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REDUCTION OF TRIETHYLLEAD CATION - A NOVEL ROUTE TO GENERATE ETHYL RADICALS

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The reduction of phenyl mercury cation with ferrocene affords phenyl mercury which readily demercurates to result in phenyl radicals.(1) However, reduction of alkylmercury cation was not achieved and demercuration led to the formation of alkyl carbonium ions. We wish to report that triethyllead acetate (m.p. 162-164°) in aqueous medium or organic solvents undergoes acidic solvolysis and subsequent reduction at room temperature to form triethyllead which further fragments to dialkyllead and ethyl radical.

$$(C_2H_5)_3PbOAc \overset{H^+}{\rightleftarrows} (C_2H_5)_3Pb^+ + CH_3COOH$$

$$(C_2H_5)_3Pb^+ + e^- \longrightarrow (C_2H_5)_3Pb\cdot$$

$$(C_2H_5)_3Pb\cdot \longrightarrow (C_2H_5)_2Pb + C_2H_5\cdot \longrightarrow \text{Products}$$

In aqueous solution with titanous trichloride as a reductant, ethane and a small amount of butane were the gaseous products from the above reaction. In organic solvents with a catalytic amount of perchloric acid and organometallics, such as ferrocene and vanadium acetylacetonate as reductants, ethane was the only gaseous product. No ethylene was detected in either case. Since no thermal decomposition of triethyllead acetate at room temperature was noticed and butane from the experiments in aqueous solution was obtained, the formation of ethyl radical in this reaction seems to be beyond doubt.

The result of reduction in different organic solvents with equal moles of triethyllead acetate, reductants and perchloric acid at 25°C over a period of 90 hours is shown in the following table:

TABLE

Solvent	Reductant	Ethane Yield
Benzene	Ferrocene	1.5%
Chlorobenzene	Ferrocene	2%
Acetonitrile	Ferrocene	0%
Ethylene Chloride	Ferrocene	8%
Acetic Acid	Ferrocene	18%
Acetic Acid	$TiCl_3$	16%
Acetic Acid	$V(C_5H_7O_2)_2$*	8%
Acetic Acid	$Fe(C_5H_7O_2)_2$**	11%

*Vanadium Acetylacetonate

**Ferrous Acetylacetonate

The absence of butane and ethylene from the product of the above experiments is in accord with the theory advanced by Szwarc(2), Bradley(3) and Kerr and Trotman-Dickenson(4) that bimolecular encounter of ethyl radicals does not happen except by two ethyl radicals formed from a single molecule such as propionyl peroxide in the solvent cage whereby they either combine to form butane or disproportionate to yield ethane and ethylene.

In the present case only one ethyl radical is derived from a molecule of triethyllead, thus hydrogen abstraction from a solvent to form ethane becomes the only possible reaction. The difference in yields of ethane from different solvents may reflect the difference of ethyl affinities(5) of such solvents whereas olefinic and aromatic compounds have higher activites toward ethyl radical addition. This also suggests that the other possible mode of ethane formation directly from triethyllead rather than from ethyl free radicals is less attractive, unless we assume that these solvents have approximately the same affinity for both ethyl and triethyllead species. The over-all low yield of ethane from solvents such as acetic acid, ethylene chloride which exhibits low ethyl affinity may be either attributed to the dimerization of triethyllead from the reduction of the cation or to other reactions such as oxidation of ferrocene by perchloric acid or addition of ethyl radicals to the cyclopentadienyl ring of ferrocene which is not clear to us at the present time. In working up the residual reaction fragments from the experiment of ferrocene, triethyllead acetate in acetic acid, after removal of the solvent, the residue was taken up with benzene and extracted with water. In the aqueous portion, ferrocenium ion was the major component. From the benzene layer it furnished some unchanged ferrocene among other gummy substances. Hexaethyl lead and the products derived from diethyllead(6) were not identified, and a material balance for the reaction was not attained.

In acetic acid, triethyllead acetate also undergoes solvolysis and reduction with ferrocene in the absence of perchloric acid at a slower rate, as indicated by the gradual appearance of the characteristic ferrocenium ion color, and this reaction furnished a comparable yield of ethane as in the case with perchloric acid. On the other hand, acetic acid solution of triethyllead acetate with perchloric acid undergoes rather slow displacement to produce ethane and presumably diethyllead diacetate. Thus in acetic acid, ethane formation from triethyllead acetate with reductants involves at least two concurrent reactions, namely:

$$(1) \quad (C_2H_5)_3Pb^+ + e \longrightarrow (C_2H_5)_3Pb\cdot$$

$$(2) \quad (C_2H_5)_3PbOAc \xrightarrow{H^+OAc^-} C_2H_6 + (C_2H_5)_2Pb(OAc)_2$$

The detailed kinetic studies will be reported later.

When the reaction was carried out in water with titanous chloride as the reductant, the yield of ethane (~10%) was lower than that of acetic acid, and a trace amount (0.1-0.2%) of butane was detected. Furthermore, in the presence of .02 mol percent of nickel acetate or cobalt acetate the yield of ethane was not affected, but the yield of butane was raised from trace amount to 1-2% in both cases. The higher yield of butane in the presence of cobalt and nickel ions agrees well with the experiments reported by Kochi and Rust(7) that metal ion-free radical complexes lengthen the life of alkyl radicals; thus, bimolecular combination is made possible.

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