[CONTRIBUTION FROM THE CATHOLIC UNIVERSITY OF AMERICA]

The Pyrolysis of Isobutylene

BY FRANCIS OWEN RICE AND LEO A. WALL[1]

In a previous investigation[2] it was established that when isobutylene is passed through a quartz tube under proper conditions of temperature, pressure and contact time, methane, propylene, allene and methylacetylene are the main products of the decomposition, which proceeds without appreciable formation of tarry or oily materials. In the work described in this paper we continued the investigation on a much larger scale which enabled us to make a more thorough examination of the nature and yields of the reaction products. Furthermore, we did some of the experiments using a large quartz decomposition tube and others using a similar tube of chrome steel and obtained identical results.

In these experiments we charged two to three kilograms of isobutylene in each run and separated and estimated all the products as well as the undecomposed isobutylene. Even for quite low percentage decompositions we obtained enough product to make accurate analysis and we also prepared allene and methylacetylene in quantity. Our results confirmed those obtained earlier in all but one respect. In the larger scale runs we found on evaporating the undecomposed isobutylene that a high boiling residue remained, which was missed in the earlier work due to its small quantity.

Experimental Method.—The apparatus used was designed to handle a charge of two to three thousand grams of isobutylene. The amount of isobutylene used was obtained by using small tanks having a tare of approximately 10 kilograms. These tanks were evacuated and weighed to ±2 g. and then cooled to −80°. When connected by means of refrigeration fittings and quarter inch copper tubing to an inverted tank of isobutylene they filled in about twenty minutes. Before closing and disconnecting the small tank it was warmed above room temperature to avoid any possibility of explosion through having the tank full of liquid at −80°. The tank was then disconnected and weighed. During the run the tank was kept in a vessel of water warmed electrically to provide the heat necessary for the evaporation of the isobutylene. The tank was connected to the apparatus through a calibrated needle valve which delivered 3–4 liters of gas at atmospheric pressure per minute. The loss in weight after the experiment gave the amount of isobutylene used. The isobutylene was better than 95% pure and contained less than 1% of C_3 hydrocarbons.

Most of the runs were made in a quartz furnace approximately four feet long and one inch internal diameter. However, in several experiments a 28% chrome steel tube of approximately the same size as the quartz tube was used. All the furnaces used were designed with an extension on either end which was covered with a flat piece of optically clear glass. Through these windows one could see through the entire length of the inside of the furnace. The furnace was heated electrically in the usual manner and the temperature was measured by an iron-constantan thermocouple located in a well running the length of the furnace. The couple was connected to a Brown recording potentiometer graduated from 500° to 1000°. The pressure was always recorded by a mercury manometer at the exit end of the furnace.

The exit gases from the furnace were first cooled to about −80° and the condensate caught in two five-liter traps. The gases not caught by these traps passed through a Cenco Hyvac pump containing glycerol instead of oil and the gases leaving the pump, now at atmospheric pressure, were passed through two more traps at −80°. The uncondensed gases then passed to a precision wet-test gas meter. In some experiments a third trap cooled by liquid air was inserted just before the gas meter.

A vapor density determination which was carried out on the gases leaving the apparatus, together with the volume of gas recorded by the gas meter, gave the total weight of gases leaving the apparatus.

The liquid contents of the various traps were combined and analyzed by low temperature distillation in a 25-mm. i. d. Podbielniak column using a specially made cooling system which circulated acetone cooled with Dry Ice through the top of the column. The distillation analysis was supplemented in various ways by gas analysis. The presence of allene was confirmed by hydrogenation and by its reaction with mercuric chloride[3]; that of methylacetylene by hydrogenation and by its reaction with silver ammonia solution.

Analytical Data.—We are presenting the analytical data for one experiment in which the gases at about 100 mm. pressure were first passed through two five-liter traps at −80° and then after passing through the pump and coming to atmospheric pressure were passed through two more traps at −80°. The remaining gas passed through a precision wet test meter, the volume and density were measured and a sample was analyzed. In experiment S.24.4, the contents of the four traps were mixed and distilled in a 25-mm. Podbielniak column as described in the previous section. The following results were obtained:

Fraction	B. p. range, °C.	% Total dist.	Substances
1	<−50	Trace	.....
2	−50 to −40	23	Propylene
3	−40 to −35	5	Propylene, allene
4	−35 to 34	37	Allene (b. p. −34.3°)
5	−34 to −24	6	Allene, methylacetylene
6	−24 to −23	26	Methylacetylene(b. p.−23.3°)
7	−23 to −10	3	Methylacetylene, isobutylene

Fractions (3), (5) and (7) were separately analyzed on a 5-mm. Podbielniak column. Fraction (3) contained 58% of allene and fraction (5) contained 34% of allene and the rest methylacetylene. Fraction (7) contained 72% of methylacetylene and the rest isobutylene. The total weight of fractions (1) to (7) inclusive was 160 g.

The gas not condensed at −80° occupied 277 liters at N. T. P. and weighed 198 g. It had the following composition:

	Wt. %
H_2	3
CH_4	64
C_2H_4	Trace
C_2H_6	2
C_3H_6	4

(1) This is taken from the dissertation presented by Leo A. Wall for the degree of Doctor of Philosophy in the Catholic University of America.

(2) Rice and Haynes, THIS JOURNAL, **70**, 964 (1948).

(3) Lossen and Dorno, *Ann.*, **342**, 185 (1905).

TABLE I

THERMAL DECOMPOSITION OF ISOBUTYLENE

The first four experiments were done using a quartz decomposition tube, 60 cm. long by 3 cm. diameter. The second test of four experiments were done in a 28% chrome steel tube of approximately the same size.

Expt.	J7.4	J30.4	A15.4	A19.4	S22.4	S24.4	03.4	07.4
Moles C_4H_8 through furnace	50.2	38.5	47.0	81.0	40.2	48.0	47.0	37.8
% decomposed	24	31	38	13	12	16	28	38
Temp. furnace, °C.	875 ± 25	875	855	855	850	850	835	875
Press in furnace, mm.	60–90	60–70	80–130	60–80	45	80–120	175	180
Contact time, sec.	0.14	0.12	0.26	0.13	0.14	0.16	0.39	0.49
Moles C_3H_6 per mole C_4H_8 decomposed	.07	.07	.06	.12	.09	.15	.10	.08
Moles C_3H_4[a] per mole C_4H_8 decomposed	.24	.26	.23	.54	.50	.43	.32	.18
Residue per g. C_4H_8 decomposed, g.	.23	.41	.25	.17	.12	.18	.25	.18

[a] $CH_2{=}C{=}CH_2$ plus $CH_3{-}C{\equiv}CH$.

	Wt. %
$CH_2{=}C{=}CH_2$	5
$CH_3{-}C{\equiv}CH$	3
C_4H_8	21

We obtained this analysis by combining the products from several experiments in the following way. A liquid air trap was inserted before the gas meter in order to condense everything except hydrogen and methane. The volume and density of the gas was measured and it was analyzed by fractional combustion for hydrogen and methane. The material condensed by liquid air was analyzed by distillation in a small Podbielniak column.

After distilling off all substances boiling lower than −10° we had 2335 g. of liquid which was mainly isobutylene. We distilled off the isobutylene and combined the residue (77 g.) with the residues of other experiments. This material consisted chiefly of benzene, toluene and naphthalene, together with somewhat lesser amounts of the xylenes, anthracene, and other solids of an aromatic nature. Mesitylene was not found although we looked carefully in order to avoid missing a small amount of it.

Discussion and Results.—Eight runs were made altogether at temperatures in the range 850–900° and in the pressure range 50–200 mm. The contact time was a few tenths of a second. The data are shown in Table I from which it will be seen that the results obtained with the quartz tube and the chrome steel tube are not significantly different.[4]

The conditions under which the decomposition is conducted are very important and if the pressure, temperature and contact time are not regulated as described in the previous investigation,[2] there is copious formation of tar and oils. Presumably these are produced by polymerization of the allene and methylacetylene which are either not mentioned by previous workers[5] or definitely reported to be absent.

Summary

1. The mechanism of the thermal decomposition of isobutylene is very sensitive to the conditions of pressure, temperature, and contact time under which it is conducted.

2. If the decomposition is conducted as described in this paper, the major low molecular weight products are methane, allene and methylacetylene accompanied by much smaller amounts of hydrogen, propylene, ethane and ethylene.

3. Although we avoided the formation of tar and carbon, there is some formation of various aromatic compounds, such as benzene, toluene, naphthalene, anthracene, etc. Mesitylene was found to be absent.

(4) See Hurd and Eilers, *Ind. Eng. Chem.*, **26**, 776 (1934).

(5) Noyes, *Mass. Inst. Tech., Quarterly*, **1** 278 (1888); Tropsch, Parrish and Egloff, *Ind. Eng. Chem.*, **28**, 581 (1936); Hurd and Spence, THIS JOURNAL, **51**, 3561 (1929); Hurd and Blunck, *ibid.*, **59**, 1869 (1937).

WASHINGTON, D. C. RECEIVED JANUARY 31, 1948