The Decomposition of Propane and *n*-Butane at Carbon Filaments

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In a previous communication[2] it was shown that methylene and ethylene, respectively, were the primary products of the decomposition of methane and ethane at hot carbon surfaces. The methods employed in this work have now been extended to an investigation of the reactions of propane and *n*-butane.

Propane was found by Hague and Wheeler[3] to decompose at 700° mainly to methane and ethylene and to a less extent to hydrogen and propylene, a view supported by the work of Pease.[4]

$$C_3H_8 \longrightarrow CH_4 + C_2H_4 \tag{1}$$
$$C_3H_8 \longrightarrow H_2 + C_3H_6 \tag{2}$$

Attempts to distinguish between the primary and secondary reactions by progressively varying the rate of flow of the gas at a given temperature and extrapolating the data obtained were made by Schneider and Frolich,[5] who were able to show that at 725° and one atmosphere pressure, 48% of the reaction proceeded according to (1) and 42%, according to (2). The order of importance of these processes was however reversed at 600°.

In the case of *n*-butane, Hague and Wheeler[3] determined the main reactions at 750° to be

$$C_4H_{10} \longrightarrow C_2H_6 + C_2H_4 \tag{1}$$
$$C_4H_{10} \longrightarrow CH_4 + C_3H_6 \tag{2}$$
$$C_4H_{10} \longrightarrow \text{Butylenes} + H_2 \tag{3}$$

occurring, respectively, to the extent of 40, 35 and 20%. The reaction at 700°, according to Hurd and Spence,[6] occurred in a similar manner, but propylene and methane proved to be the principal products at 600°. Essentially the same conclusions were arrived at by Neauhaus and Marek,[7] who applied the method of Schneider and Frolich[5] for propane to the investigation of the primary decomposition of *n*-butane.

Rice and his co-workers have[8,10] obtained radicals on passing propane and *n*-butane through a hot silica tube at 800°, and on the assumption that methyl and ethyl radicals are produced in the primary rupture of the hydrocarbon chain, have developed a chain mechanism to account for the olefinic products of decomposition.

Experimental.—To avoid as far as possible the occurrence of secondary reactions, the hydrocarbon vapors were passed at a high streaming velocity and low pressure (0.1 mm.) across a heated carbon filament situated 2–3 mm. from a tellurium mirror maintained at 100°, with which any radicals formed could react. These conditions are most favorable for the detection of methylene radicals as the polymer of telluroformaldehyde[9,2] and of methyl radicals as dimethyl ditelluride.[10] Separate experiments under corresponding conditions of temperature and pressure, but in the absence of tellurium, were also performed for the purpose of identifying the olefin products of reaction, these being condensed out together with excess hydrocarbon in a liquid air trap and distilled into a side tube containing bromine. Bromination was allowed to proceed at about −10°, excess of the reagent being avoided.

The Decomposition of Propane on a Carbon Filament.—In experiments performed at 1650°, 1,2-dibromopropane (b. p. 141°) was the only liquid product which could be isolated, while experiments with tellurium indicated that no radicals were being simultaneously produced. These, however, were detected at 1750° at which temperature also it was possible to separate ethylene dibromide (b. p. 132°) from the brominated olefin products.

The action of the products of decomposition at 1750° on hot tellurium gave rise to a small quantity of a yellow solid, finally identified as the polymer of telluroformaldehyde, as well as an orange liquid resembling dimethyl ditelluride. When, however, a boiling point determination of the latter was attempted by the micro method, decomposition of some constituent of the oil to metallic tellurium occurred between 140–160°. The addition of ether to the oil precipitated a yellow solid, which, since it decomposed at about 150° to metallic tellurium, proved to be the methylene–tellurium complex $(TeCH_2)_n$, of Rice

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[2] Belchetz and Rideal, THIS JOURNAL, **57**, 1168 (1935).

[3] Hague and Wheeler, *ibid.*, **51**, 378 (1929).

[4] Pease, *ibid.*, **50**, 1779 (1928).

[5] Schneider and Frolich, *Ind. Eng. Chem.*, **23**, 1405 (1931).

[6] Hurd and Spence, THIS JOURNAL, **51**, 3353 (1929).

[7] Neauhaus and Marek, *Ind. Eng. Chem.*, **24**, 401 (1932).

[8] Rice, THIS JOURNAL, **53**, 1959 (1931); *ibid.*, **55**, 3035 (1933); Rice, Johnston and Evering, *ibid.*, **55**, 3529 (1933).

[9] Rice and Glasebrook, *ibid.*, **56**, 2381 (1934).

[10] Rice and Glasebrook, *ibid.*, **56**, 2472 (1934).

and Glasebrook.[9] With cold tellurium mirrors, dimethyl ditelluride and dimethyl telluride only were obtained.

Previous work[2] has shown that unless the accumulation of the non-volatile polymer of telluroformaldehyde on the tellurium acceptor is entirely prevented—this being partially achieved by maintaining the mirror at 100°—reduction of this substance by atomic or hot molecular hydrogen to the methyl tellurides readily ensues. It is believed that the dimethyl ditelluride and dimethyl telluride obtained in these experiments were produced in an analogous manner.

Experiments with Mercury.—If the dimethyl ditelluride isolated in the above experiments was in fact due to methyl radicals produced by the scission of the propane chain, ethyl radicals in quantities equivalent to those of methyl should be capable of detection among the reaction products. Experiments with mercury similar to those devised by Rice, Johnston and Evering[8] and Rice and Rodowskas[11] for the identification of alkyl radicals were therefore performed. As a result of ternary collisions between methylene, atomic hydrogen and mercury, it was expected that mercury dimethyl, at any rate, would be obtained in appreciable amounts.

In these experiments a filament temperature of 1800° was employed. The products of decomposition were allowed to react with mercury continuously condensing on a water cooled bulb, and the mercury alkyls frozen out in a liquid-air trap from which they were extracted with ether. On filtering this solution into an alcoholic solution of mercuric bromide, a copious precipitate of mercurous bromide (in some cases a mixture of mercury and mercurous bromide) was obtained. This was filtered off, the filtrate evaporated to dryness *in vacuo*, and the residue steam distilled. The white solid so separated after being washed with a little alcohol and dried *in vacuo*, melted at 160° (m. p. of CH_3HgBr, 160°).

In other experiments, the mercury alkyls were diffused into a liquid-air cooled side tube where they condensed as a white solid. After the liquid propane had evaporated, part of the mercury compound was observed to decompose to mercury, leaving a clear colorless liquid which boiled at 95° (b. p. $Hg(CH_3)_2$, 95°).

The product obtained in these experiments behaved as if it were a compound of the formula $HgCH_3$, decomposing at room temperatures in contact with, and in the absence of, air as follows

$$2HgCH_3 \longrightarrow Hg + Hg(CH_3)_2$$

It was, however, stable in a cold ether solution, reacting with mercuric bromide in the following manner

$$2HgCH_3 + HgBr_2 \longrightarrow Hg + 2CH_3HgBr$$

No evidence was thus obtained for the formation of ethyl radicals.

The Decomposition of Normal Butane on Carbon Filaments.—These experiments were performed in exactly the same manner as those for propane. At 1650°, about two-thirds of the olefin product proved to be propylene, 1,2- and 2,3-butylene constituting the remaining third. It is significant that radical formation at this temperature was appreciable.

The products at 1750° contained butadiene, identified as the solid tetrabromide, propylene also being present in relatively increased proportions. No ethylene could be isolated.

The radicals produced here also appeared to be methylene, while experiments with mercury again failed to reveal the presence of ethyl radicals.

The Decomposition of Propylene on Carbon Filaments.—Since these experiments suggest that methylene radicals are produced in the secondary decomposition of the olefin products, probably before they are desorbed from the filament, the reactions of propylene were investigated from the point of view of free radicals. Here also hot tellurium was employed as the radical acceptor. The products obtained were essentially those reported for the decomposition of propane and butane at high temperatures, telluroformaldehyde and dimethyl ditelluride being produced. The presence of hydrogen telluride indicated that dehydrogenation of propylene also occurred. As propadiene and methylacetylene do not appear as products of the decomposition of propane, it is probable that their formation cannot take place when hydrogen is present in appreciable quantities.

In this connection, it is significant that Schneider and Frolich[4] obtained principally ethylene and butylene as decomposition products of propylene. This reaction clearly proceeds in the following stages:

$$CH_3CH{=}CH_2 \longrightarrow CH_2{=}CH_2 + CH_2$$
$$CH_2 + CH_3CH{=}CH_2 \longrightarrow CH_3CH_2CH{=}CH_2$$

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[11] Rice and Rodowskas, THIS JOURNAL, **57**, 350 (1935).

Certain discrepancies in the experimental work of Rice and his co-workers give rise to some doubt as to whether ethyl radicals are formed at all in the reactions of propane and butane. Thus when the decomposition products of butane were allowed to react with mercury and the mercury alkyls converted to mercury alkyl bromides and fractionally sublimed, Rice, Johnston and Evering[8] obtained a product corresponding in melting point to a mixture of CH_3HgBr and C_2H_5HgBr in the ratio of 2.3 to 1. The corresponding experiments of Rice and Glasebrook[10] with tellurium as an acceptor, however, resulted in the formation of pure dimethyl ditelluride only. One must conclude, therefore, that the mercury alkyl bromides of Rice, Johnston and Evering were imperfectly separated from mercuric bromide, and that only methyl radicals were produced in these experiments. In view of the experience of Rice and Glasebrook[9] with the decomposition of diazomethane in the presence of butane or ether at temperatures above 650°, when only methyl and no methylene radicals could be detected, it is not unlikely that all the methyl radicals formed in hot tube decompositions of the hydrocarbons, are in reality only secondary products of methylene.

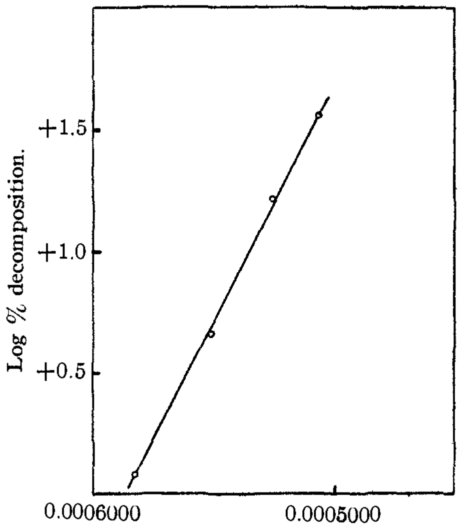

Fig. 1.—Decomposition of *n*-butane on carbon: E = 93,200 cal.

The Energy of Activation for the Decomposition of Propane and *n*-Butane on Carbon Filaments.—Except for the fact that the products of decomposition were made to pass through a liquid-air trap placed between the Gaede pump and the 2-liter bulb in the forevacuum side of the apparatus instead of being adsorbed on charcoal, the experimental procedure was identical with that employed in the corresponding work with methane and ethane.[2] Here also the rate of reaction was followed with respect to hydrogen, hydrocarbons being frozen out of the sample with liquid nitrogen boiling under reduced pressure. The results for propane are given in Table I, the percentage of the gas decomposing to propylene and hydrogen being calculated on the assumption that this was the only reaction occurring at the temperature of the investigation.

TABLE I

Temp., °K.	H_2 in product, %	Decomposition, %
1723	1.03	1.04
1843	4.75	4.99
1948	17.4	21.4
2023	34.0	51.5

The energy of activation for the decomposition of propane on carbon works out to be 94.2 kcal. (Fig. 1) a value very close to that obtained for methane and ethane.

TABLE II

Temp., °K.	Hydrogen in product, %	Decomposition, %
1713	1.17	1.19
1813	4.31	4.50
1903	14.0	16.3
1973	26.6	36.2

The corresponding data for the decomposition of *n*-butane are shown in Table II, from which an energy of activation of 93.2 kcal. is obtained (Fig. 2).

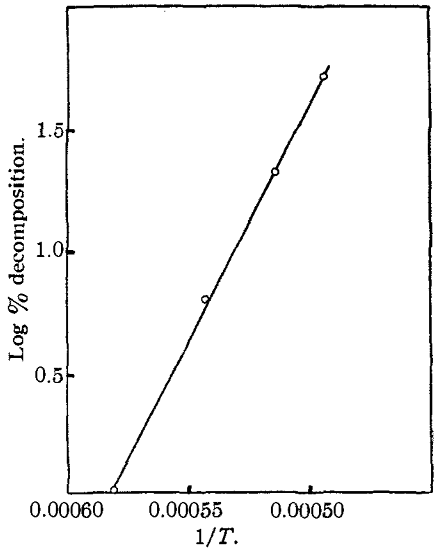

Fig. 2.—Decomposition of propane on carbon: E = 94,200 cal.

It will be observed that although high percentages of propane and butane passed through the reaction vessel decompose in the region of 1700°, the linearity of the energy of activation curve is very closely preserved. This must mean that secondary processes involving the production of methylene radicals do not appreciably alter the total volume of gaseous products, and that interaction between methylene and the parent hydrocarbon molecules must occur readily. Methane can only have constituted a small percentage of the products (not exceeding 5% at the highest temperatures) as evidenced by the negligible diminution in partial pressure of the residual gas when condensable hydrocarbons were first frozen out with liquid nitrogen boiling under atmospheric pressure, and later with liquid nitrogen boiling under reduced pressure.

Discussion

It would appear from these results that the primary reaction at a carbon surface involves the dissociation of hydrogen from the parent hydrocarbon.

$$CH_3CH_2CH_3 \longrightarrow CH_3CH{=}CH_2 + H_2$$

$$CH_3CH_2CH_2CH_3 \begin{cases} \nearrow CH_3CH{=}CHCH_3 + H_2 \\ \searrow CH_3CH_2CH{=}CH_2 + H_2 \end{cases}$$

The next stage consists in the further decomposition of the olefin with the production, in the case of propane, of ethylene and methylene.

$$CH_3CH{=}CH_2 \longrightarrow CH_2{=}CH_2 + CH_2$$

Whereas 2,3-butylene dissociates to propylene and methylene

$$CH_3CH{=}CHCH_3 \longrightarrow CH_3CH{=}CH_2 + CH_2$$

1,2-butylene is capable of undergoing further dehydrogenation to butadiene

$$CH_3CH_2CH{=}CH_2 \longrightarrow CH_2{=}CHCH{=}CH_2 + H_2$$

The propylene formed from 2,3-butylene can of course decompose still further to ethylene and methylene, although this step was never realized in our experiments.

It is interesting to note that the energy of activation for the decomposition at a carbon surface is constant, and has the relatively high value of *ca.* 94 kcal. for the four hydrocarbons investigated. Separate experiments indicated that the rate of reaction was approximately proportional to the pressure. We must thus conclude that the reaction velocity is not governed by the desorption of hydrogen but rather by some reaction taking place at collision. The energy of activation may well represent a complex mechanism involving the transformation of a relatively inert carbon surface into a reactive carbon pair similar to that found in dehydrogenation of hydrocarbons. We should thus obtain conditions permitting of a quantum mechanical transfer of two hydrogen atoms from one to another carbon pair at the moment of collision.

In conclusion, one of us (L. B.) would like to express his thanks to the governing bodies of Emmanuel College, Cambridge, and to the University of South Africa, for scholarships, and to the Philgas Co., Bartlesville, Oklahoma, for their gift of C. P. propane and *n*-butane.

Summary

The decomposition of propane and *n*-butane on carbon filaments has been investigated from the point of view of radicals and olefin products.

The experiments indicate that the initial act is the production of hydrogen and the complementary olefin. The latter can then dissociate to methylene and the next lower olefin, except in the case of 1,2-butylene which is capable of further dehydrogenation to butadiene. Methylene subsequently undergoes reaction with the surrounding molecules.

The energies of activation for the two reactions have been determined at 94.2 and 93.2 kcal.

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