[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF NORTHWESTERN UNIVERSITY]

The Pyrolysis of Isobutylene at Very Low Conversions

BY CHARLES D. HURD AND FORD H. BLUNCK[1]

A few years ago, Schneider and Frolich[2] presented an ingenious plan which attempted to distinguish the primary and secondary reactions in the thermal decomposition of hydrocarbons by progressively varying the rate of flow and extrapolating the yields of reaction products back to zero per cent. conversion. The moles produced from each 100 moles of substance were plotted against the per cent. of substance reacting. Regarding the method, the authors stated: "It will readily be seen that, when plotted in this way, the curves representing products formed by secondary and subsequent reactions must go through the origin. The method obviously does not distinguish between products formed directly and those formed indirectly through an intermediate not stable enough to be detected in the cracked products."

The same method was used by Neuhaus and Marek, who stated[3] "that although this method differentiates between secondary and primary products, it does not permit the detection of unstable intermediates, such as free radicals."

Although not intended to apply to radicals, it is clear that those sponsoring the method intended it to apply to all compounds which were isolable in the reaction products, and any compound which persisted in the products as zero conversion was approached would meet the requirements of being a primary product.

A serious limitation of this method was mentioned by Hurd and Eilers.[4] They pointed out that situations might arise wherein secondary products would persist along with the primary compounds as zero conversion was approached. As a matter of fact, this should occur in all instances except those wherein the substances formed (A) are more stable than the original substance (B). This appears self-evident because a temperature which will initiate the breakdown of B will also cause pyrolysis of part of A before its escape from the hot zone. The new compounds from A would be secondary products but they should persist even toward zero conversion.

In a study of isobutylene at 700°, Hurd and Eilers were able to confirm this reasoning. The gaseous products which remained when the yields formed at real conditions were extrapolated to zero conversion were methane, propylene and ethylene. Hydrogen and acetylene vanished from the products during the extrapolation. Methane and ethylene are both known to be more stable than isobutylene, whereas propylene and isobutylene are about equally stable.[5] Methane and propylene may be visualized readily as primary products, but ethylene may not be so regarded because its production requires the splitting of two carbon-to-carbon bonds.

Since the conversions used by Hurd and Eilers extended to a minimum value of only 8%, it was decided to investigate isobutylene at much lower conversion values. At conversions below 1%, ethylene should practically vanish from the products if the assumptions of the zero conversion method as originally proposed were correct. For reasons set forth above, however, it seemed that ethylene should persist and such was found to be the case. Obviously, this limits the usefulness of the zero conversion method, although there should be many reactions where its application would not be open to question.

In Hurd and Eilers' experiments the unsaturated hydrocarbons were analyzed by selective absorption, and the methane by combustion. A much more delicate analytical method was required in the present work. The plan adopted was to condense the products with liquid air and to separate the methane, ethylene and propylene fractions by distillation through an analytical column of the Podbielniak[6] type. In this manner, the great bulk of undecomposed isobutylene was removed from the reaction products and each reaction product was isolated as such. To identify the substances in the various fractions, each was analyzed in turn by selective absorption and combustion. The results showed definitely that methane, propylene and ethylene were formed at these low conversions. There was no detectable production of hydrogen, acetylene, ethane or iso-

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[1] Universal Oil Products Company Fellow, 1934-1935.

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

[3] Neuhaus and Marek, *ibid.*, **24**, 401 (1932).

[4] Hurd and Eilers, *ibid.*, **26**, 776 (1934).

[5] Hurd and Meinert, THIS JOURNAL, **52**, 4981 (1930).

[6] Podbielniak, *Oil Gas J.*, **28**, 58 (1929); **29**, 235 (1930).

butane. The quantity of ethylene in the gaseous reaction products varied from 11 to 13%, and there was no indication that the yield was tending to drop to zero.

Undoubtedly, the ethylene from these experiments originates in part from the propylene, since propylene is known to break down in this manner. To a certain extent, however, the ethylene may originate in another manner. Higher hydrocarbons and polymeric substances are known to be formed from isobutylene[7] and other olefins[8] at high temperatures. Breakdown of these compounds as the reaction progressed would give rise to ethylene in the reaction products. No attempt was made in the present study to isolate the higher-boiling products.

Experimental Part

Isobutylene was prepared by the dehydration of redistilled *t*-butyl alcohol with oxalic acid. It was dried thoroughly and condensed in a steel tank. To make sure that no other gases were included, some of the isobutylene in the tank was allowed to distil out before closing the valve. The hydrocarbon was then transferred to 18-liter bottles (by displacement of saturated salt solution) and it was displaced from the bottles by a steady stream of saturated salt solution. The gas was directed into the top of a vertical Pyrex reaction tube which was heated electrically to 650°. A wet test meter and a drying tower were placed between the bottles and the tube. The bottom of the tube was connected to an ice-cold receiver which, in turn, was attached to the gas-collecting bottle. In the large run when only 0.1% of the isobutylene was decomposed it was impractical to collect all the products as gas. Therefore, the isobutylene and propylene were liquefied from the gas stream as follows. The ice-cold receiver was attached to a flask at −80°. The latter was topped with a Davis column,[9] the head of which was cooled also to −80°. The gas which was not liquefied by this reflux condenser was taken to the gas collecting bottle. At the conclusion of the run, the propylene and about 7000 cc. of the isobutylene were distilled into the gas bottle through the Davis column. This gas was then fractionated through the Podbielniak column in the usual way. The results are summarized in Table I.

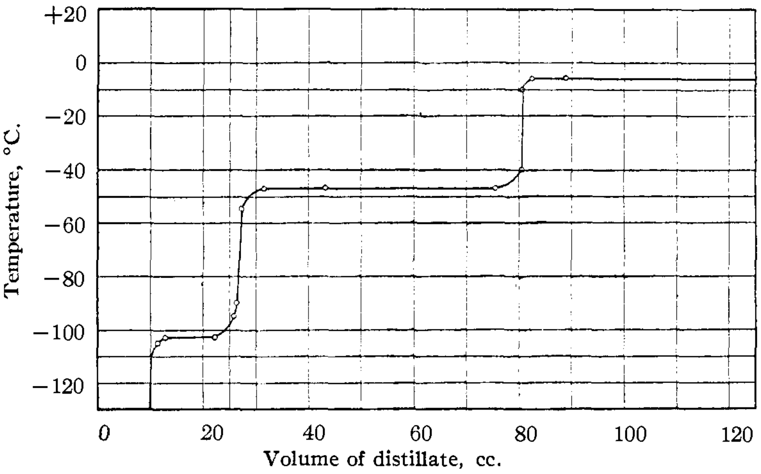

Fig. 1.—Distillation curve for hydrocarbons from isobutylene.

TABLE I

PYROLYSIS OF ISOBUTYLENE AT 650°

Vol. tube, cc.	32.3	32.3	24.5
Isobutylene taken, cc.	6500	6665	110960
Rate of flow, cc./min.	233	320	350
Contact time, sec.	2.7	2.0	1.3
Vol. of gases formed per 1000 cc. of C_4H_8 taken, cc.	13.1	4.5	1.2
Extent of decomposition, %	1	0.4	0.1
SUMMARY OF GAS ANALYSIS			
Methane formed, cc.	50.0	15.5	67.2
Ethylene formed, cc.	10.1	3.0	18.3
Propylene formed, cc.	24.8	9.4	48.6
H_2, C_2H_6, C_2H_2, C_4H_{10}, cc.	0.0	0.0	0.0
PERCENTAGE OF REACTION PRODUCTS			
Methane	59	55	50
Ethylene	12	11	13.6
Propylene	29	34	36

Analytical Details.—The volumes of the fractions which were collected by distilling the reaction products through the Podbielniak column were read from distillation curves. Each fraction was analyzed further by selective absorption or combustion. The curve for the experiment at 0.1% decomposition is shown in Fig. 1. The other analytical values were obtained similarly.

The unliquefied portion and that which distilled up to −110° represented methane and air. Its volume was 294.4 cc. Analyses for carbon monoxide, hydrogen or olefins were negative. By combustion, 61.0 cc. of the gas yielded 13.9 cc. of carbon dioxide; therefore, 67.2 cc. of methane was present in the fraction.

The fraction (16.1 cc.) collected at −110 to −90° was insoluble in 83% sulfuric acid but soluble in fuming (8%) acid. Therefore, ethylene was the only olefin in this fraction. Paraffin hydrocarbons were absent also.

The fraction (54.2 cc.) collected between −55 and −40° was chiefly propylene but it contained ethylene and isobutylene as well. Analysis of 49.1 cc. of it gave these data: 3.05 cc. soluble in 63% sulfuric acid; 44.0 cc. soluble in 83% acid; 2.05 cc. soluble in fuming acid. Therefore, the fraction contained 3.4 cc. of isobutylene, 48.6 cc. of propylene and 2.2 cc. of ethylene.

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(7) Hurd and Spence, THIS JOURNAL, **51**, 3569 (1929).

(8) Wheeler and Wood, *J. Chem. Soc.*, 1819 (1930).

(9) Davis, *Ind. Eng. Chem., Anal. Ed.*, **1**, 61 (1929).

The final isobutylene fraction (b. p. about −6°) dissolved completely in 63% sulfuric acid solution.

Summary

Isobutylene, when decomposed at 650° to the extent of 0.1–1.0%, gives rise to methane, propylene and ethylene as the only gaseous reaction products. The fact that ethylene persists even at 0.1% conversion emphasizes the need for caution in interpreting the "initial products of reaction" by the zero-extrapolation method.

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[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY OF THE UNIVERSITY OF PENNSYLVANIA]

The Reaction of Brom Phenol Blue, Iodo Phenol Blue and Chlor Phenol Blue with Hydroxyl Ion[1]

BY FRANK W. PANEPINTO AND MARTIN KILPATRICK

In the study of the dissociation constants of indicators it has been shown that brom phenol blue reacts with hydroxyl ion to give a colorless solution.[2] This paper presents the results of a study of this reaction and the reaction of tetrachloro- and tetraiodophenolsulfonphthaleins with hydroxyl ion. From a study of the kinetic electrolyte effect it will be shown that the reaction is between the bivalent anion and the hydroxyl ion.

Experimental Part

The indicators used in this study were specially purified products.[3]

Analysis gave the following:

	M. p. °C corr.	Found, %	Calcd., %
Tetrabromophenolsulfonphthalein (Brom phenol blue)	270–271	S, 4.55 Br, 47.76	4.77 47.73
Tetraiodophenolsulfonphthalein (Iodo phenol blue)	259–260	I, 59.05	59.12
Tetrachlorophenolsulfonphthalein (Chlor phenol blue)	255	Cl, 28.70	28.80

Stock solutions of the indicators were prepared by dissolving the acid in alcohol, adding sufficient carbonate-free sodium hydroxide to form the monosodium salt, evaporating off the alcohol and dissolving the salt in water. All stock solutions were approximately 2 × 10^{-4} molar and were diluted tenfold for the experiments. The reaction was followed by measuring the disappearance of the blue color by means of a Duboscq colorimeter. All solutions were referred to standard solutions which were freshly prepared from stock solutions. The experiments were carried out in a thermostat regulated to ±0.005° and the solutions were protected from light except during the transfer of samples for analysis. All salts were C. P. products purified by crystallization.

Preliminary experiments had shown that the rate of disappearance of the blue color followed the monomolecular law[2] as shown in Table I.

TABLE I

FADING OF BROM PHENOL BLUE AT 30°

	NaOH (moles per liter)			
	0.009		0.005	
Days	k	k_1	k	k_1
0.875	0.590	65.5	0.287	57.3
1.0	.585	64.9	.298	59.6
1.167	.581	64.5	.290	58.0
1.875	.574	63.8	.302	60.5
2.17	.578	64.2	.295	59.0
2.83	.592	65.6	.299	59.8
3.0	.583	64.8	.285	57.0
3.167	.566	62.8	.305	60.9
	Average	64.5		
3.83			0.286	57.1
4.0			.293	58.7
4.83			.288	57.5
5.0			.303	60.6
5.21			.290	57.9
6.0			.295	59.0
6.17			.299	59.7
6.83			.297	59.3
7.0			.285	57.0
7.83			.302	60.4
8.0			.300	60.0
			Average	58.9

The velocity constant k is calculated from the equation $k = 2.30/t \log a/(a-x)$ where a represents the initial concentration of the bivalent anion, $a-x$ the concentration at time t. The unit of time is the day. From Table I it is seen that the reaction at constant hydroxyl ion concentration follows the monomolecular law and from

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[1] Abstracted from the dissertation of Frank W. Panepinto presented to the Faculty of the Graduate School of the University of Pennsylvania in partial fulfilment of the requirements for the degree of Doctor of Philosophy, April, 1937.

[2] Chase and Kilpatrick, THIS JOURNAL, **54**, 2284 (1932); Kilpatrick, *Chem. Rev.*, **16**, 57 (1935).

[3] The authors take this opportunity to acknowledge the kindness of Dr. W. C. Harden of Hynson, Westcott and Dunning Co. in supplying these indicators.