carried out at low temperatures[4-9].

The catalytic activity of various Cu^{I} species is no doubt partly related to the availability of coordination sites on copper since it also parallels the sensitivity of these complexes to oxygen, the conversion to Cu^{II} being an inner-sphere process[14,28]. Furthermore, Cu^{I} salts of weakly coordinating anions are the most effective catalysts of all. The catalytic activity of such catalysts unfortunately cannot be measured quantitatively in acetic acid due to the leveling effect caused by ligand exchange. For example, the trifluoromethanesulfonate (T = triflate) salt of Cu^{I} shows remarkable electrophilic properties[29,30]. It is an effective agent for the decomposition of tetraethyllead, but undergoes rapid metathesis with the product, *i.e.*,

$$Cu^{I}T+Et_3PbOAc \rightleftarrows Et_3PbT+Cu^{I}OAc \tag{19}$$

so that the catalytic rate observed after more than 10 percent conversion is essentially that associated with Cu^{I} acetate. The study of the reaction in the very early stages shows, however, that Cu^{I} triflate is at least 100 times more reactive than Cu^{I} acetate.

The addition of lithium perchlorate accelerates the uncatalyzed decomposition of tetraethyllead as shown in Fig. 4. Only a part of this enhancement in rate is associated with the formation of the stronger perchloric acid by the equilibrium given in eqn. (20)[31,32], since lithium acetate has a similar effect, albeit of reduced magnitude.

$$\mathrm{LiClO_4 + HOAc \rightleftharpoons LiOAc + HClO_4} \tag{20}$$

The salt effects in the decomposition of tetraethyllead are greatly magnified in the presence of the $\mathrm{Cu^I}$ catalyst as also shown in Fig. 5. Lithium perchlorate can be involved in ligand exchange with $\mathrm{Cu^I}$ acetate [eqn. (21)]. However, such a metathesis does not account for the enhancement in rate, since the addition of the salt of a common ion such as lithium acetate causes no depression in rate. In fact, acetate is almost as effective as perchlorate in the copper catalyzed reaction in contrast to its role in the uncatalyzed reaction (Fig. 5). The absence of a common ion depression in the rate is also inconsistent with dissociation of the ligand.

$$\mathrm{Cu^IOAc + LiClO_4 \rightleftharpoons Cu^IClO_4 + LiOAc} \tag{21}$$

$$\mathrm{CuOAc \rightleftharpoons Cu^+ + OAc^-} \tag{22}$$

The influence of added salt (best interpreted qualitatively at this point) is associated with charge separation in the transition state for alkyl transfer. The salt effect observed in the catalytic system is similar to that already examined intensively by Abrahams and co-workers[33] in the analogous alkylation of $\mathrm{Hg^{II}}$ by tetraalkyltin compounds. The magnitude of the salt effect as well as the influence of solvent in the latter studies have been discussed in terms of an open S_E2 transition state [*cf.* (I)] for the transfer of the alkyl group.

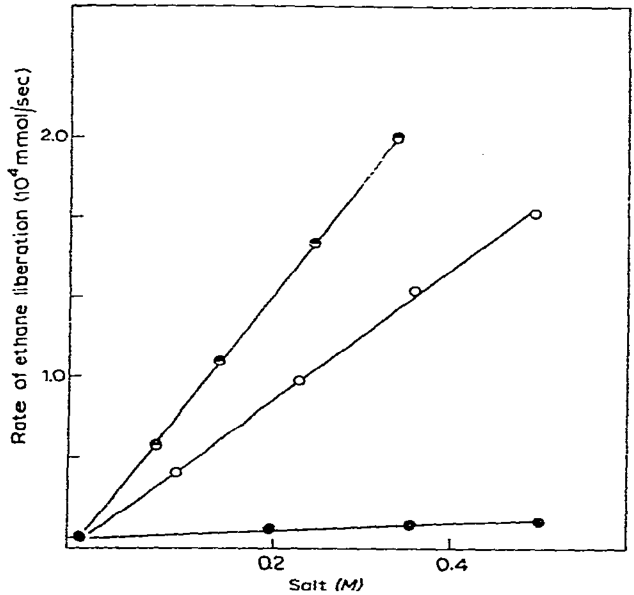


Fig. 5. Salt effect on the copper(I) catalyzed decomposition of tetraethyllead in acetic acid. ● none, ○ lithium acetate, ◓ lithium perchlorate.

Copper(I) acetate in acetic acid

Mass spectral studies based on the pyrolysis of Cu^{II} acetate indicate that Cu^{I} acetate is dimeric in the gas phase[34]. The methods available for the determination of the degree of association of Cu^{I} acetate in acetic acid are unfortunately limited since it is only sparingly soluble. Moreover, these solutions are extremely sensitive to air and we are unable to determine the molecular weight by vapor phase osmometry. Solutions of Cu^{I} acetate are also metastable and undergo disproportionation on standing for prolonged periods which precludes a molecular weight determination by isothermal distillation.

Although Cu^{II} acetate is extensively dimerized in acetic acid[35], it is not clear that Cu^{I} acetate must also be so. The kinetic studies show that the rate of acetolysis varies linearly with the gross concentration of Cu^{I} acetate. Such a behavior does not allow for a partial dissociation [eqn. (22)], *i.e.*, the Cu(I) species must be either monomeric or *completely* dimeric.

$$2\,Cu^{I}(OAc) \rightleftharpoons Cu^{I}_{2}(OAc)_{2} \qquad (22)$$

The mechanism given by eqns. (10)–(11) is formulated for monomeric Cu^{I} acetate. This assumption is supported by the high catalytic activity shown by Cu^{I} triflate which should be monomeric, based on the studies of Cu^{II} triflate in acetic acid[12]. However, the basic conclusions of the mechanism for copper catalysis are not altered if alkyl transfer occurs to a binuclear Cu^{I} species in eqn. (10).

EXPERIMENTAL SECTION

Materials

Tetraethyllead was prepared from ethylmagnesium bromide, plumbous chloride and ethyl iodide according to the procedure described by Gilman and Jones[36].

Cu^{I} acetate was prepared by dissolving Cu^{I} oxide[37] in acetic acid containing sufficient acetic anhydride to remove all the water generated from the oxide. Since the metathesis was slow, the unreacted cuprous oxide was separated from the precipitated cuprous acetate by extraction with hot acetic acid. Pure cuprous acetate separated in poor yield as a colorless crystalline precipitate on cooling. Alternatively, Cu^{I} oxide was treated with acetic acid containing 10% acetic anhydride under an hydrogen atmosphere[38]. The mixture after heating at reflux for 12 h produced a blue solution in contact with unreacted cuprous oxide and a white crystalline precipitate of cuprous acetate. The hot solution was transferred to a centrifuge tube and allowed to cool, whereupon Cu^{I} acetate crystallized. It was washed repeatedly with dry deaerated acetic acid until the wash solution was colorless.

Cu^{I} triflate is readily prepared as a molecular complex with benzene[39]. For purposes here, however, it is more convenient to prepare it, *in situ* from the direct and rapid reduction of Cu^{II} triflate with tetraethyllead[13].

Cu^{II} triflate was prepared from Cu^{II} carbonate and triflic acid in acetonitrile solution and isolated as a colorless anhydrous salt[12].

Bis(triphenylphosphine)copper(I) acetate was prepared according to the procedure described by Hammond, Jardine and Vohra[27].

Tetrakis(acetonitrile)copper(I) acetate was prepared *in situ* by carrying out the reaction in 10% vol acetonitrile/acetic acid solutions. Both the triphenylphosphine and acetonitrile complexes of Cu^I are much less readily oxidized by oxygen than Cu^I acetate and solutions are stable to air over relatively prolonged periods. Lithium perchlorate was anhydrous reagent grade material (G. F. Smith, Co.).

Acetic acid was redistilled after refluxing with acetic anhydride. The results were the same as that obtained from Mallinckrodt reagent grade material used as such. Acetic acid-d_1 was prepared from deuterium oxide and 20% excess of freshly distilled acetic anhydride. The deuterio-acetic acid was redistilled twice. The purity of deuterio-acetic acid was determined by mass spectral analysis to be 93.5% deuterated by using the prominent (≈70%) parent ion peak. The mass spectra of both HOAc and DOAc contained the same m/e fragments at 43 and 15 for the acetyl and methyl moieties, and there was no evidence for deuteriation of the methyl group. Similarly, integration of the proton magnetic resonance spectrum for the methyl and hydroxyl resonance indicated 91–92% deuterium incorporation on oxygen.

Acetolysis of tetraethyllead

A flask containing a weighed amount of copper salt and a known volume of acetic acid was sealed with a gas-tight rubber serum. The solution was then swept with argon and equilibrated in a constant temperature bath. Measured volumes of methane and isobutane as marker gases were added with hypodermic syringes. The reaction was initiated by adding a known amount of deaerated tetraethyllead with a 50 microliter syringe to the magnetically stirred solution.

Analysis

Ethane and ethylene were analyzed by gas chromatography on a 6 ft Porapak Q column at 80° using methane as the internal standard. Butane was analyzed on the same column at 135° with isobutane as the marker. Quantitative analysis was effected by carefully calibrating the system with known amounts of these gases under reaction conditions. Kinetics were determined by periodically extracting a small volume (< 0.01%) of the equilibrated gas phase.

The ethane produced in the reactions carried out in mixtures of HOAc and DOAc was introduced into the mass spectrometer either through a gas chromatographic inlet (6 ft Porapak Q at 80°) or from a gas bulb. In the latter method, samples were first purified by passing the gas through a small column of alumina. The parent ion peak was used in the analysis.

The concentration of Cu^I acetate was determined in acetic acid solutions by oxidation to Cu^{II} acetate with oxygen. The latter was determined spectroscopically by its absorption at 680 nm (ε_{app} 176 $cm^{-1} \cdot M^{-1}$)[12].

Acetate was determined by titration with a standard solution of trifluoromethanesulfonic acid in acetic acid using Cu^{II} acetate as a visual indicator. At the end-point, the color of the solution changed abruptly from a deep blue-green color of Cu^{II} acetate to a pale blue color of Cu^{II} triflate. The method was standardized with samples of alkali metal acetates and should be generally applicable to the determination of other carboxylate salts in acetic acid solutions. Some representative results are summarized in Table 3.

The stoichiometric relationship between ethane liberated during the acetolysis of tetraethyllead and acetate (triethyllead acetate) produced is given in Table 4.

Triethyllead was isolated from the reaction mixture by removal of acetic acid

TABLE 3

TITRATION OF ACETATES IN ACETIC ACID WITH TRIFLIC ACID[a]

Metal acetate	*Amount (mmoles)*	*Acetate det'd. (mmoles)*
NaOAc	0.188	0.189
NaOAc	0.188	0.186
$(CH_3)_3PbOAc$	0.190	0.193

[a] Using 0.331×10^{-3} mmoles Cu^{II} triflate.

TABLE 4

ETHANE AND ACETATE FROM THE ACETOLYSIS OF TETRAETHYLLEAD[a]

Cu catalyst (mmole)	*Etane produced (mmole)*	*Acetate det'd. (mmole)*
3.36×10^{-3}	0.45	0.49 ± 0.1
1.12×10^{-3}	0.237	0.235 ± 0.005

[a] From 0.17 *M* tetraethyllead in acetic acid at 20°. Reaction quenched with oxygen immediately before analysis.

in vacuo. The crude crystalline residue containing the catalytic amounts of copper salts melted at 147–149° and comprised 99% of the expected weight of triethyllead acetate. Trituration of this crude sample with acetone removed most of the blue color due to Cu^{II} salt and produced a white solid melting at 156–157° (70% of the theoretical yield). The reported melting point of triethyllead acetate is 160° [2] and that of diethyllead diacetate is 130° [40].

ACKNOWLEDGEMENT

We wish to thank the National Science Foundation for generous financial support of this work.

REFERENCES

1 H. Shapiro and F. W. Frey, *The Organic Compounds of Lead*, Interscience Pub., New York, N.Y., 1968, p. 25ff.

2 O. H. Browne and E. E. Reid, *J. Amer. Chem. Soc.*, 49 (1927) 830; H. Gilman and L. D. Apperson, *J. Org. Chem.*, 4 (1939) 162.

3 H. Gilman and L. A. Woods, *J. Amer. Chem. Soc.*, 65 (1943) 435; H. Gilman, R. G. Jones and L. A. *J. Org. Chem.*, 17 (1952) 1630.

4 C. E. H. Bawn and F. J. Whitby, *J. Chem. Soc.*, (1960) 3926.

5 C. E. H. Bawn and R. Johnson, *J. Chem. Soc.*, (1960) 4162.

6 G. Costa, A. Camus and E. Pauluzzi, *Gazz. Chim. Ital.*, 86 (1956) 77, 997.

7 G. Costa, G. DeAlti and L. Stefani, *Rend. Acc. Naz. Lincei, Class. Sci.*, 31 (1961) 267.

8 G. Costa and G. DeAlti, *Gazz. Chim. Ital.*, 87 (1957) 1273.

9 G. Semerano and L. Riccoboni, *Ric. Sci.*, 11 (1940) 269.

10 C. E. H. Bawn and F. J. Whitby, *Disc. Faraday Soc.*, 2 (1947) 228; *Cf.* also C. E. H. Bawn, W. H. Janes and A. M. North, *J. Polym. Sci.*, 58 (1962) 335; G. Costa, G. DeAlti, L. Stefani and G. Boscarato, *Ann. Chim. (Rome)*, 52 (1962) 289.
11 Reference 1, p. 79ff.
12 C. L. Jenkins and J. K. Kochi, *J. Amer. Chem. Soc.*, 94 (1972) 843.
13 N. A. Clinton and J. K. Kochi, *J. Organometal. Chem.*, 42 (1972) 241.
14 R. D. Gray, *J. Amer. Chem. Soc.*, 91 (1969) 56.
15 R. L. Schowen, *Progr. Phys. Org. Chem.*, 9 (1972) 275.
16 F. R. Jensen and B.Rickborn, *Electrophilic Substitution of Organomercurials*, McGraw-Hill Book Co., New York, N.Y., 1968, p. 6ff.
17 F. H. Westheimer, *Chem. Rev.*, 61 (1961) 265; J. Bigeleisen, *Pure Appl. Chem.*, 8 (1964) 217; S. B. Hanna, C. Jermini and H. Zollinger, *Tetrahedron Lett.*, (1969) 4415; W. A. Pryor and K. G. Kneipp, *J. Amer. Chem. Soc.*, 93 (1971) 5584; E. S. Lewis and M. M. Butler, *Chem. Commun.*, (1971) 941.
18 K. B. Wiberg, *Chem. Rev.*, 55 (1955) 713.
19 H. Gilman and J. M. Straley, *Recl. Trav. Chim. Pay-Bas*, 55 (1936) 821; K.-H. Thiele and J. Kohler, *J. Organometal. Chem.*, 12 (1968) 225.
20 G. Costa, A. Camus and N. Marsich, *J. Inorg. Nucl. Chem.*, 27 (1965) 281 and references therein.
21 (a) M. Tamura and J. K. Kochi, *J. Amer. Chem. Soc.*, 93 (1971) 1485;
(b) G. M. Whitesides, E. J. Panek and E. R. Stedronsky, *ibid.*, 94 (1972) 232.
22 *Cf.* W. H. Urry, F. W. Stacey, E. S. Huyser and O. O. Juveland, *J. Amer. Chem. Soc.*, 76 (1954) 450.
23 W. Braun, L. Rajbenbach and F. Eirich, *J. Phys. Chem.*, 66 (1962) 1591.
24 J. C. Martin and S. A. Dombchik, *Oxidation of Organic Compounds, Amer. Chem. Soc., Advan. Chem. Ser.*, 75(I) (1968) 269.
25 (a) B. J. Hathaway, D. G. Holah and J. D. Postlethwaite, *J. Chem. Soc.*, (1961) 3215;
(b) S. Manahan and R. T. Iwamoto, *J. Electroanal. Chem.*, 14 (1967) 213.
26 M. Kubota and D. L. Johnston, *J. Inorg. Nucl. Chem.*, 29 (1969) 769.
27 B. Hammond, F. H. Jardine and A. G. Vohra, *J. Inorg. Nucl. Chem.*, 33 (1971) 1017.
28 P. M. Henry, *Inorg. Chem.*, 5 (1966) 688; *cf.* also K. Shaw and J. H. Espenson, *ibid.*, 7 (1968) 1619.
29 R. G. Salomon, unpublished results.
30 *Cf.* A. Scott and H. Taube, *Inorg. Chem.*, 10 (1971) 62; M. M. Jones, E. A. Jones, D. F. Harmon and R. T. Semmes, *J. Amer. Chem. Soc.*, 83 (1961) 2038.
31 S. J. Cristol, T. C. Morrill and R. A. Sanchez, *J. Org. Chem.*, 31 (1966) 2719.
32 I. M. Kolthoff and A. W. Willman, *J. Amer. Chem. Soc.*, 56 (1934) 1014.
33 M. H. Abraham and F. Behbahany, *J. Chem. Soc. A*, (1971) 1061, 1469; M. H. Abraham and M. J. Hogarth, *ibid.*, (1971) 1474; M. H. Abraham and G. F. Johnston, *ibid.*, (1971) 1610; M. H. Abraham, F. Behbahany and M. J. Hogarth, *ibid.*, (1971) 2566.
34 C. Reichert, D. K. C. Fung, D. C. K. Lin and J. B. Westmore, *Chem. Commun.*, (1968) 1094.
35 J. K. Kochi and R. V. Subramanian, *Inorg. Chem.*, 4 (1965) 1527; A. T. A. Cheng and R. A. Howald, *ibid.*, 7 (1968) 2100.
36 H. Gilman and R. G. Jones, *J. Amer. Chem. Soc.*, 72 (1950) 1760.
37 G. G. Schlessinger, *Inorganic Laboratory Preparations*, Chemical Publ. Co., Inc., New York, N. Y., 1962, p. 10.
38 S. Weller and J. G. A. Mills, *J. Amer. Chem., Soc.*, 75 (1953) 769.
39 R. G. Salomon and J. K. Koshi, *Chem. Commun.*, (1972) 559.
40 E. M. Panov and K. A. Kocheshkov, *Dokl. Akad. Nauk SSSR*, 85 (1952) 1037.