

tallized from petroleum ether. The final product melted at 128° (corr.). A very small quantity of triphenyltin was recovered in this reaction and identified by its melting point, 231°. The tin content of the compound was determined as SnO<sub>2</sub> in the usual way.

*Anal.* Calcd. for [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn]<sub>3</sub>CH: Sn, 33.51. Found: Sn, 33.47, 33.49, 33.46.

The molecular weight of the compound was determined cryoscopically in benzene. Calcd. for [(C<sub>6</sub>H<sub>5</sub>)<sub>3</sub>Sn]<sub>3</sub>CH: mol. wt., 1063. Found: mol. wt., 1040, 1070, 1040.

Tri-triphenylstannylmethane is a white, crystalline solid melting at 128°. It is very soluble in benzene, ether, chloroform and trichloroethylene. It is soluble in hot petroleum ether but only slightly soluble in the cold ether. It is sparingly soluble in alcohol and insoluble in water and liquid ammonia. It is best recrystallized from petroleum ether, evaporating under reduced pressure.

**Reaction with Carbon Tetrachloride.**—Carbon tetrachloride was found to react readily with sodium triphenylstannide in liquid ammonia. The residue remaining in the reaction tube, after evaporation of ammonia, was extracted with benzene and from this was obtained triphenyltin and a very small amount of material that failed to melt at 360° and which carbonized on heating in a flame. The main product of the reaction was triphenyltin which was identified by its melting point and by analysis. In two reactions there were obtained 0.5794 and 0.5818 g. of sodium chloride, respectively, as against 0.5846 g. required according to the amount of material used. No gases were given off in the course of the reaction and no product could be found indicating what became of the carbon atom of the carbon tetrachloride.

### Summary

Di-triphenylstannylmethane and tri-triphenylstannylmethane have been prepared by the action of sodium triphenylstannide on methylene chloride and chloroform, respectively, in liquid ammonia. The corresponding quaternary derivative was not obtained with carbon tetrachloride.

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## The Pyrolysis of *n*-Butane at Low Decomposition Temperatures

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In the preceding paper<sup>1</sup> it was mentioned that Norris and co-workers studied the pyrolysis of paraffin hydrocarbons at incipient decomposition temperatures and stated that under these conditions the breakdown of the molecule occurred at a specific C-C location. This is in contrast to the results of earlier investigators who, however, employed higher temperatures. In these higher temperature studies, the results pointed to scission at several places in the molecule rather than at an exclusive location although differences in the strengths of the various C-C bonds were evident. It became a matter of importance, therefore, to check Norris' results for they seemed to indicate that this slight difference in the strength of C-C bonds could be capitalized if low enough decomposition temperatures were used.

(1) Hurd and Pilgrim, *THIS JOURNAL*, **55**, 4902 (1933).

Norris listed 400° as the decomposition temperature of *n*-butane. His work included other hydrocarbons than butane but the conclusions were identical for all. With a contact time of one hour, each was stated to have a definite decomposition temperature which was considered to represent the breaking of an individual C-C bond in the hydrocarbon chain. This conclusion was based on two factors.

**First**, the presence of a so-called "second break" which was at 450° for *n*-butane and which was usually 30-50° above the "initial decomposition temperature." These "breaks" were made visible by graphical methods. In the graph<sup>2</sup> (for *n*-pentane), rates of decomposition were plotted against °*T*. The points were connected by three straight lines which intersected each other at the "breaks." A smooth curve could have been drawn through the points. It may be noted that a straight line curve with no breaks is obtained by plotting the rates logarithmically (thus, log (rates) vs. °*T* or 1/*T*).

**Second**, analyses of the products. In the first temperature range, for example, *n*-butane was stated to give methane and propylene but no ethane or ethylene until the "second break" was reached. It is apparent that the first of these factors is meaningless unless supported by the second. In other words, the crux of the problem is the analysis of the reaction mixture. Inasmuch as the total extent of decomposition is slight the analytical procedure must be capable of detecting traces.

In the present work, pure *n*-butane was passed slowly through an empty Pyrex tube at temperatures which were considerably below Norris' second temperature range. As a matter of fact, we were able to decompose butane at temperatures below its "decomposition point." Norris used a similar method. He passed the gas slowly through a tube (one to two minutes contact time) at a temperature near but below the second break.

In our analysis of the reaction products, the following procedure was employed. The gaseous products were liquefied and separated by precise fractional distillation<sup>3</sup> through a Podbielniak column into four fractions which contained in turn essentially the C<sub>1</sub>, C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> hydrocarbons. Then each fraction was analyzed by the usual absorption and combustion methods.<sup>4</sup>

Our results were not in agreement with those claimed by Norris and co-workers. The products from *n*-butane were found to contain not only methane and propylene but also ethane, ethylene and even small amounts of hydrogen. The same products were observed in the experiments at higher temperatures. Further evidence against Norris' claim is to be found in the recent work of Frey and Hepp,<sup>5</sup> who studied the low tempera-

(2) Norris and Thomson, *THIS JOURNAL*, **53**, 3108 (1931).

(3) Podbielniak, *Oil Gas J.*, **28**, 58 (1929); **29**, 235 (1930).

(4) Hurd and Spence, *THIS JOURNAL*, **51**, 3353 (1929).

(5) Frey and Hepp, *Ind. Eng. Chem.*, **26**, 447 (1933).

ture (396–398°) pyrolysis of *n*- and isopentane. Since the first temperature range for the former is listed by Norris and Thomson as 391–426° and for the latter as 383–423°, it is evident that Frey and Hepp's temperatures were well within these ranges. Frey and Hepp found that *n*-pentane gave rise to considerable C<sub>1</sub> + C<sub>4</sub> hydrocarbons as well as to the more abundant C<sub>2</sub> + C<sub>3</sub> hydrocarbons which Norris claimed were the exclusive products. Some hydrogen was found as well. With isopentane, Frey and Hepp found C<sub>2</sub> + C<sub>3</sub> hydrocarbons as well as the C<sub>1</sub> + C<sub>4</sub> hydrocarbons which were stated by Norris to be formed exclusively.

These studies with *n*-butane, *n*-pentane and isopentane at low decomposition temperatures suggest that other paraffin hydrocarbons will be found to behave similarly. In other words, there is no evidence of a "first decomposition range," wherein an exclusive C–C bond of a paraffin hydrocarbon may be severed.

### Experimental Part

**Butane Used.**—Two specimens of pure *n*-butane were employed. One was the purified sample from a petroleum fraction, mentioned in the previous paper. It was used in the 400 and 415° experiments. The other was synthetic material and it was used in the 365° experiment.

The synthetic butane was prepared by the hydrolysis of *n*-butylmagnesium bromide. To prepare the latter, pure *n*-butyl bromide, b. p. 100–100.5°, was mixed with four volumes of isoamyl ether<sup>6</sup> (b. p. 170–172°). Magnesium turnings were added and the mixture heated at 100° for half an hour. The Grignard reagent was decomposed (four hours) with dilute sulfuric acid. The effluent butane was scrubbed with concd. sulfuric acid, liquefied and distilled twice through a Davis column; b. p. 0.0–0.5°. It did not decolorize bromine in carbon tetrachloride. Three runs (one mole quantities in each) gave yields of 55–70%.

**Pyrolysis.**—Experiments, using the same set-up as described in the previous paper, were carried out at 415, 400 and 365°. All temperatures were ±5°. Immediately prior to the 365°-experiment, the temperature recorder (chromel–alumel thermocouple) was calibrated and found to be correct at the boiling point of mercury: found, b. p. of mercury 355–356° at 744.6 mm. This coincides with the accepted value.

**Experiment at 415°.**—The details follow: butane used, 15.47 liters; rate of flow, 106 cc./min. Exit gas: volume, 16.78 liters; rate of flow, 115 cc./min. Room temp., 29°. Volume of heated part of tube, 460 cc. Contact time, 1.8 minutes. Extent of decomposition, 5%.

**Analysis.**—The exit gas was collected and subjected to fractional distillation on the Podbielniak column. Liquid air was used as the cooling agent. Four fractions were collected (see Table I) each fraction showing distinct temperature plateaus when the temperature was plotted against the gaseous volume of the distillate. Each fraction was analyzed separately in the usual way (absorption and combustion methods). Acetylenes were not formed. Whether any butene was formed cannot be answered. No more than 13 cc. (≈ H<sub>2</sub>) of it could have been present. This would represent but 0.09% of Fraction 4 and would escape identification by absorption in 83% sulfuric acid.

**Experiment at 400°.**—Data: butane used, 6.19 l.; rate of flow, 62 cc./min. Exit gas: volume 6.67 l.; rate of flow, 67 cc./min. Room temp., 25°. Volume of heated part of tube, 215 cc. Contact time, 1.5 minutes. Extent of decomposition, 2.6%.

(6) Ethyl ether was avoided because of its low boiling point.

TABLE I  
ANALYSIS OF GAS FROM PYROLYSIS OF *n*-BUTANE AT 415°

Fraction	1	2	3	4	Summary	
Distn. limits, °C.	-180 to -105	-105 to -50	-50 to -20	-20 to 0		
Volume, cc.	900	390	550	14,440	16,280	
	Analysis of each fraction, % by volume				Cc.	% (air-free basis)
Propylene	3.36	8.95	92.78	...	575	3.55
Ethylene	13.65	43.80	4.34	...	319	1.95
Oxygen	2.22	0.93	...	...	23	...
Hydrogen	1.42	...	...	...	13	0.70
Methane	69.20	...	...	...	623	3.86
Ethane	...	44.34	...	...	174	1.07
Butane	...	...	2.88	100.0	14,456	89.50
Nitrogen	9.81	1.98	...	...	97	...

The Podbielniak distillation of the reaction products revealed 81 cc. in the methane fraction, 118 cc. in the C<sub>2</sub> fraction, and 121 cc. in the propylene fraction. The C<sub>2</sub> fraction was composed as follows: ethylene, 60.2 cc.; ethane 56.2 cc.; propylene, 1.6 cc. Little interest attached itself to the methane and propylene fractions, but the identity of these substances was confirmed.

**The 365°-Experiment.**—In this run 62.9 g. (equivalent to 24.26 liters of gas at S. T. P.) of synthetic butane was distilled through the furnace at a uniform speed during 131 minutes. Thus, the rate of flow was 0.48 g./min. This is equivalent to 200 cc./min. at 25°. The contact time was 0.49 min. (vol. of tube, 215 cc.). These conditions were selected, especially the lower temperature, to ensure a very small extent of decomposition. Actually, it was 0.46%.

To facilitate the isolation of the more volatile reaction products, the unused butane was condensed in a flask at -80°; the uncondensed portion was collected separately. At the end of the experiment the butane condensate was distilled through a Davis column to recover any admixed C<sub>2</sub> and C<sub>3</sub> hydrocarbons. These were united with the original uncondensed portion and distilled through the Podbielniak column using liquid air. The first fraction (to -105°) was 84.6 cc. Besides methane, this consisted of 1.95 cc. of ethylene and a trace of hydrogen. The second fraction (-105 to -50°) was 87.1 cc. It contained 42.2 cc. of ethane, 40.8 cc. of ethylene and 4.1 cc. of propylene. For the purpose of this investigation, this second fraction was the important one. The third fraction (-50 to -20°) was 72.3 cc. It contained 1.5 cc. of ethylene and 70.8 cc. of propylene.

Thus, from the 24,260 cc. of original synthetic butane these totals of reaction products were isolated and identified, calculated to standard conditions: methane, 62.3 cc.; propylene, 67.4 cc.; ethane, 38.0 cc.; ethylene, 39.8 cc.

### Summary

It has been demonstrated that the pyrolytic products from *n*-butane at incipient decomposition temperatures include ethane, ethylene and traces of hydrogen as well as methane and propylene. No evidence could be found to support the contention that there is scission at an exclusive C-C location in the molecule if temperatures near the "initial decomposition temperature" are used.