hydroxide and 170 cc. of water was treated with a solution of 43.3 g. (0.2 mole) of mercuric oxide in 40 cc. of glacial acetic acid and 70 cc. of water and refluxed for sixteen hours. At the end of that time no more carbon dioxide was evolved and the precipitate which had formed was soluble in sodium hydroxide. The product was separated by filtration, washed and dried to constant weight at 105°; weight, 70.2 g. of anhydro-2-hydroxymercuri-isophthalic acid (96% yield).

Anal. Calcd. for $C_8H_4O_4Hg$: Hg, 55.0. Found: 55.0.

Ten grams of the mercury compound was dissolved in dilute sodium hydroxide, filtered from a slight residue and refluxed for two hours with enough excess hydrochloric acid to make the solution about 6 *N* in hydrochloric acid. The isophthalic acid obtained weighed 3.6 g. (79% yield). It sublimed without melting or decomposing. The dimethyl ester prepared by means of thionyl chloride and methanol melted at 67–68°.

Ten grams of the mercury compound was powdered and dissolved in 75 cc. of 20% potassium iodide solution. To this was added 7.5 g. of iodine. After standing for one hour, the small excess of iodine was removed by concentrated sodium thiosulfate solution. The mixture was acidified and cooled. Highly twined colorless needles separated almost immediately; weight of 2-iodo-isophthalic acid, 5.9 g. (73% yield), m. p. 241.5–243°. Crystallization from water raised the melting point to 243–244°.[3] Treatment of the acid with thionyl chloride and methanol gave the dimethyl ester, m. p. 49.5–50.50°.[4]

Summary

1. Hemimellitic acid reacts with mercuric acetate with the replacement of the 2-carboxyl by mercury.
2. Treatment of this mercury compound with halogens gives the best method of preparing 2-halogenated isophthalic acids.

EVANSTON, ILLINOIS

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

THE PYROLYSIS OF HYDROCARBONS: NORMAL-BUTANE AND ISOBUTANE[1]

BY CHARLES D. HURD[2] AND L. U. SPENCE[3]

RECEIVED JANUARY 21, 1929 PUBLISHED NOVEMBER 8, 1929

The present investigation with *n*- and *iso*butane inaugurates a series of studies dealing with the behavior of individual hydrocarbons at high

---

[3] The melting point of this substance is given as 236–238° by James, Kenner and Stubbings, *J. Chem. Soc.*, **117**, 774 (1920).

[4] *Cf.* Mayer, *Ber.*, **44**, 2301 (1911).

[1] This paper contains results obtained in an investigation on "The Non-Catalytic Thermal Decomposition of Pure Hydrocarbons and Related Compounds," listed as Project No. 18 of American Petroleum Institute Research. Financial assistance in this work has been received from a research fund of the American Petroleum Institute donated by the Universal Oil Products Company. This fund is being administered by the Institute with the coöperation of the Central Petroleum Committee of the National Research Council.

[2] Director, Project No. 18.

[3] American Petroleum Institute Junior Research Fellow.

temperatures. The evidence which was obtained with *n*-butane points to two equations for the representation of the major part of the pyrolysis

$$CH_3CH_2CH_2CH_3 \longrightarrow CH_4 + CH_3CH{=}CH_2$$
$$CH_3CH_2CH_2CH_3 \longrightarrow CH_3CH_3 + CH_2{=}CH_2$$

At 600° the first of these appears to proceed to the extent of about 55% and the second to 40%. Dehydrogenation reactions into butene or butadiene appear to represent less than 5% of the total. These results were obtained by exposing the hydrocarbon at 600° for thirty seconds or less by a single passage through a pyrex tube. The rate of flow was about 6 cc. per second, and about one-fifth of the butane suffered decomposition. Similar results were obtained when a temperature of 700° was used. The chief points of difference are these. The extent of the decomposition was 75% instead of 22%. Indicative of secondary reactions, the propylene–ethylene ratio changed so that ethylene was somewhat in excess. This is reasonable since propylene is known[4] to decompose more readily than ethylene, and since ethane is known to pyrolyze into ethylene.

In similar experiments *iso*butane differed noticeably from *n*-butane in giving rise to a large production of hydrogen. Except for the considerable excess of methane, which is a characteristic feature, the primary decomposition of *iso*butane at 600° may be represented by the equations

$$(CH_3)_3CH \longrightarrow H_2 + (CH_3)_2C{=}CH_2$$
$$(CH_3)_3CH \longrightarrow CH_4 + CH_3CH{=}CH_2$$

Since 38.5% of the unsaturated hydrocarbons (formed at 600°) is propylene and 50.8% is *iso*butylene, it would appear superficially that the first reaction takes place to the extent of 51% and the second, 39%. However, since the methane–propylene ratio is over 2:1, and since ethylene is present in appreciable quantities, quantities in fact which become rather formidable at 700°, it may be fortuitous that the hydrogen–*iso*butylene ratio is approximately 1:1. In the absence of evidence to the contrary, these facts may be explained by postulating that the hydrogen which was momentarily liberated failed to appear entirely as molecular hydrogen. Instead, it may have caused scission of some of the *iso*butylene into "methane + propylene," and also have converted part of the propylene into "methane + ethylene." In a subsequent paper we will show that at 700° *iso*butylene very definitely consumes large quantities of hydrogen with the consequent production of the anticipated excess of methane.

The general course of pyrolysis of *iso*butane is the same at 700° as at 600°, but the extent of the change was found to be considerably greater and the secondary reactions assumed greater prominence. Whereas more *iso*butylene than propylene was noted at 600°, the reverse was true at 700°. Small amounts of a liquid tar were formed at 700°, but in

---

[4] Frey and Smith, *Ind. Eng. Chem.*, **20**, 950 (1928).

quantities insufficient for identification. Experiments (unpublished data) with olefins lead us to believe that this tar formation was caused by the *iso*butylene or propylene formed in the reaction. As stated above, ethylene was formed in fair amounts at 700°.

It is believed that the results of this study may be interpreted satisfactorily by assuming an initial scission of the saturated hydrocarbons into radials. Such splitting may occur at C–C or C–H bonds. If this is the case, scission with *n*-butane is largely of the C–C type, division occurring at the terminal position slightly more readily than at the central position. Although rupture of the C–C bond is a large factor in the pyrolysis of *iso*butane, the C–H type of scission predominates, possibly because of the low attraction which the tertiary butyl radical is known to have for electrons.

Since this work on the butanes has been completed, a paper by Pease[5] has appeared which deals with the decomposition of the butanes as well as of ethane and propane. Pease approached the problem from a different point of view. His chief concern was the rate of dissociation of the various hydrocarbons, rather than the mechanism of the reaction. In his work the individual hydrocarbons which were formed in the pyrolysis were, for the most part, not identified. It was practically assumed, for example, that methane was the only saturated hydrocarbon which was formed, and no effort was made to identify the individual unsaturated hydrocarbons. It is with the latter problem in particular that this paper deals.

Two methods were developed for the analysis of the unsaturated content of the gaseous hydrocarbon mixtures which were produced. In one the olefins were converted in quantity into their bromide derivatives and then, if possible, fractionated into pure fractions or into two-component mixtures. Each such fraction was analyzed by the index of refraction method. For this work it was necessary to construct index of refraction curves for reference from synthetic mixtures of ethylene–propylene bromides, and of propylene–*iso*butylene bromides.

Another analytical method, better than the first, was developed. In this each of the gaseous unsaturated hydrocarbons was directly absorbed in a modified Orsat apparatus. Acetylene and methylacetylene were dissolved in alkaline potassium iodomercurate[6] solution, following which the remaining unsaturated hydrocarbons were removed in turn by sulfuric acid of progressively greater concentration. This is essentially the method suggested by Dobryanskii,[7] but critical studies were carried out

---

[5] Pease, THIS JOURNAL, **50**, 1779 (1928).

[6] Lebeau and Damiens, *Ann. chim.*, **8**, 221 (1917).

[7] Dobryanskii, *Neftyanoe Khozyaistvo*, **9**, 565 (1925); *Chem. Zentr.*, I, **97**, 2220 (1926); *Petroleum Domain*, 565 (1925); *C. A.*, **20**, 1576 (1926).

with it to adapt it to our needs. Dobryanskii suggested 63–64% sulfuric acid as the proper solvent for *iso*butylene; 83–84% acid for propylene; and 100–102% acid for ethylene. We obtained more satisfactory results with the acid concentrations, respectively, of 62.4, 82.5 and 100% acid which contained 8% of sulfur trioxide. We found allene to be nearly insoluble in the *iso*butylene pipet, but readily soluble in the propylene pipet. Although the absorption method, for obvious reasons of convenience, economy and precision, is superior to the bromide method, it must be used advisedly, since more than one hydrocarbon in a hydrocarbon mixture may be appreciably dissolved in the reagents employed.

Experimental Part

Apparatus.—A flow method was used. The gaseous hydrocarbon was passed directly from the tank through a wet test meter, then through a differential pressure flowmeter of the capillary type, was dried by calcium chloride and passed into the reaction tube. This tube was of pyrex, one inch in diameter, and was heated over 30 inches of its length in an unsegmented electric tube furnace. The furnace was supported in a vertical position to facilitate the escape of any liquid products from the heated portions. Butane was passed through the tube at a controlled rate of flow, and the effluent gases were passed through cooling coils at 0° to remove liquid products. The gaseous products were then analyzed.

Gas Analysis.—A modified Orsat gas analysis apparatus was constructed and the values for carbon dioxide, oxygen, total unsaturated hydrocarbons, hydrogen, carbon monoxide and saturated hydrocarbons were determined in the usual way. Presumably methane and *iso*butane are the only saturated hydrocarbons present in the mixture from *iso*butane. Combustion analysis is satisfactory for such a mixture. From *n*-butane, however, it is likely that three saturated hydrocarbons are present, methane, ethane and *n*-butane; combustion data give the average molecular weight of such a mixture. By assuming that ethane and ethylene are formed in equivalent amounts and that methane and propylene are also, the relative amounts of methane, ethane and butane may be estimated.

To analyze the individual unsaturated hydrocarbons, 3 pipets filled with glass tubes were incorporated in the apparatus. They were for acetylene, *iso*butylene and propylene[8] in turn, after which ethylene was removed with fuming sulfuric acid (8% SO_3). The acetylene reagent was made up from 500 g. of potassium iodide, 200 g. of mercuric chloride and 40 g. of sodium hydroxide, and diluted with water to one liter. The *iso*butylene pipet contained 62.4% sulfuric acid and the propylene pipet 82.4% sulfuric acid. The ethylene reagent was prepared by adding 120 g. of sulfur trioxide to 200 cc. of 95% sulfuric acid. The sequence of the analysis is: carbon dioxide, acetylenes, *iso*butylene, propylene, ethylene, oxygen, hydrogen and carbon monoxide, saturated hydrocarbons. In the sulfuric acid pipets the sample of gas was left in contact with the acid for two minutes, then withdrawn, and the process repeated until constant volume was attained.

With sulfuric acid of 60.7% strength, the rate of solution of diluted *iso*butylene (mixed with 70% air) was very slow. By changing the acid strength to 62.4%, *iso*-

---

[8] Allene, butene-1 and butene-2 are also rapidly absorbed in the propylene pipet. These three gases were shown, however, to comprise less than 2% of the total gases. Butadiene, also present in traces, would be taken up in this pipet and to some extent also in the *iso*butylene pipet.

butylene dissolved rapidly. About twenty to thirty minutes was required for complete absorption and most of this time was taken to remove the last 2 cc. of *iso*butylene from the 70 cc. of air. Propylene (31% by volume, mixed with air) was not dissolved by this 62.4% acid in a total contact time of ten minutes, but pure propylene was absorbed at the slow rate of 0.03–0.08 cc. per minute of contact. Since the gases from a thermal decomposition will never produce undiluted propylene, this becomes a separation of high accuracy. No loss of ethylene could be detected in a total contact time of twelve minutes with either 62.4 or 82.4% sulfuric acid, but a solution of 84.4% acid absorbed it at a rate of about 0.02 cc. per minute. Since propylene was rapidly dissolved in 82.4% acid, this concentration was adopted. The time of complete absorption for a mixture with air (45% C_3H_6) was twenty to twenty-five minutes. Allene, $CH_2{=}C{=}CH_2$, was found to be nearly insoluble in 62.4% sulfuric acid when the allene was of 40% concentration (60% air). It was quickly absorbed by 82.4% acid, however.

In the absorption of ethylene of 75% concentration (25% air) by fuming sulfuric acid (8% SO_3), completion was reached after seven two-minute passes. The final reading was preceded by an alkaline wash. Both butanes interfere in this analysis, but since they appear to be absorbed at a constant rate, a correction may be made for this effect. A measured sample of *iso*butane was kept in the "ethylene pipet" for two minutes. Then it was transferred to the potassium hydroxide pipet and the volume again read. Six consecutive passes gave a mean loss of 0.71 cc. for a mean volume of 92.5 cc. With *n*-butane, the loss was about 0.6 cc. In mixtures of ethylene with butane, these values obviously depend on the residual volume of butane, but one or two two-minute passes after final absorption of the ethylene will indicate the "constant" for the experiment in question. Correction may then be made.

Refractive Indices of Synthetic Mixtures of Olefin Bromides.—Ethylene bromide, propylene bromide and *iso*butylene bromide were purified by vacuum distillation. The synthetic mixtures used for these determinations were ethylene–propylene bromides and propylene–*iso*butylene bromides. The refractive indices were determined with a water-jacketed Abbé refractometer equipped with a standardized thermometer. The results are listed in Table I.

TABLE I

REFRACTIVE INDICES OF SYNTHETIC OLEFIN BROMIDE MIXTURES

Ethylene–Propylene			Propylene–*Iso*butylene		
Per cent. by weight			Per cent. by weight		
$C_2H_4Br_2$	$C_3H_6Br_2$	n^{20}_D	$C_3H_6Br_2$	$C_4H_8Br_2$	n^{20}_D
0.00	100.00	1.5198	100.00	0.00	1.5198
9.79	90.21	1.5208	74.8	25.2	1.5165
28.90	71.10	1.5240	56.6	43.4	1.5150
44.96	55.04	1.5268	41.0	59.0	1.5143
67.80	32.20	1.5313	0.00	100.0	1.5118
89.20	10.80	1.5356			
100.00	0.00	1.5379			

Temperature Measurements.—The temperature of the reaction was measured by a chromel–alumel thermocouple which was within the reaction tube and which was protected by a thin pyrex tube. This temperature was recorded and automatically controlled by a Leeds and Northrup potentiometer type recorder-controller. The usual sensitivity of this system was ±2°, but with a carbon coating on the protecting tube there was a lag, the extreme case of which was ±8°.

Source and Purity of the Butanes.—Cylinders of the liquefied gases were purchased from the Carbide and Carbon Chemicals Corporation; high purity was claimed for them; combustion analysis showed them to be fairly pure. Analysis of *n*-butane gave values of 4.04 and 3.96 for *n* in C_nH_{2n+2}; *iso*butane gave values of 3.93, 3.92 and 3.97. These are all sufficiently near the theoretical value of 4.00 to be satisfactory. The *n*-butane contained traces of pentane and 1–2% of *iso*butane as impurities. *Iso*butane contained a small amount of propane and 1–2% of *n*-butane as impurities.

Increase in Volume, Percentage Decomposition, Rates of Decomposition.—In the preliminary experiments the influence of the temperature and the rate of flow of the hydrocarbon into the tube was studied and the progress of the reaction was followed by analyzing the gases for total unsaturated hydrocarbons and hydrogen. The contact time was calculated by dividing the volume of the heated portion of the tube by the mean volume of gas entering and leaving the tube, this mean volume being corrected to the temperature of the tube.

The primary pyrolytic reactions of *n*-butane are: (1) into $C_3H_6 + CH_4$, (2) into $C_2H_4 + C_2H_6$, (3) into $C_4H_8 + H_2$. The primary changes of *iso*butane are: (1) into $C_3H_6 + CH_4$, (2) into *iso*-$C_4H_8 + H_2$. Assuming no secondary changes into acetylene, allene, butadiene, etc., it is evident that from 100 volumes of *n*- or *iso*butane there

TABLE II

VOLUME INCREASE OF THE BUTANES DURING PYROLYSIS

Butane	Temp., °C.	Rate of flow into tube, cc. per min.	Unsatd. hydrocarbons in exit gas, % by volume	Volume increase, %	
				Calcd.	Obs.
n-	600	360	17.3	20.9	16 ± 3
n-	600	336	19.2	23.8	15 ± 4
n-	700	312	38.8	63.5	88 ± 5
n-	700	315	41.6	71.5	82 ± 5
iso-	600	320	20.6	26.0	17 ± 3
iso-	700	297	36.3	57.0	79 ± 4

TABLE III

RESULTS WITH *n*-BUTANE

Temp., °C.	Contact time, sec.	Rate of inflow (20°, 760 mm.), cc./min.	Analysis of effluent gas, %		Extent of dec., %	Extent of dehydrogenation, %
			Unsat.	H_2		
400	31	300	1.3	0.9	1.3	1.0
500	27	300	1.8	1.1	1.85	1.2
600	19	360	17.3	1.8	21.0	..
600	19	336	19.2	1.0	23.8	1.1
600	22	300	13.8	1.4	16.0	1.6
			Results with *Iso*butane			
400	30	310	1.1	0.9	1.1	0.9
500	27	295	6.9	1.3	7.4	1.1
600	21	320	16.3	6.2	19.5	7.2
600	17	400	11.7	5.5	13.2	6.1
500	8	1000	1.4	0.5	1.5	0.5
550	8	900	5.1	1.3	5.4	1.3
550	10	720	7.0	0.4	7.5	0.5
600	9	800	9.9	2.0	11.0	2.3
650	7	920	16.2	5.8	19.4	7.2
700	6	1040	27.8	10.7	38.6	15.2

TABLE IV

DATA FOR THE PYROLYSIS OF THE BUTANES

	n-Butane				*Iso*butane			
Temperature, °C.	600	600	700	700	600	600	700	700
Entering rate of flow, cc./min.	345	430	390	350	346	395	330	400
Vol. of heated part of tube, cc.	550	550	550	550	550	500	550	360
Exit rate of flow (20°, 760 mm.); cc./min.	395	500	740	630	400	455	595	720
Hot contact time, sec.	30	24	18	20	27	26	21	12
Final vol. from 1000 cc. of orig. butane, cc.	1155	1150	1870	1820	1150	1190	1800	1790
Extent of decomp., %	22	20	75	76	22	25	70	70
	Anal. of effluent gas Percentage by volume							
Acetylenes	0.2	..	1.2	..	0.4	..	0.6	..
*Iso*butylene	0.6	..	2.0	..	7.2	..	11.6	..
Propylene	7.7	..	16.2	..	5.5	..	13.2	..
Ethylene	6.1	..	19.0	..	1.1	..	6.4	..
Total unsatd. gases	14.6	19.2	38.4	41.6	14.2	20.2	31.8	36.3
Hydrogen	2.0	1.0	8.5	7.8	6.8	6.2	12.7	15.2
Methane	..	..	..	..	11.3	11.0	31.3	26.3
*Iso*butane	..	..	..	..	67.9	62.8	16.6	17.0
Nitrogen	..	..	..	..	..	..	7.5	5.0
	Comp. of the unsatd. hydrocarbons Percentage by volume							
	Abs.[a]	Brom.[a]	Abs.	Brom.	Abs.	Brom.	Abs.	Brom.
Ethylene	40.1	32.6	49.3	46.0	7.8	..	20.1	2.5
Propylene	55.4	64.6	42.2	43.7	38.8	50.8	41.5	74.8
Butylenes	..	1.3	..	4.8	..	..	..	..
*Iso*butylene	3.4	..	5.3	..	50.7	46.6	36.5	19.8
Acetylenes	1.2	1.5	3.1	3.7	2.8	..	1.9	..
Acetylenes and dienes	..	..	..	..	..	2.5	..	2.9
Butadiene	..	..	..	1.6	..	..	..	..
	Vol. of prods. formed per liter of butane taken Cubic centimeters							
Ethylene	71	..	356	..	13	..	115	..
Propylene	89	..	304	..	63	..	238	..
Butenes and butadiene	7	..	39	..	..	..	..	..
*Iso*butylene	..	..	..	..	83	..	209	..
Acetylene	2	..	22	..	5	..	11	..
Total unsatd. gases	..	222	..	760	..	240	..	650
Hydrogen	23	12	159	142	78	74	228	272
Methane	80	..	312	..	130	131	563	468
Ethane	65	..	370	..	..	..	..	..
Methane + ethane	..	128	..	686	..	..	..	..
Undec. butanes	780	798	250	241	780	750	299	302

[a] The abbreviation Abs. indicates that the unsaturated hydrocarbons were analyzed by the absorption method; the abbreviation Brom. signifies the bromine method of analysis.

should be produced ((100 − P) volumes of C_4H_{10}) + (P volumes of C_2H_6, CH_4 and H_2) + (P volumes of olefins). The sum of these three quantities represents the total new volume, or V. Thus

$$V = (100 - P) + P + P = 100 + P$$

From this the percentage by volume of olefins, U, in the escaping gas is related to the percentage decomposition, P, of the butane as follows

$$U = \frac{100P}{100 + P} \qquad P = \frac{100U}{100 - U}$$

Experimentally it was determined that the agreement with both butanes was fair at 600°, but the rather wide divergence at 700° indicated considerable secondary decomposition. In these measurements of volume increase, the volumes were measured roughly in bottles of 8-liter capacity and calibrated in 100-cc. divisions. Table II lists a few of the results.

The decomposition of *n*-butane showed a rapid increase in rate between 500 and 600°. The rates of decomposition at 600° of *n*- and of *iso*butane are of the same order of magnitude, as is apparent from Table III. The data also show strikingly the limited extent of the dehydrogenation reaction with *n*-butane and the importance of it with *iso*butane, which at 600° is seen to represent 36–47% of the total reaction.

The more representative data for two representative runs at 600° and for two at 700° with *n*-butane and the same for *iso*butane are collected in Table IV. It will be noticed that the unsaturated hydrocarbons in one 600° experiment and in one 700° experiment for each of the butanes were determined directly by absorption methods. In the other four runs the olefins were estimated by the bromine method. These two methods are seen to check each other fairly well with *n*-butane, but not with *iso*butane. This is due to the more complex olefin mixture in the latter case. For the simple olefins, the absorption method is considered much more trustworthy, but the bromine method was especially useful in the search for butadiene, allene and methylacetylene. From *iso*butane it is apparent that allene and butadiene either were not present or were present in very limited amounts, since the acetylene values by the absorption method were of the same order of magnitude as the "acetylene and diene" values by the bromine method.

Data for the Bromine Method of Analysis Referred to in Table IV.—From *n*-butane at 60° the weight of bromides which were fractionated with a Vigreux column was 148 g. The percentage composition of each fraction is taken from the index of refraction curves.

Boiling range mm.	°C.	Weight, g.	n^{20}_D	Composition by weight, % $C_2H_4Br_2$	$C_3H_6Br_2$	$C_4H_8Br_2$
25	42–43	92.8	1.5259	40	60	..
23	43–45	41.7	1.5220	17	83	..
23	47–57	4.97	1.5172	..	50	50
22	107–125	3.32	....			
Residue		5.0	....	Some butadiene tetrabromide		
		Loss, 1.9 g., or 1.2%				

A total of 43 liters (20°, 760 mm.) of *n*-butane in the 700° experiment yielded 219 g. of bromides, which, twice fractionated, gave these results.

Boiling range mm.	°C.	Weight, g.	n_D^{20}	Composition by weight, % $C_2H_4Br_2$	$C_3H_6Br_2$	$C_4H_8Br_2$
24	40–43.5	85.0	1.5295	60	40	...
22	41–43	95.7	1.5260	40	60	...
21	43–44	2.04	1.5183	..	80	20
7	28–45	8.71	1.5220	..	..	100 ?
6	56–100	5.12	1.5542	..	..	...
4	104–120	7.24	....	Some butadiene tetrabromide		
Residue		7.05	....	Much butadiene tetrabromide		
		Loss, 5.07				

Butadiene tetrabromide was present in quantity in the 104–120° (4 mm.) fraction and the residue. After several recrystallizations from alcohol, there was separated 3 g. of the material which melted at 115–115.5°.

Anal. Calcd. for $C_4H_6Br_4$: Br, 85.4. Found: Br, 86.0, 85.9.

The bromides from *iso*butane at 600° weighed 107 g., and gave these data.

Boiling range mm.	°C.	Weight, g.	n_D^{20}	Apparent composition[a] (% by wt.) $C_3H_6Br_2$	*iso*-$C_4H_8Br_2$
38	54.5–55.0	4.15	1.5175	85	15
32–28	52.3–51.0	40.04	1.5162	72	28
27	51.0–52.0	26.38	1.5144	44	56
27	52.0–52.5	8.09	1.5123	4	96
2	63.0–69.0	11.92	1.5650	Almost pure $CH_3CBr(CH_2Br)_2$	
Residue		4.15	....		

[a] The presence of ethylene bromide is masked by the *iso*butylene bromide in the n_D values.

The residue represents the tetrabromide fraction (acetylenes and dienes) but it was too small to investigate satisfactorily. The fraction, b. p. (2 mm.) 63–69°, was shown to be almost pure tribromo-*iso*butane, formed by the action of *iso*butylene and bromine water. This material, therefore, represents *iso*butylene. It was united with similar material from the 700° experiment and was purified by vacuum fractionation. A fraction which weighed 13 g. had these properties: b. p. (3 mm.) 69–70°; d_4^{20} 2.1887; d_4^{25} 2.1803; n_D^{20} 1.5669.

Anal.[9] Subs. 0.1915, 0.2005: $N/15$ $AgNO_3$ soln., 29.25, 30.55 cc. Calcd. for $C_4H_7Br_3$: Br, 81.35. Found: Br, 81.4, 81.2.

The weight of olefin bromides formed from 46.72 liters of *iso*butane at 700° was 212 g. A very small quantity of butadiene tetrabromide, m. p. 113–115°, was isolated from the fraction, b. p. (4 mm.) 91–110°, and the residue.

---

[9] Analysis was by the method of Drogin and Rosanoff, THIS JOURNAL, **38**, 713 (1916).

Boiling range		Weight,	n_D^{20}	Apparent composition (% by wt.)		
mm.	°C.	g.		$C_2H_4Br_2$	$C_3H_6Br_2$	*iso*-$C_4H_8Br_2$
25	45–46	71.6	1.5204	6	94	..
24	45–46	45.7	1.5197	..	100	..
22	46–48	38.2	1.5160	..	70	30
3	28–60	4.0	....	..	...	..
2	62–72	31.7	1.5667	Entirely tribromo-*iso*butane		
4	91–110	4.4	....			
Residue		5.6	....			

Summary

Two concurrent reactions predominated in the pyrolysis of *n*-butane at 600°, namely, that into propylene and methane, and that into ethylene and ethane. The first of these reactions was slightly favored. Also, two major reactions occurred in the pyrolysis of *iso*butane at 600°, the formation of *iso*butylene and hydrogen, and to a lesser extent the formation of propylene and methane. An explanation is suggested for the observation that considerably more methane was formed from *iso*butane than would be accounted for by the latter reaction. These reactions were still the major ones with *n*- and *iso*butane at 700°, but not in the same proportions. Secondary reactions of importance were also encountered and studied.

Two methods were developed for the estimation of the individual unsaturated hydrocarbons in the gaseous mixtures which were encountered. One method, with limitations which were noted, consisted in determining the refractive index of the various bromide fractions (obtained from the olefins) and referring the values to index of refraction curves for similar synthetic mixtures. In the second analytical method, which is superior in most respects, the individual unsaturated hydrocarbons were selectively absorbed from the mixture by reagents in a modified Orsat apparatus. The various conditions for the analysis have been indicated.

EVANSTON, ILLINOIS