779. *Alkyl Derivatives of Group I Metals. Part I. Ethylsilver: Kinetics of Decomposition in Solution.*

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Ethylsilver, prepared by the reaction of tetraethyl-lead with silver nitrate in ethanol solution, has been shown to decompose in accordance with the rate equation $k = 5.0 \times 10^8 \exp(-14{,}200/RT)$ sec.$^{-1}$ over the range $-50°$ to $-20°$. The products, namely, C_2H_4, C_2H_6, and C_4H_{10}, are in agreement with the decompositon: AgEt $\longrightarrow$ Ag + Et. The reasons for the non-quantitative yield of hydrocarbons are discussed.

A STABLE alkylsilver is formed on reaction of tetra-alkyl-lead with silver nitrate in alcohols at a sufficiently low temperature. At higher temperatures the alkylsilver decomposes to hydrocarbon products. Semerano and Riccobini [1] prepared methyl-, ethyl-, and propyl-silver by the reaction $R_4Pb + AgNO_3 \longrightarrow RAg + R_3Pb\cdot NO_3$, and Glockling [2] showed that triethylisobut-1-enyl-lead gave exclusively isobut-1-enylsilver. All these alkyl metals decomposed readily either in suspension or in solution in alcohols above $0°$, with deposition of silver and liberation of alkyl radicals. Bawn and Whitby [3] showed that methylsilver in homogeneous solution decomposed according to a first-order law with the quantitative formation of ethane, AgMe $\longrightarrow$ Ag + $\frac{1}{2}C_2H_6$, and a detailed study of this reaction has recently been made by Costa and Camus. [4] In the present work decomposition of ethylsilver has been shown to have similar kinetics and it is proposed that the initial reaction is liberation of the ethyl radicals. The hydrocarbon products (ethane, ethylene, and butane) are shown to be formed by reaction of C_2H_5 with the solvent and by inter-radical reactions.

EXPERIMENTAL

Kinetic measurements were carried out under conditions in which the alkylsilver was completely in solution (approx. 0.2 g. in 100 c.c. of alcohol), and a five-fold excess of alkyl-lead was used to avoid complex formation. [1]

It was established that at all temperatures used the yield of silver was quantitative. The procedure was as follows: Solutions of silver nitrate and tetra-ethyl-lead in alcohol were pre-cooled to the reaction temperature and rapidly mixed. Ethylsilver was formed immediately and after a finite time the mixture was quickly cooled to $-78°$. The silver was collected on a No. 4 sintered-glass filter covered with a layer of Gooch asbestos and cooled to $-78°$. The silver was dissolved in concentrated nitric acid and titrated with ammonium thiocyanate.

[1] Semerano and Riccobini, *Ber.*, 1941, **74**, 1089, 1297.
[2] Glockling, *J.*, 1955, 716.
[3] Bawn and Whitby, *Discuss. Faraday Soc.*, 1947, **1**, 228.
[4] Costa and Camus, *Gazzetta*, 1956, **86**, 77.

In the determination of the gaseous products the apparatus, procedure, and methods of analysis were similar to those described by Bawn and Whitby [3] for their study of methylsilver.

Glycols were estimated and determined by Reinke and Luce's method.[5]

Commercial tetraethyl-lead (Associated Ethyl Co.) was purified by Calingaert's method.[6]

Ethyl alcohol was freed from aldehyde by refluxing it with potassium hydroxide and silver nitrate, and then distilling it.

Kinetic Measurements.—The rate of production of silver at four temperatures, as shown in Figs. 1 and 2, obeyed the first-order law $kt = \log_e [V_\infty/(V_\infty - V_t)]$ where V_∞ is the volume of 0·00965N-ammonium thiocyanate used after complete reaction and V_t is the volume used at

FIG. 1. FIG. 2.
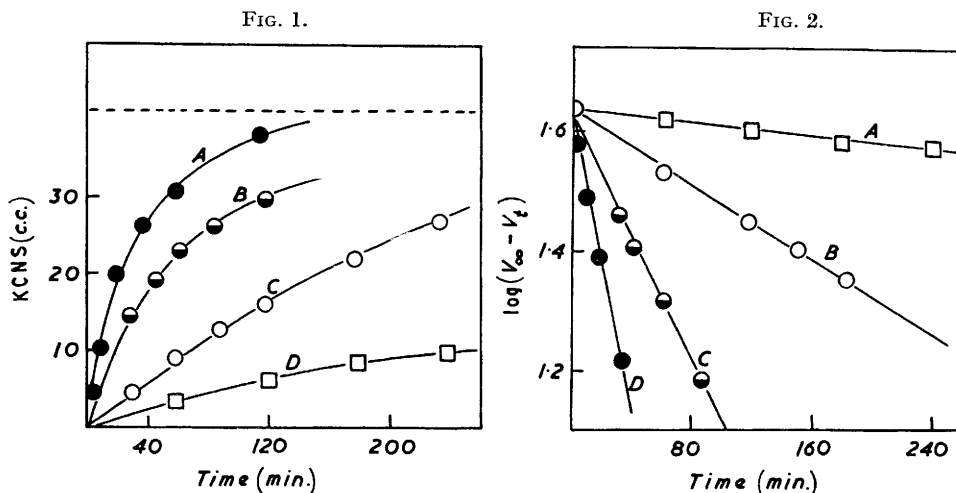
Decomposition of ethylsilver at (A) $-20°$, (B) $-30°$, (C) $-40°$ *and* (D) $-50°$. FIG. 1 *is in terms of* KCNS *used in titration of metallic silver formed.* FIG. 2 *gives first-order plots.*

time t. The plot of log k against $1/T$ was linear and corresponded to the rate law $k = 5 \times 10^8 \exp(-14,200/RT)$ sec.$^{-1}$. A further check on the first-order decomposition law was provided by the lack of dependence of the time of half-change on the initial concentration (Table 1). The change in concentration was limited by the low solubility of the ethylsilver.

TABLE 1. *Time of half-change*, AgEt $\longrightarrow$ Ag + Et.

Concn. of AgC$_2$H$_5$ (10^{-3} mole l.$^{-1}$)	9·94	7·22	9·94	7·22	9·94	7·22
Temp.	$-20°$	$-20°$	$-30°$	$-30°$	$-40°$	$-40°$
Time of half-change (min.)	19	18	57	58	180	184

TABLE 2.*

Temp.	AgNO$_3$ (10^{-4}M)	PbEt$_4$ (10^{-4}M)	Acrylo-nitrile (10^{-4}M)	Gases (c.c. at N.T.P.)			Yield (Ag$^+$ = 1C$_2$H$_5$)
				C$_2$H$_4$	C$_2$H$_6$	C$_4$H$_{10}$	
15°	2·82	23·0	—	0·38	2·46	0·37	56·8
18	3·27	24·5	—	0·25	2·85	0·37	53·3
18	3·08	24·5	—	0·28	2·59	0·35	54·1
−23	3·08	24·5	—	0·44	3·00	0·43	63·8
18	3·50	29·9	300	0·03	0·15	0·07	4·7

* Many of these analyses were carried out independently by Dr. G. T. Powell and each is the average of three or more results.

Gaseous Products.—Analyses of the gaseous products are summarised in Table 2. The concentrations were chosen so that the ethylsilver initially formed was in solution. The results differ little for experiments at different temperatures and the yield of hydrocarbon corresponds to about 60% of the silver deposited.

[5] Reinke and Luce, *Ind. Eng. Chem. Analyt.*, 1946, **18**, 244.
[6] Calingaert, *Chem. Rev.*, 1926, **2**, 55.

In the presence of a large excess of acrylonitrile the formation of polymer was observed from the commencement of the decomposition, and gaseous hydrocarbons were practically eliminated. A typical result is shown in Table 2. In several other runs no measurable gaseous products were obtained.
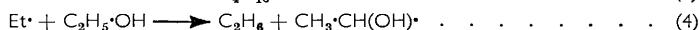
In view of the low carbon yield and the possibility that this may have arisen from the polymerisation of ethylene formed, experiments were carried out in which the reaction vessel was connected to a large storage vessel in which ethylene was maintained at atmospheric pressure. No noticeable pressure decrease occurred and thus under reaction conditions similar to those in the experiments of Table 2 it appears that neither soluble ethylsilver nor its decomposition products bring about the polymerisation of ethylene at temperatures from $-50°$ to room temperature.

DISCUSSION

In alcoholic solution silver nitrate reacts with excess of tetra-ethyl-lead very rapidly even at $-78°$, to form ethylsilver. At high concentrations of nitrate the ethylsilver is precipitated but under conditions used in the kinetic studies in which the alkylmetal was in solution it decomposed according to a first-order law with quantitative deposition of silver. The formation of ethane, ethylene, and butane can be explained if the initial reaction is the formation of the free alkyl radical, *viz.*,

$$AgEt \longrightarrow Ag + Et\cdot \qquad \qquad \qquad (1)$$

The gaseous products result from the following inter-radical and solvent-transfer reactions:

$$2Et\cdot \longrightarrow C_2H_6 + C_2H_4 \qquad \qquad \qquad (2)$$
$$\longrightarrow C_4H_{10} \qquad \qquad \qquad \qquad (3)$$
$$Et\cdot + C_2H_5\cdot OH \longrightarrow C_2H_6 + CH_3\cdot CH(OH)\cdot \qquad \qquad (4)$$

Initiation of polymerisation of acrylonitrile supports this scheme and a detailed kinetic study of the reaction substantiates it.[7] The preponderance of ethane in the products indicates the major occurrence of reaction (4) since disproportionation should yield equivalent amounts of ethane and ethylene. It is interesting that if all the ethane came from a reaction between ethyl radicals or between the ethyl radical and ethylsilver, and if an equivalent of ethylene were formed simultaneously, then the hydrocarbon yield would have been equivalent to the silver formed. Experiments showed, however, that ethylene was not lost by polymerisation or by complex formation with the silver or its salts. Semerano and Riccobini[1] also observed a difficiency of hydrocarbon in their measurements of the decomposition of ethylsilver in suspension. They identified diethyl ether as a product and suggested that the ethylene was produced in a special reactive form and formed ether by reaction with the solvent. It is more probable that the ether-forming reaction was *via* radicals from the alcohol, *viz.*: $C_2H_5\cdot O\cdot + C_2H_5 \longrightarrow (C_2H_5)_2O$. That formation and reaction of radicals from the alcohol did occur was proved by the identification of a glycol, probably butane-2,3-diol, in the products: $2CH_3\cdot CH(OH)\cdot \longrightarrow CH_3\cdot CH(OH)\cdot CH(OH)\cdot CH_3$. Quantitative determination showed that the yield of glycol corresponded to 7—13% of the ethyl radicals reacting according to (4), when calculated on the ethane yield. It seems likely that low yields of hydrocarbons, in spite of the quantitative deposition of silver, may be due to reaction between the silver ion or undissociated salt and an intermediate free radical behaving as a reducing agent, *e.g.*: $Ag^+ + CH_3\cdot CH(OH)\cdot \longrightarrow Ag + CH_3\cdot \overset{+}{C}H(OH)$.

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[7] Bawn and Powell, unpublished work.