[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF PRINCETON UNIVERSITY]

THE KINETICS OF THE THERMAL DISSOCIATION OF PROPANE AND THE BUTANES[1]

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Recent work[2] has indicated that the thermal dissociations of the paraffin hydrocarbons (other than methane) are homogeneous first-order reactions yielding as primary products mono-olefins, and a lower paraffin or hydrogen. This work has all been of a more or less exploratory nature, and it has seemed worth while to make a somewhat more thorough study of the behavior of these compounds. Of especial interest are the alternative reactions which take place. These can be conveniently studied for propane and the butanes, since in these cases the reactions are not too numerous, and yet exhibit considerable variety. Consequently, we have carried out an investigation of the dissociation of these compounds, paying special attention to the rates as affected by dilution and by contact with glass surface, and to the relative rates of the simultaneous reactions and their temperature coefficients.

Method.—From the experimental standpoint the chief problem is one of analysis. The exit gas contains (in the case of butane) much of the original hydrocarbon along with nitrogen, hydrogen, methane, ethane, ethylene, propylene and butylene. A complete quantitative separation is a matter of considerable difficulty. What we were interested in was a determination of the fractions of hydrocarbon reacting according to (for butane)

$$C_4H_{10} \longrightarrow C_4H_8 + H_2 \qquad (1)$$

$$C_4H_{10} \longrightarrow C_3H_6 + CH_4 \qquad (2)$$

$$C_4H_{10} \longrightarrow C_2H_4 + C_2H_6 \qquad (3)$$

Assuming that no other reactions enter in, a determination of hydrogen, methane and ethane in comparison with the amount of hydrocarbon taken would give the necessary data. A comparison of the total of these three in the off-gas with the amount of hydrocarbon reacting and the total of olefins formed would give a check on the correctness of the assumption that the above reactions are the only ones of importance.

It will be noted that in the case of butane the saturated hydrocarbons

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[2] Pease, THIS JOURNAL, **50**, 1779 (1928); Frey and Smith, *Ind. Eng. Chem.*, **20**, 948 (1928); Hurd "Pyrolysis of Carbon Compounds," The Chemical Catalog Company, Inc., New York, **1929**, pp. 46, etc.; Hurd and Spence, THIS JOURNAL, **51**, 3353 (1929).

in the off-gas divide into the highly volatile methane and ethane, and the relatively non-volatile butane. A separation by fractionation should then be easy, and is found to be so. In the case of propane, only hydrogen, methane and propane are to be determined, and, of course, the gas analysis always permits of expressing total hydrocarbons in terms of two such. We have in both cases resorted to fractionation, and have obtained unequivocal results as to the proportions of saturated hydrocarbons and hydrogen. The proportions of olefins do not stand out so clearly but the relative amounts in different fractions are such as would be expected from the nature of the saturated products.

Our method of fractionation was as follows. The off-gas was collected over mercury in an aspirator bottle. This bottle could be connected to another such through a small trap of 5 cc. capacity. This trap was cooled either to −180° (with liquid air) or to −116° (with solid–liquid ethyl bromide). The first goal was the removal of the bulk of the original hydrocarbon, which always preponderated in the off-gas. This was done by passing the gas slowly through the trap at −116°, and then evaporating one-fourth to one-half of the condensate. The remainder contained no saturated hydrocarbon but the original, along with varying amounts of olefins. The remaining gas (uncondensed plus evaporated) was again passed through the trap at −116°, where a part condensed. Keeping the trap at −116°, the condensate was pumped (using one aspirator bottle as a sort of Töpler pump) until only minimal amounts of gas could be removed. The residue again contained nothing but the original hydrocarbon and olefins. Finally, the remaining gas was condensed at −180°, and again pumped. The pumped-off gas consisted only of hydrogen, nitrogen and methane. This left a residue which was warmed to −116°, and pumped for the removal of ethane (and ethylene) and the rest of the methane. The residue from this treatment usually amounted to 1 to 2% of the total gas. It was combined with the residue from the second pumping at −116° on the assumption that it represented the last traces of original hydrocarbon and higher olefins.

By this method, we obtained one fraction containing hydrogen and methane, another containing methane and ethane, and a third containing the original hydrocarbon. Results could then be expressed in terms of these substances and of the total of olefins.

Experiments were carried out by the flow method. The gases passed from tanks through flowmeters to a reaction tube of known volume contained in an electric tube-furnace. The temperature of the latter was taken with a two-junction chromel–alumel thermocouple. The gases had the following analyses

				Percentage			
	C_5H_{12}	C_4H_{10}	C_3H_8	C_2H_6	H_2	N_2	O_2
n-Butane	2.6	94.8	..	...	..	1.2	1.4
Isobutane	...	98.3	..	...	..	1.2	0.5
Propane	...	..	96.3	3.0	..	0.5	0.2
Hydrogen	...	..	..	...	99.3	0.5	0.2
Nitrogen	...	..	..	...	..	98.5	1.5

Calculation of Velocity Constants.—The first-order velocity constants which appear in the tables were calculated from the ordinary expression

$$k_1 = \frac{2.303}{t} \log_{10} \frac{100}{100 - x}$$

where t is time in seconds and x is percentage conversion. The time was calculated from the volume of the reaction tube and the average of the inflow and outflow rates. The percentage dissociation is the average calculated from the amount of hydrocarbon reacting, the amount of olefins formed and the amount of hydrogen, methane and ethane formed.

Results

Effect of Packing.—If the reactions take place exclusively in the gas phase, an increase in glass surface, brought about by packing the reaction tube with broken glass, should not alter the percentage conversion. Data are presented in Table I in which the reactions in empty and in packed tubes are compared. It will be noted that in general the rate is slightly greater in the packed tube. However, in view of the fact that the packing increases the surface by a factor of about 10, and only increases the rate at most by 10%, we can safely conclude that not more than 1% of the reaction in the empty tube is heterogeneous. The rate increase in the packed tubes may also be due to somewhat better heat transfer in this case, since the reactions are endothermic and would tend to maintain a somewhat lower temperature in the empty tube.

TABLE I

EFFECT OF PACKING THE REACTION TUBE

H.C. and temp.	Reaction tube	Time, sec.	Volumes in cc. at 0° and 1 atm.						Conv., %	k_1
			H.C.		Formed					
			In	Reacted	H_2	CH_4	C_2H_6	C_nH_{2n}		
C_3H_8 at 650°	Empty	12.0	346	69	31	45	..	68	20.5	0.019
	Packed	11.5	345	70	31	41	..	71	20.6	.020
n-C_4H_{10} at 625°	Empty	12.5	341	69	8	48	20	79	22.0	.020
	Packed	12.4	351	78	9	50	21	86	23.7	.022
	Packed[a]	12.4	358	77	8	50	22	85	22.6	.021
Iso-C_4H_{10} at 600°	Empty	25.8	356	62	31	28	4	64	17.7	.0076
	Packed	26.1	354	62	33	31	3	67	18.4	.0078
Iso-C_4H_{10} at 650°	Empty	5.3	315	84	38	43	7	81	26.7	.0059
	Packed	5.1	319	86	35	38	4	74	24.8	.0056

[a] This tube was rinsed with 20% potassium chloride solution, with the view of poisoning any "active spots" on the glass surface.

Effect of Dilution with Nitrogen.—If the reactions are first-order, the rate should be independent of the concentration Consequently, dilution with an inert gas should not affect the first-order rate-constant. If the reactions were in reality second or higher order, dilution should decrease the first-order constant in proportion. Actually, dilution with an equal volume of nitrogen in general increases the constants somewhat. Pertinent data are presented in Table II. An examination of the results indicates that it is probably the dehydrogenation reaction which causes the trouble. There is relatively more hydrogen formed from the diluted gas than from the undiluted gas. It may be that the dehydrogenation reaction is reversible as is known to be the case with ethane.[3] If this is true, better constants could be obtained with greater dilution and smaller conversions. This, however, would involve greater error in the analysis. Another possible explanation is in terms of heat transfer.

In any case, these data on effect of packing and dilution leave no question but that the reactions are essentially first-order homogeneous gas reactions. It should be pointed out that the discrepancies may be in part the result of analytical error, but since they point so consistently in one direction it is probable that they are real.

TABLE II

EFFECT OF DILUTION WITH EQUAL VOLUME OF NITROGEN

H.C. and temp.	Time, sec.	Diluent	Volumes in cc. at 0° and 1 atm. H.C. In	Reacted	Formed H_2	CH_4	C_2H_6	C_nH_{2n}	Conv., %	k_1
C_3H_8 at 625°	25.7	None	368	60	27	39	..	61	16.9	0.0072
	25.9	N_2	187	37	18	23	..	36	20.4	.0088
C_3H_8 at 650°	12.0	None	346	70	31	45	..	69	22.0	.021
	12.1	N_2	188	44	20	28	..	43	23.9	.023
n-C_4H_{10} at 625°	12.5	None	341	69	8	48	20	79	22.0	.020
	12.5	N_2	186	44	7	26	13	47	24.8	.023
Iso-C_3H_{10} at 600°	25.8	None	356	62	32	28	4	64	17.7	.0076
	26.3	N_2	202	33	20	14	4	40	18.3	.0077
Iso-C_4H_{10} at 625°	5.6	None	367	60	26	25	1	54	15.0	.029
	6.3	N_2	187	29	18	14	1	31	16.6	.029
Iso-C_4H_{10} at 650°	3.5	None	362	68	33	33	2	66	18.5	.058
	3.4	N_2	186	37	20	17	2	36	19.9	.065

Effect of Varying Heating Time.—If the dissociations of propane and the butanes were pure first-order homogeneous gas reactions, the first-order rate constant should not change as the percentage conversion is increased by prolonging the heating time. A number of experiments were carried out to determine whether the constant is in fact constant. The results, which are presented in Table III, show that this is not the case. The constants fall rather rapidly as reaction proceeds. This is in line with what had already been found regarding the effects of diluting with nitrogen. In certain cases it appears that the dehydrogenation reaction is most affected, indicating some re-hydrogenation. In fact, when hydrogen was added initially in one experiment on isobutane at 625°, the amount of hydrogen formed was found to be distinctly decreased.

The lack of constancy is so great that no justifiable extrapolation to zero conversion to give a true constant can be made. This is borne out by the fact that no reasonably constant temperature coefficients and heats of activation can be obtained. Experiments at much lower conversions

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[3] Pease and Durgan, THIS JOURNAL, **50**, 2715 (1928).

TABLE III

RUNS AT 1 ATMOSPHERE PRESSURE IN EMPTY REACTION TUBES

H.C.	Temp., °C.	Time, sec.	Volumes in cc. at 0° and 1 atm. H.C.		Formed				Conv., %	k_1
			In	Reacted	H_2	CH_4	C_2H_6	C_nH_{2n}		
C_3H_8	625	25.7	368	60	27	39	..	61	16.9	0.0072
	625	53.2	339	92	32	59	..	81	26.0	.0057
C_3H_8	650	5.5	313	43	21	26	..	47	14.7	.029
	650	12.0	346	70	31	45	..	69	20.8	.019
n-C_4H_{10}	600	26.0	368	67	6	46	15	70	18.5	.0079
	600	57.0	329	94	8	62	27	101	29.5	.0061
n-C_4H_{10}	625	12.5	341	69	8	48	20	79	22.0	.020
	625	24.2	330	95	10	68	28	107	31.2	.016
n-C_4H_{10}	650	5.3	317	81	10	52	21	89	26.5	.058
	650	11.4	308	103	13	71	29	114	35.7	.039
Iso-C_4H_{10}	600	25.8	356	62	32	28	4	64	17.7	.0076
	600	57.7	334	79	40	44	4	86	25.2	.0050
Iso-C_4H_{10}	625	5.6	367	60	26	25	1	54	15.0	.029
	625	11.9	356	91	39	41	4	82	24.2	.023
	625	25.7	305	117	48	62	11	104	37.4	.018
Iso-C_4H_{10}	650	3.5	362	68	33	33	2	66	18.5	.058
	650	5.2	316	90	39	43	6	86	27.9	.063
	650	7.5	323	109	46	52	12	97	32.5	.052
	650	13.8	299	137	55	73	14	115	43.8	.042

are called for, but these must necessarily introduce serious errors in analysis. Nevertheless, further work in this direction should be carried out. Several points deserve additional investigation. There is, for example, a good indication that the proportions of the products do not change with temperature. This would say that the heats of activation for the alternative reactions are the same—a fact which, if true, would be of some theoretical importance as evidencing an activation of the molecule as a whole with the alternative reactions sharing in accordance with certain probability factors which were independent of temperature. There is also an indication that the temperature coefficients for the different hydrocarbons are the same, being about 2.75 per 25° on the average corresponding to a heat of activation of 65,000 cal.

Rate at Low Pressures.—The results of three determinations of rate at a pressure of 2 mm. are of interest. These are compared with results at 1 atm. pressure in Table IV.

TABLE IV

RESULTS AT LOW PRESSURE (TEMP., 625°)

Gas	Pressure	Time, sec.	Conv., %	k_1
C_3H_8	2 mm.	41	10	0.0026
	1 atm.	53	26	.0057
n-C_4H_{10}	2 mm.	42	21	.0056
	1 atm.	24	31	.016
Iso-C_4H_{10}	2 mm.	41	16	.0043
	1 atm.	26	37	.018

The rate is seen to be distinctly less at these lower pressures, as has been found for other first-order reactions, such as the decomposition of ethyl ether.[4] The rate is, however, definitely not lowered sufficiently to suggest a second-order reaction. These results suggest the desirability of carrying out similar measurements over a wide pressure range between a few millimeters and 1 atmosphere. We plan to study this aspect of the problem further.

Summary

Further investigation of the thermal dissociations of propane and the butane has confirmed the earlier conclusion that these are fundamentally first-order, homogeneous gas reactions. Due probably to such secondary reactions as re-hydrogenation, the first-order constants fall rather rapidly as reaction proceeds. Dilution with nitrogen has the effect of increasing the rate constants somewhat. At pressures of a few millimeters the constants are distinctly less than at 1 atmosphere, but the difference is not sufficient to indicate a reaction order higher than the first.

The temperature coefficient of rate is about 2.75 per 25°, and the heat of activation is about 65,000 cal. for all three substances, and appears to be of the same order of magnitude for the alternative modes of dissociation.

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IDENTIFICATION OF NITRILES. PREPARATION OF ALKYL PHENYL KETONES

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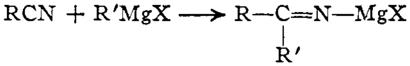
Nitriles are usually identified by hydrolyzing them to acids and identifying the latter. When the acid so obtained is aromatic no great difficulty is experienced but in the case of aliphatic acids from alkyl cyanides the isolation and preparation of a solid derivative is more difficult. In an attempt to find an easier means of identifying alkyl cyanides, the reaction with the Grignard reagent was studied.

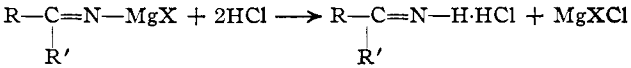
The following main reactions, involving addition of the Grignard reagent with subsequent decomposition and hydrolysis, were studied by Blaise[1] but no yields were recorded.

(a)



$$\mathrm{RCN} + \mathrm{R'MgX} \longrightarrow \mathrm{R{-}\underset{\displaystyle R'}{C}{=}N{-}MgX}$$

(b)



$$\mathrm{R{-}\underset{\displaystyle R'}{C}{=}N{-}MgX} + 2\mathrm{HCl} \longrightarrow \mathrm{R{-}\underset{\displaystyle R'}{C}{=}N{-}H{\cdot}HCl} + \mathrm{MgXCl}$$

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[4] Hinshelwood, *Proc. Roy. Soc. London*, **114A**, 84 (1927).

[1] Blaise, *Compt. rend.*, **132,** 38 (1901).