

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

THE THERMAL DISSOCIATION OF ETHANE, PROPANE, NORMAL BUTANE AND ISOBUTANE. PRELIMINARY STUDY¹

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In view of the fundamental importance in petroleum chemistry of the thermal dissociation of hydrocarbons, it is surprising to find how few quantitative data on the subject have been published. Only methane and ethane, the lowest members of the series of aliphatic saturated hydrocarbons, have been studied at all thoroughly, and in these cases the published work is by no means exhaustive. This field is attractive in both its theoretical and practical aspects. It is to be hoped that catalytic methods may prove of value. Before these are applied, however, some information as to the uncatalyzed reactions is highly desirable. On this account we have made a preliminary study of the thermal dissociation of propane, normal butane and *isobutane*. A somewhat more thorough investigation on ethane is in progress. The results of the preliminary investigation are given in this report. The work is being continued.

Experimental Method

The flow method has been used. The gases were passed at measured rates through a heated tube of known volume and the products collected, analyzed and measured.

The only experimental difficulty concerns the gas analysis, and this is a serious one. It is an easy matter to determine the total unsaturated hydrocarbons by absorption in dilute bromine water, hydrogen by fractional combustion with copper oxide at 300–350°, and the total saturated hydrocarbons by combustion with copper oxide at 500–550°, as well as the average composition of the latter by absorption in caustic solution of the carbon dioxide formed on combustion. A more detailed analysis requires liquefaction and fractionation, which must be closely controlled if it is desired to distinguish isomers such as normal butane and *isobutane*. In this preliminary investigation, we have limited ourselves to a single separation at –79°, measuring and analyzing both the condensed and uncondensed fractions. At this temperature about $\frac{1}{6}$ of the hydrogen

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and probably $1/4$ to $1/2$ of the methane dissolves in the condensate. Analysis of the uncondensed portions proved that the saturated hydrocarbons therein must be chiefly methane, and when allowance was made for the original hydrocarbon uncondensed (the vapor pressure of propane at -79° is 0.18 atm., and of butane is 0.015 atm.) the balance corresponded very closely to methane. This separation therefore sets a minimum to the amount of methane formed. A maximum is obtained by assuming that the only saturated hydrocarbons in the analyzed gases are the original and methane.

The gases which were used were obtained compressed in cylinders. Their behavior on condensation indicated a high degree of purity of all except the ethane. The analyses which follow have been calculated in terms of the chief constituent and that next higher or lower in the series according as the ratio of carbon dioxide to hydrocarbon was higher or lower than the ideal value. Ethane— C_2H_6 , 83.5%; CH_4 , 15.0%; N_2 , 1.5%. Propane— C_3H_8 , 97.5%; C_2H_6 , 2.0%; N_2 , 0.5%. *n*-Butane— C_4H_{10} , 97.5%; C_3H_8 , 2.0%; N_2 , 0.5%. *Isobutane*— C_4H_{10} , 97.5%; C_3H_8 , 2.0%; N_2 , 0.5%.

The arrangement of apparatus and the procedure were as follows. The gas passed from the cylinder to a calibrated resistance-tube flowmeter, equipped with a water overflow to keep the inlet pressure constant. The gas was then dried with calcium chloride and entered the heated reaction tube (of Pyrex) through a capillary tube. The outlet capillary was connected through a 3-way stopcock to a 500cc. gas receiver filled with mercury. When the gas was being collected, mercury was run out of the latter into a large leveling bulb through a capillary stopcock. By delicate regulation of this stopcock, it was possible to keep the flowmeter level exactly on the mark while collecting the whole of the off-gas.

The furnace consisted of a sheet iron core, 4 inches in diameter and 15 inches long, wound with heavy nichrome ribbon over asbestos paper. It was jacketed with magnesia pipe covering. The reaction tube occupied the middle 4 inches. The ends of the furnace were packed with loose magnesia and stopped with pieces of asbestos board. The middle section was found to be uniform in temperature to $\pm 2^\circ$.

Temperatures were measured with a calibrated chromel-alumel thermocouple encased in a Pyrex tube which was ordinarily in contact with the center of the reaction tube.

In making a run, the furnace was brought to temperature and the gas flow started, ample time ($1/2$ -1 hour) being allowed to attain a steady state. The exit tube was then connected with the gas receiver on the minute and the whole of the off-gas collected for exactly ten minutes. During this time the flow was kept constant as already indicated, and the temperature was closely controlled by hand regulation of the heating current. The off-gas was then divided into two fractions by passing through a trap held at -79° into another reservoir. Five slow passages back and forth were carried out. Each fraction was then measured and analyzed.

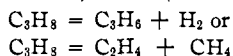
The contact time was obtained by dividing the volume of the reaction tube by the mean of the volumes of entering and exit gas passing per second, this mean being corrected to the temperature of the tube.

Interpretation of Experimental Data

Our results give the composition and volume of gas introduced, the volume of each of the two fractions, and their composition in terms of total unsaturated hydrocarbons, hydrogen and total saturated hydro-

carbons together with the average composition of the latter. The following preliminary conclusions concerning the reactions can be drawn.

There is always a volume increase on reaction, and this increase is very nearly equal to the volume of unsaturated hydrocarbons obtained. It is also true that the volume of saturated hydrocarbon plus hydrogen in the off-gas is equal to that of saturated hydrocarbon introduced. These facts suggest a primary dissociation into olefin and hydrogen, or into olefin and saturated hydrocarbon; thus (in the case of propane)



If this view is correct and there are no secondary reactions, the volume of original hydrocarbon dissociated, the volume of lower saturated hydrocarbon formed plus the hydrogen formed, and the volume of unsaturated hydrocarbon should all be the same. Since the composition of saturated hydrocarbon in the off-gas is only known as an average, this comparison cannot be made directly. We can, however, make some assumption as to the nature of the saturated hydrocarbon formed, and then compare the result with the above deduction. When this is done, it is found that if the equality of volumes is to hold, the hydrocarbon cannot be higher than methane in any case. Our analysis of the fraction uncondensed at -79° gives a lower limit to the amount of methane, which accounts for a half to three-quarters of the total. The remainder remains indefinite, but for the present we prefer to calculate the whole as methane and we have reported it as such. Work now under way will give more definite results on this point.

In the following tables we give the contact time in seconds, the volume of hydrocarbon introduced in ten minutes (the time over which the off-gas was collected), the volume of original hydrocarbon recovered (calculated by difference, assuming the balance is methane) and the volumes of methane, hydrogen and total unsaturated hydrocarbons formed. In addition we give the percentages of dehydrogenation, "demethanation," and of loss.

Results

In Table I are given the results of comparable experiments on the dissociation of ethane, propane, *n*-butane and *isobutane* at 650° and 1 atm. pressure at an average contact time of 11 seconds (reaction tube 15.2 cc. volume; volume of hydrocarbon in, 250 cc. in ten minutes).

It is evident from Table I that under these conditions the total amount of hydrocarbon dissociated increases with the number of atoms in the molecule, the butanes being most rapidly dissociated and ethane least rapidly. The amount of hydrogen obtained from ethane, propane and *n*-butane is of the same order, while the amount of methane increases, so that it is to increased amount of demethanation that the greater disso-

TABLE I
THERMAL DISSOCIATION OF C_2H_6 , C_3H_8 , $n-C_4H_{10}$ AND $Iso-C_4H_{10}$ AT 650°

Hydro-carbon	Contact time, secs.	Vol. H.C. ^a in cc.	Off-gas in cc.				Loss	Percentage to		
			Orig. H.C.	C_nH_{2n}	CH_4	H_2		CH_4	H_2	$CH_4 + H_2$
C_2H_6	12	208	187	17	0	17	2	0	8	8
C_3H_8	11	249	172	53	41	22	6	16	9	25
$n-C_4H_{10}$	10	248	144	88	82	15	3	33	6	39
$Iso-C_4H_{10}$	11	248	138	73	57	40	5	23	16	39

^a We include in the totals of hydrocarbons introduced the small amounts of foreign hydrocarbons, except in the case of ethane, when 38 cc. of methane was also present.

ciation of the higher normal hydrocarbons is due. *Isobutane* dissociates at the same rate as normal butane but gives a very different ratio of products. Thus, 40% of the *isobutane* dissociated is dehydrogenated as against 15% of the normal butane. It would seem, therefore, that the total rate of dissociation is a function of the size of the molecule only, while the nature of the products depends on the structure.

Further data on the dissociation of propane, normal butane and *iso*-butane at other rates are given in Table II.

TABLE II
INFLUENCE OF CHANGING CONTACT TIME ON THE DISSOCIATION OF C_3H_8 , $n-C_4H_{10}$ AND $Iso-C_4H_{10}$ AT 650° AND 1 ATM.

Hydro-carbon	Contact time, secs.	Vol. H.C. in cc.	Off-gas in cc.				Loss	Percentage to		
			Orig. H.C.	C_nH_{2n}	CH_4	H_2		CH_4	H_2	$CH_4 + H_2$
C_3H_8	6	254	208	37	31	18	-1	12	7	19
	11	249	172	53	41	22	6	16	9	25
	21	272	177	69	64	29	1	24	11	36
$n-C_4H_{10}$	8	226	164	67	54	10	-1	24	4	28
	10	248	144	88	82	15	3	33	6	39
	21	242	140	105	86	17	0	36	7	43
$Iso-C_4H_{10}$	8	206	144	51	37	29	-2	18	14	32
	11	248	138	73	57	40	5	23	16	39
	22	239	123	96	77	45	-2	32	19	51

Table II shows that the ratio of demethanation to dehydrogenation does not vary greatly with the total amount of dissociation. It also would appear that the rate diminishes rather rapidly with the concentration of hydrocarbon, but under the conditions of the experiment, and in view of the uncertainty as to the precise nature of the products, it is not possible to state definitely what the reaction order is.

In order to determine whether the hydrogen which is formed enters into secondary reaction with the hydrocarbons, two experiments were carried out with normal butane, in one of which the butane was diluted with one-half its volume of hydrogen and in the other with one-half its volume of nitrogen. The latter experiment was to serve as a check on the effect of dilution by hydrogen as opposed to chemical reaction. The results are given in Table III.

TABLE III
EFFECT OF DILUTION OF NORMAL BUTANE WITH HYDROGEN AND WITH NITROGEN AT 650° AND 1 ATM.

2 Vols. C ₄ H ₁₀ plus 1 vol. of	Contact time, secs.	H.C. in, cc.	Orig. H.C.	Off-gas in cc.				Percentage to			
				C ₇ H ₁₆	CH ₄	H ₂	Loss	CH ₄	H ₂	CH ₄ +H ₂	
Hydrogen	7	248	161	71	61	17 ^a	3	25	7	32	
Nitrogen	7	248	162	72	63	12	3	25	5	30	

^a Exclusive of 125 cc. of hydrogen introduced.

Since the results of the two experiments correspond within experimental error, we conclude that hydrogen acts simply as a diluent, and that in the other experiments there is no appreciable reaction of the hydrogen formed either with the saturated hydrocarbons or with the olefins.

Comparison of these results with that obtained with *n*-butane alone at 1 atm. pressure and 8 seconds' contact (instead of 7 seconds) shows that the percentage conversion is nearly the same. This is what would be expected if the reactions are unimolecular. The fractional conversion should then be independent of dilution.

Finally, we have carried out comparable experiments on propane, *n*-butane and *isobutane* at 625 and 650° to get an idea of the temperature influence. The results of these are given in Table IV.

TABLE IV
TEMPERATURE INFLUENCE ON THE DISSOCIATION OF C₃H₈, *n*-C₄H₁₀ AND *iso*-C₄H₁₀ EXPERIMENTS AT 625 AND 650°

Hydro- carbon	Contact Temp., °C.	Time, secs.	H.C. in cc.	Orig. H.C.	Off-gas in cc.				Percentage to			
					C ₇ H ₁₆	CH ₄	H ₂	Loss	CH ₄	H ₂	CH ₄ +H ₂	
C ₃ H ₈	625	22	272	204	43	39	21	3	14	8	22	
	650	21	272	177	69	64	29	1	24	11	35	
<i>n</i> -C ₄ H ₁₀	625	24	242	165	69	63	11	1	26	5	31	
	650	21	242	140	105	86	17	0	36	7	43	
<i>iso</i> -C ₄ H ₁₀	625	24	239	170	59	39	30	0	16	13	29	
	650	22	239	123	96	77	45	2	32	19	51	

We find that the ratios of the percentage dissociation at the two temperatures are of the order of 1.5 to 2 per 25° under these conditions. This would correspond to an activation energy of 25,000–50,000 cal. per mole. Since dissociation has taken place to a considerable extent, these figures are lower than the true values for these quantities.

Discussion

The general results of these experiments can be satisfactorily accounted for qualitatively. Modern theories of reaction rate indicate that a molecule which is about to react contains energy in excess of the average of all molecules. More particularly, the excess is associated with one or more degrees of freedom which, in the cases under consideration, doubtless represent the oscillation of atoms about their positions of equilibrium.

Heat capacity data prove that the total energy available for concentration on some particular degree of freedom increases with the number of atoms in the molecule (and also with the temperature, of course). The frequency with which a molecule finds itself active will therefore be greater the more complex the molecule, so that if the energy required for activation is of the same order for molecules of two substances of differing complexity, the frequency with which the more complex molecules react will be the greater.

If the molecule can undergo more than one type of reaction, the relative ratio of the different types will depend on the relative magnitude of the energy quantities required for activation. There is evidence based on thermal data that the energy required for the complete destruction of a carbon-carbon linkage is about 72,000 cal. per mole and for a carbon-hydrogen linkage about 92,000 cal. per mole. If we assume that in order to produce methane a carbon-carbon linkage must first be broken, while to produce hydrogen a carbon-hydrogen linkage must first be broken, we have an explanation of the fact that when both these reactions can take place, demethanation occurs to the greater extent (because it is associated with a lesser energy of activation). Some variation from strict constancy of the ratio of demethanation to dehydrogenation is to be expected due to minor variations in the energies of C-C and C-H linkages in different hydrocarbons. Thus, it is well known that a tertiary hydrogen atom, such as exists in *isobutane*, is in general more reactive than hydrogen formed in other ways. We thus may expect, and find, a greater proportion of dehydrogenation in this case.

Recent experiments having shown that the dissociation of ethane and of propane is unaffected by an increase in glass surface, we conclude that all these reactions are homogeneous gas reactions. The order is probably the first, as already pointed out.

The above considerations appear to give a rational explanation of the results which have been obtained and we propose to adopt them as a working hypothesis in the succeeding work.

Summary

The thermal dissociations of ethane, propane, normal butane and *isobutane* have been studied at 625 and 650°, and 1 atm. We find that the total rate of dissociation increases with the complexity of the molecule. The two principal reactions are dehydrogenation and demethanation. The ratios of hydrogen to methane decrease in the series ethane, propane, *n*-butane. *Isobutane* decomposes at about the same rate as *n*-butane but gives relatively much more hydrogen. The hydrogen formed undergoes no appreciable secondary reaction. The reactions seem to be somewhat more rapid than normal in the first few seconds but dilution experiments

indicate a first order reaction. The temperature coefficients are as a minimum 1.5–2 per 25°, giving a minimum activation energy of 25,000–50,000 cal.

An explanation of the relative rates of the reactions is given in terms of activation energies as a function of the size of the molecule and the nature of the linkages to be broken.

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[CONTRIBUTION FROM THE CHEMICAL ENGINEERING LABORATORY OF SYRACUSE UNIVERSITY]

THE MELTING POINT OF META-DINITROBENZENE

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Answering a call issued by J. E. Zanetti,¹ we have carefully determined the melting point of *m*-dinitrobenzene; ninety degrees is commonly given in the textbooks. We used Washburn's² method, employing an unsilvered half pint thermos bottle furnished by the Icy Hot Company. The bottle, padded with asbestos except for a small opening through which the thermometer was read, was heated carefully on the sand-bath to about 100 degrees and then allowed to cool during half an hour or forty-five minutes. The solidification temperature was constant over a period of from ten to fifteen minutes. With recrystallized material from the DuPont Company, the following (corrected) results were obtained.

I	89.583	IV	89.553
II	89.593	V	89.563
III	89.563	Mean	89.57

The determinations represent fresh samples in each case, for the melting was found to cause discoloration and decomposition which lowered the solidification point several tenths of a degree. Material that had been melted was recrystallized from alcohol. The solidification point was no higher than that of the DuPont material which was labeled "89.8–89.95 degrees." We made three capillary tube melting point determinations, using hot water as the bath, and found 89.85 degrees for the average. An Anschuetz thermometer, calibrated by the Bureau of Standards, was used throughout.

The work was done at Sweet Briar College in the spring of 1924. The International Critical Tables give 89.7 as the melting point.

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¹ Zanetti, *Ind. Eng. Chem.*, **16**, 88 (1924).

² Washburn, *ibid.*, **16**, 275 (1924).