The deposit formed in leaded gasolines needs special study, and it appears possible that a leaded gasoline should meet different breakdown requirements than lead-free products.

Work is at present under way with the hope of so modifying the bomb test that the copper-dish operation, with its lack of controls, may be discarded ultimately.

Acknowledgment

The work described here represents the efforts of many workers. The early studies of E. B. Hunn and C. L. Gutzeit along this line have been heavily drawn upon, and much of the experimental data used herein has been obtained by R. H. Decker, J. F. Dudley, L. Z. Wilcox, and other members of these laboratories. To E. W. Dean and H. G. M. Fischer much appreciation is due for frequent thorough criticisms and helpful suggestions, and to C. R. Wagner and the Pure Oil Company for assistance in securing samples.

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Thermal Decomposition of Isobutane into **Primary Products**

L. F. MAREK AND MAX NEUHAUS

Research Laboratory of Applied Chemistry, Massachusetts Institute of Technology, Cambridge, Mass.

ROM a practical standpoint the study of the thermal dissociation of the aliphatic hydrocarbons of lower molecular weight has as an object the utilization of the large quantities of these materials available in the form of natural It is posand refinery gases. sible, also, that information regarding the rates and mechanism of dissociation of the lower hydrocarbons will be applicable, by extrapolation, to the cracking of petroleum oils. From a theoretical standpoint the thermal dissociation of these hydrocarbons offers an approach to a refined theory of reaction velocity. The tendency to examine these homogeneous reactions from the point of view of the kineticist rather than from that of the descriptive organic chemist has

made necessary the accumulation of data of greater accuracy than that formerly available with relatively impure materials and inexact methods of analysis.

The present work forms a portion of a general program which has as its object the accumulation of accurate information regarding the mechanism and rate of dissociation of the lower paraffinic and olefinic hydrocarbons, this information to be used in the formulation of generalizations regarding the thermal stability and chemical nature of the materials. It is obvious that a program such as this could be most satisfactorily conducted by a division into separate phases, each of which could be thoroughly investigated as a separate project. The results of the studies on the primary dissociation of ethane (9), propane (9), and n-butane (5), and on the rate of dissociation of ethane and propane (4) have already been published.

The pyrolysis of isobutane at 600° and 650° C. was investigated for the purpose of determining the primary products of the thermal dissociation. Decomposition was varied over a wide range, and the results plotted in such a way that the curves could be extrapolated to zero per cent cracked in order to indicate primary-product distribution. Listed in the order of their relative importance, the primary dissociation products were found to be: (1) hydrogen and isobutylene, (2) methane and propylene, and (3) ethane. Velocity constants for the thermal dissociation rates at 600° and 650° C. have been calculated. By use of over-all dissociation-rate constants and primarydissociation distribution, rate constants for the individual primary-dissociation reactions of ethane, propane, n-butane, and isobutane over the temperature range of 550° to 650° C. have been calculated.

PREVIOUS WORK

The literature contains little data on the thermal dissociation of pure isobutane into primary products. Pease (θ) , Pease and Durgan (7), and Hurd and Spence (3) have reported on the thermal decomposition of isobutane in the pure state. Pease, and Pease and Durgan were concerned mainly with over-all decomposition rates, and made no attempt at complete product analyses. Hurd and Spence, while interested in yields, carried out more detailed analyses of the reaction products, but did not make runs in which the amount of isobutane reacting was varied over a wide range. Interpretation of these data for the purpose of determining distri-

bution of primary products necessitates rather wide extrapolations and certain assumptions regarding secondary reactions which may be questioned.

A summary of the product yields obtained in previous investigations of the thermal decomposition of isobutane is as follows:

	VARIATIONS OBTAINED IN MOLES OF EACH PRODUCT
Product	Formed per 100 Moles of Isobutane Reacting
Hydrogen	29.6 to 62.1
Isobutylene	29.8 to 37.7
Methane	41.7 to 80.3
Propylene	28.6 to 33.9
Ethane	0 to 12.1
Ethylene	5.9 to 16.4

The primary reactions that have been suggested are:

$(CH_3)_3CH = (CH_3)_2C:CH_2 + (CH_3)_3CH = CH_3CH:CH_2 +$	-	${ m H_2} { m CH_4}$	(1) (2)
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Hurd and Spence (3) postulated that the molecular or nascent hydrogen present during the dissociation reacted with the isobutylene to form methane and propylene, and with the propylene to form methane and ethylene. This was suggested in order to account for the high methane yields obtained. In the presentation of data on the cracking of isobutylene, Hurd and Spence also state that the addition of hydrogen increased the quantities of methane and propylene formed.

DECOMPOSITION OF ISOBUTANE

As has been previously pointed out (5, 9), the determination of primary products formed in the thermal decomposition of a hydrocarbon requires that secondary reactions be eliminated entirely or that their influence on the nature of the products formed be known. The first alternative could, perhaps, be achieved by cracking the original hydrocarbon to only a very small extent. However, the difficulty of separating extremely small quantities of products from the original hydrocarbon and the limitations placed on their analysis by methods now available make the successful application of this procedure very doubtful. The influence of the secondary reactions of the product compositions may, however, be determined quite simply without an investigation of the nature of these secondary reactions. This is done by decomposing the hydrocarbon under investigation in varying degree and plotting the data so obtained in such a way as to permit the extrapolation of the curves to zero per cent decomposed. The extrapolation may be carried out most conveniently by drawing curves representing the moles of each product formed per 100 moles of isobutane reacting vs. the percentage of isobutane reacted. Thus, curves for the primary products intercept the vertical axes at points corresponding to the proportions in which they are first formed, while curves for the secondary products pass through the origin. Obviously, the method distinguishes between primary and secondary products, but it does not allow the detection of unstable, intermediate reaction products.

tor. The true temperature of the gas leaving the reactor was measured by means of a compensated thermocouple, and the temperature was held at the desired value by suitable manipulation of the control rheostats. After leaving the reactor, the unchanged isobutane passed with the reaction products through a preliminary cooler of copper tubing immersed in a mixture of solid carbon dioxide and acetone, and then into a cold trap submerged in a similar bath. The gas not condensing in the cold trap was collected in a calibrated gas bottle by displace-ment of saturated zinc sulfate solution. This gas contained methane, ethane, ethylene, propylene, some isobutane, and most of the hydrogen formed in the pyrolysis. The condensate con-tained the remainder of the products as well as the greater part of the unchanged isobutane.

Immediately at the end of each run, fractionation of the liquid which had collected in the cold trap was accomplished in a Davis column (1). The several fractions obtained were collected over zinc sulfate solution in displacement burets or in 20-liter bottles, depending on the volumes of the cuts. Analyses of the fractions were made in a Williams gas analysis apparatus, except in cases where the olefin concentrations were so low as to render absorption methods inaccurate. Under those conditions, the olefins were determined by titration of gas samples with 0.02 N potassium bromide-potassium bromate solution, using a modifica-tion of the method described by Francis (2). This method was also employed in distinguishing between mono- and diolefins in the analyses of the products from runs in which the degree of decomposition was large. The total percentage of olefins in a given fraction was determined by absorption in 92 per cent sulfuric acid, and the number of double bonds per mole of gas estimated by means of the titration method. From data obtained in this way, the concentrations of, say, isobutylene and butadiene in the C₄ fraction, could be calculated. The following absorbents were employed in the Williams apparatus: 64 per cent sulfuric acid for isobutylene, 92 per cent sulfuric acid for propylene, bromine in 10 per cent potassium bromide solution for ethylene, pyrogallol for oxygen, and 33 per cent potassium hydroxide for carbon dioxide. In absorbing propylene, the usual correction for the partial absorption of ethylene was applied. Hydrogen was determined by combustion over copper oxide at 300° C., and the saturated hydrocarbons were estimated from data obtained in exploding small samples of the residue gas from the absorption analysis with excess oxygen. From three to six explosions were made in each case in order to obtain good average values for the ratio of contraction to carbon dioxide.

The noncondensed gas, however, contained three paraffins-i. e., methane, ethane, and isobutane-and the explo-

	AMOUNT	<u> </u>	Mo	DLES PRODUC'	трев 100 Мо:	LES OF ISOBU	TANE REACTI	NG		MATERIAL
Run	Reacting	H_2	C_4H_8	CH_4	C_3H_6	C_2H_4	C_2H_6	C_4H_6	Liquid ^a	BALANCED
	%									%
					AT 600° C.					
330	1.38	60.5	64.0	37.9	32.2	0.8	3.4			- 3.5
340	1.93	62.3	61.9	38.6	35.5	0.9	3.6			- 1.1
29	4.57	64.3	63.6	46.3	31.7	1, 0	0.7			-16.1
310	7.35	62.7	63.1	43.4	32.7	1.4	1,6			- 4.7
32	10.76	66.8	55.8	48.3	39.4	3.2	1, 4			+12.1
30	12.90	68.4	46.5	49.6	46.5	2.8	7,2			- 6.8
37	17.33	71.8	42.3	61.3	49.2	5.8	2.1			-12.9
43c	46.1	48.1	41.9	55.6	36.6	9.1	3.8	5.4	4.73	+ 4.6
42¢	68.3	43.1	36.2	67.1	36.5	11.7	8.5	4.2	4.65	0.0
					AT 650° C.					
394	6.93	59.8	61 2	42 3	34 8	2.3	1.8			- 5.6
380	13.30	58.8	58.1	47.9	36.3	3.1	1.6			- 2.3
360	16.67	63.6	52.3	55.0	40.9	3.9	1.2			- 9.1
41¢	43.7	49.4	40.7	55.7	38.9	13.5	1.0	7.4	4.4	0.0
400	73.8	48.5	29.5	78.6	32.6	15.5	2.3	7.0	9.4	+ 8.9
^a Yield of	liquid hydrocarb	ons expressed	as grams per	100 grams of	f isobutane rea	eting.				
b Gain or	loss based on inn	ut as measure	d by flowmete	r						
e Runs nlo	otted.									

TABLE I. CRACKING OF ISOBUTANE

PROCEDURE. The isobutane used in this work was kindly furnished by the Phillips Petroleum Company. As received, the material contained small amounts of ethane and propane but no heavier hydrocarbons. Ethane and propane were completely removed by distilling off a portion of the liquid under a high reflux ratio in a low-temperature fractionating column.

The isobutane was passed through an all-glass flowmeter, scrubbed with concentrated sulfuric acid, and dried over calcium chloride. The gas was then passed through a 24 imes 1 linch (61×2.5 cm.) fused silica preheater maintained at a wall temperature of 540° C. From the preheater the gas entered directly into a 24 × 0.5 inch (61×1.25 cm.) fused silica reacsion data alone were not sufficient to fix the composition. But, since the moles of ethane and of ethylene in the liquid could be determined from the analyses of the Davis column fractions, and since the concentrations of ethylene in the noncondensed gas were known from absorption data, the ethane percentage could be calculated through the use of a proper relative volatility factor. The relative volatility of ethane with respect to ethylene at the cold trap temperature of -78° C. was calculated from the respective vapor pressures with the introduction of a Raoult's law deviation factor of -10 per cent for the ethylene. The value used was 0.525. By means of this calculation of the ethane concentration independently of the explosion data, it was possible to calculate the percentages of the two remaining hydrocarbons present from the experimentally determined ratio of contraction to carbon dioxide.

DISCUSSION OF RESULTS

The calculated results obtained in the runs at temperatures of 600° and 650° C. are presented in Table I. The temperatures given are not average temperatures through the cracking zone, but are exit gas temperatures as indicated by a compensated thermocouple in the gas stream. As will be shown later, the effective temperatures, as calculated



FIGURE 1. CURVES SHOWING AMOUNT OF EACH PRODUCT . FORMED AT 600° C.

from over-all reaction velocity constants obtained from the present data, differed from these exit temperatures but approached them at long times of contact.

In Figures 1 and 2 the data are plotted as described abovei. e., as moles of each product formed per 100 moles of isobutane reacting. It was found that those runs at 600° C. in which the material balances were in error by 6 per cent or more, gave points which did not lie very well on the curves obtained from runs with good material balances. Since the data from runs with good material balances sufficed to define the curves and since greater clarity of presentation is obtained, the points for the inferior runs are omitted from the plots. In Table II the product distributions obtained by extrapolating the curves to the ordinate axes are listed. Ethane definitely seems to be a primary product, although the mechanism by which it is formed is not clear. It is possible that ethane may be formed in a bimolecular reaction such as that found by Schneider and Frolich (9) in the pyrolysis of propane. A reaction of this type would be expected to yield ethane and 2,3-dimethylbutane, but the latter compound was not positively identified among the reaction products. Whether this was due to its relative instability or to a fault in the analytical procedure is not known. However, only a very small fraction of the isobutane reacts in this way.

TABLE II. DISTRIBUTION OF PRIMARY PRODUCTS FROM THERMAL DISSOCIATION OF ISOBUTANE

	Moles Formed pe	r 100 Moles	0
PRODUCT	ISOBUTANE I At 600° C.	Reacting At 650° C.	
Hydrogen Isobutylene	63.0 63.0	63.0 63.0	
Methane	35.0	36.0	
Ethane	2.5	1.5	

The formation of large quantities of methane and the accompanying consumption of hydrogen as the percentage of isobutane decomposed was increased simulates the results of Hurd and Spence (3). However, the data do not indicate the increase in propylene yields which would be expected if the methane were produced by the destructive hydrogenation of isobutylene. It may well be that the hydrogen reacted in the same manner with the propylene present to form ethylene and more methane, or that the isobutylene reacted to form not propylene but ethylene. The curves from the runs made at 600° C. indicate that the latter reaction might have occurred, for the slope of the methane curve is approximately twice that of the ethylene curve, while the line drawn through the propylene points is flat.

The heavier hydrocarbons, liquid at room temperature, which began to appear among the products as the fraction of isobutane decomposed reached some 40 per cent, were bright yellow in color, had a density of 0.8 to 0.9 at 25° C., exhibited great affinity for bromine even at subzero temperatures, and reacted violently with strong sulfuric acid. Owing to a lack of sufficient material, a more complete investigation of the polymers could not be carried out, but their reactivity suggests a highly unsaturated character.

The small shift in product distribution over the 50° C. temperature range investigated is of interest when it is considered that the change is marked in the case of propane and of *n*-butane. In the case of propane, a change of temperature from 725° to 650° C. reverses the order of importance of the two major primary reactions (9). At 650° C. dehydrogenation to propylene predominates:

$$C_{3}H_{8} = C_{3}H_{6} + H_{2}$$

and at 725° C. there is more tendency for the carbon linkage to rupture with formation of methane and ethylene:

$$C_3H_8 = C_2H_4 + CH_4$$

In the case of *n*-butane, a change of temperature from 650° to 600° C. has little effect on the dissociation to methane and propylene:

$$n-C_4H_{10} = C_3H_6 + CH_4$$

changes the distribution of the ethane-ethylene dissociation from about 37 to 34.5 per cent:

$$n-C_4H_{10} = C_2H_4 + C_2H_6$$

and increases the hydrogen-butylene reaction from 12.3 to 16 per cent of the total dissociation:

$$n-C_4H_{10} = C_4H_8 + H_2$$

This indicates that the energies of activation of the reactions taking place when isobutane is cracked are much more nearly the same than are the activation energies of the reactions involved in the pyrolysis of the other two hydrocarbons.

The agreement of the experimental results given in this paper with the predictions of Rice (8) based on primary free radical formation and the occurrence of reaction chains is not as good as that found in the pyrolysis of *n*-butane (5). The ratios of the number of moles of isobutane reacting to form methane and propylene to the number of moles reacting to form hydrogen and isobutylene as predicted by Rice and as obtained by experiment are:

	METHANE -	+ PROPTLENE (REACTION 2)
	HYDROGEN +	- ISOBUTYLENE (REACTION 1)
TEMP.	Predicted	Determined
° C.		
600	0.91	0.55
650	1.04	0.57

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It has already been pointed out that the gas temperatures measured were exit temperatures, and that there was a temperature gradient along the reactor. The wall temperature of the preheater was known, however, and an arithmetic mean of this and the true exit-gas temperature was taken for the purpose of calculating times of contact. These times of contact were used in calculating velocity constants by means of the first-order rate equation:

 $2.303 \log (1/1 - x) = kt$ where x = fraction of isobutane undergoing dissociation t = av. time of contact, sec. k = velocity constant

These rate constants were calculated on the assumption that negligible dissociation occurred in the preheater. The effect of reverse reactions on dissociation rates was neglected.



CURVES SHOWING AMOUNT OF EACH PRODUCT FIGURE 2. Formed at 650° C.

To determine whether the arithmetic mean gave correct values for the effective reactor temperatures, the rate constants found in the manner outlined above were compared with those obtained in a separate investigation now in progress. These latter experiments are being conducted in copper and quartz apparatus, specially designed to permit accurate determinations of temperature and time of contact. The data are presented in Table III.

TABLE III. RATE OF DECOMPOSITION OF ISOBUTANE

TEMP. OF Exit Gas ° C.	Arithmetic Mean Temp. ° C.	Isobutane Reacting %	Velocity Constant, k	Temp. Correspond- ing to Velocity Constant ° C.
600	570	1 38	0 00594	571
000	010	1.93	0.00632	011
		4.57	0.00767	
		7.35	0.00952	
		10.76	0.00928	
		12.90	0.00916	
		17.33	0.00773	
		40.1 68.3	0.0228	600
650	595	6.93	0.0463	617
		13.30	0.0633	
		16.67	0.0424	
		43.70	0.1014	
		73.80	0.1460	648

From the results of previous work on the dissociation into primary products of ethane (9), propane (9), and n-butane (5), and of the present work with isobutane, it is possible to determine the rates for the individual primary-dissociation reactions within certain temperature ranges by making use of the published data on the over-all dissociation rate of ethane (4) and of unpublished data on the over-all dissociation rates of propane, n-butane, and isobutane. This

is of interest because it makes possible a comparison of the relative strengths of similar bonds in hydrocarbons of different molecular weights and structures.

The results of this compilation are shown in Table IV, and give a comparison of the rates at which the parent hydrocarbon disappears by the various primary reaction routes. Thus, $k_{\rm H_2}$ gives the rate at which the saturated hydrocarbon disappears by splitting off hydrogen, $k_{\rm CH}$, the rate of disappearance when methane is split off, and $k_{C_2H_6}$ the rate when ethane is split off. A temperature range from about 550° to 650° C. is covered by the data.

TABLE IV.	DISSOCIATION	RATES	FOR	INDIVIDUAL
	Primary Ri	EACTION	s	

Hydrocarbon			R SPLITTING OF	OF:
Gab	T	H2	CH_4	C ₂ H ₆
Dilana	- 0,	0.00010		
Ethane	800	0.00019		
	625	0.00000		••••
	650	0.00203		
	675	0.00000	• • • •	• • • •
_	070	0.01850		• • • •
Propane	550	0.00026	0.00019	
	575	0.00100	0.00076	
	600	0.00360	0.00274	
	625	0.01175	0.00895	
	650	0.03725	0,02830	
	675	0.11000	0,08360	
n-Butane	525	0.00096	0.00029	0.000207
	550	0.00040	0.00121	0.000863
	575	0.00157	0.00475	0.00338
	600	0.00552	0.01671	0.01190
	625	0.01540	0.05330	0.04050
	650	0.04610	0.18000	0.13900
Isobutane	550	0,00132	0.000735	
	575	0.00454	0,00252	
	600	0.01368	0.00759	
	625	0.03750	0.02083	
	650	0.10400	0.05880	

Conclusions

The primary products of the thermal dissociation of isobutane at exit-gas temperatures of 600° and 650° C. were found to be as follows:

	Moles Formed p Isobutane	ER 100 Moles of Reacting
PRODUCTS	At 600° C.	At 650° C.
Hydrogen and isobutylene	63.0	63.0
Methane and propylene	34.5	36.0
Ethane	2.5	1.5

The average temperatures as estimated from the velocity constants were 571° and 617° C., respectively, under conditions where the amount of dissociation was small.

The small variations obtained in the primary-product distribution indicate that the energies of activation of the two principle dissociation reactions of isobutane are very nearly equal over the temperature range investigated.

Reaction rates for the individual primary dissociation reactions of ethane, propane, n-butane, and isobutane over the temperature range of 550° to 650° C. have been shown.

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