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The Pyrolysis of Hydrocarbons. Further Studies on the Butanes¹

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Recent work on the pyrolysis of the butanes⁴⁻¹⁰ has elucidated much of the problem but such questions as the following seemed important for further study: (1) the reaction products at incipient decomposition, (2) the importance of the contact time, (3) the relationship of temperature and contact time, (4) the influence of metal reaction tubes. These items, among others, have been considered in the present paper.

The Reaction Products at Incipient Decomposition.—There are two approaches to this problem. One is to extrapolate the quantities of products formed at real conditions to their value at zero decomposition.⁸ This method has been considered in the present paper. The other, which will be taken up in the following paper, is to carry out the pyrolysis at a very low decomposition temperature.¹⁰

The set-up for the pyrolysis experiments was essentially the same as that of Hurd and Spence.⁴ The gas was forced through the reaction tube by a head of water. The customary flowmeters, manometer, drying towers and collecting bottles were in the train. Various size reaction tubes and furnaces were used. The gases were analyzed either by the absorption and combustion method⁴ or by precision fractional distillation in a column of the type described by Oberfell and Alden¹¹ and Podbielniak,¹² or by a combination of these methods. The *n*-butane for this work was generously furnished by F. E. Frey of the Phillips Petroleum Company. Distillation analysis confirmed its purity. Less than 1% of low boiling material and

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

(5) Pease, *ibid.*, **50**, 1779 (1928); Pease and Durgan, *ibid.*, **52**, 1262 (1930).

(6) Hague and Wheeler, *J. Chem. Soc.*, 378 (1929).

(7) Frolich, Simard and White, *Ind. Eng. Chem.*, **22**, 240 (1930).

(8) Schneider and Frolich, *ibid.*, **23**, 1405 (1931); Neuhaus and Marek, *ibid.*, **24**, 400 (1932).

(9) Frey and Huppke, *ibid.*, **25**, 54 (1933).

(10) Norris and Thomson, *THIS JOURNAL*, **53**, 3108 (1931); Norris, *J. Chem. Educ.*, **9**, 1890 (1932); Norris and Standley, paper before the Organic Division, A. C. S. meeting at New Orleans, April, 1932.

(11) Oberfell and Alden, *Oil Gas J.*, **27**, 142 (1928).

(12) Podbielniak, *ibid.*, **28**, 58 (1929); **29**, 235 (1930).

less than 1% of higher boiling material was indicated by the Podbielniak type of analysis.¹³ Its boiling point was 0°.

The extrapolation experiments were essentially similar to those of Neuhaus and Marek so the data will be omitted for brevity. As a primary effect it was confirmed that more propylene than ethylene was formed in the range of 0–30% decomposition and that the dehydrogenation reaction was considerably less than the ethylene reaction. Secondary changes were noticeable in the region of high decomposition for the propylene yield diminished in the 600°-experiments at about 80% decomposition to such an extent that ethylene then predominated. In the 700°-experiments, this occurred in the 60% region.

The Contact Time, VT'/FT'' .—(V = vol. of tube; T' = abs. temp. of entering gas; T'' = abs. temp. of heated gas; F = average rate of flow of gas through the tube.)

Experiments were conducted at varying temperatures in tubes of varying sizes and with gas flow of varying rates to ascertain the effect of these factors. As might be expected, no single factor governed the extent of the decomposition but the combination of the various factors, as expressed in the contact time, did do so. The following comparisons make this evident.

New data were obtained with the butanes at 700° in a tube whose heated volume was 5.9 cc. so as to compare them with the published data of Hurd and Spence,⁴ who used a tube over ninety times larger, namely, 550 cc. As shown in Table I, contact times of similar magnitude were obtained by maintaining a 75–85 times smaller rate of flow in the smaller tube. The extent of decomposition was comparable and the analysis of the reaction products from the small tube so nearly coincided with the earlier published results with the large tube that, for brevity, it will be omitted here.

TABLE I
FACTORS INFLUENCING THE EXTENT OF DECOMPOSITION

Vol. of tube, cc.	Rate of flow, cc./min.	n-Butane		Isobutane	
		entering	exit	entering	exit
5.9	4.45	550	390	5.9	330
	8.6	740	7.8	595	
Final vol. from 1000 cc. of butane		1815	1870	1679	1800
Contact time, sec.		15	18	17	21
Extent of decomposition, %		73	75	77	70

Relationship of Temperature (T) and Contact Time (t).—Since $t = VT'/FT''$ it follows that $tT'' = \text{constant}$ if V , T' and F are held constant. This inverse relationship between temperature and contact time is in keeping with the fact that the products formed from *n*-butane at about 400° (see the following paper) were similar to those formed at 600 or

(13) Considerable trouble was experienced with the tanks of the so-called "pure" *n*-butane on the market. For example, on a sample for which 99% purity was claimed, distillation analysis revealed 14.1% propane, 9.1% isobutane and 76.8% *n*-butane.

700° with a shorter contact time. It is apparent also from the data of Table II which show, for example, that at a constant contact time of 0.3 sec. the extent of decomposition may be adjusted at will between 6–95% by selecting a suitable temperature between 650–850°. Or, with a constant temperature of 600 or 700°, one may govern the extent of decomposition by suitable adjustment of the contact time.

TABLE II

TEMPERATURE, CONTACT TIME AND EXTENT OF DECOMPOSITION															
600°				650°		700°				750°		800°		850°	
Sec.	%	C ₂ H ₄	C ₃ H ₆	Sec.	%	Sec.	%	C ₂ H ₄	C ₃ H ₆	Sec.	%	Sec.	%	Sec.	%
0.36	9	..	4.1	0.33	6	0.31	12	4.2	5.5	0.27	24	0.25	70	0.24	95
2.5	24	10.5	11.9			3.7	60	20.0	16.4						
5.2	32	12.7	15.1			4.7	65	19.5	18.7						
24.0	56	18.3	20.1			14.6	73	21.8	15.8						
						20.3	68	15.2	9.8						

The yields of propylene and ethylene from *n*-butane increase with increasing percentage decomposition as the similarity of curve III (propylene yield at 600°) in Fig. 1 with

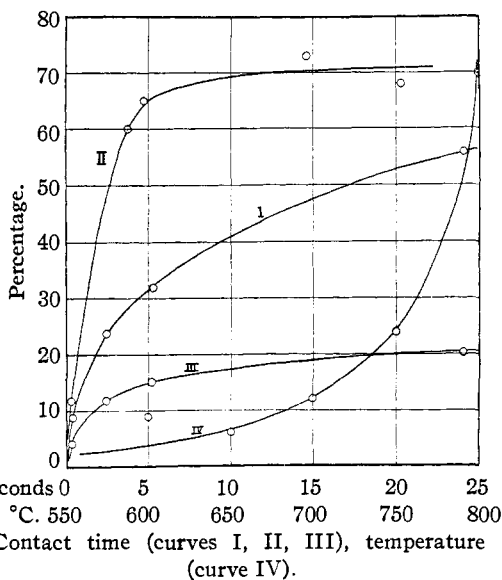


Fig. 1.—Pyrolysis of *n*-butane: curve I, percentage decomposition vs. contact time, constant temperature of 600°; curve II, same, for a constant temperature of 700°; curve III, percentage formation of propylene vs. contact time, constant temp. of 600°; curve IV, percentage decomposition vs. temperature. constant contact time of 0.3 sec.

curves I and II (% decomposition at 600 and 700°) bears witness. A curve for ethylene at 600° would be lower than the propylene curve but otherwise similar. Were these two curves plotted for the 700° experiments, the prominence of secondary reactions would be emphasized for the curves would bend downward with increasing contact time.

Curves I, II and III (Fig. 1) are isotherms. Curve IV is not. It represents experiments at a constant contact time of about 0.3 sec., the abscissas representing temperature. The inverse relationship between temperature and contact time is apparent by comparing curves I and IV. If the abscissas (contact time) for curves I, II and III and the ordinates (% decn.) for curve IV are plotted logarithmically, straight line curves are indicated.

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The Extent of Decomposition.—Hurd and Spence⁴ obtained this value indirectly by averaging the percentage increase in volume with the value of the percentage decomposition (P) from the formula $P = (100 U)/(100 - U)$, wherein U represented the percentage of olefins formed. Since P may now be determined directly by the Podbielniak type of distillation, some experiments were carried out to compare the two methods. The results in Table III show that the indirect method agrees to within 1-4% for isobutane whereas deviations of 5% or more may be expected with n -butane.

TABLE III
DETERMINATION OF UNUSED BUTANE

n -Butane				Isobutane			
Temp., °C.	Contact time, sec.	Decomposition, % I ^a	D ^a	Temp., °C.	Contact time, sec.	Decomposition, % I ^a	D ^a
600	5.2	32	37	600	6.2	22.8	22.6
700	2.0	33	29	700	3.8	58.0	62.0
				700	5.1	71.5	70.8

^a I = Indirect method, calcd. on basis of olefins and increase in volume. D = Direct method, based on combined distillation and absorption analysis.

Pyrolysis Experiments in Metal Tubes.—Three metals were used: iron, nickel and monel. Monel (a Ni-Cu-Fe alloy) was decidedly catalytic. For example, with n -butane at 600° and 7.5 seconds the increase in volume was over 200%. The change was largely into carbon and hydrogen. At 500°, however, carbon formation was slight and the reaction appeared to follow a normal course.

TABLE IV
DECOMPOSITION OF THE BUTANES IN METAL TUBES

Metal tube	n -Butane					Isobutane				
	Iron	Ni	Monel	Iron	Ni	Monel	Iron	Ni	Monel	
Temp., °C.	550	600 ^a	605	500	600	550	600 ^a	600	500	600
Rate of flow, cc./min.	131	102	127	183	205	171	117	331	176	268
	137	124	151	192	620	184	139	353	190	500
Vol. of heated part of tube, cc.	62	62	121	151	151	62	62	121	151	151
Contact time, sec.	10	9.7	17.8	21	7.5	7.7	9.9	7.2	19.3	8
Final vol. from 1000 cc. butane	1042	1222	1185	1045	3040	1075	1184	1068	1078	1870
Extent of dec., %	14	24	21	20	80	9	19	17	20	70

Analysis of Exit Gases in Per Cent. by Volume

Isobutylene	8.7	8.9	4.6	6.8	10.3
Propylene	..	12.0	2.9	6.9	3.7	4.7	7.1
Butenes	..	3.1
C ₃ H ₆ + C ₄ H ₈	11.8	..	12.8	8.9	1.4
Ethylene	2.4	7.4	5.5	0.9	0.8	0.2	1.2	0.0	0.0	2.5
Hydrogen	..	2.3	4.8	2.6	70.0	1.9	6.7	5.7	5.2	41.5
Methane	..	11.1	2.3	7.5	8.8
Ethane	..	2.1
Butane (unused)	..	62.1	84.0	68.9	77.2
C _n H _{2n+2}	85.8	..	77.0	87.6	28.0	83.3	38.6
n	3.70	..	3.5	3.66	2.40	3.72	2.00

^a Analysis of the exit gases was by a combination of precision distillation and absorption. For the other runs, analysis was by the absorption method alone.

Iron and nickel tubes differed materially from monel. Pyrolysis in them was practically the same as when Pyrex or quartz tubes were used. Carbonization, which was so prominent in monel at 600°, was negligible in iron or nickel. Representative data are collected in Table IV. If similar experiments in Tables II and IV are compared the essential similarity of results in the quartz, nickel and iron tubes is apparent.

In another article¹⁴ it will be shown that iron and nickel tubes exert a considerable catalytic influence (dehydrogenation and carbonization) on the decomposition of such unsaturated hydrocarbons as ethylene, propylene, isobutylene and 2-pentene. This shows that the effect is governed not only by the nature of the metal but also by the type of hydrocarbon.

Seamless nickel, iron and monel tubes were used in this investigation. The iron tube was calorized on the outside (but not on the inside). The thermocouple within each tube was encased by a Pyrex sheath. The metal tubes were encased at the furnace limits with tight-fitting copper coils through which cold water circulated. This permitted the use of rubber connections at the ends of the tubes. After each run the tubes were searched for carbon and scraped clean if any was present. The monel tube produced much carbon but almost none was formed in the nickel and iron tubes. For example, in the 600° runs with *n*- and isobutane in monel, 15 and 46%, respectively, of the carbon content of the entering gas was scraped from the walls of the tube as carbon.

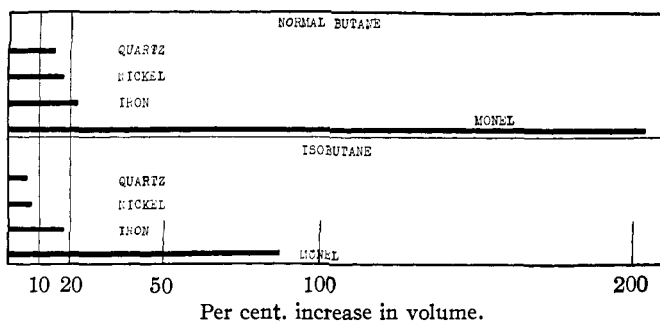


Fig. 2.—Relative catalytic effect of various tubes.

The percentage increase in volume in the 600°-experiments was calculated from the data (listed as "final vol. from 1000 cc. butane") in Table IV and the results portrayed graphically in Fig. 2. Although the contact times vary somewhat, the striking behavior in monel is evident.

Search for Isobutylene in the Products from *n*-Butane.—In the absorption method of analysis for hydrocarbons, isobutylene is removed by 62.5% sulfuric acid. Slight absorption in this reagent was noticed when the gases from pure *n*-butane pyrolyses were analyzed. Using a solution of

(14) With L. K. Eilers.

nitric acid and mercuric nitrate which was shown by Denigès¹⁵ to be a specific reagent for isobutylene, Mr. A. R. Goldsby demonstrated the absence of isobutylene in these gases. Hence, the slight absorption in the 62.5% acid was an absorption either of propylene or of butane which was present in large amounts. Thus, it is obvious that the absorption method, which is quite satisfactory for isobutylene when appreciable quantities are present, must be used with caution when only traces are present.

The test reagent for isobutylene was prepared by dissolving 20 g. of mercuric oxide in 40 cc. of concd. nitric acid and 500 cc. of water. It was found that 300 cc. of the reagent absorbed 150 cc. of pure 1-butene gas readily enough but there resulted no precipitate even on standing overnight. Similarly, there was absorption but no consequent precipitation when 2-butene or trimethylethylene was taken. With isobutylene, however, a distinct precipitation (yellow) was observed in two hours with a 0.1-cc. sample. A similar orange colored precipitate was produced in a few minutes if the solution was heated.

A sample of butane, pyrolyzed at 675° and twenty-three seconds contact time, was analyzed as follows: 1.7% absorbed by 62.5% acid and usually interpreted as isobutylene, 22.8% propylene, 19.2% ethylene, 5.3% hydrogen, 51% saturated hydrocarbons. When this gaseous mixture was tested with the acidified mercuric nitrate reagent no trace of precipitation occurred. Hence, no isobutylene was formed during the pyrolysis.

Summary

Experiments with the butanes have demonstrated that similar results may be expected in tubes of widely varying sizes if a constant contact time is maintained in the various tubes. The inverse relationship between temperature and contact time is pointed out.

Decomposition of *n*- or isobutane in iron or nickel tubes at 600° pursued practically the same course as that observed in quartz tubes. Monel, however, exerted a vigorous catalytic action at this temperature. The change was largely one into carbon and hydrogen.

The fact that no isobutylene was formed during the pyrolysis of *n*-butane is sufficient evidence that the carbon chain does not undergo rearrangement in this process.

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(15) Denigès, *Compt. rend.*, **126**, 1043 (1898).