

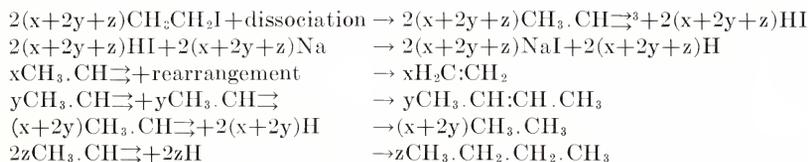
5. Indium chloride is soluble in a mixture of ether and strong hydrochloric acid saturated with hydrochloric acid gas, consequently the method of Gooch and Havens for the separation of aluminum and iron cannot be applied to indium and iron.

THE SECONDARY REACTIONS IN THE PREPARATION OF ZINC ETHYL

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In 1849 in his research on free radicals, Frankland (1) treated zinc with ethyl iodide in a sealed tube at 150° C. As products of the reaction, he obtained a gas mixture, crystals of ethyl zinc iodide, and a clear liquid, zinc ethyl. His analysis of the gas gave 50.03 per cent butane, 25.79 per cent ethane, 21.7 per cent ethylene, and 2.48 per cent nitrogen. But neither Frankland nor subsequent workers have offered a satisfactory explanation of the mechanism of this reaction.

Various theories have been proposed to explain reactions of this type. Nef² proposed alkylidene dissociation, and produced experimental data for the Würtz reaction which indicated that sodium reacts with ethyl iodide to give 50 per cent butane, 25 per cent ethane, and 25 per cent ethylene. But alkylidene dissociation should also foster the formation of some butylene, and the relative quantities of the products formed if the alkylidene radical is the active intermediate in reactions of this type can be shown to be x mols of ethylene, y mols of butylene, $(x + 2y)$ mols of ethane, and z mols of butane. Expressed in equation form,



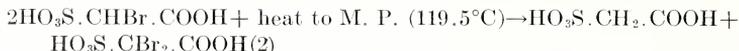
However, these relationships are not satisfied by the data of either Frankland or Nef, which indicates either a faulty theory or faulty data.

Another theory that has been advanced to interpret reactions of this type is disproportionation. Experimental data seem to indicate that disproportionation reactions may involve either molecules or radicals or both, as illustrated by the following equations:

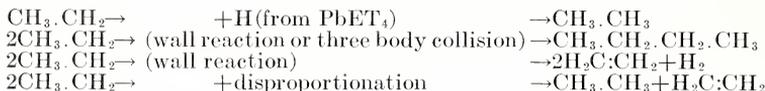
¹ Abstract of a thesis presented to the faculty of Purdue University by Rush Fox McCleary in partial fulfillment of the requirements for the degree of Master of Science.

² Data obtained from lecture notes of Dr. F. W. Upson, student of J. U. Nef.

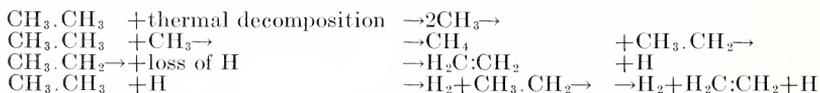
³ Free radicals are indicated by use of arrows.



To account for the thermal decomposition products of lead tetraethyl, Minert assumed the formation of ethyl radicals which he believed might react according to the following equations (5):



The work of Rice on the thermal decomposition of ethane is also of interest in this connection because alkyl radicals appear to be the active intermediates (6). He accounted for his products by the following formulation:



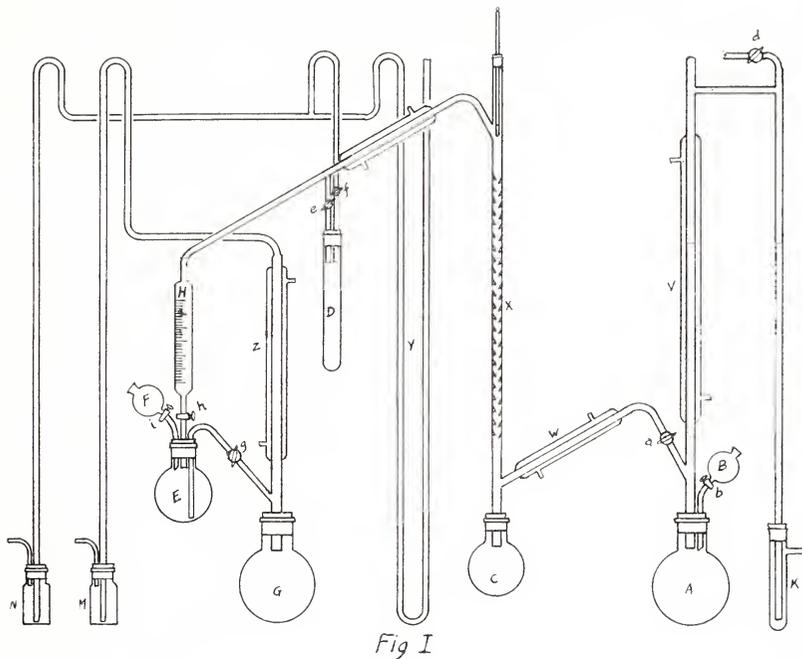
Doubtless either the alkyldene or alkyl radical is involved as an active intermediate in these secondary reactions in the preparation of zinc ethyl; hence it seemed advisable to make a quantitative study of the gaseous products of the reaction of zinc with ethyl iodide under controlled conditions, thus obtaining additional information on the mechanism of reactions of this type.

EXPERIMENTAL

Four hundred grams of powdered zinc and 60 grams of granular zinc were introduced into a one liter flask and activated by heating over a luminous flame for approximately two hours (7). During this heating the contents of the flask were stirred frequently to prevent caking. The flask was then attached to the apparatus as shown in Fig. I (flask *A*) and heated more strongly while the apparatus was being filled with carbon dioxide. The zinc was allowed to cool and 200 cc. of pure ethyl iodide were added through dropping funnel *B*. Then flask *A* was heated for 19 hours at 80°C by means of an oil bath equipped with a temperature regulator, and subsequently the temperature was raised and maintained at 105°C for four hours. The gases evolved were collected over water (previously saturated with the gases) and analyzed.

The type of apparatus devised for this research is quite suitable for the preparation, purification, and use of zinc ethyl as a reagent. The zinc ethyl iodide may be prepared as above, and then the zinc ethyl distilled off under reduced pressure and subjected to purification by fractional distillation by heating the initial receiver *C* with an oil bath. The first portion of the distillate is bypassed into receiver *D*. When the desired boiling point is reached, stopcocks *e* and *f* are closed and the pure zinc ethyl is collected in the graduated receiver *H*, from which any desired amount may be withdrawn into flask *E*. Here it can be diluted with a suitable solvent or introduced directly into reaction flask

G by the application of a slight vacuum. The other reagent can be added directly to flask *G* before the introduction of the zinc ethyl, or subsequently through separatory funnel *F*. If a reduced temperature is desired, flask *E* may be immersed in an ice or alcohol-carbon dioxide bath. Likewise flask *G* may be kept at the desired temperature. After a preparation, the entire apparatus is readily cleaned by distilling about 200 cc. of crude hydrochloric acid through the system, followed by a similar distillation with alcohol or acetone.



In order to determine the effect of a higher temperature upon the amount and composition of the gases evolved, a series of runs was made in which the bath was heated to 90°C and maintained at this temperature for two hours. It was then heated to and maintained at 105°C for three hours. Subsequently it was allowed to rise slowly until it reached a maximum of 135°C at the end of ten and one-half hours.

The gases were freed of carbon dioxide by passage through a drying train, followed by an ascarite train, the hydrocarbons being collected over water, previously saturated with the gases. The gases were then bubbled through bromine at 0°C , the olefine constituents being absorbed without appreciable substitution. The volume of the olefines was determined by difference and the individual constituents identified by the physical properties of the resulting bromides. The residual saturated gases were measured and passed through a condenser coil immersed in an alcohol-carbon dioxide bath at -65°C to -70°C , where the butane was liquified. The liquified butane was then fractionated to remove any

dissolved ethane. Representative analyses of the ethane and butane fractions of the various runs, are respectively,

Analyses. Calc. for ethane fraction: C, 79.87; H, 20.13. Found: C, 79.97, 80.53, 80.16, 80.10, 80.00; H, 20.02, 19.47, 19.84, 19.90, 20.00. Calc. for the butane fraction: C, 82.65; H, 17.35. Found: C, 82.03, 82.42, 82.61, 82.20, 82.65; H, 17.97, 17.58, 17.39, 17.80, 17.34.

Should free hydrogen have been present the analytical separation would have placed it in the ethane fraction. In this event the ethane rather than the butane should have analyzed high in the percentage of hydrogen. However, the ethane fraction analyzed low in percentage of hydrogen, and the butane analyzed high in percentage of hydrogen. This was doubtless due to the difficulty in obtaining complete fractionation of the ethane from the butane.

The yield of zinc ethyl in each case was an inverse function of the volume of the gases evolved. The time required for the reaction to reach completion (8) and the temperature of the reaction are the chief factors in determining the volume of the gases evolved, the temperature being the more important variable.

At the lower initial temperature, the analysis of the gases evolved showed the following percentage composition for three separate determinations.

Volume of Gases Evolved with Temperature at 80°C for 19 hrs., then raised to and maintained at 105°C for four hours.				Volume of Gases Evolved with Temperature at 90°C for 2 hrs., then raised to 105°C for 3 hrs., and finally raised to 135°C.			
No.	% Butane	% Ethane	% Ethylene	No.	% Butane	% Ethane	% Ethylene
1	42.55	28.76	28.65	1	51.66	23.93	23.81
2	43.78	27.64	28.57	2	49.02	25.33	25.64
3	39.81	30.09	30.10	3	52.36	24.48	23.15

Whereas the amount of butane varied over a narrow range, the percentage of ethane and ethylene for a given run were in close agreement. In the bromine addition products there was no indication of the presence of butylene bromide, hence it seems that no butylene was formed in the reaction.

CORRELATION OF DATA

The above data are not in agreement with the theory of Nef, hence it seems that the alkylidene radical is not an intermediate in this reaction. However, if we assume the formation of free ethyl radicals, as Minert and other workers have done (9), the products obtained in the secondary reactions of zinc upon ethyl iodide may be accounted for by the following mechanisms:

(1) For the formation of butane, two ethyl-radicals may combine directly in a wall reaction or in a three body collision (10).

(2) For the formation of ethane and ethylene *in equi-molar quantities*, two ethyl radicals may react either by (a) a limited chain re-

action in a three body collision ($\text{CH}_3\text{CH}_2 \rightarrow \text{H}_2\text{C}:\text{CH}_2 + \text{H}$; and $\text{CH}_3\text{CH}_2 \rightarrow + \text{H} \rightarrow \text{CH}_3\text{CH}_3$), or (b) by disproportionation in a three body collision ($\text{CH}_3\text{CH}_2 \rightarrow + \text{H}\cdot\text{CH}_2\text{CH}_2 \rightarrow \text{CH}_3\text{CH}_3 + \text{H}_2\text{C}:\text{CH}_2$).

SUMMARY

1. An improved apparatus for the preparation, purification, and use of zinc ethyl as a reagent, is illustrated.

2. The data obtained indicate the mechanism of the secondary reactions of zinc upon ethyl iodide to be: (a) two ethyl radicals may combine directly in a wall reaction or in a three body collision to form butane, and (b) two ethyl radicals appear to react to form equi-molar quantities of ethane and ethylene. This appears to be a ternary collision involving a chain reaction or disproportionation.

3. The data indicate that the formation of gases is favored at higher initial temperatures, the formation of butane being especially so favored.

4. There was no indication of the formation of hydrogen nor of the formation of butylene, the only products of the reaction being butane, ethane, and ethylene.

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