

[CONTRIBUTION FROM THE FRICK CHEMICAL LABORATORY, PRINCETON UNIVERSITY]

Kinetics of the Decomposition of *n*-Butane. I. Normal Decomposition

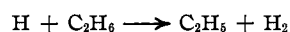
BY LEONARD S. ECHOLS AND ROBERT N. PEASE

In the earlier work¹ from this Laboratory on the pyrolysis of propane and the butanes, it was concluded that the reactions were clean-cut dissociations (designated dehydrogenation, demethanation and so on), and were first-order and homogeneous. These conclusions were based on flow experiments at one atmosphere. Rates were little affected by dilution with nitrogen, or by packing or coating (with potassium chloride) the reaction vessel. At the same time it was recognized that the over-all first-order rate constants fell as reaction proceeded, and probably also fell as the pressure was diminished, indicating that the reactions were not free of complication.

The implication that the reactions are simple unimolecular processes was shortly cast in doubt by the speculations and experimental work of F. O. Rice and others.² Rice asserted that the primary process in this and other organic pyrolyses is a dissociation into alkyl radicals, which set up reaction chains. Although this view that an over-all endothermic reaction can give rise to a chain mechanism was received with some skepticism, there was much to support it. Thus, Rice and Herzfeld³ showed how the over-all reaction might give a first-order constant, as it was then supposed to do. Further, it was already known from the work of Taylor and Jones⁴ that metal alkyls would induce hydrogenation (along with polymerization) in ethylene-hydrogen mixtures, and from the work of Paneth and Hofeditz⁵ that metal alkyls yield free alkyl radicals. It thus appeared that at least one reverse reaction (hydrogenation) is sensitive to alkyl radicals. In addition, it was shown by Rice⁶ that many organic compounds (butane included) yield alkyl radicals when investigated by the Paneth technique, the substance being heated briefly at high temperature and low pressure. Finally, it was shown by Frey⁷ that mercury dimethyl would sensitize the decomposition of *n*-butane at 525°

under conditions such that the normal reaction was negligible.

Although all this argued most persuasively for a radical chain mechanism, it still did not prove that the normal decomposition at moderate temperatures and pressures actually occurs in this way. In fact, there was some experimental evidence against the particular mechanisms proposed by Rice. Thus, in the case of ethane, the reaction



appeared to have too low an activation energy.⁸ Also, the rate of ortho-para hydrogen conversion, which should be catalyzed by free atoms or radicals, was unexpectedly low in presence of decomposing ethane.⁹ As pointed out by Steacie¹⁰ these results throw considerable doubt on Rice's mechanism for ethane and, by implication, on those for related substances.

One important test of mechanism remained to be made. Whereas acceleration may represent simply a homogeneous catalysis rather than the initiation of chains, retardation or inhibition almost certainly denotes chains. In his studies of homogeneous catalysis, Hinshelwood made the fundamental discovery that nitric oxide will inhibit the decomposition of acetylene and propionaldehyde.¹¹ A means of demonstrating chain breaking and hence a chain mechanism was thus at hand.

The authors had been working on the accelerated decomposition of gaseous paraffins in presence of ethylene oxide,¹² and determined to extend the investigation to include possible effects due to nitric oxide as well. After some preliminary difficulties with obtaining nitric oxide free of impurities such as oxygen and nitrous oxide, which accelerate the reaction, it was found that nitric oxide does inhibit *n*-butane decomposition, though the effect is in part a transient one.¹³

(1) Pease, *THIS JOURNAL*, **50**, 1779 (1928); Pease and Durgan, *ibid.*, **52**, 1262 (1930).

(2) F. O. Rice, *ibid.*, **53**, 1959 (1931); see Taylor, *Trans. Faraday Soc.*, **21**, 560 (1925).

(3) Rice and Herzfeld, *THIS JOURNAL*, **56**, 284 (1934).

(4) Taylor and Jones, *ibid.*, **52**, 1111 (1930).

(5) Paneth and Hofeditz, *Ber.*, **62**, 1335 (1929).

(6) Rice, Johnston and Evering, *THIS JOURNAL*, **54**, 3529 (1932).

(7) Frey, *Ind. Eng. Chem.*, **26**, 198 (1934).

(8) Steacie and Phillips, *J. Chem. Phys.*, **5**, 1568 (1937); Trenner, Morikawa and Taylor, *ibid.*, **5**, 203 (1937).

(9) Patat and Sacchse, *Z. Elektrochem.*, **41**, 493 (1935); Sacchse, *Z. physik. Chem.*, **B31**, 79 (1935).

(10) Steacie, *Chem. Rev.*, **22**, 311 (1938).

(11) Staveland and Hinshelwood, *Proc. Roy. Soc. (London)*, **154A**, 335 (1936); *J. Chem. Soc.*, 812 (1936).

(12) Echols and Pease, *THIS JOURNAL*, **58**, 1317 (1936); see Heckert and Mack, *ibid.*, **51**, 2706 (1929).

(13) Echols and Pease, *ibid.*, **59**, 766 (1937); **60**, 1701 (1938).

With this additional confirmation of a chain mechanism, we returned to an investigation of the normal reaction in the hope that a more detailed analysis than had previously been made would reveal additional features of significance. This hope has been rewarded. In particular, strong evidence of inhibition by products has been obtained. A subsequent conversation with F. O. Rice having indicated that propylene was suspect in this connection,¹⁴ effects due to this substance were investigated. As a result, propylene has been found to exhibit transient inhibition, just as does nitric oxide. Finally, an investigation of acceleration by nitrous oxide, and of surface effects, was made.

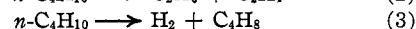
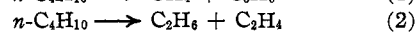
Our data and conclusions are to appear in a series of papers. This, the first of the series, deals with the normal decomposition.

Method.—Kinetic data were obtained from pressure measurements at constant volume, supplemented by analysis. The apparatus was for the most part of familiar type. Special attention was given to temperature control. The reaction bulb (of Pyrex, 3.7 cm. diameter by 22 cm. long) was wrapped in aluminum foil. This bulb and three chromel–alumel thermocouples were placed in an "inner furnace," consisting of an aluminum tube wound with asbestos-covered chromel wire. This in turn was contained in a considerably larger "outer furnace" which was kept about 10° below the inner furnace. The latter was held to the desired temperature (within less than 0.5°) by a photoelectric cell, vacuum-tube control actuated by a mirror galvanometer in the thermocouple circuit.

A special type of graphite-lubricated mercury-sealed stopcock was used to avoid solution of gases in stopcock grease.¹⁵

Gases were analyzed after fractionation, the method being checked with mixtures of known composition.

A comparison of data on composition and on pressure increase showed that the latter is a fairly satisfactory measure ($\pm 5\%$) of extent of reaction up to about 25% reaction. Thus, for example, at 520° and an initial pressure of 200 mm., after about thirty-five minutes the pressure increase was 49.8 mm.; the residual butane corresponded to a loss of 50.0 mm.; the total olefins corresponded to a gain of 47.9 mm. This is the relation to be expected if the reactions are



It may be mentioned that at 520° and 25% decomposition, the ratios of reactions 1:2:3 was found to be as 10:4:1. This compares with Frey and Hepp's result at 575° and 11% reaction of 6:3:1, and of Neuhaus and Marek's data at 600° extrapolated to 0% reaction of 5:3.5:1.5.¹⁶ Steacie and Puddington,¹⁷ on the other hand, were unable to identify butenes at 500–600°.

A word should be said regarding the values of initial pressures. These cannot be determined satisfactorily by extrapolation to zero time because of the high initial rates. The values given are calculated from the amounts of gas in a storage reservoir before and after admission to the reaction bulb. They are believed to be accurate to about 1%. The uncertainty is due to the high initial rate. Partially reacted gas may "push back" into the reservoir during the finite time required for admission.

It may be mentioned here that *n*-butane was chosen as a type substance for this work because it is of intermediate complexity, and because the amount of dehydrogenation, which is reversible, is small.¹⁸

The *n*-butane was supplied by the Ohio Chemical and Manufacturing Company. It was fractionated before use in a Podbielniak-type still.

Results

Normal Decomposition.—The normal decomposition was investigated between 480 and 535°, and from 100 to 600 mm. pressure in a potassium chloride-coated Pyrex bulb (3.7 × 22 cm.). Results are given in Table I and Fig. 1, the latter being for 520°.

These data at once made it clear that only in a most approximate sense could the reaction be called first-order. Comparison of times to 10% decomposition for different initial pressures would indicate an order of about 1.3, while if the initial portions of any one curve are to be fitted, an order of as high as 5 or 6 is required.

It is quite obvious from these observations alone that the reaction is complex. Our first efforts were directed at determining whether this is due to an impurity in the butane, possibly acting as a

(16) Frey and Hepp, *Ind. Eng. Chem.*, **25**, 441 (1933); Neuhaus and Marek, *ibid.*, **24**, 400 (1932).

(17) Steacie and Puddington, *Can. J. Research*, **16B**, 176 (1938).

(18) Frey and Huppke, *Ind. Eng. Chem.*, **25**, 54 (1933); Frey and Hepp, *ibid.*, **25**, 441 (1933).

(14) Rice and Polly, *J. Chem. Phys.*, **6**, 273 (1938).

(15) Echols, *Ind. Eng. Chem., Anal. Ed.*, **10**, 527 (1938).

TABLE I
 DATA ON NORMAL REACTION

Temp., °C.	p_0 , mm.	Time (min.) to indicated % reaction									
		t_6		t_{10}		t_{16}		t_{20}			
		Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.	Exptl.	Calcd.
480	200	29.5	29.2	77.5	78.5
490	200	13.2	15.5	42.2	45.0	82.0	80.0	130	120
	400	11.8	13.0	34.5	35.5	62.5	62.0
500	200	9.0	9.0	25.8	25.8	47.2	47.2
	400	8.6	..	21.3
	600	6.4	6.4	16.6	17.5
510	200	5.2	..	14.4	..	26.4	..	41	42
520	100	2.4	3.2	8.8	9.6	18.2	19.0	31.0	31.0
	200	3.3	3.4	9.3	9.3	16.8	17.2	26.0	26.0
	400	2.7	2.8	7.7	7.6	14.0	13.5	21.7	20.2
	600	2.1	2.2	6.4	6.4	11.8	11.8	17.8	16.8
535	200	1.5	1.5	4.0	4.5	7.5	8.2	12.0	13.0
	400	1.3	1.3	3.7	3.7	6.7	6.7	10.4	10.0

sensitizer. To this end, samples of butane were taken as follows: 1, directly from cylinder; 2, first, middle, and last fractions on evaporation; 3, after "blowing-off" cylinder to remove fixed gases (*e. g.*, oxygen); 4, from middle fraction of a Podbielniak-type distillation; 5, from fractionation of a sample of partially reacted gas.

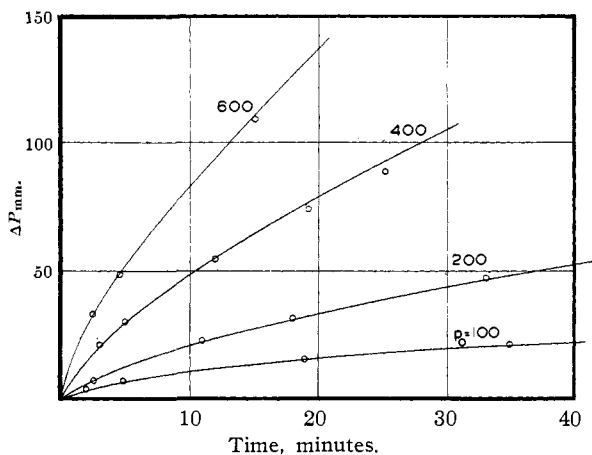


Fig. 1.—Decomposition of normal butane at 520°: initial pressures, p_0 , in mm. Hg., curves—by equation, points—experimental.

Since in no case was there a deviation in rate outside of experimental error, it was concluded that the observed behavior was characteristic of the *n*-butane decomposition itself.

An attempt was made to fit the experimental data by means of a semi-empirical equation. For this purpose, the form

$$-\frac{d\hat{p}_B}{dt} = k_1\hat{p}_B^{1.5} + k_2\hat{p}_B^2/(\hat{p}_{0B} - \hat{p}_B)$$

in which \hat{p}_B = pressure of butane at time t and \hat{p}_{0B} = pressure of butane at zero time, proved

satisfactory. Values of the constants were obtained by a process of graphical differentiation. Reversal of the procedure, using these constants, permitted the construction of curves for each initial pressure and temperature. These curves are plotted in Fig. 1. Calculated times are compared to observed values in Table I. Values of the constants are given in Table II and Fig. 2.

 TABLE II
 CONSTANTS FOR THE NORMAL REACTION
 (Units are mm. of Hg and minutes)

Temp., °C.	$k_1 \times 10^4$	$k_2 \times 10^4$
480	0.642	0.182
490	1.043	.338
500	1.80	.625
510	2.85	1.126
520	4.50	1.95
535	8.30	4.77

These data lead to activation energies: $E_1 = 58,000$ cal.; $E_2 = 72,000$ cal.

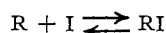
We attach no profound significance to the particular form of the equation given above. Nevertheless, in its application the following points emerge: 1, the "effective" order with respect to initial pressure is between 1.0 and 1.5; 2, the rapid initial deceleration appears as a "product effect" (denominator of second term); 3, this latter effect exhausts itself largely in the first 10% of reaction, beyond which the second term contributes very little; 4, the subsequent reaction is of 1.5 order (first term).¹⁹

(19) The equation

$$kt = \ln \left(\frac{1}{1-x} \right) - bx \quad (x = \text{fraction reacted})$$

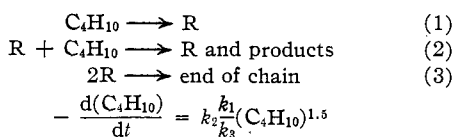
given by Dintses and Frost, *J. Gen. Chem. U. S. R. S.*, 6, 68 (1936), was based on flow experiments for various hydrocarbons at 1 atm. pressure. Such an equation is inadequate to express the variation of rate with initial pressure.

As will be shown in a later paper, the "product effect" is attributable largely to propylene. When this substance is added, there is an initial inhibition. However, the effect is a transient one, the rate subsequently duplicating that of the normal decomposition. This result, which is also observed on addition of nitric oxide, we believe to be due to a "feed-back" of radicals by an active intermediate formed with the inhibitor. Effectively, the combination of chain carrier, R, and inhibitor, I, is in part reversible



At the steady state a constant fraction of chain carriers, R, is being returned to the reaction. That all radicals are not returned is shown by the fact that rates equivalent to the initial rate when propylene is not added are not subsequently attained.

According to our equation, the rate subsequent to the attainment of this steady state corresponds to a 1.5 order (first term of the equation). The mechanism thus reduces to something essentially equivalent to



We do not mean to imply more by this than that the reaction orders in terms of butane and radical concentrations should be as indicated. Further discussion of mechanism is postponed to the next paper, which will deal with inhibitor action.

Recent work of Steacie and Puddington¹⁷ on the *n*-butane decomposition is in good numerical agreement ($\pm 10\%$) with our data. These authors attempted an analysis of the change in initial rate with initial pressure in terms of the theory of quasi-unimolecular reactions. This seems to have been recognized to be unsatisfactory, a fact which we regard as most significant in view of our own findings. As a matter of fact, the possibility that the reaction had characteristics of a quasi-unimolecular mechanism was considered by us. Experiments were carried out in which *n*-butane at 200 mm. and 520° was mixed with nitrogen or with hydrogen. The effect of nitrogen (200 mm.) was, if anything, to cause a slight diminution in rate throughout. Hydrogen, on the other hand, caused an appreciable

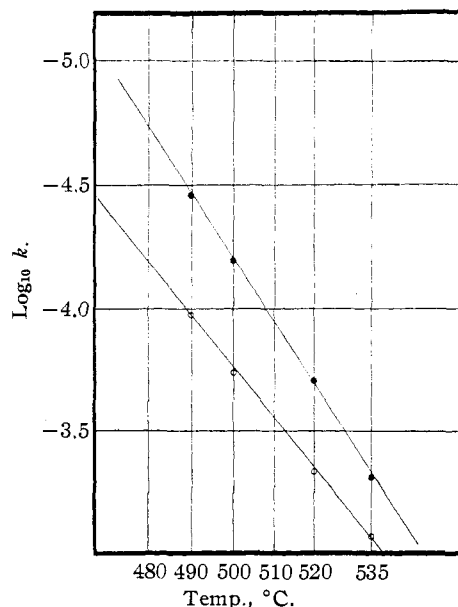


Fig. 2.—Activation energies for k_1 and $k_2 \log k$ vs. $1/T$: O = k_1 ; ● = k_2 .

increase in initial rate, amounting to about 25%. The effect is thus in the same direction as for such substances as ethyl ether.²⁰ Subsequent rates were diminished appreciably. There was no analytical evidence of loss of hydrogen or olefin by association. This might be considered significant in relation to quasi-unimolecular reaction theory. However, in view of the fact that the ethyl ether decomposition itself is doubtless a chain reaction, we are not inclined to stress this result unduly.

Summary

A re-investigation of the kinetics of decomposition of *n*-butane has shown that the reaction is very far from being the simple unimolecular reaction originally postulated on the basis of flow experiments at 1 atm. The variation of fractional reaction times with initial pressure indicates more nearly an order of 1.3. However, this can have no primary significance since the rapid initial decrease in rate at any one pressure would require an order of as high as 5 or 6. Data are fitted by the semi-empirical equation

$$-\frac{d(p_{C_4H_{10}})}{dt} = k_1 p_{C_4H_{10}}^{1.5} + k_2 \frac{p_{C_4H_{10}}^2}{p_{OC_4H_{10}} - p_{C_4H_{10}}}$$

The second term indicates inhibition by products, and drops out after about 10% reaction. This

(20) Hinshelwood, *Proc. Roy. Soc. (London)*, **114A**, 84 (1927).

leaves the first term, corresponding to an order of 1.5, predominating over the remainder of the reaction.

This is the first of a series of papers on the characteristics of *n*-butane decomposition.

PRINCETON, NEW JERSEY RECEIVED NOVEMBER 25, 1938

NOTES

The Preparation of Methyleneaminoacetonitrile

BY LAWRENCE H. AMUNDSEN AND RUTH VELITZKIN

After repeated experimentation the method of preparing methyleneaminoacetonitrile as described in "Organic Syntheses"¹ has been improved. The following modifications have been made: (1) time of reaction decreased; (2) higher temperatures; (3) internal cooling with solid carbon dioxide;² (4) acetic acid added in one portion before the addition of sodium cyanide.

Experimental

A mixture of 150 cc. (1.9 moles) of 35% formaldehyde, 54 g. (1 mole) of ammonium chloride and 38 cc. (0.66 mole) of glacial acetic acid was cooled to below 15° by the addition of crushed ice. When as much as 10% more formaldehyde was used, no significant difference in yield or purity of the product was observed but 50% more formaldehyde appeared to decrease the yield. It has been found possible to add small pieces of solid carbon dioxide instead of crushed ice. When one works with ten times the quantities stated here, the necessity for handling such a large volume of solution is thus avoided. There is probably no advantage in making this substitution if sufficiently large vessels are available. The mixture was stirred vigorously and a solution of 49.5 g. (0.98 mole) of 96-98% sodium cyanide in approximately 100 cc. of water was added from a dropping funnel over a period of fifteen to twenty minutes. The temperature was kept at 15-20° by the addition of crushed ice. When the temperature was permitted to go as low as 0°, no difference was noted in the results. Also momentary increases in temperature above 20° caused no significant change but when the temperature was maintained throughout at 35-40° an oily product was formed. After the addition was completed, the stirring was continued for fifteen minutes while the same temperature was maintained. Somewhat longer periods of stirring gave identical results, but if the solution was filtered at once, a small additional

quantity of the compound was deposited from the filtrate. The precipitate was filtered off and washed well with water. It seemed to be best to filter off the product the same day for the product was less pure, as indicated by the melting point, when the reaction mixture was allowed to stand for several days. This may be due to the formation of the lower melting isomer.³ When the product was not thoroughly washed, the melting point was low and suspended solid material seemed to be present in the melt. This may have been ammonium chloride. The yields with few exceptions have been from 45-55% of the theoretical and the melting points have been between 124 and 129° (uncorr.) with a 2 or 3° range. Although these yields are somewhat lower than those reported by Adams and Langley,¹ they are equal to those obtained in this Laboratory by following their directions. This method has given equally satisfactory results with batches ten times the size of the one described, *i. e.*, the same size batch used by Adams and Langley.¹ When solid carbon dioxide was used for cooling these larger batches, 3-4 kg. was sufficient to keep the temperature at 15-20°.

(3) Johnson and Rinehart, *THIS JOURNAL*, **46**, 772 (1924).

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RECEIVED NOVEMBER 10, 1938

Comment on "Absence of Combined Fatty Acid in Cereal Starches"

BY LEO LEHRMAN

No doubt all the workers in the field of starches will note with a great deal of interest the above entitled communication of Schoch.¹ The author reports the complete removal of the fatty acids in three cereal starches by extraction with water-miscible fat solvents, particularly methanol, the cellosolves and 80% dioxane. He gives two other results, *viz.*, (1) the de-fatted starch retains the usual properties of starch; (2) fatty acid can be reintroduced into the defatted starch by treatment with alcoholic oleic acid, and then concludes that "the fatty acid is distributed throughout the starch granule as an extraneous impurity."

It is with the interpretation of the experimental work that I think exception must be taken.

(1) Schoch, *THIS JOURNAL*, **60**, 2324 (1938).

(1) Adams and Langley, "Organic Syntheses," edited by Gilman, John Wiley and Sons, Inc., New York, N. Y., 1932, Coll. Vol. I, p. 347. This method in a more or less modified form has been described or mentioned several times in the literature. A complete bibliography is given in "Organic Syntheses." As far as the authors have been able to determine, no more recent information has appeared.

(2) The authors are indebted to Raymond I. Longley, Jr., for proposing temperature control by adding solid carbon dioxide directly to the mixture.