

# KINETICS AND MECHANISMS OF THE PYROLYSIS OF *n*-BUTANE

## PART I. THE UNINHIBITED DECOMPOSITION

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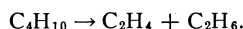
### ABSTRACT

The kinetics of the pyrolysis of *n*-butane have been studied at temperatures from 520° to 590° C, and at pressures from 30 to 600 mm Hg; the rate was followed from pressure changes and by gas chromatography. The reaction was accurately of the three-halves order; the activation energy was found to be 59.9 kcal mole<sup>-1</sup>, and the frequency factor  $3.24 \times 10^{15}$  cc<sup>1/2</sup> mole<sup>-1/2</sup> sec<sup>-1</sup>. The reaction is sensitive to surface; packing the vessel and 'conditioning' it usually led to a decrease in rate and an increase in activation energy. The reaction is concluded to be largely homogeneous, and to occur almost entirely by a free-radical mechanism; the initiation reaction is considered to be the dissociation of a butane molecule into two ethyl radicals, in its first-order region, and termination is believed to be the second-order combination of ethyl radicals. The mechanism proposed is shown to account satisfactorily for the observed behavior. The surface effect is attributed to a certain amount of initiation by abstraction, by a surface atom, of a hydrogen atom from butane, and to surface catalysis of the recombination of ethyl radicals.

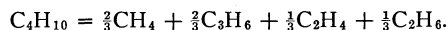
### INTRODUCTION

Recent papers from this laboratory have dealt with the kinetics and mechanisms of the thermal decomposition of ethane (1) and propane (2). The *n*-butane decomposition presents an interesting contrast in that hydrogen atoms are no longer predominant as chain carriers; the free-radical mechanisms are therefore of a different character. A considerable amount of recent work has been done on the pyrolysis of *n*-butane, but certain features of the mechanism have still remained obscure; in particular may be mentioned the order of the initiating reaction, the nature of the main chain-ending step, and the role of the surface. A reinvestigation of the reaction was therefore considered to be worthwhile, and was carried out in conjunction with the study of the inhibited reaction described in the following paper (Part II).

The main features of the previous work on this reaction may be summarized as follows. Pease (3) and Pease and Durgan (4) established that the reaction is largely homogeneous and approximately of the first order; the overall reaction could be represented mainly by the equations



Steacie and Puddington (5) found that the reaction products could initially be represented by the equation



They reported the first-order rate constant as

$$k = 5.1 \times 10^{12} e^{-58,700/RT} \text{ sec}^{-1}.$$

Echols and Pease (6) found that the order was closer to 3/2 than to unity.

The presence of free radicals in the reaction system was demonstrated by Rice, Johnston, and Evering (7), and Rice and Rice (8) proposed a free-radical mechanism which has been modified by Steacie (9), Semenov (10), and Benson (11). The latter proposed termination steps of the  $\beta\beta$  type, leading to 3/2-order kinetics.

Purnell and Quinn have made a detailed investigation of the effect of surface on the pyrolysis of *n*-butane (12(a)), and in a recent paper\* (12(b)) have described a study of the overall kinetics, in which they pay particular attention to the rate of production of the chief products. They concluded (12(a)) that 'conditioning' the surface, by carbon deposition, increases the rate of the heterogeneous removal of the radicals. Much of the work in their second paper (12(b)) was concerned with the breakdown of the ethyl radical, which they conclude to be in its pressure-dependent region. Kuppermann and Larson (13) have recently reported a first-order rate constant given by

$$k = 1.7 \times 10^{10} e^{-52,500/RT} \text{ sec}^{-1}.$$

Their frequency factor and activation energy are significantly smaller than those of other investigations, including the present one. They found that packing the vessel and adding carbon dioxide had very little effect on the rate.

### EXPERIMENTAL

The apparatus was essentially as described in previous papers (14, 1, 2). The reaction was carried out in vessels of approximately 200-ml capacity supported inside a large metal block the temperature of which was electrically controlled to within 0.2° C. Two quartz reaction vessels were used; one was unpacked and the other packed with quartz tubing to give a 11.6-fold increase in the surface:volume ratio. Except for runs carried out to investigate special surface effects, the results were obtained in vessels cleaned by three washings at 60° C with concentrated nitric acid, followed by rinsing with distilled water. A quartz spiral pressure gauge was used to follow pressure changes, the pressures being recorded on a Beckman photo-pen recorder; rates were determined by measuring the slopes of these records.

The *n*-butane used was research grade (99.9% pure), obtained from the Phillips Petroleum Company; it was further purified by one bulb-to-bulb distillation and was rigorously degassed.

Analyses were carried out on a Perkin-Elmer Vapor Fractometer. The C<sub>1</sub> to C<sub>3</sub> hydrocarbons and *n*-butane were analyzed using a 2-m silica gel column at 60° C; butenes were analyzed using a 3-m column containing 30% (w/w) 2,5-hexanedione on 30- to 60-mesh firebrick.

### RESULTS

The pyrolysis of *n*-butane was studied in the temperature range from 520 to 590° C, and at pressures from 30 to 600 mm Hg. Figure 1 shows a typical pressure-time record.

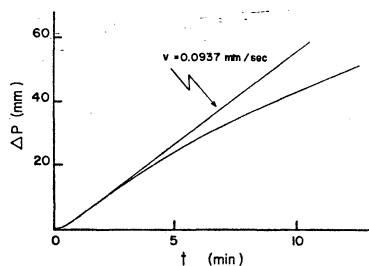


FIG. 1. A typical pressure-time curve. Temperature = 530° C, initial butane pressure = 386 mm, unpacked vessel.

There is seen to be a short induction period, and slopes were measured at the inflection point. Figure 2 shows double logarithmic plots of initial rate against pressure at various temperatures, in both packed and unpacked vessels. The order in the unpacked vessel is close to 3/2, while that in the packed vessel is slightly lower. Table I lists the 3/2-order rate constants obtained in the unpacked vessel, and Table II gives the rates at 200 mm

\*This paper appeared while our paper was in course of publication.

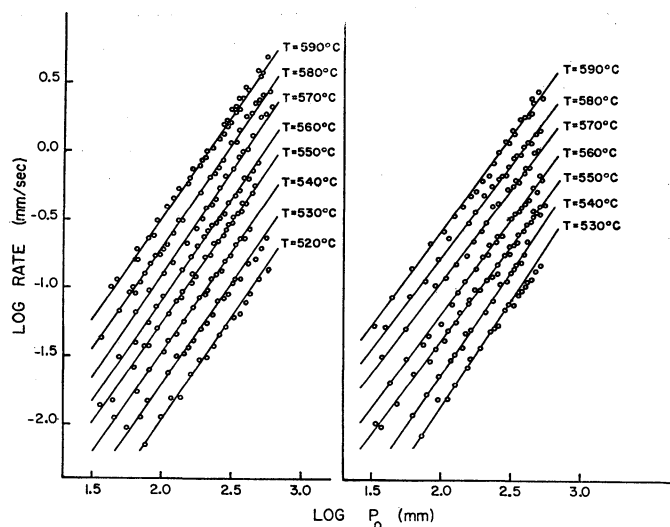


FIG. 2. Logarithmic plots of rate against pressure. The left-hand plots are for the unpacked vessel, the right-hand ones for the packed vessel.

TABLE I  
Three-halves-order rate constants in the unpacked  
unconditioned vessel

Temperature (°C)	$10^5 k$ (mm <sup>-1/2</sup> sec <sup>-1</sup> )	Temperature (°C)	$10^5 k$ (mm <sup>-1/2</sup> sec <sup>-1</sup> )
520	1.09	560	7.92
530	1.94	570	13.0
540	3.29	580	20.4
550	5.50	590	32.5

TABLE II  
Rates at 200 mm initial pressure in the packed vessel

Temperature (°C)	Rate $\times 10^2$ (mm sec <sup>-1</sup> )	Temperature (°C)	Rate $\times 10^2$ (mm sec <sup>-1</sup> )
530	4.34	570	28.1
540	7.24	580	43.7
550	11.0	590	70.5
560	16.8		

Hg in the packed vessel. Figure 3 shows a comparison of the rates in the packed and unpacked vessels at 550°C; there is seen to be a small but significant inhibition by surface, accompanied by a slight decrease in order of reaction.

Figure 4 shows an Arrhenius plot, on which the results of other workers (5, 6, 15) are included for comparison; where necessary the results were converted from first-order constants to 3/2-order ones. The activation energy is calculated to be 59.9 kcal mole<sup>-1</sup>. Figure 5 shows that the addition of a 2½-fold excess of carbon dioxide leads to no significant increase in the rate.

Figure 6 shows the effect of packing the reaction vessel and of conditioning it by pyrolyzing butane in it at 300 mm Hg for 48 hours. The reaction is quite sensitive to the state of the surface, and almost any change from a clean unpacked vessel tends to raise the activation energy; that in the packed vessel is 62.3 kcal mole<sup>-1</sup>.

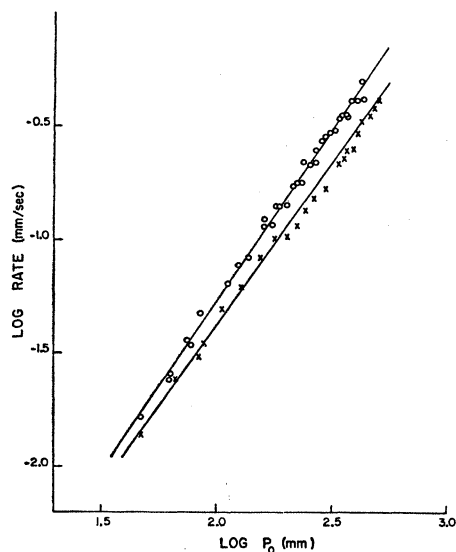


FIG. 3. Rates in the packed (X) and unpacked (O) vessel at 550°C, plotted logarithmically against the initial pressure of butane.

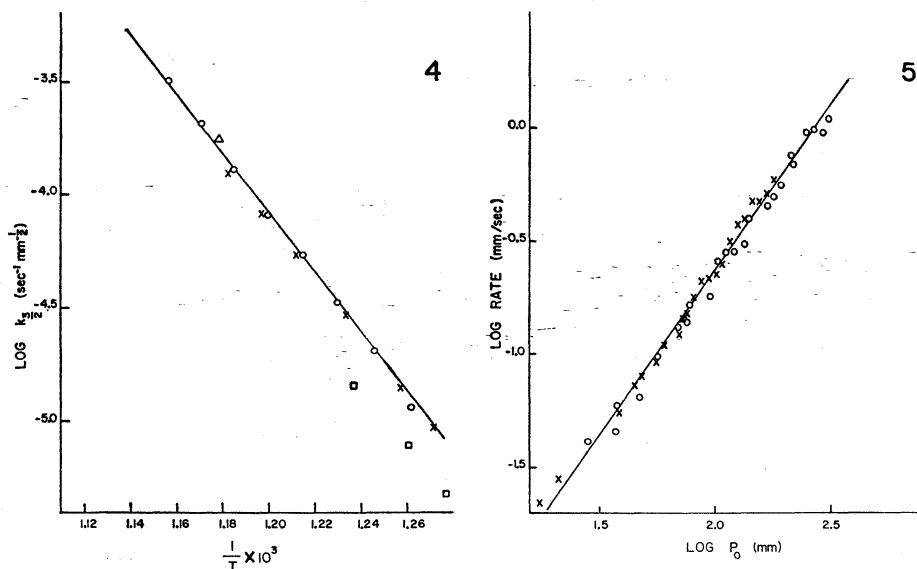


FIG. 4. Arrhenius plot for the unpacked vessel. The results of this investigation are shown as O, those of Steacie and Puddington (5) as X, those of Frey and Hepp (15) as Δ, and those of Echols and Pease (6) as □.

FIG. 5. Plot of the logarithm of the rate against the logarithm of the pressure at 580°C, showing the effect of added CO<sub>2</sub>. O denotes no added CO<sub>2</sub>, X denotes rate measured with CO<sub>2</sub>/C<sub>4</sub>H<sub>10</sub> ≈ 2.5.

Some of the analytical results are presented in Fig. 7. Figure 7(a) shows that unit decrease in butane pressure corresponds roughly to unit increase of the total pressure, while Fig. 7(b) represents the production of methane and ethane. Additional analytical data are shown in Table III; it gives some product ratios at three temperatures, all at 15% conversion and 200 mm Hg initial pressure.

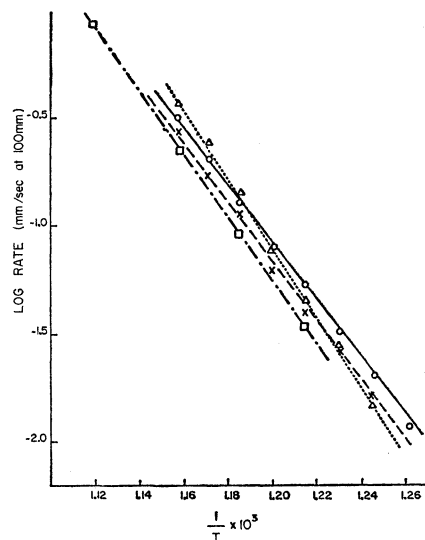


FIG. 6. Arrhenius plot showing the effect of surface. Rates measured in the clean, unpacked vessel are given by O, in a clean packed vessel by X, in a conditioned unpacked vessel by  $\Delta$ , and in a conditioned packed vessel by  $\square$ .

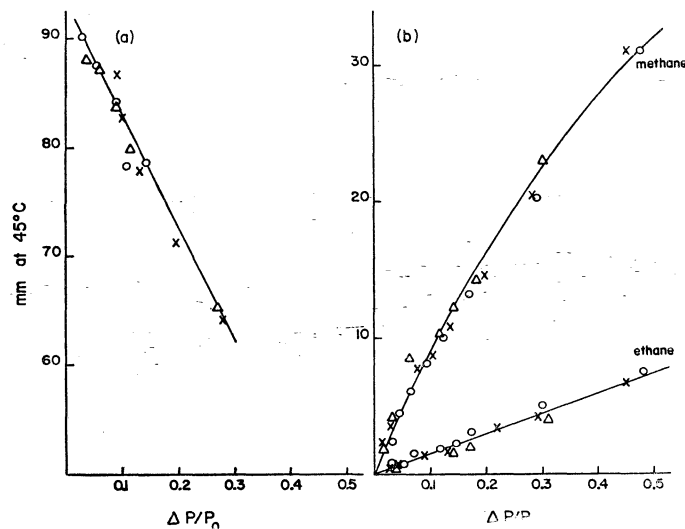


FIG. 7. Analytical results. The left-hand plot shows the correlation between the increase in total pressure and decrease in partial pressure of butane, the right-hand gives that between the increase in total pressure and appearance of methane and ethane, at 550°C (O), 570°C (X), and 590°C ( $\Delta$ ).

TABLE III  
Ratios of decomposition products  
(Initial pressure 202 mm Hg; 15% decomposition)

Temperature (°C)	$\frac{C_2H_6}{C_2H_4}$	$C_4$ products	Alkanes	$\frac{CH_4 + C_3H_8}{C_2H_4 + C_2H_6}$
		$C_1, C_2,$ and $C_3$ products	Alkenes	
550	0.616	0.012	1.08	1.92
570	0.523	0.014	1.03	1.81
590	0.467	0.021	1.02	1.80

On the basis of the present work the 3/2-order rate constant for the reaction is concluded to be

$$k_{3/2} = 3.24 \times 10^{15} e^{-59,900/RT} \text{ cc}^{1/2} \text{ mole}^{-1/2} \text{ sec}^{-1}.$$

## DISCUSSION

*Overall Reaction Mechanism*

The work of Purnell and Quinn (12(a)), and the results described in Part II, indicate that the molecular component of the reaction is of minor importance; this conclusion is supported by the fact that the order in a clean unpacked vessel is accurately three-halves. The following free-radical mechanism, which is very similar to that of Echols and Pease (6), is proposed to explain the facts:

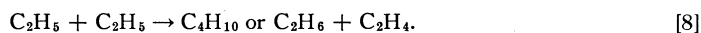


Table IV lists the known and estimated rate constants, activation energies, and frequency factors.

TABLE IV  
Kinetic parameters for elementary reactions

Reaction	Frequency factor*	Activation energy (kcal mole <sup>-1</sup> )	Rate constant* at 570° C	Reference
[1]	$1.0 \times 10^{17}$	80.0	$1.85 \times 10^{-4}$	Trotman-Dickenson (16)
[2]	$7.7 \times 10^{11}$	10.4	$1.55 \times 10^9$	Boddy and Steacie (17)
[3]	$6.5 \times 10^{11}$	24.0	$3.92 \times 10^5$	Gruver and Calvert (18)
[4]	$1.6 \times 10^{10}$	22.0	$3.18 \times 10^5$	Kerr and Trotman-Dickenson (19)
[5]	$2.7 \times 10^{11}$	9.0	$1.26 \times 10^9$	Jones and Steacie (20)
[6]	$3.0 \times 10^{14}$	39.5	$1.74 \times 10^4$	Bywater and Steacie (21) and Trotman-Dickenson (22)
[7]	$1.0 \times 10^{14}$	7.9	$8.97 \times 10^{11}$	Schiff and Steacie (23)
[8]	$1.6 \times 10^{13}$	0.0	$1.60 \times 10^{13}$	Ivin and Steacie (24)

\*In the units sec<sup>-1</sup> or cc mole<sup>-1</sup> sec<sup>-1</sup>.

The proposed mechanism gives rise to the following expressions for the steady-state radical concentrations:

$$[\text{H}] = \frac{k_6}{k_7} \left( \frac{2k_1}{k_8} \right)^{1/2} [\text{C}_4\text{H}_{10}]^{-1/2}$$

$$[\text{C}_2\text{H}_5] = \left(\frac{2k_1}{k_8}\right)^{1/2} [\text{C}_4\text{H}_{10}]^{1/2}$$

$$[\text{C}_4\text{H}_9] = \frac{k_2}{k_4} \left(\frac{2k_1}{k_8}\right)^{1/2} [\text{C}_4\text{H}_{10}]^{3/2} + \frac{k_6}{k_4} \left(\frac{2k_1}{k_8}\right)^{1/2} [\text{C}_4\text{H}_{10}]^{1/2}.$$

With the assumption of long chains, so that the removal of butane by reaction [1] is negligible, the overall rate is found to be

$$v = \left(\frac{k_3}{k_4} + 1\right) \left\{ k_2 \left(\frac{2k_1}{k_8}\right)^{1/2} [\text{C}_4\text{H}_{10}]^{3/2} + k_6 \left(\frac{2k_1}{k_8}\right)^{1/2} [\text{C}_4\text{H}_{10}]^{1/2} \right\}.$$

The data from Table IV indicate that  $k_3$  and  $k_4$  are very close to each other, although  $k_3$  is usually slightly higher.

Experimentally it is found that the reaction is strictly of the 3/2 order over the range of conditions employed, and this requires that the second term in the rate equation be negligible compared with the first. At first sight the mechanism proposed would not seem to lead to this conclusion; thus, insertion of the values of the rate constants from Table IV leads to the result that, at 570° C and 500 mm Hg,

$$\frac{\text{term 1}}{\text{term 2}} = \frac{k_2}{k_6} [\text{C}_4\text{H}_{10}] = 0.85,$$

so that the two terms appear to be comparable in magnitude. The reason for this apparent discrepancy is presumably that, as found by Purnell and Quinn (12(b)), the decomposition of the ethyl radical is not in its first-order region, but in the pressure-dependent region, the apparent order of the reaction being slightly greater than unity. In view of this the rate of decomposition of the ethyl radical is less than it would be if the reaction were of the first order. The predominance of the first term in the rate equation is therefore explained.

In the scheme as written above all butyl radicals are treated as the same. In fact *s*-butyl radicals are formed slightly more easily, as shown by Kuppermann and Larson (13) and by McNesby and Gordon (25). Kuppermann and Larson (13) estimate that for abstraction reactions such as [2] and [5] the ratio of secondary to primary hydrogen atom abstraction is

$$\frac{k_p}{k_i} = 2.43e^{-2640/RT}.$$

This ratio is about 0.5 at 570° C. About one-third of the  $\text{C}_4\text{H}_9$  produced is thus *n*- $\text{C}_4\text{H}_9$ , and two thirds is *s*- $\text{C}_4\text{H}_9$ . The ratio (propylene+methane)/(ethylene+ethane) should therefore be about 2, in reasonable agreement with the experimental ratios of 1.8–1.9 (Table III). According to McNesby and Gordon (25) the ratio  $k_p/k_s$  is  $1.50e^{-2100/RT}$ , and this leads to a  $(\text{CH}_4 + \text{C}_3\text{H}_6)/(\text{C}_2\text{H}_4 + \text{C}_2\text{H}_6)$  ratio of 2.4. The fact that our ratios are significantly less than this may be due to the fact that there is hydrogen-atom abstraction from propylene; the resulting radical may combine with a methyl or ethyl radical, giving butene-1 in the former case. This suggestion is related to the conclusion by Dintses and co-workers (27) that the butane decomposition is inhibited by products. Some isomerization of butyl radicals is possible, but Gordon and McNesby (26) detected none at somewhat lower temperatures (up to 450° C).

The mechanism proposed does not explain the small amounts of butenes formed in the reaction. The kinetic parameters for the decomposition of either *n*-butyl or *s*-butyl

radicals into butenes and hydrogen atoms have not been determined, but the activation energy is probably (21) well above 40 kcal mole<sup>-1</sup>. On this basis, assuming normal frequency factors, the amounts of butenes should be less than 0.1% of the total products; actually they are 10 to 20 times this (Table III). Possibly the butenes arise from surface dehydrogenation or from a small molecular component of the reaction. It is to be noted that the butenes are about one-quarter butadiene, the formation of which is difficult to explain by any chain mechanism.

According to the rules of Goldfinger, Letort, and Niclaude (28) (cf. Table 2 of ref. 2), in order to have 3/2-order overall kinetics one must postulate one of the following possibilities:\*

- (1) first-order initiation,  $\beta\beta$  recombination;
- (2) second-order initiation,  $\beta\mu$  recombination;
- (3) second-order initiation,  $\beta\beta M$  recombination.

The first is the one that is believed to apply. The second can be eliminated since it predicts a positive inert gas effect, which was not found, and also the  $\beta\mu$  termination can be shown, by the insertion of kinetic parameters, to be considerably slower than the  $\beta\beta$  recombination (by  $\sim 50$  times at 500 mm Hg). This termination might become important at very low pressures, when the order should change to unity (assuming initiation to remain first order). The third possibility cannot be positively eliminated on the basis of the present work, since it predicts the same kind of behavior as the first; our reasons for preferring the first possibility are considered in the next section.

In connection with the lack of inert gas effect found for this system it is to be noted that a small inert gas effect was reported by Jach and Hinshelwood (29, 30), who used mainly sulphur hexafluoride. This substance was shown in an investigation of the propane decomposition (2) to be not inert, and results with it are therefore suspect.

#### *The Initiation and Termination Reactions*

The initiating reaction has been postulated to be the breakdown of *n*-butane into two ethyl radicals, in its high-pressure first-order region. Brinton and Steacie (31) have shown that at 250° C the recombination of ethyl radicals is certainly first-order at pressures of 0.5 mm and higher, and is probably first-order at pressures as low as 0.02 mm Hg. The Kassel-Rice-Ramsperger theories predict that the transition pressure should vary with the  $(s - 1/2)$ th power of the temperature, where  $s$  is the number of effective degrees of vibrational freedom. If  $s$  is taken as 12 in this case the initiating reaction should be first-order down to very low pressures; even if  $s$  were as large as 19 the reaction is probably still first-order at 100 mm Hg. It therefore seems most reasonable to consider that the initiation is in its first-order region under all of the experimental conditions employed in this work, and that the termination step [8] is in the second-order region. Support for this view is provided by the fact that for the ethane decomposition the evidence strongly supports the conclusion that the ethyl radical recombination is in its second-order region (1).

Another possible initiation reaction is the split into a methyl and a propyl radical. However, Trotman-Dickenson (16) has estimated that the dissociation energy for this process is some 4 kcal mole<sup>-1</sup> higher than for the split into two ethyl radicals. The frequency factor may be slightly higher and may partly compensate for this; on the whole, however, it seems likely that the split into two ethyl radicals will predominate.

\*A  $\beta$  radical is one which undergoes second-order propagation reactions, a  $\mu$  radical one that undergoes first-order reactions. In the present scheme the ethyl radical is both a  $\beta$  and a  $\mu$  radical (reactions [2] and [6]), but is predominantly a  $\beta$  radical since reaction [2] is more rapid than reaction [6].



If initiation is first order the termination step must be  $\beta\beta$ . The reactions



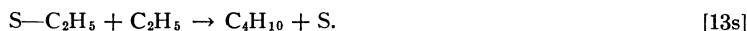
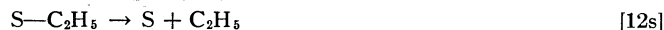
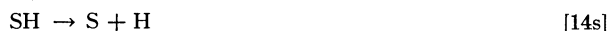
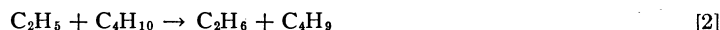
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occur in their third-order regions (1, 2) under the conditions of these experiments; the termination must therefore be by reaction [8]. By inserting numerical values it can in fact be shown that this reaction should be the predominant one.

### Surface Effects

The rates in the packed clean vessel are seen from Fig. 6 to be lower at all temperatures than those in the unpacked clean vessel. They are most depressed at lower temperatures, so that the activation energy is slightly higher in the packed vessel. It is suggested that free surface sites (S) on the quartz can abstract hydrogen atoms from the butane molecule, in a manner similar to nitric oxide. According to this view the reaction occurs in part as



Application of the steady-state treatment leads to the following expression for the overall rate:

$$v \approx k_2 \left( \frac{k_3}{k_4} \right) \left( \frac{k_{1s}k_{12s}}{k_{11s}k_{13s}} \right)^{1/2} [\text{C}_4\text{H}_{10}]^{3/2}$$

No reliable estimates of the individual rate constants can be made. The surface-controlled reaction should become more important as the temperature is lowered, and an increase in activation energy is to be expected.

The results in the 'conditioned' vessel are of some interest. The reaction in the conditioned unpacked vessel has a very high activation energy, and its rate at high temperatures is greater than that in the clean vessel. The effect of packing in the conditioned vessel is much more pronounced than in the clean vessel. These results confirm the conclusion that some of the initiation and termination is taking place at the vessel walls. The larger effect of packing indicates that the conditioned surface is a better inhibitor than initiator, compared with the clean surface. As graphite consists of a two-dimensional fused ring it is not surprising that atoms and small free radicals are able to recombine readily on the surface. The slight increase in rate over that in the clean vessel at the highest temperatures suggests that a small, purely heterogeneous decomposition may be taking place in addition.

### Kinetic Parameters

If the reaction is assumed to be completely homogeneous the predicted activation energy is

$$E = E_3 - E_4 + E_2 + \frac{1}{2}(E_1 - E_8).$$

Insertion of the values in Table IV leads to 52.4 kcal mole<sup>-1</sup>, to be compared with the experimental value of 59.9 kcal mole<sup>-1</sup>. The calculated frequency factor is  $2.5 \times 10^{14}$  cc<sup>1/2</sup> mole<sup>-1/2</sup> sec<sup>-1</sup>, to be compared with the experimental value of  $3.2 \times 10^{15}$ . The calculated absolute rate is 6.5 cc<sup>1/2</sup> mole<sup>-1/2</sup> sec<sup>-1</sup> at 570° C, to be compared with the experimental value of 0.97.

The agreement is not as good as with ethane (1) and propane (2); this is probably to be attributed to the greater importance of the heterogeneous reaction. This, as seen in the previous section, tends to raise the experimental activation energy.

#### ACKNOWLEDGMENTS

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