Initiation of the Homogeneous *n*-Butane Oxidation

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Initiation of the oxidation of hydrocarbons, an important part of many flame systems' remains largely unsolved. This paper reports a study of the oxidation of butane under conditions that yield information on the homogeneous initiation reactions.

A sequential reaction mechanism is proposed involving activation of an oxygen molecule followed by attack on a butane. This leads to rate equations which accurately describe the observed butane decomposition rates. Activation energies have been calculated from experimental data with this equation and are found to check values obtained from the literature and from theoretical considerations.

The tentative initiation mechanism is used to explain the existence of three classes of products in the exit gases: hydrocarbons other than butene, butene, and oxygenated products.

Under some operating conditions periodic cool flame phenomena are observed, and their effect on the course of the reaction has been explained.

Although considerable progress has been made in the field of low-temperature hydrocarbon oxidation, kinetic data which could be used as a basis for the formulation of reaction mechanisms are lacking. Methane and formaldehyde, the two simplest members of their respective series, have been studied extensively, and their oxidation reaction kinetics has been clarified by Norrish and his co-workers (*10*). However for hydrocarbons above methane only a few systematic kinetic studies have been made, and virtually no information is available for hydrocarbons above heptane. The large number of reaction products, their isolation, identification, and quantitative analysis have without the use of expensive mass spectrographic techniques presented a considerable barrier to the characterization of the oxidation reaction. Although the development of gas chromatography as an analytical device has given a powerful new tool to investigators in this field, nevertheless the myriad chemical reactions occurring simultaneously in the oxidation of even such apparently simple molecules as ethane prohibits the writing of any single rate equation descriptive of the entire process. An excellent review article by Tipper (*14*) points up the complexity of the problem.

There are at least three different regions of interest: a precool-flame region in which slow, partial oxidation occurs, usually accompanied by a faint luminescence; the cool flame region, evidenced by higher rates of partial oxidation, usually characterized by periodic pressure fluctuations which correspond to the alternate formation and extinction of cool flames; and two-stage ignition, leading to complete reaction. The last of these is always preceded by a single cool flame. Which of the above phenomena is realized in a given experiment depends on the pressure, temperature, concentration, and reactor geometry.

By far the large majority of partial-oxidation studies have been performed in batch systems in which reaction rates are followed by a measurement of pressure increase, and quenching of the reaction is accomplished by removing the system from its oven and plunging it into a cold bath. There are, however, several advantages of flow system over batch systems for partial oxidation studies. In addition to their obvious manipulatory advantages, flow systems are capable of yielding much larger quantities of product for analysis and are far more flexible to operate. Flow systems have been used by King, Sandler, and Strom (*8*), Kovijman (*9*), Garner and Petty (*6*), Frank and Blackham (*5*), Quon, Dalla Lana, and Govier (*11*), and others. Stable (nonperiodic) cool flames have been obtained in flow systems of the proper configuration by Boord and associates (*2*) and Williams, Johnson, and Carhart (*15*).

The effect of surface on the partial oxidation of hydrocarbons is particularly difficult to characterize. The nature and state of the surface and surface-to-volume ratio often play important roles in the reaction. Surface is generally acknowledged to have an inhibitory effect on the reaction by free radical destruction. Although free radicals can be destroyed and initiated both homogeneously and heterogeneously, surface destruction is more efficient than gas-phase destruction. Hence an increase in surface to volume ratio should yield a decreased reaction rate. This has been observed experimentally. However surface initiation is known to play an important role in many partial oxidation reactions (*13*). One of the goals of this research was to attempt clarification of this point.

The paper then reports results from a kinetic investigation of the initiation of normal-butane oxidation in a flow reactor. As will become evident, wall effects were proved negligible, and only the homogeneous reaction was studied. Normal butane was chosen because less attention has been paid to it than to any normal hydrocarbon in the C_1 to C_5 range and because it is the logical precursor to an understanding of the combustion of higher hydrocarbons which may be of more practical interest. The latter arises because butane is the first member of the series having both primary and secondary carbon atoms adjacent to the points of most probable attack.

EXPERIMENTAL PROGRAM: EQUIPMENT

The equipment used in this project consisted of the normal sequence of reaction system and analytical apparatus. The reactor is shown diagrammatically in Figure 1. A mixture of oxygen and normal butane of better than 99.5% purity was fed to the reactor through standard flow regulation and metering devices. Gas pressure at all flow meters and in the reactor was measured manometrically, and temperatures were measured throughout the apparatus by iron-constantan, glass-insulated thermocouples. Surface temperatures were measured at the inlet to the reactor, at the axial center of the reactor, and at the reactor outlet (Figure 1). All temperatures were recorded continuously. The reactor and gas preheaters were surrounded by a high-temperature oven providing the primary heat source.

The reactor consisted of three parts. The first was a packed inlet section, the second the reactor proper, the third a packed outlet section. The packing was random chips and turnings of stainless steel washed with acetone and dried overnight at 110°C. It was supported by a stainless steel screen. The conical inlet and outlet sections served two purposes. They served as smooth enlarging and reducing sections, thus eliminating any large stagnant areas upstream or downstream to the reaction zone, and they provided effective heat transfer sections.

Product gases were led to a cold-finger type of condenser. Liquid product was collected in standard 0°C, cold traps,

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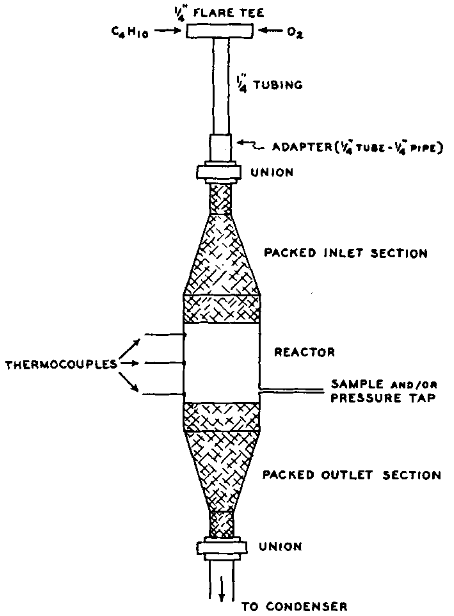

Fig. 1. Reactor assembly.

and the uncondensed gases were sampled in conventional gas-collecting bulbs.

For analysis a gas chromatographic unit was constructed. Helium of 99.99% minimum purity was used as a carrier gas. Details of the construction, operation, and use of this device as well as of the complete experimental apparatus are available (*12*).

Because of the large number of products present in the exit gases, five separate columns were used for the analysis. All columns were made of ¼-in. copper tubing and were packed tightly by use of an electric vibrator. The following columns were used:

1. Column 1, 7 ft. of 30 to 60–mesh type 5A molecular sieve, was used for analysis of hydrogen, oxygen, nitrogen, methane, and carbon monoxide.

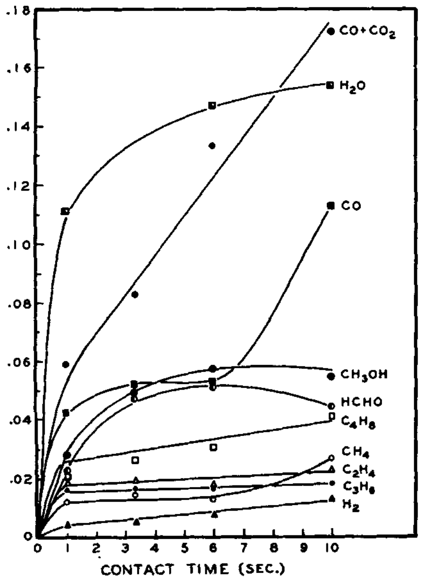

Fig. 2. Sample product distribution; moles of product formed vs. contact time at 350°C., 20% initial oxygen concentration.

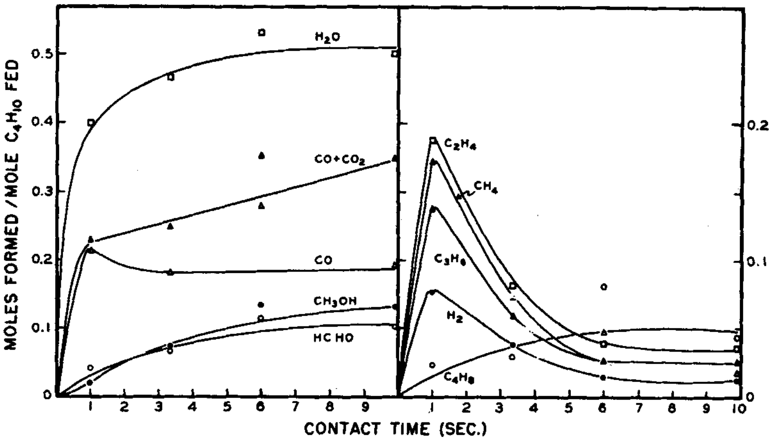

Fig. 3. Sample product distribution; moles of product formed vs. contact time at 350°C., 40% initial oxygen concentration.

2. Column 2, 4 ft. of 80-mesh activated charcoal, was used for analysis for methane, ethylene, and ethane. This column could also be used for carbon dioxide but was not nearly so sensitive for this as was column 3.

3. Column 3, 3½ ft. of 40 to 60–mesh silica gel, was used for analysis of carbon dioxide.

4. Column 4, 3 ft. of 20-mesh activated alumina, was used for analysis of ethylene, propane, acetylene, propylene, butane, and the butylenes.

5. Column 5 was 10 ft. in length, 4 ft. of which were packed with di-*n*-octyl phthalate supported on 60 to 100–mesh acid-washed celite, and the remaining 6 ft. consisted of celite impregnated with glycerol. The packing of each section was prepared by contacting 35 wt. % of the liquid with 65 wt. % celite in an acetone slurry. The acetone was subsequently removed by overnight oven drying at 110°C. Column 5 was used for analysis of the liquid product (aldehydes, alcohols, ketones, and water).

The chromatographic columns and the thermal-conductivity cell were enclosed in a constant-temperature oven, with heat supplied by nichrome-resistance wire coils mounted on the inner surface of the oven. Temperatures in excess of 200°C. were obtainable and were measured at the center of the oven. Temperature control was effected by standard devices.

EXPERIMENTAL PROGRAM: PROCEDURE

After preliminary start-up operations had been completed, a reaction was initiated and the reaction temperature was adjusted to the desired value. The system was allowed to equilibrate and was operated continuously for 2 hr. before any product was collected. The duration of any single run was usually determined by the rate of liquid-product formation, 2 cc. being required for all analyses. If more than one run was made in any given day, 2 hr. was allowed for the system to reequilibrate at the new conditions.

Preliminary experimentation established that reaction temperatures from 275° to 350°C., contact times between 1 and 10 sec., and from 20 to 40% inlet oxygen concentrations would be suitable for the purposes of this work. To randomize errors throughout the program an experimental sequence was set up in which the runs were made in random order. To obtain information regarding the reproducibility of the work, a set of check runs was superimposed on the random series. Complete details of the experimental work and the results obtained are, again, available in reference *12*.

The preliminary work also served to prove the absence of surface effects. For this purpose the entire reactor assembly was packed with stainless steel chips and turnings. The reactor temperature was adjusted to 335°C., and the reactor was fed with a 30% oxygen-to-70% butane mixture at a rate such that the contact time was 7 sec. Over 7½ hr. of operation no measurable reaction of any kind was found. After the detailed experimental program had been completed, a check on this was made with the conditions under which the highest reaction rate had been observed. At a temperature of 350°C., 40% initial oxygen concentration, and 1.09 sec. contact time no reaction was observed in 2 hr. of operation with the completely packed

TABLE 1. TYPICAL PRODUCT DISTRIBUTION
Run conditions: temperature = 300°C., contact time = 3.35 sec., initial oxygen concentration = 40%

Constituent	Total moles exit reactor × 10^3
H_2	3.61
O_2	72.1
CH_4	9.61
CO	84.1
C_2H_4	14.7
C_2H_6	0.37
CO_2	16.5
C_3H_8	0.05
C_3H_6	14.0
C_4H_8	17.5
C_4H_{10}	299.0
HCHO	37.0
CH_3CHO	3.56
$(CH_3)_2CO$	1.28
CH_3OH	30.0
H_2O	161.0
Acid	2.58

Butane conversion, oxygen conversion, material balances, mole fractions, etc., may be calculated from these data.

TABLE 2. MATERIAL BALANCE

Run (12)	Carbon balance	Oxygen balance
24	100.9	99.6
25	102.1	97.6
26	100.0	97.9
47	105.8	92.9
48	93.0	98.0
49	98.1	97.5

The data are reported as percentage of reactant fed which was accounted for in the exit stream. For the carbon and oxygen the mean balances yield 100.0 and 97.4% respectively, and the coefficients of variation are 3.63 and 2.13.

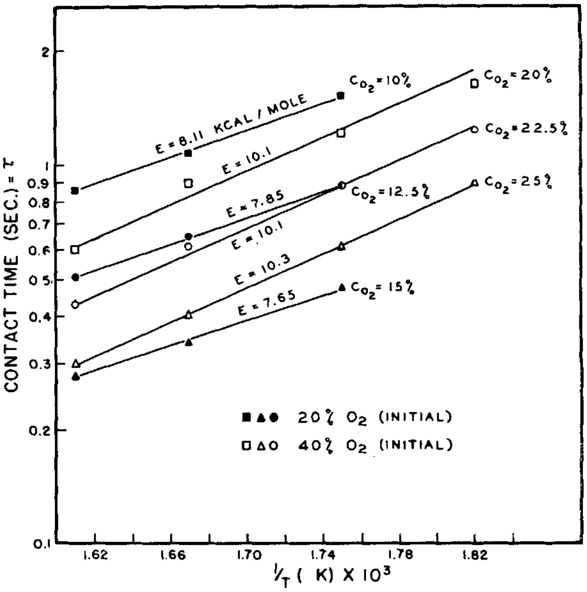

Fig. 4. Estimation of activation energy from

$$\log \tau = \log \left[\frac{\rho}{A} \int_0^{x_A} \frac{dx_A}{\prod^{i} (C_i^{\,i})} \right] + E/2.\,3RT.$$

reactor. The reactor temperature was then gradually increased. At 420°C. a reaction was obtained. This reaction was characterized by a very low carbon monoxide formation, approximately 2.5% of the methane-formation and approximately ⅓ of the hydrogen-formation rates previously observed. This reaction was sustained as the reactor temperature was decreased below 420°C., but the rate dropped off very sharply. At 370°C. the reaction was again below the detectable level. Since the maximum operating temperature throughout this work was 350°C., it is evident that reaction in the inlet packed section may be ignored in this study.

To study the quenching action of the packed outlet section, samples were taken directly from the reactor and compared with those removed from the condenser outlet. The samples from the reactor were removed at a rate slower than the flow rate in order to avoid sucking of gas back from the packed section. There was no detectable difference between the concentrations of products in the sample taken just prior to the packed section and in those taken from the condenser.

RESULTS

A typical list of products obtained at one set of operation conditions is shown in Table 1. Forty-nine experimental runs were made, approximately half at 20% inlet oxygen concentration (the remainder being normal butane) and approximately half at 40% inlet oxygen concentration. Contact time was varied between 1 and 10 sec. and the temperature between 275° and 350°C. All product analyses were obtained by means of gas chromatography with the exception of analyses for acid, formaldehyde, and peroxide in the liquid, which were made chemically. The absence of peroxides in the products is interesting but easily explained by the configuration of the reactor and condenser system; peroxides are known to be unstable and to decompose on the walls of a reactor or on other surfaces.

Figures 2 and 3, which illustrate typical product distributions as a function of contact time, formed the basis for the kinetic analysis which was made. Complete material balances were made for six of the runs; the results are shown in Table 2. A reproducibility study was made on five of the runs. Statistical analysis of the results indicated that all deviations from the mean were random, and the standard deviation for all constituents varied between 0.50 and 2.06.

Table 3 presents a sample of the experimental data which formed the basis for the conclusions presented in this paper. Similar tables were obtained for each run and are available (*12*). These data were correlated graphically by the preparation of plots of product distribution as a function of contact time. Because of the configuration of the reactor and condenser system, the presence of peroxides in more than trace quantities is not to be expected. Chemical analysis of the liquid product indicated an average peroxide concentration of 0.5% based on the liquid product.

It will be noted that the data from runs using 40% initial oxygen concentration show a maximum in the conversion-contact time curve which is not observed in the 20% data. This peak was due to periodic cool-flame formation which manifested itself by strong pressure fluctuations and marked increases in the cracking reactions leading to the formation of unusually large amounts of hydrogen, methane, ethylene, and propylene. The final conversion rate at high contact time in this 40% data is approximately double that observed in the 20% data.

ANALYSIS OF THE RESULTS

Wall Effect

As previously noted, surface was shown to have an inhibitory effect on the over-all oxidation reaction. To estimate the effect of surface in the unpacked reactor (the effect of any quenching at the wall), it was necessary to calculate a range of effectiveness of the wall. The *range of effectiveness* may be defined as that distance from the wall at which the probability of a free radical-wall collision (and subsequent destruction) is equal to the probability of a radical-molecule collision (leading to chain continuation). When one assumes a free radical at distance δ from the wall, and when one assumes that in its next move it moves toward the wall, the ratio of the probability of a collision with the wall to that of a collision with another molecule may be calculated (as a function of δ) and set equal to unity. For $T_R = 600°K.$, a typical reactor temperature, and with $r_m = 4 \times 10^{-8}$ cm., such a calculation yields $\delta \cong 4.06 \times 10^{-6}$ cm. Hence the range of effectiveness of the wall extends approximately 10^{-6} cm. into the reactor. The authors have assumed in this calculation that all collisions between free radicals and surface or molecules are effective. Even if the wall collisions are 1,000 times as effective as homogeneous collisions, δ is only $\approx 10^{-3}$ cm. Thus the volume bounded by δ is negligible by comparison with the total reactor volume, and the wall effect in the homogeneous section may be neglected.

Temperature Gradient

To employ the surface temperature measured at the axial center of the reactor in subsequent calculations of the activation energy, it is necessary to show that this temperature is an adequate representation of the true reactor temperature. Since it was not feasible to obtain a radial temperature profile experimentally, this gradient was calculated for the most drastic conditions (that is, run 34, in which the maximum heat generation

Table 3. Sample Data Sheet—Run 26

Initial oxygen concentration = 39.9%, reactor temperature = 299°C. (572°K.)
contact time = 3.34 sec., room temperature = 29°C.

Constituent	Mole oxygen	Reacted carbon, %	Mole %	Moles formed/ mole C_4H_{10}fed
H_2			0.47	0.0094
O_2	0.144		9.39	
N_2				
CH_4		2.75	1.25	0.0249
CO	0.084	24.1	10.9	0.218
CH_4(c)				
C_2H_4		8.39	1.91	0.0381
C_2H_6		0.21	0.048	0.00096
CO_2	0.033	4.72	2.15	0.0427
$C_2H_4(Al_2O_3)$				
C_3H_8		0.04	0.007	0.00013
C_3H_6		16.0	1.82	0.0362
C_4H_8		20.0	2.28	0.0454
C_4H_{10}			38.9	
HCHO	0.037	10.6	4.81	0.0959
CH_3CHO	0.0036	2.04	0.463	0.0092
$(CH_3)_2CO$	0.0013	1.10	0.167	0.0033
CH_3OH	0.030	8.56	3.90	0.0777
H_2O	0.161		20.9	0.417
*Acid	0.0052	1.48	0.336	0.0067
Totals	0.499			

Rate of liquid product formation = 4.28 g./hr.; 5.35 g. total
Moles O_2 fed = 0.255
Moles C_4H_{10} fed = 0.386; moles carbon fed = 1.544 = C
Total mass fed = 30.57 g.
$R_1 = 1.65$
$R_2 = 0.925$
$R_3 = CO_2/C_2H_4 = 1.12$

$T_i = 28.3/224 \times 273/302 \times 0.465\ N_i = 0.0531\ N_i$

Material Balances:

Oxygen 97.9%
Carbon 100%
Conversions:

Oxygen 71.7%
Butane 22.7%
% C_4H_{10} to: oxygenated products 11.9%

per unit volume per unit time was obtained).

Assuming radial symmetry and no axial gradient, one can solve the heat transfer equation with a heat-generation term. Assuming that half the butane reacts (all going to carbon dioxide and water), one obtains a generation rate of 0.00125 cal./(cc.) (sec.) This is undoubtedly much higher than the values realized during the experimentation. An average value of the thermal conductivity was estimated to be 1.03 × 10^{-4} cal./(sec.) (cm. °C.), and a maximum temperature difference between reactor center and wall was calculated to be 6.9°C. The axial temperature gradient, as measured by surface thermocouples, was found to be 2°C./cm. Since the length of the reactor is 3 cm., this represents a 6°C. maximum variation in temperature under the worst possible conditions. Thus the assumption of an isothermal reactor is justified, and the reaction temperature (as measured by a center axial-wall thermocouple) is subject to an uncertainty of approximately 6°C. This represents a temperature variation of less than 2% on the Kelvin scale.

Preliminary Estimate of Over-all Activation Energy

In order to postulate a set of initiation reactions which would lead to a rate equation to be tested against the experimental data, some information concerning the energies of the reaction was required. An estimate of the over-all activation energy was made as follows. In a flow reactor

$$r\,dV = F\,dX_A \tag{1}$$

when one rearranges and integrates, with

$$r = \frac{dC_B}{dt} = -k[\prod^{i} (C_i{}^j)] \tag{2}$$

where dC_B/dt = rate of consumption of butane, $\pi^i\ C_i{}^j$ = the product of all of the molecular concentrations upon which the rate depends, raised to the appropriate power j, and with

$$F = \rho Q \tag{3}$$

one obtains

$$\frac{V}{\rho Q} = \frac{1}{k}\int_0^{X_A} \frac{dX_A}{\prod^{i} C_i{}^j} \tag{4}$$

But

$$\frac{V}{Q} = \tau$$

= contact time based on inlet flow rates. Then

$$\frac{\tau}{\rho} = \frac{1}{k}\int_0^{X_A} \frac{dX_A}{\prod^{i} C_i{}^j} \tag{5}$$

Taking the logarithm of each side and substituting the Arrhenius form for k, one obtains after slight rearrangement

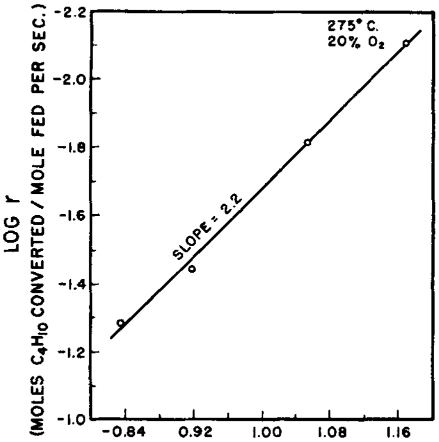

Fig. 5. Test of second-order oxygen dependence (20% oxygen data).

$$\ln \tau = \ln\left[\frac{\rho}{A}\int_0^{X_A} \frac{dX_A}{\prod^{i} C_i{}^j}\right] + \frac{E}{RT} \tag{6}$$

Since butane is present in large excess, oxygen is the limiting reactant and to a first approximation will be the major term in $\pi^i\ C_i{}^j$. At constant oxygen concentration the second log term will be approximately constant, and a plot of ln τ vs $(1/T)$ should yield an activation energy. At very low contact times, conversions are small and the oxygen concentration does not change radically through the reactor. Plots of outlet oxygen concentration as a function of contact time were made, and from these curves for each value of oxygen concentration values of τ and T were taken and plotted as log τ vs. $(1/T)$. These results are shown in Figure 4 for both 40 and 20% initial oxygen concentrations. Activation energies between 7.7 and 10.3 kcal./mole were obtained.

Initiation Reaction

With a knowledge of the approximate activation energy, obtained in the previous section, some tentative statements can be made regarding the nature of the controlling step or steps in the partial oxidation reaction. Over-all activation energies in the range of 8 to 10 kcal./mole could indicate either a diffusion-controlled step or a low-energy gas phase or wall activation. Since the reaction has been shown to be surface inhibited, a diffusion or activation involving the wall can play no part in the activation process. This leaves the possibility of a low-energy gas-phase bond-activation step, involving either O_2/C_4H_{10}, C_4H_{10}/C_4H_{10}, or O_2/O_2 collisions.

Of the three possible types of initiating collisions the oxygen-butane and the butane-butane collisions may be eliminated from consideration due to the number of degrees of freedom involved. The energy transferred by the collision is dissipated among these many degrees of freedom, and as a result no one of the

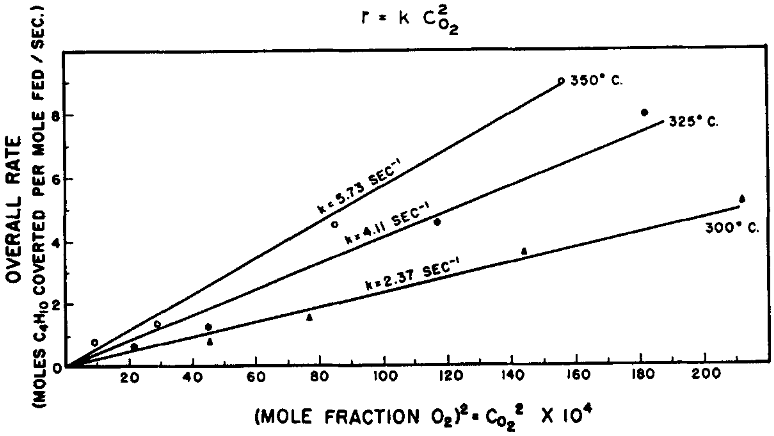

Fig. 6. Test of rate equation (20% oxygen data).

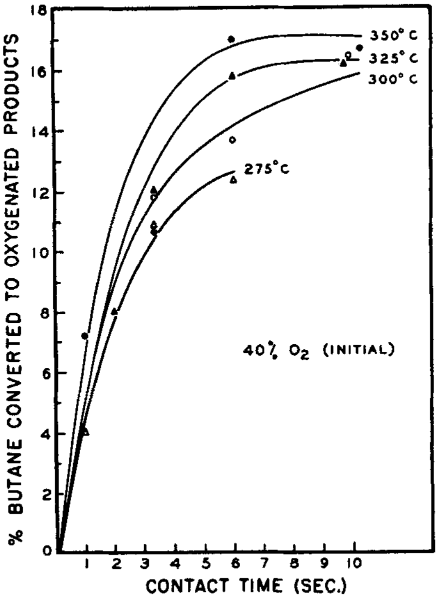

Fig. 7. Conversion to oxygenated products (40% oxygen data).

bonds is likely to undergo activation. However in an oxygen-oxygen collision only one bond is available for activation in each of the two participating molecules. The following tentative mechanism, descriptive of the initiation process, may now be written

$$O_2 + O_2 \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} O_2^* + O_2 \qquad (7)^*$$

$$O_2 + A \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} O_2^* + A \qquad (8)$$

$$O_2^* + C_4H_{10} \xrightarrow{k_3} C_4H_9\cdot + HO_2 \qquad (9)$$

Equation (7) represents a collisional activation-deactivation process resulting in the formation of excited oxygen molecules. Equation (8) indicates that the activation and deactivation could also involve another species A, where A may be any other molecule present with the exception of O_2 and O_2^*. Equation (9) is the free radical initiation step. The rate of O_2^* formation is then

$$\begin{aligned}\frac{dC_{O_2*}}{dt} &= k_1 C_{O_2}^{\ 2} + k_2 C_{O_2} C_A \\ &- k_{-1} C_{O_2*} C_{O_2} - k_{-2} C_{O_2*} C_A \qquad (10) \\ &- k_3 C_B C_{O_2*}\end{aligned}$$

when one makes the steady state assumption for the active species

$$\frac{dC_{O_2*}}{dt} = 0 \qquad (11)$$

and

$$C_{O_2*} = \frac{k_1 C_{O_2}^{\ 2} + k_2 C_{O_2} C_A}{k_{-1} C_{O_2} + k_{-2} C_A + k_3 C_B} \qquad (12)$$

Since butane is present in large excess, $C_A \approx C_B$, and

$$C_{O_2*} = \frac{k_1 C_{O_2}^{\ 2} + k_2 C_{O_2} C_B}{k_{-1} C_{O_2} + k_{-2} C_B + k_3 C_B} \qquad (13)$$

It seems reasonable to assume that $k_2 C_{O_2} C_B$ is much smaller than $k_1 C_{O_2}^{\ 2}$, and similarly that $k_{-2}\ C_B \ll k_{-1}\ C_{O_2}$. Hence

$$C_{O_2*} \cong \frac{k_1 C_{O_2}^{\ 2}}{k_{-1} C_{O_2} + k_3 C_B} \qquad (14)$$

The rate of butane conversion from (9) is

$$\begin{aligned}\frac{dC_B}{dt} &= -k_3 C_{O_2*} C_B \\ &= -\frac{k_3 k_1 C_B C_{O_2}^{\ 2}}{k_{-1} C_{O_2} + k_3 C_B}\end{aligned} \qquad (15)$$

An approximate second-order oxygen dependence, confirmed in the next section, indicates that the term $k_{-1}\ C_{O_2}$ must be negligible in comparison with $k_3\ C_B$ and that for subsequent development and testing the following over-all rate equation may be used:

$$\frac{dC_B}{dt} = -k_1 C_{O_2}^{\ 2} \qquad (16)$$

Test of Rate Equation

The validity of Equation (16) was tested by the experimental data. Figure 5 shows a check of the second-order dependence on oxygen concentration. A plot of log r vs. log C_{O_2} should have a slope of 2 if the proposed rate equation is correct. The rates were obtained from the butane conversion-contact time curves. At a given contact time the rate was measured graphically, and the corresponding value of oxygen concentration at this contact time was used to prepare

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*Bleakney (1) has recently reported the relaxation time for excited oxygen to be approximately 10^{-5} sec. under the conditions of this work. Since the collision frequency is many orders of magnitude greater than this, the proposed mechanism involving vibrationally excited oxygen molecules appears not to be unreasonable from this point of view.

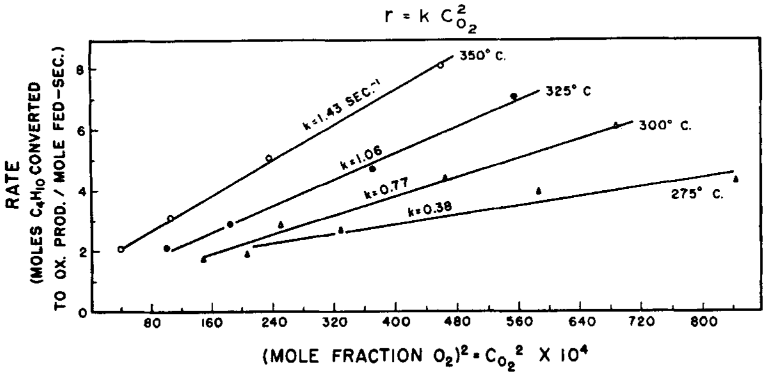

Fig. 8. Test of rate equation (40% oxygen data).

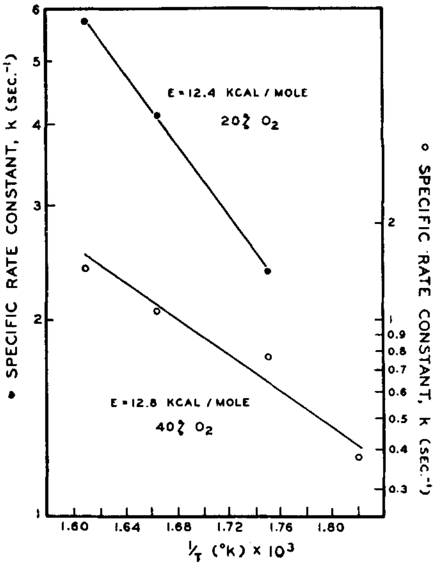

Fig. 9. Arrhenius plot.

Figure 5. A slope of 2.2 was obtained in excellent agreement with the proposed second-order oxygen dependence.

The entire rate equation was next tested for constancy of the specific rate constant. To satisfy the rate equation, plots of rate of butane conversion vs. $C_{O_2}{}^2$ must be linear and pass through the origin. Rates were obtained by graphical differentiation of the data. These data are plotted for the 20% oxygen runs in Figure 6. The results are in definite agreement with the rate equation.

As has previously been noted, cool-flame formation was observed in some of the runs made at 40% initial oxygen concentration. The innate unsteadiness of this periodic phenomenon precludes the direct use of the proposed rate equation for this data. However some interesting information can be obtained by a modification of the rate term itself. If, instead of over-all butane conversion, butane converted only to oxygenated products is plotted against contact time, a smooth curve is obtained (Figure 7). Bearing in mind that the rates obtained from this data are of different significance than the rates used previously one may make a similar type of analysis (Figure 8). In Figure 8 the rate of conversion to oxygenated products only is plotted against $C_{O_2}{}^2$. The linearity of these plots confirms the validity of the rate equation and indicates that the initiation mechanism is probably the same as for the 20% runs.

Values of k were obtained from the slopes of the lines shown in Figures 7 and 8. The over-all energy of activation of the process was then determined from plots of log k vs. $1/T$ (Figure 9). The values obtained for E_A are in good agreement with those estimated in the previous section.

The postulate of an activated oxygen molecule resulting from an oxygen-oxygen collision seems to be in agreement with the over-all activation energies obtained. The energy E_1 required for a transition from the oxygen ground state to the first vibrational level is 4.6 kcal./mole, and 10 kcal./mole is required for the second (*7*). Excitation to the second or third level then seems necessary for this process.

Over-all Reaction

Over twenty products of the partial oxidation of *n*-butane were observed; there are no doubt traces of many more. To set up a reaction sequence which not only leads to all the observed products but also agrees with the distributions obtained experimentally is an insurmountable task at this time. Many of the products react further, and it is not feasible to specify completely the interrelations of these products with the reactants, radicals, and other products involved. A partial list of reactions which probably occur has been prepared (*12*).

Three general types of products have been found: butenes, cracking reaction products, and oxygenated products. The reactions leading to the formation of each of the classes depend either directly or indirectly on the fate of the butyl radical. Butene formation by hydrogen abstraction from the butyl radical seems most probable. The butyl-peroxide radical formed by oxygen addition to the butyl radical leads to the oxygenated products. Decomposition of the butyl radical leads to formation of cracking products. Reactions of the types suggested are validated in the literature (*3, 4*).

CONCLUSIONS

1. An initiation step for the homogeneous butane oxidation involving activated oxygen molecules resulting from oxygen-oxygen collisions has been proposed. A rate equation involving a second-order oxygen dependence was derived and confirmed by testing against experimental data. The initiation step was shown to be the same for both cool-flame and noncool-flame regions.
2. Activation energies resulting from the use of the derived rate expression are in agreement with those obtained by other techniques and were comparable with those found in other investigations.
3. The products and product distributions obtained indicated that the butyl radical is a critical intermediate in the partial oxidation process studied. The types of products obtained and their relative importance depend in large measure on the fate of this radical.

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NOTATION

A = Arrhenius frequency factor, sec.$^{-1}$
A = symbol for a gas-phase constituent
cc. = size of sample analyzed
C = total moles carbon fed
C_B = butane mole fraction
C_i = mole fraction of i
C_{O_2} = mole fraction of oxygen
$C_{O_2^*}$ = mole fraction of activated oxygen molecules
C_P = specific heat, cal./(g. mole) (°K.)
E_A = apparent activation energy, kcal./mole
E = activation energy, kcal./mole
F = feed rate, mass per unit time
k = specific reaction rate constant, sec.$^{-1}$
$M.W.$ = molecular weight
N_i = cc.^{i}/10cc. total exit gas
Q = inlet flow rate, cc./sec.
R = gas constant, cal./(mole) (°C.)
R = gas-phase concentration ratio
r = reaction rate, moles/(mole feed) (sec.)
r_m = molecular radius, cm.
T = temperature, °K.
T_i = total moles i leaving reactor during run
T_R = reactor temperature, °K.
T_W = wall temperature
V = reactor volume, cc.
X_A = moles of A converted per unit mass of feed

Greek Letters

δ = range of effectiveness of the wall, cm.
ν = molecular concentration, molecules/cc.
ρ = gas density, g./cc.
τ = contact time based on inlet flow rate, sec.

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