containing copper and manganese, in the atomic proportions 2:1 and varying amounts of indium have about the same Curie temperatures. He ascribed the magnetism to the presence of the superlattice, even at low indium concentrations. This would seem to be a plausible explanation, although it appears that the superlattice is stable at high temperatures only in the immediate vicinity of the composition Cu_2MnIn. Elsewhere the β-phase may break down into α and β' at lower temperatures. Complete ordering of the β-phase cannot occur, since there is always an excess of copper atoms in its lattice. Should it decompose, however, a certain quantity of the β'-phase can be formed, with the excess copper going into a second constituent, probably the copper-rich α-phase. The Curie temperature of this alloy would then be a high value corresponding to the β'-phase. Should incomplete conversion of the β into α and β' occur it would be possible to observe two Curie temperatures for a single alloy, a lower one for the β-phase and a higher one for the β'-species. It will be noted that this is the case for several alloys, although no attempt was made to identify the phases present.

On the basis of the above results it appears that a situation exists here which is somewhat similar to that existing in the Cu–Mn–Sn and Cu–Mn–Al systems. A β-phase region has been located which is believed to consist of an unordered body-centered cubic lattice, since it is the extension of the binary Cu–In β-phase. This phase does not include the point Cu_2MnIn. However, as pointed out previously, the composition Cu_2MnIn also has a body-centered cubic structure, although it is an ordered phase and appears to be distinguishable from the β under the microscope. Since both of these phases exhibited ferromagnetism, this phenomenon definitely appears to be associated with the body-centered structure, as is the case in the Cu–Mn–Al and Cu–Mn–Sn systems.

The Decomposition of *n*-Butane in the Presence of Oxygen

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RECEIVED MARCH 21, 1952

The reaction of butane and oxygen at low oxygen concentrations has been studied in the temperature range 486 to 526°. Complete analysis of the reaction product was accomplished by the method of multiple isothermal distillation supplemented by chemical and spectroscopic tests. The effects of variations of concentration of oxygen from zero to 35 volume per cent. of variation of reaction time, and of Pyrex and KCl coated surfaces were observed under static and flow conditions. An important result of the study was the observation that the initial reaction product at low oxygen concentrations consists primarily of butene and water, indicating that oxygen acts primarily as a dehydrogenating agent under these conditions. Oxygen is shown to have a pronounced accelerating effect on the thermal cracking of butane; 0.5% of oxygen producing a hundred-fold increase in the rate of decomposition of butane. At oxygen concentrations below about 8%, the reaction products within the limits of sensitivity of the analysis consist only of hydrocarbons and water. The rate of reaction was found to be approximately proportional to the square root of the oxygen concentration and to the three-halves power of the butane concentration. The apparent activation energy of the reaction was found to be 21 kcal./mole.

Introduction

The acceleration of the decomposition of hydrocarbons by low concentrations of oxygen has been referred to in the literature by various workers,[2,3] and the reaction was investigated manometrically by Rice and Polly and Bell, Folkins and Thacker.[4] The influence of concentrations of oxygen in the range typical of combustion (production of appreciable concentrations of CO and CO_2) was investigated by Pease.[5]

As part of a broader study of hydrocarbon decom-

(1) (a) Shell Oil Company, Inc.; (b) The Johns Hopkins University, Applied Physics Laboratory.

(2) F. D. Rice and O. L. Polly, *J. Chem. Phys.*, **6**, 278 (1938).

(3) See also L. S. Echols and R. N. Pease, THIS JOURNAL, **61**, 208 (1939).

(4) F. D. Rice and O. L. Polly, *Trans. Faraday Soc.*, **35**, 850 (1939); R. T. Bell, H. O. Folkins and C. M. Thacker, U. S. Patent 2,397,638 (April 2, 1946).

(5) R. N. Pease, THIS JOURNAL, **51**, 1853 (1929).

positions in these laboratories, the influence of oxygen on *n*-butane decomposition in the range of oxygen concentrations below 25% was investigated. None of the above authors had published detailed analyses of the reaction products obtained in their work, nor studied the reaction over a wide range of oxygen concentration.

The experimental work reported here was done in 1942. The investigation was interrupted by the war, and subsequent activities by the authors have prevented completion of the paper although the general results of the work were presented at the American Chemical Society Meeting at Chicago in 1948, and at the Symposium on Combustion held at the University of Wisconsin in 1948.

Experimental

Both static and flow experiments were carried out. The former gave information on the influence of oxygen on the

product composition, but the reaction was so fast in the temperature range of interest (450–550°), that rate data could be obtained only in the flow apparatus where reaction times of the order of one second were possible.

The static experiments were carried out in a typical apparatus using a Pyrex reactor coated on the inside with KCl. In the flow apparatus the two gases were conducted through separate preheater tubes, where they were preheated to a temperature appropriate to the desired reaction temperature, mixed in a small volume (0.25 ml.) mixing chamber, and passed through the reactor (5.43 ml. volume, 15 mm. i.d., 35 mm. length, with thermowell). Preheater and reactor were of Pyrex and were KCl coated in all experiments but one wherein the effect of an uncoated Pyrex surface was studied.

The n-butane used in all experiments was obtained from the Phillips Petroleum Company and shown by isothermal distillation to be more than 99% pure. Oxygen was obtained from the Linde Air Products Company of Houston, Texas. A trace of nitrogen was the only impurity.

Before each static experiment the n-butane was condensed at $-195°$, pumped for 15 minutes with a two-stage Hg diffusion pump, then liquefied, refrozen, repumped, etc., until it had been through this process at least three times.

The products of reaction were analyzed by a modified method of multi-isothermal distillation.[6,7] Since in the products from the reaction with oxygen a higher concentration of n-butene was found than is characteristic of the normal "oxygen-free" decomposition, the products from one experiment were analyzed by another method to obtain an independent check of the composition. In this method the fixed gases and material boiling above n-butane were removed in the usual way.[6,7] The remaining products, composed of C_2-, C_3- and C_4-saturates and olefins, were divided into two samples, one of which was brominated to remove olefins and the other was hydrogenated to convert olefins to saturates. The differences in the C_2-, C_3- and C_4-saturate contents of these samples as determined by the combined multi-isothermal and isothermal method,[6,7] represented the C_2-, C_3- and C_4- olefin content of the product. A comparison of results obtained by the two methods of analysis is given in Table I. While the standard multi-isothermal method[6,7] gave slightly high results for butenes and correspondingly low results for ethylene and propylene, essentially good agreement was obtained between the two sets of data.

Several experiments were carried out with the static apparatus at 500° and contact time of 10 sec. using a n-C_4H_{10} initial pressure of 380 mm. and O_2 initial pressure of 30 mm. to obtain sufficient product to test for the presence of aldehydes, ethers, acids and butylenes.

The hydrocarbon fractions, C_2 through C_4 gave negative tests for aldehydes by the silver mirror method. Previous tests on blends of air and acetaldehyde vapors had shown that concentrations of acetaldehyde as low as 0.4% by volume gave a definite mirror test by the above procedure. Consequently, it was concluded that aldehydes having a vapor pressure ≥ 0.1 mm. in the temperature range -195 to $-78°$ (the temperature range of the multi-isothermal distillation analysis) were absent, in any significant amounts, from the reaction products of a n-butane–oxygen mixture containing 8–9% by volume oxygen or less.

The residue (substances with vapor pressure ≤ 0.1 mm. at $-78°$) of the above sample was absorbed in distilled water and was found to be neutral to litmus and to give a negative test for aldehydes by the silver mirror test.

The infrared absorption spectrum of the C_2–C_4 fractions of the product sample was determined to get a qualitative test for the presence of butenes and ethers. The characteristic absorption bands of 1-butene were found in the spectrum obtained and no bands were found which would correspond to an ether type carbon–oxygen linkage.

By use of the flow apparatus more elaborate tests were made for aldehydes using the fuchsin–aldehyde reagent, peroxides using a starch–KI reagent, and acids using methyl orange indicator in distilled water. The tests were made by bubbling the gases issuing from the reactor directly into the test solution for about 15 or 20 minutes. In all the ex-

(6) L. S. Echols and E. Gelus, *Ind. Eng. Chem., Anal. Ed.,* **19**, 668 (1947).

(7) W. G. Appleby, W. H. Avery and W. K. Meerbott, This Jour-nal, **69**, 2279 (1947).

TABLE I

COMPARATIVE ANALYSIS OF REACTION PRODUCTS BY THE BROMINATION–HYDROGENATION AND STANDARD MULTI-ISOTHERMAL METHODS

Run no.			183-S[c]	157-S[d]
Charge	n-C_4H_{10}	cc. at S.T.P.	24.37	24.58
		mm.	377.2	380.2
	O_2	cc. at S.T.P.	1.32	1.32
		mm.	20.5	20.4
		mole fractn.	0.0515	0.0510
Time, sec.			30	30
Temperature, °C.			500	500
Reaction, %	ΔC_4H_{10}		18.8	18.2
Recovery,[a] mole %			99.6	99.9
% v. of C_4H_{10} dis-appearing	Total unsat.		103.3	101.5
	H_2 + total sat.		62.7	65.3
Products, moles per 100 moles C_4H_{10} reacted	H_2		4	3
	CH_4		45	46
	CO		0	0
	C_2H_4		25	28
	C_2H_6		10	13
	C_3H_6		47	38
	C_3H_8		4	4
	C_4H_8		31	36
	Residue[b]		31	28

[a] Recovery: C_4 equivalent of products excluding residue $\times$ 100/C_4 added. [b] Residue: all products with v.p. $\leq$ 0.1 mm. at $-78°$. [c] Analyzed by bromination–hydrogenation–multi-isothermal method. [d] Analyzed by standard multi-isothermal method.

periments herein reported, except the one run in Pyrex, no positive test was obtained for peroxides but very faint positive tests were obtained for aldehydes and acids. The latter results are contrary to the observed absence of aldehydes and acids in similar tests using the static system. We attribute the difference to the fact that only 20 to 30 ml. of gas could be tested in the static system experiments whereas from several hundred to several thousand ml. of gaseous products were tested in the flow system experiments. Also, with the longer residence time in the static system, any oxygenated compounds had more opportunity to undergo decomposition. In any case, however, the tests for aldehydes and acids were only faintly positive. The presence of even traces of such materials is not negligible, however, from the standpoint of the reaction mechanisms involved.

In the static experiments the water content of the product was calculated from the vapor pressure of the residue on the assumption that the residue was pure water. With this assumption the oxygen balance was about 15% low on the average. The low value is ascribed to condensation and adsorption of water in the apparatus. In the flow experiments, the product water content was calculated from the oxygen disappearance, allowance being made for oxygen appearing in the product as CO.

Results

Static and Flow Comparison.—It is of interest first to examine the correspondence between the data obtained in the static apparatus and that obtained in the flow apparatus. All static experiments were run at 30 seconds residence time, since no significant ($< 0.5\%$) amount of reaction was observed in this time in the absence of oxygen, and the time interval was large enough to guarantee good reproducibility. Since practically all of the oxygen had combined within about 5 seconds, as shown in the rate study in the flow experiments, the maximum residence time in the flow experiment was about 5 seconds. The data shown in Table II are nearly equivalent, the differences being ascribable to the errors of the analytical method.

Influence of Initial Oxygen Concentration.—The data of Table III show the change in the fraction of n-butane reacted in the static system at 380 mm. initial pressure, 30 seconds residence time, and 500° in the presence of various

TABLE II

COMPARISON OF STATIC AND FLOW RESULTS

Reaction system	Static	Flow
Pressure, mm.	414	756
Temperature, °C.	500	502
C₄H₁₀/O₂ in charge	10.7	10.4
Residence time, sec.	30	5
% reaction, O₂	100	99
% reaction, C₄H₁₀	21	20

Moles products per 100 moles C_4H_{10} reacted

	Static	Flow
CO	0	1
H₂	3	7
CH₄	49	43
C₂H₄	29	26
C₂H₆	13	12
C₃H₆	38	42
C₃H₈	3	0
C₄H₈	35	29
H₂O	79	95

the cube root of the initial oxygen concentration reveals a straight line relationship for initial oxygen concentrations below 9%. The relationship indicates that pyrolysis rates may be significantly affected by concentrations of oxygen as low as 0.0001%.

(4) By comparison with the pure pyrolysis, it is seen that oxygen has the effect of decreasing the production of saturates and propylene and increasing the production of ethylene and 1-butene relative to the values observed in absence of oxygen. The effect on saturates is most marked in the case of ethane. Whereas in the oxygen free reaction, ethane is produced in amounts equal to ethylene, oxygen concentrations of 5% or greater reduce the ethane relative to ethylene by roughly 50%. It is also noteworthy that methane production has been reduced by 15 to 25% in the reaction in presence of oxygen.

Data from Flow Experiments.—The rate studies were made entirely in the flow apparatus because the rates were too fast for measurement in the static apparatus.

Dependence of Reaction on Space Velocity.—The variations in percentage reaction of *n*-butane and oxygen and in product composition with space velocity are given in Tables IV and V.[8]

In Fig. 1 the fractions of butane and oxygen reacted in the 10/1 mixture at 503° are plotted as functions of the re-

TABLE III

INFLUENCE OF INITIAL OXYGEN CONCENTRATION

n-C₄H₁₀ initial pressure, 380 ± 2 mm.; reaction time, 30 sec.; temperature, 500°

Expt. no.	Initial O₂ concn. % by volume	Reaction, % *n*-C₄H₁₀ min.	O₂	CO	H₂	CH₄	C₂H₄	C₂H₆	C₃H₆	C₃H₈	C₄H₈	H₂O	Moles *n*-C₄H₁₀ reacted per mole O₂ reacted
174 S													
175 S	0.00	(2.22)ᵃ	...	0	1	67	25	27	55	3	15	0	..
166 S	0.48	8.8	100	0	0	32	16	15	39	0	43	11	15.5
156 S	2.03	13.4	100	0	0	52	22	21	42	1	34	25	6.3
157 S	5.10	18.2	100	0	3	46	28	13	38	4	36	52	3.3
158 S	8.57	21.3	100	0	3	49	29	13	38	3	35	79	2.2
182 S	12.29	27.9	100	5	0	44	28	12	39	6	28	95	2.0
172 S	15.73	34.3	100	12	5	42	32	13	37	3	27	98	1.8
181 S	22.54	50.8	100	24	6	53	42	12	42	5	15	91	1.8

ᵃ The residence time in this experiment was 3600 sec.

initial concentrations of oxygen, and the effect of varying initial concentrations of oxygen on the products of decomposition.

Examination of the data reveals these interesting points: (1) At low concentrations of oxygen (<8%) the product of reaction consists of detectable amounts of only hydrocarbons and water; no oxygenated hydrocarbons or carbon oxides were found. This rather surprising result is confirmed by the carbon–hydrogen–oxygen balances obtained.

(2) At oxygen contents greater than 10% by volume, carbon monoxide appears as a reaction product, the amount formed increasing rapidly as the oxygen content is increased. No other carbon compounds containing oxygen were found. Thus, in the run initially containing 12.3% O₂ the products contained an appreciable amount of carbon monoxide. No carbon–oxygen compounds were found in the products from experiments with lower initial oxygen concentrations. This was checked carefully by a redetermination of the infrared spectra of the C₃- and C₄-hydrocarbons and the residue in the products from a run at 500° with 380 mm. of *n*-butane and 20 mm. of oxygen. Characteristic absorption bands of *n*-butane, 1-butene and propylene were the only bands observed in the spectrum of the C₃–C₄ products and no absorption ascribable to compounds other than water was observed with the residue.

(3) Below 10% by volume of oxygen, the number of moles of butane combined with each mole of oxygen, when all the oxygen is consumed, is inversely proportional to the two-thirds power of the oxygen concentration, decreasing from a value of fifteen in mixtures containing 0.5% oxygen to a value of 2 in the mixture containing 10% oxygen. Accordingly, low concentrations of oxygen have a large effect on the rate. With only 0.5% oxygen present, the rate is approximately one hundred times that of the uncatalyzed reaction. A plot of the fraction of *n*-butane reacted *versus*

ciprocal of the space velocity. Within experimental error the moles C₄H₁₀ consumed per mole O₂ consumed is constant. However, examination of Table IV shows that the product composition changes appreciably as the residence time increases; longer times lead to a marked reduction in the butene content of the product, with a corresponding increase in methane and propylene, a small increase in ethylene, and a slight decrease in ethane.
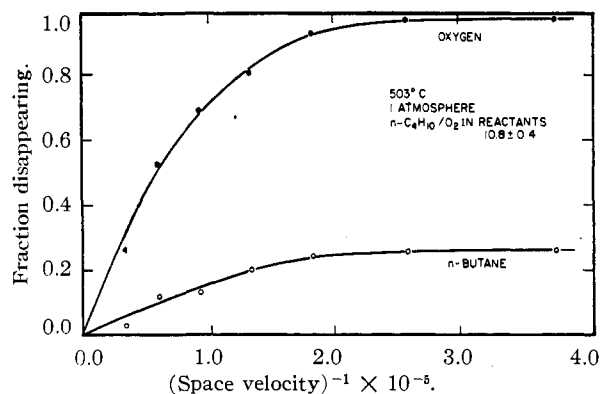

Fig. 1.—Rate of reaction of *n*-butane and oxygen in flow apparatus.

The effect of space velocity on the product composition indicates that initial products of the reaction undergo fur-

(8) In the calculation of space velocity the total reactor volume was taken to be 5.68 ml.

TABLE IV

EFFECT ON REACTION OF RESIDENCE TIME (Flow system, 1 atm. press.)

Approx. residence time, sec.	0.5	0.5	0.5	0.9[a]	1.4	2.0[a]	2.7	4.0	5.7
Temperature, °C.	503	503	503	503	503	503	503	503	503
Inlet flow rate, ml./min. at S.T.P.									
n-Butane	221.0	211.0	208.6	116.6	76.1	52.3	38.4	27.6	19.3
O_2	20.3	19.7	20.6	11.3	6.9	4.8	3.7	2.5	1.8
Total	241.3	230.7	229.2	127.9	83.0	57.1	42.1	30.1	21.1
Space velocity, mole/sec./ml. reactor									
Vol. × 10⁵	3.16	3.03	3.00	1.68	1.09	0.75	0.55	0.39	0.28
Outlet flow rate, ml./min. at S.T.P.	251.6	239.0	235.4	136.6	91.7	64.6	48.2	34.1	25.1
Butane–oxygen ratio in charge	10.9	10.7	10.3	10.3	11.1	10.7	10.5	11.2	10.4
Reaction, %									
n-C_4H_{10}	5.1	4.7	4.1	8.8	9.9	15.2	18.0	19.2	19.7
O_2	33.7	25.3	20.9	53.4	69.0	80.9	93.5	97.6	97.8
Products, % vol. of total									
H_2	3.5	0.0	0.0	2.2	0.0	1.6	1.5	1.1	2.8
CO	4.4	0.0	0.0	4.2	0.0	2.2	1.5	3.5	0.4
CH_4	6.8	5.3	5.8	8.5	10.4	12.6	15.1	16.4	16.8
C_2H_4	5.1	9.5	5.8	6.2	6.7	8.9	9.5	10.9	10.1
C_2H_6	3.5	5.0	6.1	5.5	7.0	5.7	5.2	3.9	4.6
C_3H_6	8.4	5.1	6.1	10.1	11.5	12.6	15.4	13.1	16.4
C_3H_8	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
C_4H_8	24.9	32.9	32.5	19.1	19.2	17.8	11.6	13.6	11.4
H_2O	43.4	42.9	43.6	44.3	45.2	38.1	40.2	37.9	37.5
Moles C_4H_{10} reacted per mole O_2 reacted	1.65	2.00	2.02	1.72	1.61	2.01	2.02	2.20	2.09
Moles product per mole C_4H_{10} reacted	1.75	2.34	2.50	2.45	2.79	2.44	2.38	2.20	2.54

[a] Average of 2 runs.

ther reaction at longer residence times. Accordingly, it is suggestive to extrapolate the product composition to zero residence time. This is done in Fig. 2 and leads to the following indicated initial product composition: Product (followed by volume per cent. in parentheses): C_4H_8 (37 ± 10), H_2O (46 ± 10), C_2H_4 (5 ± 2), C_2H_6 (5 ± 2), C_3H_6 (3 ± 3), CH_4 (3 ± 3), CO (1 ± 1), H_2 (1 ± 1). Insofar as the extrapolation is valid, one may conclude that oxygen in low concentrations acts at 500° predominantly as a dehydrogena-
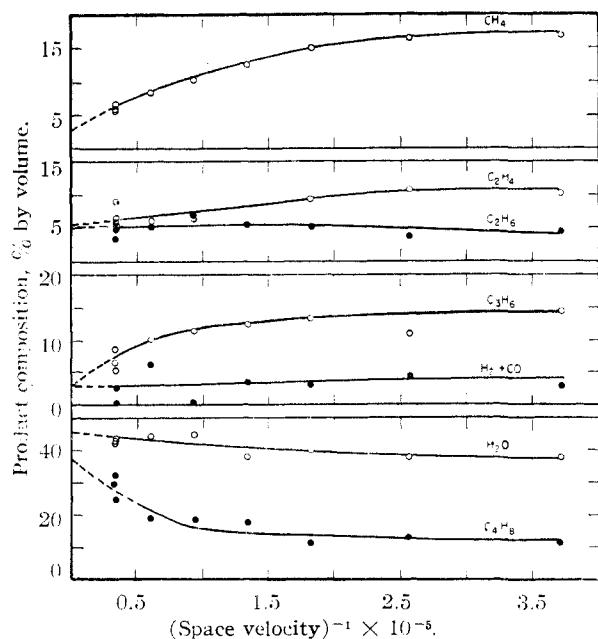

Fig. 2.—Influence of space velocity on product composition: 503°, atmospheric pressure, C_4H_{10}/O_2 —10.8 ± 0.4 moles/mole.

tion agent for butane; water and butene being formed as products. In addition, there is a small amount of induced cracking.[9]

(2) Inhibition by Products.—It was thought that the inhibition effect mentioned earlier might be caused by the reaction of oxygen with the products of the initial processes. The data of Table III show that the butene yield decreases rapidly with increase of initial oxygen concentration; hence, it is possible that butene caused the inhibition, although propylene could also be involved, as could water since it is a major product. An experiment to test the influence of 1-butene and of water indicated that addition of 10% butene-1 reduced the butane conversion about 20%. Water had no noticeable effect.

(3) Effect of Temperature on the Reaction.—The effect of temperature on the reaction is shown in Table V. It is apparent from the data shown that the over-all reaction has a low temperature coefficient.

The effect of temperature on the products of reaction involves a decrease in butene production and a corresponding increase in lower hydrocarbons as the temperature is increased. This effect is in the same direction as that obtained by increasing the initial oxygen concentration at a constant temperature or increasing the residence time.

(4) Effect of Variations in the Initial n-Butane–Oxygen Ratio in the Flow Apparatus.—The effect of variation in the initial butane–oxygen ratio at about 0.9 second residence time and 486 and 503° is shown by the data of Table V. The change in product composition with increase in initial oxygen concentration is in the same direction as shown in the static system. At some oxygen concentration between 3.6 and 8.8%, CO formation begins to become significant and the trend is toward an increase in CO formation.

It is of interest to note here also the effect of temperature at various initial n-butane–oxygen ratios. The data for

(9) An attempt was made recently (W. H. Avery) to obtain data on the product composition at conversions of the order of 1%, by mass spectrometric analysis of the reaction products. The results of six experiments at 500° with a butane–oxygen ratio of eleven were inconclusive, since the oxygen balance showed a large discrepancy between the oxygen apparently reacted and that detected. However, butene, propylene, ethylene, methane, hydrogen and water were the only products found, butene being the major constituent.

TABLE V

THE EFFECT ON REACTION OF TEMPERATURE AND n-BUTANE–OXYGEN RATIO (Flow system, atm. pressure)

Approximate residence time, sec.	0.9[a]	0.9	0.9	0.9[b]	0.9[a]	0.9
Temperature, °C.	503	503	486	486	486	526
Inlet flow rate. ml./min. at S.T.P.						
n-Butane	105.6	122.3	121.8	95.2	119.8	116.3
O_2	27.5	4.5	20.1	29.2	11.0	11.4
Total	133.1	126.8	141.9	124.4	130.8	127.7
Space velocity mole/sec./ml. reactor						
Vol. $\times 10^5$	1.74	1.66	1.86	1.63	1.71	1.67
Outlet flow rate, ml./min. at S.T.P.	148.6	133.2	149.3	134.2	136.1	142.7
Butane–oxygen ratio in charge	3.8	27.2	6.03	3.25	10.8	10.3
Reaction, %						
n-C_4H_{10}	16.7	7.2	9.3	15.2	7.2	12.4
O_2	50.7	71.3	39.3	36.8	45.1	60.7
Products. % vol. of total						
H_2	1.0	2.2	1.2	0.0	2.7	0.9
CO	5.0	0.0	5.0	7.1	2.6	5.0
CH_4	6.6	14.5	3.4	1.8	7.2	16.5
C_2H_4	7.4	9.6	3.3	5.7	5.3	10.7
C_2H_6	3.0	4.3	3.2	2.5	2.3	4.8
C_3H_6	5.7	14.5	4.4	3.4	6.5	16.9
C_3H_8	0.0	0.0	0.0	0.0	0.0	0.0
C_4H_8	16.8	20.1	25.1	24.3	24.2	12.4
H_2O	54.5	34.8	54.3	55.1	49.1	32.7
Moles C_4H_{10} reacted per mole O_2 reacted	1.30	3.00	1.0	1.35	1.73	2.12
Moles product per mole C_4H_{10} reacted	2.70	2.10	2.35	2.37	2.25	2.51

[a] Average of 2 runs.   [b] Average of 3 runs.

486° do not show the marked decrease in butenes with increase of oxygen.

(5) Effect of Surface on the Reaction.—The effect of changing the reactor surface from KCl to Pyrex is shown in Table VI. There appears to be a slight acceleration of the reaction as a result of the change in surface, but the ef-

TABLE VI

EFFECT OF SURFACE ON THE n-BUTANE–OXYGEN REACTION AT 503° AND ONE ATMOSPHERE PRESSURE

Surface	KCl	Pyrex
n-C_4H_{10}/O_2 in charge	10.4	10.5
Inlet flow rate. ml./min. at S.T.P.	128	132.3
Space velocity, total moles/sec./ml. reactor vol. $\times 10^5$	1.67	1.72
Outlet flow rate, ml./min. at S.T.P.	137	141.9
Reaction. %		
n-C_4H_{10}	8.8	10.0
O_2	53.4	60.0
Products, % by volume		
H_2	2.1	0.8
CH_4	8.5	14.4
C_2H_4	6.2	6.3
C_2H_6	5.5	2.8
C_3H_6	10.0	10.2
C_3H_8	0.0	0.0
C_4H_8	19.1	19.2
CO	4.2	3.5
H_2O	44.5	42.8
CO_2	0.0	0.0
Moles of n-C_4H_{10} reacted per mole of O_2 reacted	1.72	1.76
Moles of product per mole of n-C_4H_{10} reacted	2.45	2.37

fect is not particularly marked. The only noticeable effects on the products involved are: (1) a greater production of CH_4 and a lesser production of C_2H_6, and (2) the appearance of a slight amount of peroxides. (The test was very faintly positive as were the aldehyde and acid tests.) The latter observation is particularly significant because the absence of peroxides in the products from reaction in the KCl lined reactor indicates that KCl either destroys peroxide formed in the gas phase or prevents a surface reaction on Pyrex involving peroxide formation.

Reaction Kinetics.—Because of the changes of product composition with residence time and butane–oxygen ratio, it is evident that very extensive data must be available before conclusions of basic significance may be drawn regarding the dependence of the reaction kinetics on concentration and temperature. However, it seems worthwhile to point out the apparent relationships, as a guide to further studies and as an aid in understanding the mechanism of the reaction.

(a) Dependence of the Rate on Reactant Concentration and Residence Time.—Examination of the data of Table IV shows that the rate of the reaction is approximately proportional to the square root of the oxygen concentration and to the three halves power of the butane concentration. Thus

$$-d[C_4H_{10}]/dt = K[C_4H_{10}]^{3/2}[O_2]^{1/2} \qquad (1)$$

Letting a = initial concentration of O_2, b = initial concentration of butane, q = no. of moles oxygen reacted per mole butane reacted, x = moles butane reacted at time t. Equation (1) may be integrated to give

$$\frac{2}{(ab)^{1/2}(1 - qb/a)} \left[\left(\frac{1 - xq/a}{1 - x/b} \right)^{1/2} - 1 \right] = Kt \qquad (2)$$

Data of Table IV substituted in equation (2) to determine the value of the constant K are presented in Table VII. The equation is seen to give a reasonably satisfactory fit to the data.

(b) Temperature Coefficient.—In Table VIII values of the rate constant K calculated from equation (2) are presented for reaction of the 10/1 mixture at temperatures of

485, 503 and 526.5°. Assuming that the rate constant varies with temperature according to the expression

$$K = Ae^{-E/RT} \qquad (3)$$

the apparent activation energy of the reaction is found to be 21 kcal.

TABLE VII

CALCULATED VALUES OF THE RATE CONSTANT AT 503°

Experiment No.	Butane–oxygen ratio	Fraction reacted Butane	Oxygen	Rate constant, cc./mole sec. $\times 10^{-4}$
101, 112, 127	10.9	4.7	26.6	2.38
105, 120	10.4	8.8	53.4	2.70
108	11.1	9.9	69.0	2.24
106, 126	10.7	15.2	80.9	2.63
114	10.5	18.0	93.5	2.71
130	11.2	19.2	97.6	2.34
110	10.4	19.7	97.8	1.66
116	27.2	7.2	71.3	4.00
115, 121	3.8	16.7	50.7	4.18

TABLE VIII

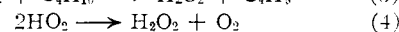DEPENDENCE OF RATE CONSTANT ON TEMPERATURE

Experiment No.	Butane–oxygen ratio	Fraction reacted Butane	Oxygen	Temp., °C.	Rate constant, cc./mole sec. $\times 10^{-4}$
122, 136, 138	10.8	7.2	45.1	486	2.10
105, 120	10.4	8.8	53.4	503	2.70
117	10.3	12.4	60.7	526.5	4.34

Reaction Mechanism.—As noted earlier, further data are required before the reaction mechanism can be established. However, the experimental results do give clear evidence that the reaction process at low oxygen concentrations represents a considerable simplification over that which has been observed in the past with nearly stoichiometric mixtures.

The most significant result of the experimental work described above is that oxygen acts predominantly as a dehydrogenating agent, when the oxygen content of the mixture is less than 10%. Since it seems unlikely that carbon–oxygen bonds when once formed would all disappear in secondary re-

actions, one may infer that the chain carriers in these mixtures consist mainly of hydrocarbon radicals and compounds of oxygen and hydrogen alone. Consideration of the energetics of the possible processes suggests the following steps for the primary reactions

$$C_4H_{10} + O_2 \longrightarrow C_4H_9 + HO_2 \qquad (1)$$
$$C_4H_9 + O_2 \longrightarrow C_4H_8 + HO_2 \qquad (2)$$
$$HO_2 + C_4H_{10} \longrightarrow H_2O_2 + C_4H_9 \qquad (3)$$
$$2HO_2 \longrightarrow H_2O_2 + O_2 \qquad (4)$$
$$H_2O_2 \xrightarrow{\text{wall}} H_2O + {}^1/{}_2O_2 \qquad (5)$$
$$2HO_2 \xrightarrow{\text{wall}} H_2O + 1{}^1/{}_2O_2 \qquad (6)$$
$$C_4H_9 \longrightarrow CH_3 + C_3H_6 \qquad (7)$$
$$CH_3 + C_4H_{10} \longrightarrow CH_4 + C_4H_9 \qquad (8)$$
$$C_4H_9 \longrightarrow C_2H_5 + C_2H_4 \qquad (9)$$
$$C_2H_5 + C_4H_{10} \longrightarrow C_2H_6 + C_4H_9 \qquad (10)$$
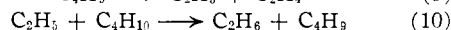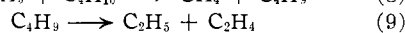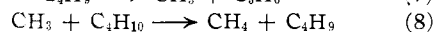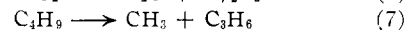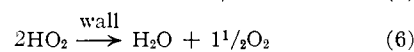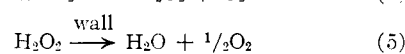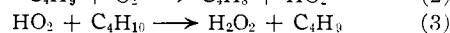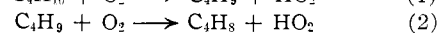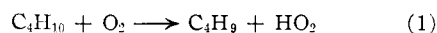
The products observed are in accord with this reaction scheme.[10]

Acknowledgment.—The authors wish to express their appreciation to Mrs. Betty Grisamore for computational assistance in this work, to Mrs. Ruth Quinn for computational and experimental help, to Dr. R. D. Schultz who constructed the flow system used for the experiments described in the footnote,[9] and to Dr. F. L. Mohler and the mass spectrographic group at the National Bureau of Standards for the mass spectrometric analyses referred to in the same note.

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(10) It may be noted that the above series of partial reactions leads to the following equation for the over-all rate of butane consumption.

$$- d[C_4H_{10}]/dt = K_1(C_4H_{10})(O_2) + (K_3(C_4H_{10})/2K_4)$$
$$[-K_6 + \{K^2_6 + 8K_1K_4 (C_4H_{10})(O_2)\}^{1/2}] +$$
$$\frac{K_7 + K_9}{2K_4K_2(O_2)} [K_1(C_4H_{10})(O_2) + K_3(C_4H_{10})$$
$$[-K_6 + \{K^2_6 + 8K_1K_4(C_4H_{10})(O_2)\}^{1/2}]] \qquad (4)$$

If reasonable numerical values are substituted for the constants, equation (4) reduces to

$$- d(C_4H_{10})/dt \cong \sqrt{2K_3}\sqrt{K_1/K_4} (C_4H_{10})^{3/2}(O_2)^{1/2} \qquad (5)$$

which is of the same form as equation (1).