815. *Alkyl Derivatives of Group I Metals. Part III.* Kinetics of Decomposition of Ethylcopper*(I) *in Ethanol.*

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The reaction between cupric nitrate and tetraethyl-lead has been shown to occur in two stages: (*a*) reaction between cupric ion and alkyl-lead to give cuprous ion and the free ethyl radical; and (*b*) formation of insoluble ethylcopper(I) by reaction of the cuprous ion with tetraethyl-lead. The kinetics of the first stage were determined by suppressing the second by formation of the cuprous complex with *p*-dimethylaminobenzylidenerhodanine. Under these conditions the yield of Et was quantitative and reaction followed a bimolecular rate law. The overall mechanism is discussed.

IN previous papers * it was shown that copper and silver salts react with alcoholic solutions of a tetra-alkyl-lead with formation of a free radical and reduction of the metal ion either to the lower valency state or to the metal. Cupric salts react in two steps: reduction to the cuprous state, and reaction of the cuprous compound with the alkyl-lead to form an alkylcopper(I). The general features had been observed by Gilman and Woods[2] but they did not propose a detailed mechanism. The reactions and the kinetics of the initial electron-transfer, $Cu^{2+} + PbEt_4 \longrightarrow Cu^+ + PbEt_3^+ + Et\cdot$ have now been studied.

Experimentally, reaction between cupric nitrate and tetraethyl-lead occurs as (*a*) discharge of the blue colour and (*b*) rapid formation of a brown precipitate. Stage (*a*) was accompanied by production of cuprous ions, as shown by the use of *p*-dimethylaminobenzylidenerhodanine. The precipitate was stable in alcohol below —30° but decomposed or reacted with the solvent at room temperature, with evolution of gas.

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* Parts I and II, *J.*, 1960, 3923, 3926.

[1] Bawn and Whitby, *Discuss. Faraday Soc.*, 1947, **2**, 228.

[2] Gilman and Woods, *J. Amer. Chem. Soc.*, 1943, **65**, 435.

The gaseous products of the overall reaction at 20° consisted of ethane, ethylene, and butane in the proportion set out in the Table. The carbon yield, based on the assumption that Cu^{2+} consumed liberated two ethyl radicals, was 73—74%.

Reaction between Cu^{2+} *and* $PbEt_4$ *in ethanol* (*typical results*).

Cu^{2+} (10^{-4} mole)	$PbEt_4$ (10^{-4} mole)	C_2H_6 (10^{-4} mole)	C_2H_4 (10^{-4} mole)	C_4H_{10} (10^{-4} mole)	Carbon balance (Cu^{2+} = 2Et)	Remarks *
1·65	12·7	1·61	0·12	0·35	74%	Total reaction at 20°
1·92	12·7	1·68	0·27	0·0	101·9	In presence of X.
3·15	12·7	1·38	0·0	0·49	75·1	Reaction at −30°. Results show gases evolved on warming to 20°.
1·81	12·7	0·0	0·19	0·0	10·1	X added after complete reaction at 20°.
1·81	12·7	0·86	0·35	0·26	50·0	In presence of excess of Y.
1·79	13·0	0·33	0·08	0	13·6	In presence of excess of Z.

* X = *p*-Dimethylaminobenzylidenerhodanine. Y = *NN*-Diphenyl-*N′*-picrylhydrazyl. Z = Acrylonitrile.

These observations suggested that during the first stage cupric copper was reduced to the cuprous state and that the second stage involved reaction of the cuprous ion. This was confirmed by suppressing the second stage by complex-formation between cuprous copper and *p*-dimethylaminobenzylidenerhodanine. The gaseous products then corresponded to the liberation of one Et radical for each Cu^{2+} consumed (see Table). The reaction which occurred was therefore analogous to that observed with tetramethyl-lead:

$$Cu^{2+} + PbEt_4 \longrightarrow Cu^{+} + PbEt_3^{+} + Et\cdot \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (1)$$

$$2Et\cdot \longrightarrow C_2H_6 + CH_4 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (2)$$

$$Et\cdot + EtOH \longrightarrow C_2H_6 + EtO\cdot \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (3)$$

At −30°, in the absence of a complex-forming agent, the cuprous ion reacted further, to form a brown precipitate of ethylcopper(I), without further gas evolution:

$$Cu^{+} + PbEt_4 \longrightarrow CuEt + PbEt_3^{+} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \ . \ . \quad (4)$$

Warming the solution caused evolution of ethane and butane (see Table). If it is assumed that the gases are produced by solvent-reaction or by decomposition of ethylcopper(I) according to the scheme:

$$CuEt + EtOH \longrightarrow CuOEt + C_2H_6 \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (5)$$

$$2CuEt \longrightarrow 2Cu + C_4H_{10} \quad . \ . \ . \ . \ . \ . \ . \ . \ . \quad (6)$$

then the yield of gases was 75%. If the free ethyl radical were liberated as in reaction (1) it would be expected to disproportionate to some extent to ethylene and ethane. The absence of ethylene was not due to its polymerisation since the reacting mixture of copper nitrate and tetraethyl-lead did not polymerise ethylene at 1 atm. and room temperature. It therefore appeared that the butane formed was not a combination product of the ethyl radical but was formed in one step by the reaction (6).

If, when gas evolution was complete, the rhodanine reagent was added to the solution ethylene was liberated (see Table) and it must therefore be postulated that this was retained in solution as a co-ordination complex with the cuprous salt. Such a complex not only prevents release of ethylene but also removes potentially reactive cuprous copper from the system. If a 1 : 1 complex is formed it produces an ethylene deficiency of about 10% in the first stage of the reaction, and modifies the second stage so that only about 90% of the cuprous ion will be available. The total deficiency in carbon yield is therefore about 20% and when this is allowed for the overall yield based on $1Cu^{2+}$ yielding 2Et· is at least 95% of that required by the scheme (1)—(6).

X-Ray analysis of the end copper product showed the presence of copper metal and cuprous oxide, with the latter in large excess. Chemical analysis agreed with a composition Cu_2O 80% + Cu 20%. The metal was produced by disproportionation of cuprous ion:

$$\mathrm{CuOEt} \longrightarrow \mathrm{Cu^+ + OEt^-}$$
$$\mathrm{2Cu^+} \longrightarrow \mathrm{Cu^{2+} + Cu}$$

and in the absence of excess of the alkyl-lead the colourless solution formed at the end of the reaction became blue and a copper mirror was deposited. The cuprous oxide was formed by hydrolysis of ethylcopper(I):

$$\mathrm{2CuOEt + H_2O} \longrightarrow \mathrm{Cu_2O + 2EtOH}$$

The other end product of the copper nitrate reaction was triethyl-lead nitrate and this was confirmed by isolation and analysis of the product (Found: Pb, 57·6; N, 4·0; C, 18·7; H, 4·2. $C_6H_{15}NO_3Pb$ requires Pb, 58·1; N, 3·9; C, 20·2; H, 4·2%). No evidence was obtained in this reaction, or in that of other alkylmetals with copper or silver ion, for the replacement of more than one alkyl group.

FIG. 1.

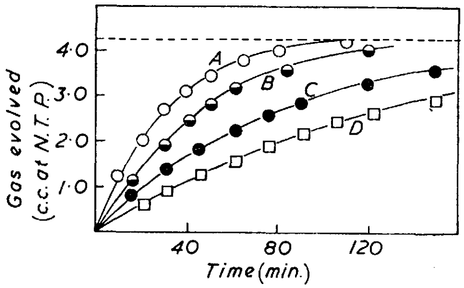


FIG. 2.

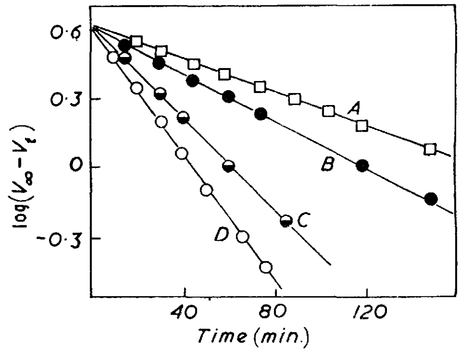
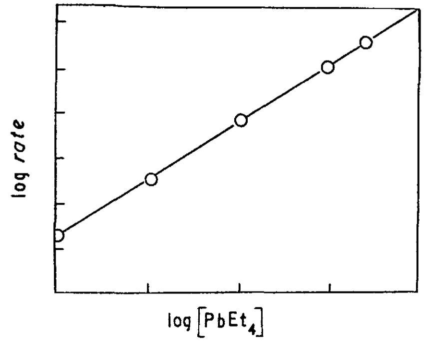


FIG. 3.



FIGS. 1—3. *Plots illustrating the kinetics of the first stage of the reaction of* Cu^{2+} *with tetraethyl-lead.*

Reaction at (*A*) +5°, (*B*) 0°, (*C*) −5°, *and* (*D*) −10°.

Formation of Free Radicals.—The free-radical mechanism was justified by measurements in the presence of free-radical capture agents. *NN*-Diphenyl-*N'*-picrylhydrazyl is decolorised by free radicals [3] and when our reaction was carried out in the presence of an excess of this hydrazyl the latter was decolorised and the gas yield was considerably decreased (see Table). The radical capture was not complete and this was partly due to the rapid competing reaction between the hydrazyl and cuprous ions.

In the presence of acrylonitrile, formation of hydrocarbons was almost completely suppressed (see Table) and polyacrylonitrile was produced in high yield. Formation of

[3] Bawn and Mellish, *Trans. Faraday Soc.*, 1951, **47**, 1216; Bawn and Margerison, *ibid.*, 1955, **51**, 780, 925.

ethylcopper(I) was also inhibited, owing to complex formation between cuprous ions and acrylonitrile. Similar observations were made with styrene and the kinetics of this polymerisation, to be reported in a later paper, substantiate the free-radical character of the reaction.

Reaction Kinetics.—Reaction between Cu^{2+} and tetra-alkyl-lead is relatively fast at room temperature and its kinetics were determined by suppressing the secondary reaction of Cu^{+} as described above. Under these conditions a 100% yield ($Cu^{2+} = 1Et$) was obtained and the rate of the reaction was observed by direct measurement of the hydrocarbon. The gases were removed continuously by a Toepler pump as described by Bawn and Whitby.[1] In a typical series (Fig. 1) of experiments the alkyl-lead was in at least a 20-fold excess, so that its concentration may be assumed to be constant. The plot of log ($V_{\infty} - V_t$) against time, where V_{∞} is the total volume of gas evolved and V_t the volume at time t, was linear, showing that the reaction was of the first order with respect to cupric ion (Fig. 2). At constant [Cu^{2+}], the rate at varying alkyl concentrations (determined from the slope of the gas evolution–time curve) showed that the rate of reaction was proportional to the alkyl-lead concentration (Fig. 3). The primary process is therefore the bimolecular reaction (1). The variation of the rate with temperature gave a linear Arrhenius plot corresponding to an activation energy of 15·2 kcal. mole^{-1} and an overall rate of reaction $k = 7{\cdot}42 \times 10^{9} \exp(-15{,}200/\boldsymbol{R}T)$ l. mole^{-1} sec.$^{-1}$.

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