adding acetone to a concentrated alcoholic solution. As thus obtained the hydrochloride melts at 219–220°. Calycanthine hydrochloride melts at 217°, but a mixture of the two began to sinter at 205° and melted completely at 208°. The free base, which will be designated β-alkaloid, was only obtained as a colorless oil, readily soluble in ether. Seeding with α-alkaloid did not induce crystallization. This base also gives a red color with Ehrlich's reagent.

Isolation of Xylose from the Epicarp of the Seeds.—The residue after thorough extraction consisted of the inner fleshy portion of the seed together with the still tough and dark brown epicarp in large flat pieces. By virtue of a difference in density, the two parts could be easily separated by a process of flotation with water, the epicarp sinking. When most of the fleshy portions had been removed by this means, the residue of hulls was hydrolyzed with 2% boiling sulfuric acid for three hours, neutralized with calcium carbonate, filtered, the solution evaporated to a thick sirup *in vacuo* and the latter extracted once with a large volume of absolute methanol. The extract, on evaporation, yielded about 6% of almost colorless crystals which, after two recrystallizations, melted at 150° alone or admixed with a genuine specimen of *l*-xylose. It may here be mentioned that the epicarp from *C. floridus* under similar treatment yielded the same sugar in approximately the same amount.

Summary

1. The alkaloid, calycanthine, has been isolated from *Meratia praecox, Rehd. and Wils.*, a shrub native to Asia. Its identity with the alkaloid from *Calycanthus floridus, L.*, has been established.

2. Two other alkaloids were isolated in small amounts, but the investigation of these is delayed until more material is available.

3. The existence of glucose, or a sugar which gives glycosazone, in the seeds has been shown.

4. Xylose was isolated from the epicarp of the seeds by hydrolysis with dilute sulfuric acid.

NEW HAVEN, CONNECTICUT

[CONTRIBUTION FROM THE LABORATORY OF PHYSICAL CHEMISTRY, PRINCETON UNIVERSITY]

CHARACTERISTICS OF THE NON-EXPLOSIVE OXIDATION OF PROPANE AND THE BUTANES[1]

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The reactions between hydrocarbon vapors and oxygen are of interest for a number of different reasons. Information as to their nature is of

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importance in connection with the utilization of hydrocarbons, especially in connection with their combustion; and from the purely chemical standpoint the mechanism of these reactions demands investigation. Other investigators have studied the oxidation of methane, ethane, ethylene, acetylene and some of the higher paraffins. We have chosen to investigate the oxidation of the intermediate paraffins, propane and the butanes. The investigation has been comprehensive rather than exhaustive. In particular, the nature of the liquid products has been disregarded and conclusions are based entirely on the analyses of gaseous reactants and products.

Apparatus and Procedure

The flow method has been used. Known volumes of reactants at known rates were passed into a reaction tube and the corresponding off-gas collected and analyzed. The gases passed from cylinders through calibrated flow meters (equipped with overflows to maintain constant head) and calcium chloride drying tubes, into $^1/_4$-inch pyrex tubes which extended into the electric furnace used for heating. These tubes were joined within the furnace to a short length of 2-mm. capillary which served as a mixing chamber, and this in turn was joined to the reaction tube. The gases then issued through a length of 2-mm. capillary to which was sealed a three-way stopcock, by means of which communication could be made either with the air or with the collecting system. The latter consisted of a trap of 5-cc. capacity and a 500-cc. mercury aspirator bottle. This was a pyrex flask to which had been sealed a three-way stopcock. The whole of the off-gas was collected in this bottle during a measured time interval, the rate of inflow of reactant gases being controlled by careful regulation of the rate of outflow of mercury from the bottle. During collection of the off-gas, the trap was cooled in carbon dioxide–ether mixture to remove liquid products. Condensable gases were, of course, trapped simultaneously. These were subsequently evaporated by allowing the trap to warm up to room temperature. The gases were then mixed by expansion and compression and submitted to analysis. After analysis the total volume of off-gas was measured and the volumes of the individuals were calculated. All gas volumes were reduced to 25° and 760 mm.

Analysis was carried out with a Williams apparatus to which had been added a copper oxide combustion tube. The confining fluid was water. Carbon dioxide was determined by absorption in potassium hydroxide solution, unsaturated hydrocarbons in dilute bromine water (less than 0.2% of bromine) and oxygen in alkaline pyrogallol. Carbon monoxide and hydrogen were obtained by oxidation with copper oxide at about 300° followed by absorption of carbon dioxide. The saturated hydrocarbons were burned over copper oxide at about 550°, with subsequent absorption of carbon dioxide.

A chromel-wire-wound furnace jacketed with magnesia pipe covering was used. Its interior dimensions were 30 inches length and 4 inches diameter. The wire was wound on a piece of stovepipe covered with asbestos paper. The ends of the furnace were packed with loose magnesia, the central third constituting the actual heating space. Temperatures were measured with a single-junction chromel–alumel thermocouple, the hot junction being at the center of the furnace.

The gases were obtained from cylinders. Their compositions were as follows

Oxygen—O_2, 98.5%; "CH_4," 1.0%; N_2, 0.5%
Nitrogen—N_2, 99.0%; "CH_4," 0.5%; O_2, 0.5%
Carbon dioxide—CO_2, 100.0%
Hydrogen—H_2, 98.5%; "CH_4," 1.0%; O_2, 0.5%

Methane—CH_4, 95.5%; N_2, 4.5%
Propane—C_3H_8, 98.5%; "CH_4," 1.0%; N_2, 0.5%
n-Butane—C_4H_{10}, 99.0%; ["CH_4," (-1.0%)]; N_2, 2.0%
*Iso*butane—C_4H_{10}, 95.5%; "CH_4," 2.0%; O_2, 1.0%; N_2, 1.0%

The boiling points of the normal and *iso*butane were nearly constant and close to −1 and −10°, respectively, thus further ensuring their purity. These and the other hydrocarbons were originally obtained from natural gas.

The experimental procedure was as follows. The furnace was brought to temperature and the gases were allowed to flow through the system for one to two hours to ensure steady-state conditions. The off-gas was then sent through the trap and connecting tubes for one minute. The carbon dioxide–ether mixture was applied to the trap (which was shut off at both ends), and one minute later connection was made through the trap with the gas collector. The whole of the off-gas was then collected for a measured time interval. At the end of this time the trap was warmed to room temperature and the condensed gases were added to the main body, which was mixed and analyzed. The flow rates and sampling times were so adjusted that in all experiments 400 cc. of gas was introduced while the sample was being collected.

Nature of Experimental Data and Interpretation

Analytical Data.—The experimental results have been expressed as follows. The gas absorbed in caustic has been called carbon dioxide. It undoubtedly consists in part of formaldehyde and probably volatile alcohols and acids. Gas absorbed by bromine water has been called simply unsaturated compounds. These are doubtless chiefly olefins. The oxygen, carbon monoxide and hydrogen determinations are unequivocal. The data on saturated hydrocarbons have been expressed in terms of the principal hydrocarbon and methane. This is, of course, arbitrary. Fortunately, however, analyses of the off-gas from the majority of the experiments indicated that the hydrocarbon introduced was the chief one present—no large quantity of new hydrocarbon had resulted from the oxidation. The same holds for the cylinder gases.

We have then to compare the volumes of carbon dioxide, unsaturates, oxygen, carbon monoxide, hydrogen, methane and original hydrocarbon in the off-gas with the volumes of oxygen and hydrocarbon introduced. We find that in general the principal gaseous products of reaction are carbon monoxide and unsaturates, sometimes one and sometimes the other predominating. Methane appears in increasing quantities as the furnace temperature is raised. Hydrogen and carbon dioxide, however, are only rarely important products.

The appearance of unsaturates, methane and hydrogen, all in amounts increasing with the furnace temperature, recalls the dissociation reactions of hydrocarbons, for example

$$C_3H_8 \longrightarrow C_2H_4 + CH_4$$
$$C_3H_8 \longrightarrow C_3H_6 + H_2$$

In most experiments, however, furnace temperatures were far below those required to produce appreciable dissociation by themselves; but off-setting this there is the exothermicity of the oxidation reactions. (The question of temperature is discussed below.) We choose therefore to regard the hydrogen and methane as products of dissociation of the hydrocarbon and to associate with them equivalent quantities of unsaturates. We therefore account for a part of the hydrocarbon reacting in terms of thermal dissociation, designating this as "Reaction I. Unsaturates by Dissociation." The amount of this type of reaction is given by the sum of the volumes of methane and hydrogen.

Thermal dissociation as thus evaluated only accounts for a portion of the unsaturates. The remainder must obviously be a product of oxidation. We cannot say what reactions are involved here, but we suggest that they be regarded as oxidations of those portions of the molecules which would be split off in dissociation leaving olefins. Thus, for example

$$\begin{array}{llll}
C_4H_{10} \longrightarrow C_4H_8 + H_2 & \longrightarrow C_4H_8 + H_2O \\
C_4H_{10} \longrightarrow C_3H_6 + CH_4 & \longrightarrow C_3H_6 + CH_3OH \\
 & \longrightarrow C_3H_6 + HCHO, \text{ etc.} \\
C_4H_{10} \longrightarrow C_2H_4 + C_2H_6 & \longrightarrow C_2H_4 + C_2H_5OH \\
 & \longrightarrow C_2H_4 + CH_3CHO, \text{ etc.}
\end{array}$$

These then are products of incipient dissociation completed by oxidation of the more saturated product of dissociation. We designate these reactions as of the type "Reaction II. Unsaturates by Oxidation." The amount of this type of reaction is given by the total of unsaturates less the sum of the volumes of methane and hydrogen.

Finally there remains that portion of the reacting hydrocarbon over and above the equivalent of unsaturates produced. In accounting for this we note that in those cases (low temperatures, empty reaction tube) in which little unsaturates, methane and hydrogen are formed, carbon monoxide is produced in amount roughly corresponding to the volume of hydrocarbon consumed, two volumes of oxygen disappearing simultaneously. This appears to be indicative of the type of reaction which Edgar and Pope[3] have found in the case of the higher hydrocarbons and of which an example would be

$$\begin{array}{c}
C_3H_8 + O_2 \longrightarrow C_2H_5CHO + H_2O \\
C_2H_5CHO + O_2 \longrightarrow CO + H_2O + CH_3CHO, \text{ etc.}
\end{array}$$

In any event we take care of the hydrocarbon unaccounted for in Reactions I and II by a third type, an oxidation which is designated "Reaction III. Aldehyde Reaction." The amount of this is obtained by subtracting the volume of unsaturates produced from the volume of hydrocarbon consumed.

We analyze our results then in terms of three reaction types of which the following would be examples: Type I, Unsaturates by Dissociation, *e. g.*, $C_3H_8 \longrightarrow C_3H_6 + H_2$; Type II, Unsaturates by Oxidation, *e. g.*,

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[3] Edgar and Pope, Swampscott Meeting, 1928.

$C_3H_8 + {}^1/_2O_2 \longrightarrow C_3H_6 + H_2O$; Type III, Aldehyde Reaction, *e. g.*, $C_3H_8 + 2O_2 \longrightarrow CO(+ CH_3CHO + 2H_2O)$. This establishes a basis for the comparisons of the effects of altering the variables. We do not insist that the possibilities are exhausted by the above types or that the method of calculating the relative amounts is infallible. Methane and hydrogen may well be formed in part by dissociation of intermediate products; the unsaturates may not represent olefins exclusively. Especially, the arbitrary method of representing the hydrocarbons as consisting only of the original and methane doubtless introduces errors. We have, however, a definite basis for the presentation and discussion of the data and we are inclined to think that the scheme and its application are not wide of the mark.

Temperature.—With respect to the reported temperatures, the following is to be kept in mind. These reactions are as a whole exothermic and take place rapidly. Exposure times are of the order of a few seconds. The gases are, therefore, unquestionably at a higher temperature than the surroundings. However, the whole question of temperature under such conditions is decidedly vague. Newly-formed molecules are necessarily highly energized. No matter what the total reaction rate may be, the unchanged molecules with which these product molecules first come in contact are subjected to far more extreme conditions than would correspond to many hundreds of degrees general rise in temperature. Only under such conditions that every newly-formed molecule made many wall collisions before meeting an unchanged molecule would anything corresponding to an isothermal state be set up. In our preliminary work much time was spent in attempting to adjust temperatures down the reaction tube by using a number of independent heating elements. Arrangements were made for determining temperatures at various positions. It was always found, however, that if reaction took place at all, the thermocouple at the entrance to the reaction tube registered from 25 to 50° above that somewhat farther down. We came, therefore, to the conclusion that a better arrangement was simply to place the reaction tube in a constant-temperature bath—the furnace—over its entire length, and to measure and record its temperature. This is at least definite and should be reproducible. The reaction then takes place in a manner that is partly adiabatic and partly isothermal. Since the gases were heated prior to mixing, the recorded temperatures are also the initial temperatures of the reaction mixture.

Heating Time.—Some uncertainty exists as to the exact times of heating in these experiments. When there is no change in the number of molecules on reaction, the temperature is known and constant and the flow is uniform across the reaction tube, the heating time is obtained by dividing the volume of the tube by the flow rate corrected to the temperature and pressure at which reaction is occurring. However, in these reactions, the number of molecules changes on reaction in so far as dissociation is a factor and the actual temperature of the reacting mixture is uncertain. Instead of trying to estimate these effects in separate experiments, and adjusting the flow rate to give a uniform contact time, we have been content to maintain a constant flow rate (measured at room temperature and pressure) throughout any one series of experiments. The average heating time in any series has then been taken as the ideal heating time at a temperature of 472° (745° A., which is $2^1/_2$ times the average room temperature, 298°). As experiments were conducted over the range 300–625°, this temperature is an average for all experiments. Room temperature might as well have been the basis of calculation, but the above gives more nearly the actual heating times.

The larger empty reaction tube had a volume of 21.6 cc. and the total flow rate at 25° and 760 mm. was 40.0 cc./min. The average heating time was therefore

$$\frac{21.6}{40.0 \times \frac{745}{298}} \times 60 = 13.0 \text{ seconds}$$

The *packed* tube had a volume of 15.8 cc., and the total flow rate was 30.0 cc./min. The average heating time was 12.6 seconds. The results of experiments in the two large tubes are therefore directly comparable as to heating time.

The smaller, empty tube had a volume of 2.6 cc. and the flow rate was 40.0 cc./min. The average heating time was 1.6 seconds. Heating times in this tube are therefore approximately one-eighth as long as in the larger tubes.

The large, empty tube was 1.65 cm. in internal diameter, 11 cm. long with 2-mm. walls. The small empty tube was 0.5 cm. in internal diameter, 10 cm. long with 1-mm. walls. The large, packed tube was 2 cm. in internal diameter, 11 cm. long with 2-mm. walls. It contained 46 g. of broken glass of 6–20 mesh. The glass surface in this tube was 10 to 15 times that in the empty tube.

Results and Discussion

Wall Action.—The first point to be settled was, of course, the influence of the walls of the reaction tube on the reaction. The result was unexpected. In order to determine whether or not the wall material (pyrex glass) catalyzed the reaction, a comparison was made between reactions taking place in an empty tube and in one packed with broken pyrex glass. (The tubes were cleaned with hot concentrated nitric acid and rinsed with water before use.) The result of the comparison was that whereas in the empty tube reaction between oxygen and propane was complete at 375°, in the packed tube there was no reaction below 500°. The glass packing therefore *strongly suppresses* reaction rather than accelerates it, and we must conclude that the walls have a predominantly negative rather than positive catalytic effect. This is in harmony with the observations of Hinshelwood and Thompson on the hydrogen–oxygen combination.[4] Related observations are those of Gautier and Hélier[5] on the explosibility of hydrogen–oxygen mixtures in a tube packed with porous porcelain.

This inhibitory influence of wall surface undoubtedly has to do with the more efficient transfer of energy from the reaction mixture to the surroundings. On the older view the initial temperature is more nearly maintained in presence of the glass packing; on the newer view excited molecules of product are de-activated by the walls instead of transferring excitation to fresh molecules of reactant. We will return to this point later.

There was still the possibility that in addition to this inhibitory influence of wall, which was regarded as physical in nature, the wall material was capable of exerting a positive catalytic effect on the oxidation. If this

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[4] Hinshelwood and Thompson, *Proc. Roy. Soc. (London)* **118A**, 170 (1928); see also Pease and Chesebro, *Proc. Nat. Acad. Sci.*, **14**, 472 (1928).

[5] Gautier and Hélier, *Compt. rend.*, **122**, 566 (1896).

were the case it should be possible to poison the active surface and obtain a further reduction in the amount of reaction. Poisoning the surface amounts to covering it with some material which is itself inactive. Alkali halides suggested themselves as substances which might fulfil this object. Accordingly the tubes were rinsed out with 20% potassium chloride solution, drained and again put to use. It was found that there was no alteration in the amount of reaction of oxygen and propane in the empty tube. In the packed, "coated" tube, however, the temperature at which reaction began was raised from around 500 to 575°, and reaction was still incomplete at 625°, whereas prior to coating it had been nearly complete at 550°. We have then to deal not only with an inhibitory action of the walls but also with a positive catalytic effect which, however, can be markedly decreased (and possibly eliminated) by poisoning. In the large, empty tube, on the other hand, we are safe in assuming that the observed reaction is almost exclusively homogeneous.

We will designate the reaction taking place in the large, empty, coated tube as the "free reaction," and that in the large, packed, coated tube as the "inhibited reaction." It is of interest to consider these two in some detail. Because it is in some respects the simpler and more normal of the two, the inhibited reaction will be first discussed.

The Inhibited Reaction

Propane.—Data on the reaction between propane and oxygen in the packed, coated tube are given in Table I. (In all these experiments close to 400 cc. of gas was introduced while the sample of off-gas was being collected, the actual amount being, of course, used in the calculations. For the sake of clearness, the amounts in round numbers are entered in

TABLE I

REACTION OF PROPANE AND OXYGEN IN PACKED, COATED TUBE

Temp., °C.	Gas in, cc.		Reacting, cc.		Formed, cc.					% C_3H_8 introduced to reaction,			
	O_2	C_3H_8	O_2	C_3H_8	Unsats.	CH_4	H_2	CO	CO_2	I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
575	300	100	8	13	4	3	2	1	1	5	0	8	13
600			33	27	20	1	4	5	2	5	15	7	27
625			35	32	25	14	3	2	2	17	8	7	32
575	100	300	6	27	14	10	1	1	1	4	1	4	9
600			39	78	64	33	3	3	2	12	9	5	26
625			84	144	119	105	1	3	5	35	4	8	47
	N_2												
600	100	300		33	22	32	3			11			11
625				45	40	32	17			15			15
Before coating with KCl													
	O_2												
550	300	100	287	88	15	8	13	167	49	15	0	74	89
	100	300	95	146	101	58	11	41	6	24	11	15	50

the tables under "Gas in." In addition, the temperature, volumes in cc. of hydrocarbon and oxygen reacting and of gaseous products formed and the percentages of total hydrocarbon introduced which have reacted according to the reaction types in which the results have been expressed are given.)

The first point to be noted is that approximately the same fraction of propane reacts whether the initial propane–oxygen ratio is 3 to 1 or 1 to 3. The conversion of propane is therefore approximately first order with respect to its own concentration. Since a large proportion of what reacts appears as dissociation products, one might suspect that the chief reaction was a purely thermal dissociation. When, however, nitrogen is substituted for oxygen as diluent, it is found that only one-third to one-half as much propane reacts. Hence it is clear that the dissociation has been for the most part excited by the simultaneous oxidation reactions. It is nevertheless significant that one has to approach conditions conducive to thermal dissociation before any reaction occurs. The oxidation reaction is evidently contingent on the possibility of dissociation, and at the same time promotes dissociation. It is as though the underlying reaction were still the unimolecular dissociation of the hydrocarbon but that the degree of activation requisite for reaction were lowered.

It is to be noted that little if any carbon monoxide, carbon dioxide or hydrogen is formed. Since less hydrogen is obtained from the oxidation than from the dissociation, it is evident that some has been burnt—under circumstances, it may be added, such that little hydrogen alone would have reacted. There is fairly clear indication here of removal of hydrogen directly from the hydrocarbon molecule by oxidation. This was given as an example of one of the type reactions, and for this reason. The absence of carbon monoxide and carbon dioxide shows that such carbon–oxygen linkages as have been formed have issued in liquid products. The marked difference in this respect between experiments before and after coating with potassium chloride will be noted.

It is a peculiarity, attributable to the unimolecular character of the reaction, that more oxygen is consumed from the mixture which is deficient in oxygen. It should be noted also that the mixtures richer in oxygen, although the more explosible because of their greater potential energy content, are under these conditions the less reactive.

The Free Reaction

Propane.—We turn now to a consideration of the very different type of reaction between propane and oxygen which takes place first at 300–400° (as compared to 575–600°) in our larger, empty tube. Carbon monoxide is now the principal gaseous product. The reaction is of a highly spontaneous character and gives every evidence of being of the chain type. Results are presented in Table II.

TABLE II

REACTIONS OF PROPANE AND OXYGEN IN THE LARGER, EMPTY, COATED TUBE

Temp., °C.	Gas in, cc.		Reacted, cc.		Formed, cc.					% C_3H_8 introduced to reaction,			
	O_2	C_3H_8	O_2	C_3H_8	Unsats.	CH_4	H_2	CO	CO_2	I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
300	300	100											
325			Nil		Nil								
350			119	51	10	0[a]	9	59	14	9	1	43	53
375			115	50	17	0	4	58	11	4	14	34	52
400			97	44	16	0	9	50	9	9	7	29	45
425			67	42	19	0	4	35	5	4	15	24	43
450			Explosive										
300	200	200	Nil		Nil								
325			183	98	20	3	4	91	15	4	7	41	52
350			192	100	24	0	3	90	17	2	11	40	53
375			193	105	31	0	11	95	14	6	11	38	55
400			187	107	37	4	5	92	11	5	15	36	56
425			Explosive										
300	100	300	Nil		Nil								
325			93	66	15	2	5	45	6	2	3	18	23
350			96	70	24	5	6	45	5	4	4	16	24
375			94	74	27	8	5	40	4	5	5	17	27
400			94	81	37	8	6	40	5	5	8	15	28
450			94	101	63	15	12	40	5	9	12	13	34
500			93	137	91	48	12	48	5	21	11	16	48
550			96	151	109	53	19	51	4	25	13	15	53
600			94	178	131	81	33	54	3	40	6	16	62
Before coating with KCl													
375	300	100	124	49	15	0	6	56	11	6	9	35	50
	200	200	189	99	30	1	11	88	13	6	9	36	51
	100	300	93	73	32	6	7	39	4	5	7	14	26

[a] In these and many other experiments with excess of oxygen, the saturated hydrocarbon in the off-gas averaged slightly higher in carbon than the original hydrocarbon. There would thus be no indication of the presence of methane. Small quantities of saturated hydrocarbons of higher molecular weight than the original appear to be formed under these conditions. The discrepancy never exceeded a few cc. and no attempt has been made to allow for it.

The reaction does not follow any conventional scheme. It starts abruptly within a 25° temperature interval, and, in the case of the $3C_3H_8{:}1O_2$ and $2C_3H_8{:}2O_2$ mixtures, runs immediately to complete consumption of the oxygen. Somewhere between $C_3H_8{:}O_2$ ratios of 2:2 and 1:3 there is another abrupt change such that at the lower propane concentrations only one-half to one-fourth of the oxygen reacts, although the start of reaction as the temperature is raised is still abrupt. Moreover, the reaction has under such conditions a quite definitely negative temperature coefficient, although it eventually becomes mildly explosive.

At first sight the diminished reactivity of mixtures low in propane appears to be in harmony with the results of the corresponding experiments in the packed tube at higher temperatures. There is, however, more than a suspicion that in the empty tube excess of oxygen rather than deficiency of propane is the important factor in limiting the reaction. Experiments were carried out in which one-third of the oxygen of the $1C_3H_8:3O_2$ mixtures was replaced by some other gas giving mixtures of the composition $1C_3H_8:2O_2:1$ diluent. The diluent gases were nitrogen, carbon dioxide, methane and hydrogen. Results are presented in Table III.

TABLE III

EXPERIMENTS ON MIXTURES OF COMPOSITION $1C_3H_8:2O_2:1$ DILUENT IN THE LARGER, EMPTY, COATED TUBE

Gas in, C_3H_8, 100 cc.; O_2, 200 cc.; diluent, 100 cc.

Temp., °C.	Diluent	Reacted, cc.		Formed, cc.					% C_3H_8 introduced to reaction,			
		O_2	C_3H_8	Unsats.	CH_4	H_2	CO	CO_2	I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
375	O_2	115	50	17	0	4	58	11	4	13	34	52
	CH_4	109	53	15	0	3	47	8	3	12	39	54
	N_2	109	47	14	0	6	45	9	6	8	35	49
	CO_2	94	46	13	0	4	45	(15)	4	9	35	48
	H_2	93	42	12	0	(2)	47	8	(2)	(10)	31	43
425	O_2	67	42	19	0	4	35	5	4	15	24	43
	CH_4	31	19	13	0	3	12	1	3	10	6	19
	N_2	11	12	10	0	1	8	1	1	9	2	12
	CO_2	12	8	6	0	4	7	(11)	4	2	2	8
	H_2	Nil										

The substitution of diluent for part of the oxygen makes very little difference in the amount of reaction at 375°. There is a small decrease in the order O_2, CH_4, N_2, CO_2, H_2. At 425°, however, this effect becomes so pronounced that, in the presence of hydrogen, reaction is almost entirely suppressed. These diluent gases clearly have specific inhibitory effects on the oxidation, the effect being more pronounced at the higher temperature. The similarity of the results when oxygen is the diluent leaves little room for doubt that this substance itself is as well inhibitor as reactant, and especially that the negative temperature coefficient observed with excess of oxygen is intimately related to the inhibitory action of this substance. That propane does not have a similar effect may be seen by comparing the results of experiments with $2C_3H_8:2O_2$ mixtures (Table II) with the above.

So far as is known, no similar observations on homogeneous gas reactions have been noted except those involved in anti-knock action, which refer, of course, to precisely this type of reaction—the oxidation of hydrocarbons.

The characteristics of the free reaction convince us that we are dealing with a chain mechanism. The reactions in question are undoubtedly those suggested by Edgar and Pope[3] as the reactions of oxidation of the higher paraffins, and may be represented by the equations

$$C_3H_8 + O_2 \rightarrow C_2H_5CHO + H_2O$$
$$C_2H_5CHO + O_2 \rightarrow CH_3CHO + H_2O + CO\text{, etc.}$$

In the case of propane the two reactions written above appear to be chiefly concerned, since in general we obtain 1 mole of carbon monoxide for 1 mole of propane and 2 moles of oxygen reacting. This is the sequence of reactions which is suppressed by diluents and KCl-coated, glass packing, and which has the chain mechanism. These reactions induce those yielding unsaturates and are the more effective in this respect as the temperature is raised.

Further information as to the nature of the free reaction is given by experiments in which 50% propane–oxygen mixtures were diluted with nitrogen. Results are presented in Table IV.

TABLE IV

REACTION OF 50% PROPANE–OXYGEN MIXTURES DILUTED WITH NITROGEN IN THE LARGER, EMPTY, COATED TUBE

Temp., °C.	Gas in cc. N_2	Gas in cc. O_2	Gas in cc. C_3H_8	Reacted, cc. O_2	Reacted, cc. C_3H_8	Formed, cc. Unsats.	Formed, cc. CH_4	Formed, cc. H_2	Formed, cc. CO	Formed, cc. CO_2	% C_3H_8 introduced, to reaction, I unsats. by dis.	% C_3H_8 introduced, to reaction, II unsats. by ox.	% C_3H_8 introduced, to reaction, III aldehyde react.	Total
350	300	50	50	Nil										
375														
450														
500				28	27	16	0	0	12	1	0	33	23	56
550				46	40	22	1	4	28	3	10	35	37	82
600				48	37	24	12	3	35	3	32	19	28	79
300	200	100	100	Nil										
350				73	39	9	0	4	33	6	4	5	32	41
400				Nil										
450				Nil										
475	Slightly explosive			76	62	37	14	17	50	6	33	6	26	65
300	100	150	150	Nil										
350				138	69	16	0	1	69	11	1	10	37	48
400				75	53	21	0	3	31	4	2	13	23	38
350	300	50	50	Nil										
	200	100	100	73	39	9	0	4	33	6	4	5	32	41
	100	150	150	138	69	16	0	1	69	11	1	10	37	48
	0	200	200	192	100	24	0	3	90	17	2	11	40	53
400	300	50	50	Nil										
	200	100	100											
	100	150	150	75	53	21	0	3	31	4	2	13	23	38
	0	200	200	187	107	37	4	5	92	11	5	15	36	56

Results with mixtures containing 50% nitrogen are particularly striking. Considerable reaction took place at 350°, but not at 300, 400 or 450°. At 475° the mixture became very mildly explosive but a sample could still be taken. The reaction rate first increases with temperature (300–350°), then decreases to zero (350–450°) and finally again increases (450–475°). When the nitrogen content is increased to 75% the whole of the low temperature reaction is wiped out, and only the higher temperature region (500–600°), with its positive temperature coefficient but without the explosive character, remains. It is to be noted that when reaction does set in, the formation of unsaturates is considerable as compared to that of carbon monoxide. This is equally true for the 50% mixture at 475°.

We have seen that the reactions of propane and oxygen can be suppressed by dilution or by the use of a KCl-coated glass packing. It was desired to determine the effect of shortening the heating time. To accomplish this it was convenient to keep the flow rate the same and use a smaller reaction tube. Accordingly a tube of the same length as the larger, empty tube (about 11 cm.) but of about one-third the diameter (0.5 cm. as against 1.6 cm.) was made up. Results are given in Table V.

TABLE V

REACTION OF PROPANE AND OXYGEN IN THE SMALLER, EMPTY, COATED TUBE

Temp., °C.	Gas in, cc.		Reacted, cc.		Formed, cc.					% C_3H_8 introduced to reaction,			
	O_2	C_3H_8	O_2	C_3H_8	Unsats.	CH_4	H_2	CO	CO_2	I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
600	300	100	12	10	11	0	7	4	1	7	4	0	11
625	Explosive												
500	100	300	Nil										
550			25	48	38	19	0	1	3	6	6	3	15
600			93	150	125	58	17	36	6	26	17	9	52

Reaction is again forced into the higher temperature region with the formation of unsaturates predominating.

The heating time in this smaller tube was one-eighth of that in the larger tube. This would be expected to decrease the amount of reaction correspondingly; but the observed decreases are so great as to warrant the conclusion that the decrease in tube diameter is effective of itself. Reaction only sets in at 500-600° instead of at 300–400°. In the smaller tube contact between gas molecules and the tube walls is facilitated. Apparently the difference in this respect between the smaller and larger tubes is sufficient to give the observed marked differences in reaction characteristics.

There is finally one more way in which the propane–oxygen reactions can be affected. This is by reducing the pressure. Experiments were carried out in which hydrocarbon–oxygen mixtures were caused to flow through a tube of large volume at 5 to 10 mm. pressure. The quantitative results were not very satisfactory owing to irregularity. Qualitatively, however, there was no question but that the suppression of reaction was very great. No reaction whatever took place below 600°. At higher temperatures there was certainly a parallelism between the amounts of hydrocarbon dissociating in nitrogen and the amount reacting in oxygen. It was not possible to conclude whether the same amount of hydrocarbon was involved in the two cases, or whether the two reactions were independent of each other. Once more, however, we find reaction finally setting in under conditions which are favorable to dissociation alone.

What has been said of the low pressure oxidation of propane applies as well to that of the butanes and also of ethane.

In the oxidation of propane we have then to deal with three types of reaction—that yielding unsaturates, and methane or hydrogen by dissociation, that yielding unsaturates and unidentified liquid products by oxidation and that yielding carbon monoxide and unidentified liquid products (again by oxidation). The first two types always appear together, sometimes one and sometimes the other predominating, and increase in amount as the temperature is raised. Unless the carbon monoxide reaction is taking place (as in the larger, empty tube) the reactions yielding unsaturates do not put in an appearance until the temperature reaches 550–600°. They give evidence of being more or less normal homogeneous gas reactions, first-order with respect to propane, which are subject to excitation by the carbon monoxide reaction in amount which is small at the lower temperatures but increases as the temperature is raised.

In the carbon monoxide reaction we meet with a wholly different state of affairs. This reaction is promoted by excess of hydrocarbon but depressed by excess of oxygen. Dilution with other gases than oxygen likewise inhibits the reaction; the extent of inhibition is a specific property of the diluent, and suppression by any of the diluents (including oxygen) is greater at higher temperatures so that the reaction under these conditions has a negative temperature coefficient. This reaction is likewise suppressed by a glass packing, particularly when this is coated with potassium chloride; it is suppressed in reaction tubes of small diameter; and it is suppressed when the pressure is lowered to a few millimeters. These are characteristics to be expected of a chain reaction, and we do not hesitate to state that a chain mechanism is here involved.[6] We have, however, no evidence bearing on the nature of the chain, though the formation of aldehydes and the possibilities of peroxide formation are to be borne in mind.[7]

That the reactions are as a whole exothermic is shown by the fact that a jacketed thermocouple will register a temperature 25–50° higher in a small region close to the inlet end than in the rest of the tube. A spontaneous development is not surprising. Rather, what requires explanation under these circumstances is the fact that other possible reactions

[6] We have recently found that this reaction is also faintly luminous.

[7] See Mardles, *J. Chem. Soc.*, **133**, 872 (1928)

are not more influenced, in particular, the fact that the excess of hydrocarbon which is always present is not more radically and more completely decomposed. The evidence is all in favor of the conclusion that the reaction energy is not as a whole available for heating the gases but is largely retained in some special form by product molecules to be given up to the walls or to be devoted by a specific mechanism to the continuance of the particular reaction to which it is due.

Reactions of the Butanes with Oxygen.—It remains now to present data on the reactions of the butanes with oxygen under conditions corresponding to those of the propane–oxygen reactions which have aready been presented and discussed in detail. The relations are essentially the same as with propane. Reaction is in general more ready and suppression is more difficult. Of the two, *n*-butane is the more reactive.

The Inhibited Reaction.—Results with the packed coated tube are presented in Table VI.

TABLE VI

REACTIONS OF THE BUTANES AND OXYGEN IN THE PACKED COATED TUBE

Temp., °C.	Gas in, cc.		Reacted, cc.		Formed, cc.					% H. C. introduced to reaction,			
	O_2	H.C.	O_2	H.C.	Unsats.	CH_4[a]	H_2	CO	CO_2	I unsats. by dis.	II unsats. by ox.	III aldehyde reacts.	Total
					*Iso*butane								
450	300	100	40	14	11	0	4	10	8	4	7	3	14
500			109	42	22	0	3	42	18	3	20	21	44
550			197	69	31	14	11	106	24	26	6	40	76
450	100	300	45	25	28	0	6	8	11	2	8	0	10
500			87	73	63	23	3	15	15	9	13	3	25
550			97	107	89	74	2	5	12	27	5	6	38
					n-Butane								
400	300	100	56	15	11	4	4	7	7	8	3	4	15
450			140	46	20	0	4	46	33	4	15	26	45
500			183	63	31	8	7	80	33	15	16	33	64
400	100	300	Nil										
450			58	35	34	9	1	4	15	3	8	0	11
500			88	85	78	22	6	23	17	10	17	2	29

[a] The interpretation of the analyses for saturated hydrocarbons in the off-gas are the more uncertain in these cases because of the probability that ethane is also present.

A comparison of these with the corresponding results for propane shows that whereas the latter only reacted at 600° with very little carbon monoxide formation, the butanes are reacting at 500° and considerable carbon monoxide is produced. The packing, therefore, does not repress the "aldehyde reaction" so readily in these cases. A finer packing might perhaps be more effective. As between the two, reaction development is the more ready in *n*-butane but the differences are not great, particularly when oxygen is in excess.

The Free Reaction.—Reaction between the butanes and oxygen in the larger, empty, coated tube takes place in a manner not very different from that with propane. A greater proportion of oxygen is consumed and reaction passes more readily into explosion. Indeed, *n*-butane–oxygen mixtures of composition 2:2 or 1:3 showed no region of quiet reaction. Results are presented in Table VII.

TABLE VII

REACTIONS OF THE BUTANES AND OXYGEN IN THE LARGER, EMPTY, COATED TUBE

Temp., °C.	Gas in, cc. diluent			Reacted, cc.		Formed, cc.					% C_3H_8 introduced to reaction, I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
	diluent	O_2	H. C.	O_2	H. C.	Unsats.	CH_4	H_2	CO	CO_2				
*Iso*butane														
350	None	300	100	181	62	12	0	5	75	17	5	7	52	64
400	Explosive													
350	None	100	300	100	60	29	4	0	37	6	1	9	11	21
400				98	77	39	11	0	34	6	4	10	13	27
450				100	100	68	33	9	41	7	15	9	11	35
400	N_2, 100	200	100	149	51	16	0	4	59	14	4	13	37	54
	H_2, 100	200	100	160	61	14	0	6	68	10	6	8	49	63
425	Both diluted mixtures explosive													
n-Butane														
Mixtures of 100 C_4H_{10}–300 O_2 or 200 C_2H_{10}–200 O_2 have no zone of quiet reaction														
350	None	100	300	93	64	30	26	6	36	9	10	0	12	22
450				96	91	77	42	7	39	12	17	10	5	32

With 3:1 hydrocarbon–oxygen mixtures (when all of the oxygen is consumed) the proportions of reactants and products are much the same as with propane. The 1:3 *iso*butane–oxygen mixture reacts only incompletely when it does not explode (*e. g.*, at 350°) as in the case of the cor-

TABLE VIII

REACTIONS OF THE BUTANES AND OXYGEN IN THE SMALLER, EMPTY, COATED TUBE

Temp., °C.	Gas in, cc.		Reacted, cc.		Formed, cc.					% C_3H_8 introduced to reaction, I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
	O_2	H. C.	O_2	H. C.	Unsats.	CH_4	H_2	CO	CO_2				
*Iso*butane													
500	300	100	43	15	15	0	2	14	5	1	14	0	15
550	Explosive												
450	100	300	22	13	18	0	0	0	5	0	7	0	7
500			54	52	46	5	0	9	7	2	14	2	18
550			99	116	101	39	8	32	9	16	19	5	30
n-Butane													
450	100	300	70	49	42	4	2	17	13	2	12	4	16
500			70	75	68	10	4	16	13	5	18	2	25
550			93	124	130	53	8	32	12	20	21	0	41

responding propane mixture, though a greater proportion of the oxygen is consumed. There is less indication of suppression by diluents, however. Data referring to the smaller, empty, coated tube are given in Table VIII.

It is seen that in the smaller, empty, coated tube the butanes again react more readily than propane, and that *n*-butane is the more reactive of the two. In this case the system of interpretation appears to be strained somewhat by the appearance of excessive quantities of unsaturates. It is possible that the formation of ethane is responsible, or that in some cases two molecules of ethylene are formed from one of butane.

A comparison between the amounts of reaction of 3:1 butane–oxygen mixtures at 450° in the larger and smaller empty tubes is available and is of some interest. It will be recalled that the two tubes give heating times in the ratio of 1 to 8 (1.6 and 13 sec., respectively) their diameters being in the approximate ratio of 1 to 3. Results are given in Table IX.

TABLE IX

COMPARISON OF 3:1 BUTANE–OXYGEN MIXTURES AT 450° IN SMALLER AND LARGER, EMPTY, COATED TUBES

	Reacted, cc.		Formed, cc.					C_3H_8 introduced to reaction, %			
Tube	O_2	H. C.	Unsats.	CH_4	H_2	CO	CO_2	I unsats. by dis.	II unsats. by ox.	III aldehyde react.	Total
					*Iso*butane						
Small	22	13	18	0	0	0	5	0	7	0	7
Large	100	100	68	33	9	41	7	15	9	11	35
					n-Butane						
Small	70	49	42	4	2	17	13	2	12	4	16
Large	96	91	77	42	7	39	12	17	10	5	32

The differences are ascribed to an increase principally in the amounts of dissociation, along with a considerable increase in the amount of carbon monoxide, which, however, does not appear in the analysis of results as due to our aldehyde reaction, though doubtless this would be the correct interpretation.

We conclude that there is no essential physico-chemical difference between the reactions of the butanes with oxygen and those of propane and that the same considerations are applicable. This being the case, we are inclined to believe that the same will be true of the higher hydrocarbons. Differences will necessarily appear in the study of the lower hydrocarbons, methane and ethane, because of the impossibility of certain types of reaction, and these will require special study. The appearance of carbon monoxide and water as the principal products of methane oxidation is suggestive of a similarity in some sense. In the case of ethane the slowness of the reactions when oxygen is in excess, as shown by Bone and Stockings,[8] is exactly in accord with results found for propane and the

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[8] Bone and Stockings, *J. Chem. Soc.*, **85**, 693 (1904).

butanes. It may be added that Bone and Wheeler[9] and Bone and Andrew[10] find the same effect in the slow oxidation of ethylene and of acetylene, pointing to chain mechanisms in these cases also.

These results are admittedly incomplete. What was aimed at was a survey of the field. The points that will interest us especially in further investigations are the nature of the chain reaction and especially of the diluent effect, and the behavior of the lower hydrocarbons.

It may be pointed out that the indications are that liquid products containing the same number of carbon atoms as the original hydrocarbon are not formed in quantity. The aldehyde with one less carbon atom should be obtainable in a fairly pure state by oxidation at the lowest possible furnace temperature with excess of hydrocarbon. High temperatures and the maximum suppression give good yields of what are undoubtedly olefins, under conditions which are more convenient than those required for ordinary dissociation. In fact, this is unquestionably a suitable method to prepare olefins from saturated hydrocarbons. We have no very clear ideas as to the nature of the reactions producing unsaturates by oxidation except that the burning off of hydrogen to give the olefin of the same chain length is one reaction, and that reactions such as

$$C_3H_8 + {}^1/_2O_2 \rightarrow C_2H_4 + CH_3OH$$
$$C_3H_8 + O_2 \rightarrow C_2H_4 + HCHO + H_2O$$

are possible. We are inclined to believe that the formation of alcohols, which probably occurs, is referable to the first of these reactions and may be regarded as due to the tendency of the hydrocarbon to undergo demethanation. The formation of acids is perhaps due to secondary oxidation of aldehydes but we have no evidence on this point for or against.

There is no question but that the proportions of these various reactions can be altered profoundly by relatively minor changes in the methods of carrying out the oxidation. This is to be borne in mind by those interested in arriving at a more precise idea of the nature of the liquid products, or in forcing the reactions in some one particular direction. One point in particular is worth bearing in mind. Probably any catalyst will act to suppress what we have called the aldehyde reaction just as a glass packing does. On top of this effect will be superimposed the specific action of the particular catalyst employed. The role of the catalyst will thus be always a dual one.

Summary

1. A study has been made by the flow method of the reactions of mixtures of oxygen with propane and the butanes. No attempt has been made to analyze the liquid products and all conclusions are based on the results of gas analyses.

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[9] Bone and Wheeler, on ethylene, *J. Chem. Soc.*, **85**, 1637 (1904).

[10] Bone and Andrew, on acetylene, *ibid.*, **87**, 1232 (1905).

2. The reactions are classified into three types, which (with examples) are as follows: (I) Unsaturates by Dissociation, Example—$C_3H_8 \longrightarrow C_3H_6 + H_2$; (II) Unsaturates by Oxidation, Example—$C_3H_8 + {}^1/_2O_2 \longrightarrow C_3H_6 + H_2O$; (III) Aldehyde Reaction, Example—$C_3H_8 + 2O_2 \longrightarrow CO + 2H_2O + CH_3CHO$.

3. Types I and II give evidence of being more or less normal homogeneous gas reactions which appear at 500–600°, but are subject to induction by Type III at lower temperatures in amount increasing with the temperature.

4. Type III may begin at temperatures of 300–350° and gives every indication of being a chain reaction. Its development is highly spontaneous, and at the same time it is sensitive to relatively minor variations in the conditions of reaction. In particular, it is subject to suppression by a broken-glass packing (especially when this is coated with potassium chloride), and by use of a reaction tube of small diameter. Lowering the pressure to a few millimeters has a like effect. Dilution with oxygen, methane, nitrogen, carbon dioxide or hydrogen depresses the reaction in amount increasing in the order named; this effect is the greater at higher temperatures. Under these conditions the reaction thus has a negative temperature coefficient, though eventually becoming explosive. Excess of hydrocarbon promotes the reaction.

5. Under suppression, there may be no reaction up to 500–600°. Types I and II then appear, accompanied by Type III in varying amount.

6. Considerations bearing on the isolation of particular reactions are set forth.

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THE STRUCTURE OF METAL KETYLS. I. THE SCHMIDLIN FORMULA

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The highly colored products formed by the addition of one atom of an alkali metal to one molecule of certain aromatic ketones were named "metal ketyls" by Schlenk and his co-workers,[2] who concluded that these substances comprised a new class of compounds containing trivalent carbon. This view was criticized by Schmidlin,[3] who contended that they should be regarded as molecular compounds analogous to those formed between

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[2] (a) Schlenk and Weikel, *Ber.*, **44**, 1182 (1911); (b) Schlenk and Thal, *ibid.*, **46**, 2840 (1913); (c) Schlenk, Appenrodt, Michael and Thal, *ibid.*, **47**, 486 (1914).

[3] Schmidlin, "Das Triphenylmethyl," Stuttgart, **1914**, pp. 186–188.