ing by sliding the rod H through the rubber connector I, thus closing the stopper G. The tube K is then closed by a short rubber tube and glass bead and the entire sorption tube and cap ensemble removed and placed in a desiccator to cool. A vacuum type desiccator carrying a bottle neck in its cover enables one to insert the weighing tube into the desiccator in a vertical position. A thin rubber sleeve attached to the bottle neck, into which the cap F fits, then seals the desiccator. When cool, the small tube D is detached at the ground joint E for weighing. A correction must, of course, be made for the steam that condenses in the free space of the tube upon cooling.

When the apparatus is used for determining the moisture content of solid materials, the steam generator is cut off and a stream of completely dried air or nitrogen passed over the material in D. The effluent gases are then passed through a series of weighed drying tubes attached at K to collect the moisture. The loss in weight of the material in D serves as a check. The dissociation of moist materials which decompose upon heating with evolution of gases not absorbable by the drying agents used may thus readily be obtained by determining the total loss in weight of the material itself as well as the amount of water vapor evolved. The ability to interrupt the experiment easily and to determine the change in weight also enables one to follow the *rate* of sorption, drying or dissociation quite readily.

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THE PYROLYSIS OF HYDROCARBONS: ISOBUTYLENE[1]

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

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In the first paper[4] of this series, data were recorded for the pyrolysis of *n*-butane and *iso*butane. The present paper concerns itself with *iso*butylene, a hydrocarbon which possesses a branched chain of four carbons,

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[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.

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

as does *iso*butane. It will be shown that *iso*butylene is much more stable than *iso*butane under similar conditions. Undoubtedly this observation is connected in some way with the greater or lesser "electron attraction" of the various radicals concerned. It leads to the inference that the carbon-to-carbon single bond in *iso*butane undergoes scission more readily than the similar single bond in *iso*butylene.

The literature furnishes no record of a quantitative study of the pyrolysis of *iso*butylene. Previous workers, however, have identified some of the products formed when this hydrocarbon is decomposed. A. A. Noyes[5] passed *iso*butylene through a glass tube heated to "low redness," and identified ethylene, propylene, butadiene, methane, hydrogen, benzene, toluene and naphthalene. Nef[6] found propylene, methane, hydrogen and a "small yield" of yellow oil as the decomposition products of *tert.*-butyl alcohol. Presumably *iso*butylene was an intermediate product. Ipatiev[7] reported that when *iso*butylene was passed over alumina at 500°, or over zinc chloride at 600°, there was no change into the isomeric butenes, but that some propylene, hydrogen and methane were formed.

Experimental

*Iso*butylene was prepared by refluxing 400 cc. (4.3 moles) of *tert.*-butyl alcohol with 150 g. (1.2 moles) of oxalic acid dihydrate. The gas evolved was collected and stored over water in a gasholder of 56-liter capacity. The yields of several runs averaged 80–90%. The only impurities in the gas were small quantities of air and the vapors of *tert.*-butyl alcohol. Before passing into the reaction tube, the gas was conducted through a wet test meter and then freed from water and alcohol vapors by a calcium chloride tower. A flowmeter was used for adjusting the flow of gas through the apparatus to a constant rate.

The reaction chamber was of pyrex tubing (2.5 × 90 cm.). It was heated in an electric tube furnace over 76 cm. of its length. The temperature was recorded and controlled accurately by a Leeds–Northrup potentiometer controller, as has been described in the first paper of this series. The volume of the heated portion was approximately 360 cc. and the inside surface was 600 sq. cm. To facilitate the removal of liquid products, the tube was placed vertically. Such liquids were condensed and removed from the escaping gases by passage through two U-tubes filled with glass wool and cooled to 0–5°. The effluent gases were measured by a second wet test meter. A sample of the gaseous products was removed for analysis toward the end of each run. For each experiment, 20–30 liters of *iso*butylene was employed. A sketch of the apparatus is given in Fig. 1.

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[5] Noyes, *Mass. Inst. Tech. Quarterly*, **1**, 278–281 (1888).

[6] Nef, *Ann.*, **318**, 24, 25, 210 (1901).

[7] Ipatiev, *Ber.*, **36**, 2008 (1903).

The gaseous products were analyzed by the absorption methods which were developed for the work on the butanes. The same sequence and the same precautions were observed. Mercury was used as the confining liquid in the Orsat buret. This work showed that the chief unsaturated hydrocarbons in the effluent gas were *iso*butylene and propylene (or allene), with a small amount of ethylene and acetylene.

A check on the values for the unsaturated hydrocarbons was obtained in a separate run by converting them into the bromides and then separating these bromides. The proportion of *iso*butylene and propylene as estimated in this manner agreed closely with the amounts found by gas analysis. The allene content was shown to be very small. Since the fuming sulfuric acid pipet should remove not only ethylene but also benzene and toluene vapors, it was to be expected that the ethylene bromide value for ethylene should be somewhat lower than the absorption value. Such was the case.

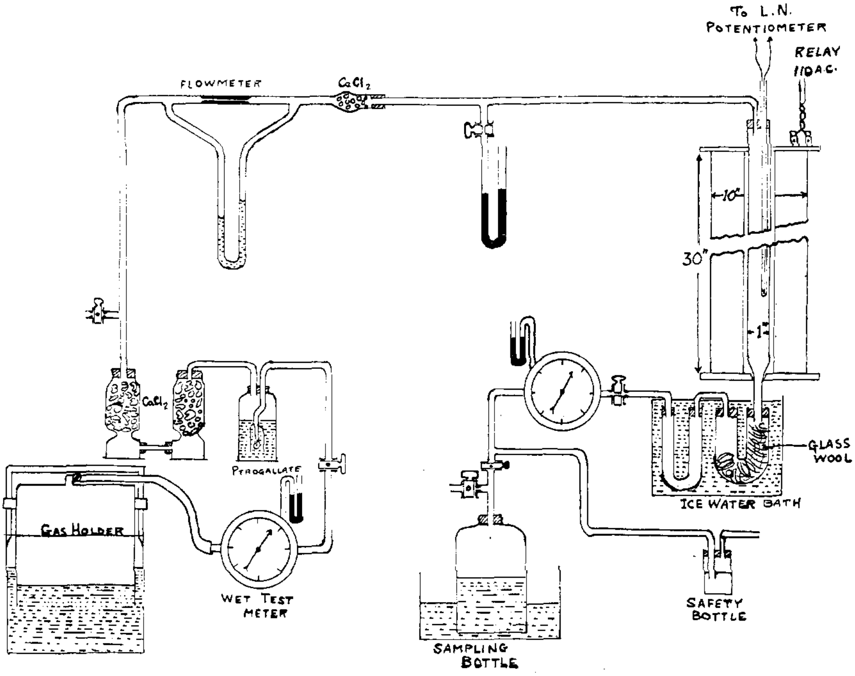

Fig. 1.

The decomposition was quite slow at 600°, but the rate increased rapidly with the temperature. In Table I is shown the amount of decomposition of *iso*butylene (97–99% purity) at the different temperatures used.

The rate of disappearance of the *iso*butylene was unchanged by dilution of the entering gas with nitrogen or with hydrogen (Table II). The rate of decomposition is therefore independent of the concentration.

TABLE I

DECOMPOSITION RESULTS

Temp., °C.	Contact time, sec.	Decompn., %	Temp., °C.	Contact time, sec.	Decompn., %
599	18	1.2	700	12	30.2
599	200	20.0	700	18	47.7
			700	23	54.0
652	18	11.1	700	25	51.4
652	27	22.7	700	32	64.3

TABLE II

DILUTION WITH NITROGEN

Temp., °C.	Contact time, sec.	Composition of entering gases Percentage by volume C_4H_8	N_2	O_2	Percentage decomposition
702	23	98.0	1.6	0.4	54.0
704	21	54.8	44.9	0.3	54.4

DILUTION WITH HYDROGEN[a]

		C_4H_4	Air	H_2	
702	23	98.0	2.0	...	54.0
704	22	51.8	3.7	44.5	56.8

[a] Although the extent of decomposition of *iso*butylene was not appreciably altered by the presence of hydrogen, still this gas was not an "inert" diluent. It was found that 62 cc. of hydrogen disappeared per liter of *iso*butylene decomposed, while the decomposition without the previous addition of hydrogen produced 265 cc. of hydrogen per liter of *iso*butylene decomposed. The disappearance of this hydrogen was accompanied by an increase in the methane content to the extent of 205 cc. per liter of *iso*butylene decomposed.

When the surface of the reaction tube was increased to twice its original value by packing the tube with small pyrex tubing, the rate of decomposition was also unchanged. This is revealed in Table III. The decomposition is, therefore, homogeneous or largely so.

TABLE III

EFFECT OF INCREASED SURFACE

Temp., °C.	Contact time, sec.	Vol. of tube, cc.	Surface, sq. cm.	Decomp., %
702	23	360	600	54.0
704	21	345	1200	51.8

Since the decomposition of *iso*butylene is independent of the concentration of the gas and is unaffected by an increase of surface, the reaction is unimolecular. The rate of decomposition should be given by the equation

$$\frac{dx}{dt} = k(a - x)$$

which, on integration, becomes

$$k = \frac{1}{t} \log_e \frac{a}{(a - x)}$$

In this equation a represents the original concentration of *iso*butylene, $(a - x)$ the concentration remaining after t seconds, and k the specific reaction rate. In the calculation of the values of k, given in Table IV, the concentrations of *iso*butylene have been expressed in moles per 22.4 liters at 0° and 760 mm.

TABLE IV

RESULTS OF EXPERIMENTS

Temp., °C.	Time, sec.	Concn. in moles per 22.4 liters Start	Finish[a]	k	Mean k
600	200	0.940	0.690	0.0016	0.0016
650	13	.990	.900	.0073	
650	27	.970	.762	.0089	.0081
700	12	.980	.634	.0362	
700	18	.975	.433	.0451	
700	22	.978	.294	.0547	
700	23	.980	.387	.0405	
700	25	.978	.380	.0378	
700	32	.983	.266	.0409	
N_2 700	21	.548	.212	.0451	
H_2 700	22	.518	.206	.0420	
700[b]	21	.978	.399	.0428	.043

[a] The final concentrations are somewhat in error, since the liquid products were removed before measuring the volume of the exit gases. Therefore, the concentration of the *iso*butylene at the end of the reaction was actually less than the figures in Table IV.

[b] Experiment with increased surface.

The heat of activation was calculated from the change in the specific reaction rate with the temperature, by means of the equation of Arrhenius

$$\frac{d(\log_e k)}{dT} = \frac{A}{RT^2}$$

wherein k is the specific reaction rate; T, the absolute temperature; R, the gas constant in calories; and A, the heat of activation. The mean values of k for the temperature of 600, 650 and 700° were used in these calculations.

Mean temperature, °C.	625	650	675
Heat of activ., A, cal./mole	52,700	55,700	59,100

A summary of the data of several experiments on the pyrolysis of *iso*butylene at 600–700° under varying conditions are arranged in Tables V and VA. In Expt. 12 the olefin was diluted with nitrogen; in No. 13, it was diluted with hydrogen. Experiment No. 15 was an increased surface experiment such as has been mentioned above. In the other 700° experiments it will be seen that for each mole of *iso*butylene decomposed, 1.3–1.5 moles of other gases was formed with an exposure of from twelve to thirty-two seconds. Methane comprised about half of the gaseous portion, but since liquid products were found to be formed to the extent of 41–63% of the weight of *iso*butylene decomposed, it is apparent that methane formation is not the exclusive major reaction. In the various 700° experiments, methane represented 46–55% of the gases exclusive of the unchanged *iso*-

butylene. Five of the six results showed the hydrogen content to be 19–20%, and the sixth dropped to 14%. In general, therefore, hydrogen comprised about one-fifth of the gases. Propylene represented one-seventh or less (14–17%), and other gases were present in lesser amounts. Expressed somewhat differently, each 100 moles of *iso*butylene undergoing decomposition under these conditions gave rise to 59–83 moles of methane, 20–30 moles of hydrogen, 20–25 moles of propylene, lesser amounts of *iso*butane and ethylene and almost negligible quantities of acetylene.

The Nature of the Unsaturated Hydrocarbons Formed at 700°.—In a separate experiment *iso*butylene was decomposed at 700° at a contact time of nineteen seconds. The unsaturated hydrocarbons in the off-gas were analyzed by the bromide method to serve as a check on the absorption method of analysis. The gaseous products were dried with calcium chloride, and were then absorbed in bromine in dry carbon tetrachloride solu-

TABLE V

THE PYROLYSIS OF *ISO*BUTYLENE

Experiment	1	2	10	11	7	4	9
Temperature, °C.	599	599	652	652	700	700	700
Contact time, sec.	200	18	27	13	12	18	19
Entering flow, cc./min.	35	420	256	522	536	330	300
Exit flow, 25°, cc./min.	38	420	252	509	578	388	363
Press. in tube, mm. of Hg	750	747	744	743	755	744	720
Concn. of *iso*butylene in the entering gas, % by vol.	94	96.5	97	99	98	97.5	97
Decomposition, %	20	1.2	22.7	11.1	30.2	47.7	...
Oil formation (% by weight of entering *iso*butylene)	...	...	9	7	14.1	30	23.3
GASEOUS PRODUCTS FORMED PER LITER OF *ISO*BUTYLENE ENTERING							
Propylene, cc.	61	4	39	16	66	109	...
Methane, cc.	118	...	65	15	177	312	...
*Iso*butane, cc.	54	...	40	22	40	29	...
Hydrogen, cc.	35	...	34	6	73	124	...
Acetylene, cc.	3	3	8	12	13	28	...
Oxides of carbon, cc.	7	4	10	9	12	6	...
Ethylene and aromatics, cc.	18	2	7	11	20	32	...
GASEOUS PRODUCTS FORMED PER LITER OF *ISO*BUTYLENE DECOMPOSED							
Propylene, cc.	305	...	172	144	218	228	...
Methane, cc.	590		286	135	586	655	
*Iso*butane, cc.	270		176	198	133	61	
Hydrogen, cc.	175		150	54	242	260	
Acetylene, cc.	15		35	108	43	59	
Ethylene and aromatics, cc.	90		31	99	66	69	
OIL FORMATION							
Yield of oil based on the weight of *iso*butylene dec., %	...	...	39.6	63	46.6	63	...

TABLE VA

THE PYROLYSIS OF *Iso*BUTYLENE

Experiment	14	6	5	8	12	13	15
Temperature, °C.	702	702	700	700	704	704	704
Contact time, sec.	22	23	25	32	21	22	21
Entering flow, cc./min.	261	258	236	172	281	284	270
Exit flow, 25°, cc./min.	322	308	296	226	331	309	320
Press. in tube, mm. of Hg	747	747	743	739	745	748	748
Composition of entering gas, percentage by volume							
*Iso*butylene	97.8	98.0	97.8	98.3	54.8	51.8	97.8
Nitrogen	1.7	1.6	2.0	1.5	44.9	3.5	1.7
Oxygen	0.5	0.4	0.2	0.2	0.3	0.3	0.5
Hydrogen	...	...	...	...	...	44.5	...
Percentage decomp.	62.7	54.0	51.4	64.3	54.4	56.8	51.8
Oil formation (% by weight of entering *iso*butylene)	26.8	25.3	21.3	29.0	15.2	13.0	20.4
GASEOUS PRODUCTS FORMED PER LITER OF *Iso*BUTYLENE ENTERING							
Propylene, cc.	127	105	133	129	146	158	129
Methane, cc.	420	372	426	534	238	507	310
*Iso*butane, cc.	20	92	53	36	15	34	23
Hydrogen, cc.	167	143	105	193	168	(−35)	131
Acetylene, cc.	9	11	10	7	4	6	14
Oxides of carbon, cc.	9	6	0	4	12	8	11
Ethylene and aromatics, cc.	79	27	38	66	84	105	58
GASEOUS PRODUCTS FORMED PER LITER OF *Iso*BUTYLENE DECOMPOSED							
Propylene, cc.	202	195	259	201	268	278	249
Methane, cc.	669	689	830	830	438	894	600
*Iso*butane, cc.	32	169?	103?	56	28	60	44
Hydrogen, cc.	266	265	204	300	309	(−62)	253
Acetylene, cc.	14	20	20	11	7	11	27
Ethylene and aromatics, cc.	126	50	74	103	155	185	112
OIL FORMATION							
Yield of oil, based on the weight of *iso*butylene decomposed, %	42.7	46.8	41.5	45	28.0	22.9	39.4

tion. A volume of 21.3 liters (53.4 g.) of *iso*butylene (0°, 760 mm.) was passed through the reaction tube. The volume increase was 20.9%.

After removing the excess bromine from the solution of the bromides, the carbon tetrachloride was distilled off. Of the residue, the lower-boiling portion (b. p. (30 mm.) 51–68°), which contained the ethylene, propylene and *iso*butylene dibromides, was found to weigh 94.3 g. The higher-boiling material weighed 43.2 g. After four fractionations with a fractionating column of the type described by Cooper and Fasce,[8] the dibromides were separated into the following fractions

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[8] Cooper and Fasce, *Ind. Eng. Chem.*, **20,** 420 (1928).

B. p., °C.	130–139	138–144	145–148
Grams	4.4	21.1	55.2
n_D^{20}	1.5178	1.5158	1.5111

and the residue was added to the first high-boiling residue. The amounts of ethylene bromide, propylene and *iso*butylene bromide were estimated from the distillation curve and also from the refractive index[4] of the three fractions.

Dibromides	Ethylene	Propylene	*Iso*butylene
From refr. index, g.	..	18	63
From distn. curves, g.	1	18	62

The higher-boiling material from the bromides was fractionated at reduced pressure and was also shown to represent *iso*butylene for the most part. The largest fraction was tribromo-*iso*butane, which is formed along with higher brominated products when *iso*butylene reacts with bromine.[9] Considerable tetrabromo-*iso*butane was found, and also a small residue containing presumably penta- and hexa-substituted *iso*butane. There was also a very small fraction containing acetylene tetrabromide and possibly allene tetrabromide. No butadiene tetrabromide was found, contrary to the work of A. A. Noyes.[5]

Most of the tribromo-*iso*butane was collected at 75.2–76° (4 mm.); its index of refraction was n_D^{20} 1.5670. Between 81 and 88°, 4.5 g. of similar material was also collected. Only half a gram distilled in the next fraction at 108–110° (9 mm.), n_D^{20} 1.5728. This fraction should represent the acetylene or allene tetrabromides. The next fraction of tetrabromo-*iso*butane weighed 5.8 g. It was collected at 134–150° (15 mm.), and its index of refraction at 20° was 1.6070. The residue weighed 1.8 g.

On the basis of 123 g. of isolated bromides, 1 g. was from ethylene, 18 g. from propylene, 95 g. from *iso*butylene (as di-, tri-, or polybromides) and 9 g. of other bromides. The mole percentage of olefins by such an analysis is ethylene 1.0%; propylene 17.2%, *iso*butylene 76.0%, others 5.8%. These results agree closely with the results by absorption methods in the modified Orsat apparatus.

	By absorption, %	Calcd. from bromides, %
*Iso*butylene	40.6	40.7 (53.6 × 0.760)
Propylene	8.4	9.2 (53.6 × 0.172)
Ethylene	2.4	0.5 (53.6 × 0.010)
Acetylene	2.2	3.2 (remainder)
	53.6	53.6

Reaction of Bromine and Isobutylene.—The proportion of the different bromination products given when *iso*butylene reacts with bromine has been calculated from the results of this fractionation. It is interesting to com-

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[9] Mereshkowsky, *Ann.*, **431**, 113 (1923).

pare our results at 0–5° with those of Mereshkowsky[9] at 45–50°. Evidently the bromination of *iso*butylene dibromide is lessened at the lower temperature, but it is still remarkably large as compared with similar experiments on other olefins which are reported in the literature.

	This investigation, 0–5°		Mereshkowsky, 45–50°	
*Iso*butylene dibromide	65.5	% by weight	45	% by weight
Tribromo-*iso*butane	25.5		44	
Tetrabromo-*iso*butanes	6.0		7	
Penta- and hexa-analogs	3.0		1	

The Liquid Products.—The pyrolysis of *iso*butylene is complicated by the formation of large amounts of liquid products in addition to the gaseous products which have been discussed. When the *iso*butylene was diluted with nitrogen before passing into the hot tube, the yield of liquid products was appreciably decreased (see Table VA, Expt. 12). Dilution with hydrogen had a similar effect on the yield of liquid products and in addition it served to increase the yield of methane and of propylene appreciably. Also it seemed to increase the yield of gaseous saturated hydrocarbons other than methane (see Table VA, Expt. 13). The accuracy of the combustion method for the determination of such saturated hydrocarbons is open to some question since all of the benzene and toluene vapors may not have been removed by the fuming sulfuric acid (8% free SO_3) before the combustion. The use of stronger acid, on the other hand, would result in the solution of appreciable quantities of such hydrocarbons as *iso*butane and propane.[10] The experiment with hydrogen is rather good evidence that the following reactions of scission and addition normally occur to some extent with the hydrogen which is liberated in the reaction.

$$(CH_3)_2C{=}CH_2 + H_2 \longrightarrow CH_4 + CH_3CH{=}CH_2$$
$$(CH_3)_2C{=}CH_2 + 2H_2 \longrightarrow 2CH_4 + CH_2{=}CH_2$$
$$(CH_3)_2C{=}CH_2 + H_2 \longrightarrow (CH_3)_3CH$$

The important part played in the reaction by the formation of the liquid products is shown in Table VI, in which the yield of liquid products is given in percentage by weight of the *iso*butylene decomposed.

TABLE VI

LIQUID PRODUCTS FROM *ISO*BUTYLENE

Temp., °C.	Contact time, sec.	Yield, %	Temp., °C.	Contact time, sec.	Yield, %
650	13	63	700	19	49
650	27	40	700	22	43
			700	23	47
700	12	47	700	25	42
700	18	63	700	32	45

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[10] Worstall, *Am. Chem. J.*, **20,** 664 (1898); THIS JOURNAL, **21,** 246 (1899); Orndorff and Young, *Am. Chem. J.*, **15,** 261 (1893).

Examination of the Oils Formed at 700°.—The density of the oil formed from *iso*butylene at 700° was found to increase with the contact time. This would be expected, since, as the contact time increases, the reaction of the aromatic hydrocarbons with each other and with the unsaturated hydrocarbons present forms the higher molecular weight aromatic hydrocarbons. The density, for a contact time of twelve seconds, was d_4^{20} 0.8511; for twenty-four seconds, d_4^{20} 0.8899; and for thirty-two seconds, d_4^{20} 0.9053.

Two samples of the liquids were fractionated, with the following results.

B. p., °C.	Weight, g.	% by weight of the oils
65–96	6.2	20.0
97–122	8.5	28.0
137–146	3.5	11.5
146–180	3.8	12.5
180–275	1.5	5.0
275–310	1.0	3.5
310–330	1.0	3.5
Pitch	2.5	8.0
Loss	2.4	8.0
	30.4	100.0

B. p., °C.	Weight, g.	% by weight of the oils
65–103	6.8	20.5
103–105	7.0	21.0
125–155	3.0	9.0
170–205	2.2	6.7
205–218	2.2	6.7
230–330	2.2	6.7
360–395	0.3	0.9
Residue	3.5	10.5
Loss	5.9	18.0
	33.1	100.0

The fractions of similar boiling point were then combined and fractionated more closely to separate the individual hydrocarbons. Much of the distillation loss in these fractionations was due to the dissolved *iso*butylene,[11] the last traces of which are removed with difficulty by distillation processes. Table VII shows the results of the final fractionation.

TABLE VII

FINAL FRACTIONATION OF OILS FROM *ISO*BUTYLENE

Fraction	Boiling range, °C.	Weight, g.	n_D^{20}	Probable composition
A	Up to 76°	1.2	....	Benzene and *iso*butylene
B	77–85	5.1	1.4850	Benzene and *iso*butylene
C	89–109	5.9	1.4860	Benzene and toluene
D	109–113	9.9	1.4912	Toluene
E	118–133	2.5	....	......
F	135–143	4.6	1.5005	Xylenes
G	153–185	3.5	1.5258	......
H	190–250	5.4	Naphthalene and homologs	
I	250–300	3.3	Diphenyl, ditolyl (?)	
J	310–395	1.3	Anthracene, phenanthrene	

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[11] Brooks, "The Non-Benzenoid Hydrocarbons," The Chemical Catalog Co., Inc., New York, **1923**, p. 583: "Kerosene and machine oil dissolve about 220 volumes of *iso*butylene at room temperature and the gas is only completely expelled on heating to 260°." Benzene–toluene mixtures would probably act similarly, since their solvent action is usually greater.

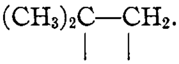
From the results in Table VII, only Fraction A gave evidence of the presence of appreciable amounts of unsaturated hydrocarbons by the usual tests. The high refractive indices of the fractions are also indicative of the aromatic nature of the hydrocarbons. The following derivatives were prepared.

Fraction	Derivative	Obs. m. p., °C.	Recorded lit. m. p., °C.	Mixed m. p., °C.
B	*m*-Dinitrobenzene	89.5–90	90	90–90.5
D	Trinitrotoluene	80–81	82	81–82
F	Nitro derivative	127–129	178, trinitro-*o*-xylene	
			182, trinitro-*m*-xylene	
			139, trinitro-*p*-xylene	
H	Picrate	128–131		
		125–134	150, naphthalene picrate	
J	Picrate	142–145	143, phenanthrene picrate	
		157–164	161, anthracene picrate	

Benzene and toluene were thus definitely characterized by their derivatives. The other fractions undoubtedly contained several compounds, since the derivatives were impure after two recrystallizations.

Isobutylene and Isobutane Compared.—Under comparable conditions *iso*butylene differs quite materially from *iso*butane in its behavior toward heat, in spite of the fact that both of these substances are branched hydrocarbons which contain four carbon atoms. For example, at 600° the unsaturated hydrocarbon decomposed only 1.2% in eighteen seconds, whereas the saturated hydrocarbon decomposed 13–19.5% in seventeen to twenty-one seconds.[4] For a 20% decomposition of *iso*butylene at 600°, a hot contact period of 200 seconds was required. With 700° temperatures, the rate of decomposition for both hydrocarbons is markedly increased although the contrast is still apparent. For a hot contact time of twelve to twenty-one seconds, *iso*butane was broken down to the extent of 70%, whereas with *iso*butylene decomposition varied between 30 and 50%.

Still more striking a difference in the two cases is to be found in the course of the two reactions. *Iso*butane was found to decompose almost exclusively into gaseous hydrocarbons which were molecularly smaller than the original substance. *Iso*butylene, on the contrary, changed quite materially into hydrocarbons of greater molecular complexity. Nearly half of the decomposed *iso*butylene gave rise to liquid hydrocarbons whereas the remainder appeared in the form of gases. The gaseous products from both *iso*butane and *iso*butylene were similar to the extent that methane, hydrogen and propylene were important products of the decomposition, with methane always predominating.

The Mechanism of the Pyrolysis.—Any mechanism for the pyrolysis of *iso*butylene must provide an explanation not only for the simpler gaseous hydrocarbons of the reaction but also for the generous formation of aromatic hydrocarbons. As major effects, it is suggested that heat may rupture the single C—C or C—H bonds, and that it may activate the C=C double bond. The univalent radicals which are thought to be formed by rupture of the single bonds, namely, $—CH_2—C(CH_3)=CH_2$ or $—C(CH_3)=CH_2$, evidently do not give rise as such to aromatics, since the quantity of liquids formed during pyrolysis of the butanes was very small and since, for the butanes, transient radical formation was also postulated. Such univalent radicals appear to give rise to gaseous products. In the case of the double bond, it is considered that the tie is sufficiently strong to resist complete rupture, thereby creating a radical with two bonds. In the case of *iso*butylene, this is  $(CH_3)_2\underset{|}{C}—\underset{|}{CH_2}$. As a working hypothesis it is considered that radicals of the latter type are the precursors of building-up processes. Three such "activated olefin molecules," by combination, would produce a cyclohexane derivative which, at the elevated temperature of formation, would be stripped into benzene derivatives.

Summary

*Iso*butylene was found to be a more stable hydrocarbon than *iso*butane or *n*-butane. It was only slowly decomposed at 600°. The pyrolytic reactions were studied at 600, 650 and 700°, especially at 700° where the rate of decomposition was rather high. It was demonstrated that the reaction was unimolecular and largely homogeneous. The velocity constant and the heat of activation for the unimolecular reaction were calculated from the data. The various products of the reaction were identified. The mechanism of the reaction is much more complicated than that of the saturated hydrocarbons studied, but a mechanism is suggested which recognizes not only the decomposition into smaller substances but also the building-up processes into aromatic hydrocarbons.

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