349. *The Oxidation of Propane. Part II. The Products of the Slow Oxidation at High Pressures.*

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It is shown that when propane is oxidised at high pressures, *iso*propyl alcohol and acetone are found in the products in circumstances suggesting that they arise from direct oxidation of the hydrocarbon molecule at the β-carbon atom.

n-Propyl, ethyl, and methyl alcohols are also formed in considerable quantities, the yield of the higher alcohols being favoured by increase of pressure.

The results suggest that propane undergoes oxidation in two ways, the initial products in the one case being *n*-propyl alcohol and propaldehyde, and in the other, *iso*propyl alcohol and acetone.

In Part I (preceding paper) it is shown *inter alia* that, in the oxidation of propane at and below atmospheric pressure, higher aldehydes of the type R·CHO are important intermediates, which, in certain circumstances, may exert a marked influence upon the course of the oxidation and give rise to the phenomenon of cool-flame combustion. The actual mechanism by which they are formed from the parent hydrocarbon is still open to question, but their occurrence in large quantities affords strong evidence that the point of initial oxygen attack on the propane molecule is at a terminal carbon atom.

When, however, propane is oxidised at high pressures the products are found to contain, in addition to most of those substances formed at normal pressures, both *iso*propyl alcohol and acetone, arising probably from some initial oxidation at the β-carbon atom. Although the rôle of pressure in bringing about such an alteration in the primary process is not obvious, there are several ways in which it might operate indirectly; *e.g.*, a sufficiently high pressure might alter the ratio of the collision period leading to activation and the vibrational periods of the C–C or C–H linkages; or, it might act by increasing the concentration of certain secondary products formed reversibly by the interaction of intermediates taking part in the main combustion process. The work described in the present paper was carried out with a view to obtain more detailed information upon its action.

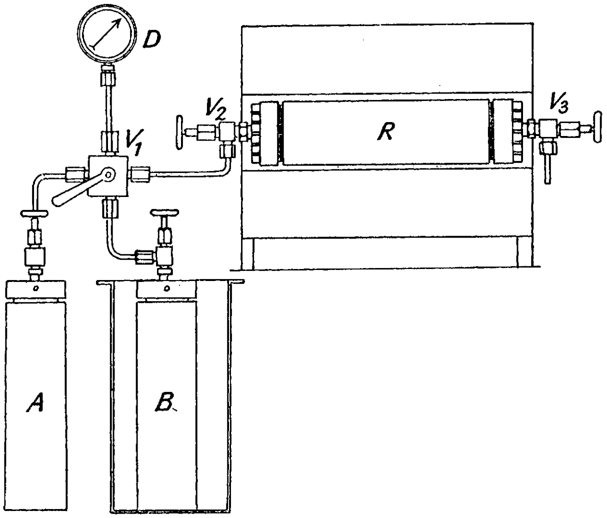
EXPERIMENTAL.

In following the progress of a highly exothermic reaction such as the oxidation of propane, it is necessary, if substantially isothermal conditions are to be maintained, to employ media containing a large excess of one or other of the reactants and/or of an inert diluent gas or vapour, and preferably to use a static method similar to that described in Part I.

The apparatus shown diagrammatically in the figure was used. The reactants and diluent gases are stored under pressure in the steel cylinders *A* and *B*, and are admitted separately through the valves V_1 and V_2 to the steel reaction vessel *R*, which is maintained at the desired temperature by external heating. Reaction normally takes place slowly with a rise of temperature seldom exceeding about 10°; on completion, the products are discharged through the exit valve V_3, and, after traversing a series of cooling coils and scrubbers in which the condensable and water-soluble products are removed, are collected in a calibrated gas-holder.

The pressure of the system is measured by the Bourdon gauge *D*, and the reaction temperature by means of a platinum–rhodium thermocouple situated in a light steel tube traversing axially the reaction chamber. In experiments employing high partial pressures of propane, the storage cylinders and all connections to the reaction vessel have to be maintained at a temperature sufficiently high to avoid condensation.

The Products from the Slow Oxidation at High Pressures.—From the slow reaction at pressures above about 10 atm., there results a complex mixture of liquid and gaseous products containing formaldehyde and higher aldehydes, normal alcohols, and *iso*propyl alcohol, acetone, the two oxides of carbon, and steam. No propylene, methane, or acetylene is found amongst the gases, and usually no peroxidic substance in the condensable liquid products. In experiments in which the contents of the reaction vessel were suddenly released before the end of reaction and were immediately cooled, traces of peroxides could, however, sometimes be detected by the titanium chloride test, but no unsaturated gases, methane, or hydrogen.



It is also noteworthy that the products from mixtures containing a large excess of propane reacting in the neighbourhood of their ignition temperatures are always found to contain considerable quantities of naphthalene, which condenses in the exit valve and cooling coils as a white solid.

Qualitative tests show the higher aldehydes to consist of propaldehyde and acetaldehyde, and the *n*-alcohols of methyl, ethyl, and propyl alcohol. The acids consist principally of acetic, with traces of propionic and possibly formic acid, although no derivatives of the last were prepared. In the tabulated results, quantitative estimates are given only for the total aldehydes, *n*-alcohols, and acids.

The Influence of Temperature upon the Distribution of Oxygen in the Products.—To ascertain the most favourable conditions for examining the pressure effect, a series of experiments was first carried out with a 1 : 5 propane–air medium at 30 atm. over a range of temperature giving from very slow to rapid rates of reaction without, however, approaching ignition; at each temperature the products were collected at the end of the reaction, when little or no free oxygen remained, and were subsequently analysed, with the results recorded in Table I.

The data show that, although the total *n*-alcohols surviving in the products increase throughout with temperature, yet the total aldehydes, *iso*propyl alcohol, and acids reach a maximum and then diminish; the ratio of the sum of the aldehydes and *n*-alcohols, *A*, to the *iso*propyl alcohol and acetone, *B*, which may be taken as a rough measure of the relative extent to which the β-carbon atom and the terminal carbon atoms are undergoing oxidation, shows a minimum at about 274°.

By a suitable adjustment of temperature and pressure it is possible to establish a cool flame in the 1 : 5 mixture and to compare the resultant products with those from slow combustion

TABLE I.

Products from the reaction of a 1 : 5 *propane–air medium at* 30 *atm. and various temperatures.*

Temp.	260°.	270°.	274°.	284°.	286°.
	Products, as % of the carbon of the propane burnt.				
Total aldehyde	5·7	8·8	12·8	16·6	8·7
Total *n*-alcohols	20·9	25·5	18·8	25·5	40·0
*iso*Propyl alcohol	2·0	6·9	12·7	8·4	6·2
Acetone	nil	1·4	0·6		0·5
Total acids	4·4	13·4	13·8	11·5	6·0
CO_2	49·8	25·0	26·9	13·0	11·0
CO	17·2	19·0	14·4	25·0	27·6
Ratio CO/CO_2	0·35	0·76	0·53	1·9	2·5
Ratio A/B *	13·3	4·2	2·4	5·0	7·3

* A = Sum of the aldehyde and *n*-alcohols; B = sum of the *iso*propyl alcohol and acetone.

under approximately the same conditions. The data for two such experiments at 30 atm. are given below :

	Products, as % of the carbon of the propane burnt in	
	Slow combustion.	Cool-flame combustion.
Total aldehydes	8·8	22·2
n-Alcohol	25·5	22·1
*iso*Propyl alcohol	6·9	4·2
Acetone	1·4	1·7
Acids	13·4	6·8
CO_2	25·0	20·4
CO	19·0	12·6

The only marked difference in the products lies in the increased quantity of total aldehydes formed in the cool-flame combustion.

The Influence of Pressure.—To obtain a true comparison of the changes in the products resulting from a progressive increase of pressure, the above results show that it is necessary to adjust the temperatures so that reaction at the different pressures will take place at approximately equal rates. In Table II the analytical data for a 1 : 3·6 propane–air medium reacting at four pressures in the range 1—100 atm. and temperatures between 373° and 250° are summarised.

TABLE II.

Products from the reaction of a 1 : 3·6 *propane–air medium at pressures from* 1 *to* 100 *atm.*

Pressure, atm.	1	20	60	100
Reaction temp.	373°	281°	252°	250°
	Products, as % of the carbon of the propane burnt.			
Total aldehydes	20·5	21·8	13·5	13·7
n-Alcohols	19·7	21·0	17·5	15·2
*iso*Propyl alcohol	1·3	2·8	6·2	16·0
Acetone	0·5	4·3	12·5	7·9
Acids	4·3	17·0	19·0	18·9
CO_2	7·3	17·1	21·4	20·6
CO	21·3	16·0	9·9	7·7
C_3H_6	25·1	nil	nil	nil
Ratio CO/CO_2	2·93	0·95	0·46	0·37
Ratio A/B	22·3	6·0	1·7	1·2

The effect of pressure is shown by the rapid diminution of the ratio A/B between 1 and 60 atm.; there is clearly an increasing tendency as the pressure is raised for the propane molecule to undergo primary oxidation at the β-carbon atom, and the quantities of *iso*propyl alcohol and acetone surviving show a corresponding increase. It should also be noted that propylene, present to the extent of 25% at atmospheric pressure, is entirely absent at high pressure.

Carbon monoxide, formed partly from the thermal decomposition of aldehydes and partly from their further oxidation, decreases with increase of pressure and lowering of the reaction temperature.

The Influence of Concentration.—In the slow oxidation of methane and ethane at high pressures, the concentration of the hydrocarbon has been shown to play an important part in determining the survival of intermediate products (*Proc. Roy. Soc.*, 1931, *A*, **134**, 591; 1933, *A*,

140, 426), and from structural and other considerations a still greater effect might be anticipated in the case of propane. Experiments at 30 atm. and 275° with a series of mixtures in which the proportions of propane to air are varied between 1 : 20 and 1 : 0·5 confirm this prediction.

In the results set forth in Table III the most noticeable feature is the extent to which the total condensable products increase with the concentration of the hydrocarbon. For instance, whereas with a 1 : 20 propane–air mixture they represent 47·6% of the carbon of the propane burnt, yet when the proportion of propane is increased to 1 : 0·5 the corresponding figure is 85·5%.

TABLE III.

Products from the reaction of various propane–air mixtures at 30 *atm. pressure and* 275°

Propane : air.	1 : 20.	1 : 5.	1 : 3·6.	1 : 2·5.	1 : 1·25.	1 : 0·7.	1 : 0·5.
	Products, as % of the carbon of the propane burnt.						
Total aldehydes	12·5	8·8	12·0	18·5	16·1	14·6	16·7
n-Alcohols	17·3	25·5	23·0	27·6	33·1	34·8	34·5
*iso*Propyl alcohol	2·7	6·9	5·2	2·8	5·2	6·0	14·4
Acetone	1·2	1·4	1·3	0·9	0·3	10·6	7·4
Acids	13·9	13·4	15·2	6·7	8·9	11·0	12·5
CO_2	31·5	25·0	22·1	8·6	10·5	9·8	7·0
CO	20·9	19·0	21·3	34·8	25·9	13·6	8·0
Total condensable products	47·6	56·0	56·7	56·5	63·6	77·0	85·5
Ratio CO/CO_2	0·66	0·76	0·96	4·05	2·46	1·39	1·14
Ratio A/B	7·6	4·1	5·4	12·4	9·0	2·9	2·4

Under comparable conditions in respect of concentration, pressure, and reaction velocity, the yields from methane, ethane, and propane respectively are as follows :

	CH_4.	C_2H_6.	C_3H_8.
Reaction temp.	380°	305°	275°
Total condensable products, as % of the carbon of the hydrocarbon burnt	7	40	64

n-Alcohols are in all cases present in larger quantities than either *iso*propyl alcohol, aldehydes, or ketones, but the change in the ratio (aldehyde + *n*-alcohol) : (acetone + *iso*propyl alcohol) shows that with increasing concentrations of the hydrocarbon a greater proportion of the oxygen is utilised in oxidising it at the β-carbon atom.

The Distribution of Alcohols in the Products.—Further light is thrown on the mechanism of the oxidation by a more detailed study of the effect of pressure upon the distribution of alcohols in the products. The absolute amount of alcohols recovered from any one experiment in our apparatus is not large, and in order to obtain a sufficient quantity for analysis, it is necessary to carry out 10—20 experiments at each pressure. The products are freed from aldehyde, and the individual alcohols estimated by a method based upon their relative solubilities in aqueous calcium chloride and in xylene. The results for a 1 : 3·6 propane–air mixture at 5, 30, and 65 atm. are given below.

Relative quantities of alcohols surviving from the reaction of a 1 : 3·6 *propane–air mixture.*

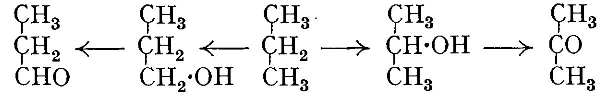
Pressure, atm.		5	30		65
Products	Methyl alcohol	76·3	58·0	55·3	50·1
	Ethyl alcohol	19·1	17·6	13·2	9·8
	Propyl alcohol	4·6	4·3	7·3	12·2
	*iso*Propyl alcohol		20·0	24·2	27·9

The results at 5 atm. confirm Pease's observation (*J. Amer. Chem. Soc.*, 1934, **56**, 2034) that methyl alcohol is the chief constituent of the alcoholic products at low pressures. As the pressure is increased, the proportions of both methyl and ethyl alcohol diminish, whilst those of propyl and *iso*propyl alcohol increase. The formation of a series of *n*-alcohols from propane is explicable on the assumption that oxidation takes place at an end methyl group, the propyl alcohol formed in the initial stages then undergoing further oxidation to propaldehyde, and the lower alcohols being subsequently formed by the reaction $R{\cdot}CHO + O_2 = R{\cdot}OH + CO_2$.

Evidence in support of this mechanism is obtained from experiments upon the slow oxidation of propyl and ethyl alcohol severally at high pressure. The former reacting at 240° and 56 atm. gives propaldehyde, acetaldehyde, ethyl alcohol, and propionic and acetic acids, whilst the latter reacting at 280° and 50 atm. gives acetaldehyde, methyl alcohol, and acetic and formic acids

(*Proc. Roy. Soc.*, **1934**, *A*, **147**, 555). It will also be recalled that Kane, Chamberlain, and Townend (this vol., p. 436) have shown that methyl alcohol is far less easily oxidisable than either propyl or ethyl alcohol even at high pressures, and its survival in comparatively large quantities is therefore to be expected.

The formation of *iso*propyl alcohol might be attributed to hydration of propylene : $C_3H_6 + H_2O = CHMe_2{\cdot}OH$, but at 250—300° the equilibrium constants for the reaction would demand the presence of considerable quantities of propylene, which, in point of fact, was absent in the high-pressure experiments. We conclude, therefore, that, in addition to attack at the terminal carbon atom, the propane molecule may undergo direct oxidation at the β-carbon atom, a process which is favoured by high pressure :



$$\begin{array}{ccccccccc} CH_3 & & CH_3 & & CH_3 & & CH_3 & & CH_3 \\ | & & | & & | & & | & & | \\ CH_2 & \longleftarrow & CH_2 & \longleftarrow & CH_2 & \longrightarrow & CH{\cdot}OH & \longrightarrow & CO \\ | & & | & & | & & | & & | \\ CHO & & CH_2{\cdot}OH & & CH_3 & & CH_3 & & CH_3 \end{array}$$

Analytical Methods.—The methods for estimating total aldehydes, alcohols, and acids have been described in Part I. In addition the following were used.

Alcohols. The products were freed from aldehydes by the addition of hydroxylamine hydrochloride, potassium hydroxide was added, and the alcohols distilled off. The aqueous-alcoholic mixture was concentrated by repeated redistillation with anhydrous potassium carbonate, and sufficient solid calcium chloride then added to give a 40% solution. The solution was shaken with xylene for several hours, and the xylene separated and washed several times with a fresh calcium chloride solution to remove any traces of methyl and ethyl alcohols. The original calcium chloride solution was also washed several times with xylene to remove the last traces of *n*- and *iso*-propyl alcohol.

Methyl and ethyl alcohols were recovered together from the calcium chloride solution by distillation, and the distillate was dried and its density determined. The alcohols were then estimated by oxidation with (1) potassium dichromate and sulphuric acid and (2) potassium permanganate in the cold.

The *n*- and *iso*-propyl alcohol were extracted from the xylene solution with water, and dehydrated by distillation with anhydrous potassium carbonate. The density of the mixture was determined, and the alcohols subsequently estimated by oxidation with potassium dichromate and sulphuric acid.

iso*Propyl alcohol and acetone.* A portion of the condensate free from aldehyde was oxidised with potassium dichromate and sulphuric acid in the cold for 3—4 hours, and the excess chromic acid reduced by adding ferrous sulphate. The mixture was then made alkaline with potassium hydroxide and steam-distilled, and the total acetone estimated by means of hydroxylamine hydrochloride. The acetone in the original condensate was estimated by the Scott-Wilson method (*Bull. Soc. Chim. biol.*, **1932**, **14**, 885), mercurous cyanide and hydrogen peroxide being used, and the *iso*propyl alcohol found by difference.

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