# CVII.—*Low-temperature Oxidation of Hydrocarbons. Part I. The Pressure–Temperature Curves of Amylene–Oxygen Mixtures.*

By J. Stanley Lewis.

In a previous paper (J., 1927, 1555) the author described the effect of increase of temperature on mixtures of paraffin hydrocarbons and oxygen kept at constant volume, and suggested that the primary reaction was a dehydrogenation of the hydrocarbon, yielding water and an unsaturated hydrocarbon, which, owing to its instability in the presence of oxygen, might yield peroxides or their decomposition products such as aldehydes. The view that peroxides or moloxides are first produced by the direct union of the paraffin with oxygen during initial combustion has many supporters, and a brief review of this subject is given by Brunner and Rideal (J., 1928, 1162). They are of opinion that moloxides are initially produced at surfaces until the concentration rises to a certain critical value, whereupon chain reactions set in, accompanied by an enormous increase in the velocity of reaction.

It has been shown by the author (*loc. cit.*) that paraffin hydrocarbons possess a characteristic initial temperature of oxidation which is lower the higher the molecular weight. In the case of *n*-hexane, this is 232°, and it was found that this temperature varied only slightly with wide variations in concentration and rate of heating. By maintaining a constant temperature somewhat below 232°, Brunner and Rideal were able to identify a preliminary slow oxidation period. Their pressure–time curves indicate a period of steady fall in pressure at constant temperature, followed by an abrupt rise in pressure. The first portion of the curve is interpreted as an induction period during which slow autoxidation occurs with the formation of moloxides or peroxides, and the final part corresponds to a period of rapid combustion or decomposition of peroxides. The predominating reactions are given as follows (J., 1928, 2824) :

$$C_6H_{14} + O_2 \longrightarrow C_6H_{14}O_2 \text{ (active moloxide)},$$
$$C_6H_{14} + C_6H_{14}O_2 \longrightarrow 2C_6H_{12} + 2H_2O,$$
$$C_6H_{12} + O_2 \longrightarrow C_6H_{12}O_2 \longrightarrow \text{decomposition.}$$

The catalytic action of water in the initial oxidation of saturated hydrocarbons has been demonstrated previously (Lewis, *loc. cit.*), and the above actions could be equally well explained by assuming in the first place that the per- or mol-oxide of hydrogen is produced by surface action, thus :

$$2H_2O + O_2 \longrightarrow 2H_2O_2 \text{ (peroxide)},$$
$$C_6H_{14} + H_2O_2 \longrightarrow C_6H_{12} + 2H_2O,$$
$$C_6H_{12} + O_2 \longrightarrow C_6H_{12}O_2 \longrightarrow \text{decomposition.}$$

There is also a possibility that the peroxide of the unsaturated hydrocarbon, if formed, might accelerate the reaction according to the equation $C_6H_{12}O_2 + 2C_6H_{14} \longrightarrow 3C_6H_{12} + 2H_2O$. This would have the merit of being in accordance with facts, for it is well known that the olefins and diolefins accelerate the oxidation of the paraffins.

The practical evidence that moloxides of saturated hydrocarbons exist is very scanty and far from conclusive. This is not the case with the olefins and dienes, which form addition products with oxygen at room temperature as shown by Engler and Weissberg (*Ber.*, 1900, **33**, 1094) in their work on autoxidation. Amylene, when allowed to stand in air in diffused daylight, gave a syrupy liquid containing oxygen of which 45% was peroxide. Trimethylethylene yielded a similar product with 30% of peroxide oxygen, and hexylene 7·2% after exposure to oxygen for 48 hours. These peroxides are unstable and under certain conditions have been known to detonate, but during slow decomposition they give rise to aldehydes, acids, carbon monoxide and dioxide, water, traces of unsaturated hydrocarbons, and hydrogen. This important point is referred to again in the discussion (p. 764).

The author still adheres to his original suggestion that the first well-defined stage in the oxidation of a paraffin hydrocarbon is the production of unsaturated hydrocarbon and water. Experimental evidence shows that the ease with which the hydrogen is removed varies with the structure of the hydrocarbon, and the various cases which present themselves have been mentioned already (Lewis, J., 1927, 1569). Moreover, it is possible to obtain unsaturated hydrocarbons from the paraffins by partial oxidation under special conditions: by passing a mixture of pentane or hexane and air over feebly ignited platinum, Stepsky (*Monatsh.*, 1902, **23**, 773) obtained amylene and hexylene amongst the oxidation products.

A comparison of the action of sulphur and of oxygen in the removal of hydrogen from saturated hydrocarbons apparently strengthens the case for primary dehydrogenation. In some experiments made by the author, hexane vapour was drawn through molten sulphur at about 350° by a current of nitrogen, and a high yield of hydrogen sulphide was obtained. The unattacked hexane recovered was found to contain 1—2% by volume of unsaturated hydrocarbons, whilst the product in the reaction vessel was a black asphaltic mass, which was not investigated. When the hydrocarbon was heated with sulphur in an atmosphere of nitrogen in a glass bulb with a manometer attached, a rapid action, denoted by pressure increase, occurred above 320°, and after the contents of the bulb had been cooled, qualitative tests indicated the presence of hydrogen sulphide and of organic sulphur compounds which gave precipitates with mercuric chloride. Spanier had previously stated that sulphur had no action on *n*-hexane when heated at 210° for 24 hours in a sealed tube. It is suggested that the mechanism of the reaction is similar to the oxidation of the paraffin whereby hydrogen atoms of the hydrocarbon are directly removed by the sulphur, yielding more active unsaturated residues. Under the conditions of temperature and pressure of the author's experiments, the paraffins can dissociate to unsaturated hydrocarbons plus hydrogen atoms, but with negligible velocity except at the surface of the containing vessel. These hydrogen atoms may then react with oxygen or sulphur, and for the former element some such sequence as the following may occur:

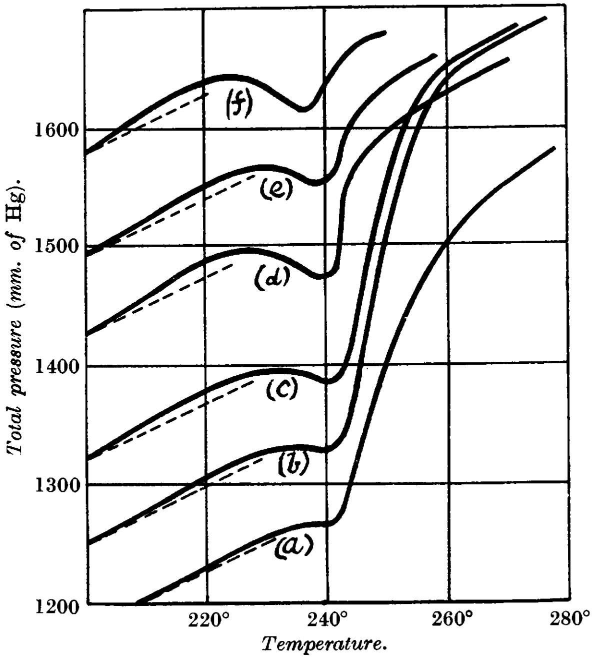
$$C_6H_{14} \rightleftharpoons C_6H_{12} + 2H \text{ (surface action)},$$
$$2H + O_2 \longrightarrow H_2O_2,$$
$$H_2O_2 \longrightarrow H_2O + O \text{ (assists primary dehydrogenation)}.$$

It being assumed that the initial stage of the oxidation of paraffins is the production of unsaturated hydrocarbons, the next step in the combustion may be a reaction between these hydrocarbons and oxygen. The chemical changes involved appear to be well defined, and the trend of evidence is in favour of initial peroxidation with subsequent decomposition and further oxidation. The present paper contains an account of some work carried out on mixtures of amylene and oxygen heated continuously with moderate rise in temperature at constant volume. The changes discerned in similar mixtures maintained at constant temperature and volume will be described in a later communication.

## EXPERIMENTAL.

*Pressure–temperature Curves.*—The hydrocarbon used in the following experiments was amylene, which was found to give a characteristic curve. It was washed with acidified potassium iodide and redistilled after drying over calcium chloride, the fraction of b. p. 34—35° being accepted. The apparatus was a slight improvement of the one used in the experiments on saturated hydrocarbons (*loc. cit.*), in which a reaction bulb (of 225 c.c. capacity) was attached to a mercury manometer by means of a capillary tube. During the heating of the bulb, the mercury was maintained at a definite mark in the capillary tube by raising the manometer, and the height of mercury above this mark plus the barometric pressure gave the pressure of the bulb contents. Typical pressure–temperature curves are given in Fig. 1. In order that reproducible results may be

FIG. 1.



obtained it is essential that the amylene be freshly distilled and that moisture be absent. Before each experiment the bulb was washed with chromic acid, water, and alcohol, dried in an oven at about 150° whilst a current of dry air was blown into it, cooled in a desiccator, and filled with dried carbon dioxide-free oxygen. The form of the curve is not greatly affected by fairly wide variations in the rate of heating, but for very slow rates the slope is somewhat greater than for rapid heating. The above curves were obtained when a temperature of 240° was attained after approximately 2½ hours' heating. The dotted lines in Fig. 1 show the slope of an amylene–nitrogen curve for comparison. In Table I will be found the composition of the mixtures for each of the several curves. The initial part of the curve of a weak mixture (*a*) changes almost in accordance with the gas laws, but in the case of (*d*), with a composition approximating to $C_5H_{10} + O_2$, there is a maximum deviation. Analysis of mixtures during this part of the heating afforded positive information of slight chemical action occurring, carbon oxides as well as aldehydes being present at 190°.

The second part of these curves is characterised by a fall in pressure until a minimum point is reached, indicating that a slow chemical action is proceeding with a decrease in the number of molecules present. The temperature of minimum pressure varies to a small extent with the concentration of amylene and with the total pressure; thus, for mixture (*a*) the minimum point is at 241°, but it gradually falls to 237° for mixture (*f*). It will be observed that the contraction is greatest in the case of the equimolecular mixture (*d*).

TABLE I.

| | Amylene, % by vol. | Residual gas at *N.T.P.* after oxidation. | Gas analysis, %. | | | % Amylene (by wt.) oxidised to CO and $CO_2$. |
|---|---|---|---|---|---|---|
| | | | $CO_2$. | CO. | $O_2$. | |
| (*a*) | 17·8 | 142 c.c. | 31·0 | 30·8 | 18·2 | 44·3 |
| (*b*) | 25·8 | 137 ,, | 35·0 | 35·1 | 4·9 | 32·4 |
| (*c*) | 35·3 | 112 ,, | 33·3 | 39·5 | 3·7 | 22·5 |
| (*d*) | 46·7 | 100 ,, | 35·2 | 42·3 | 2·7 | 16·0 |
| (*e*) | 54·9 | 86 ,, | 36·6 | 43·1 | 2·2 | 13·5 |
| (*f*) | 62·2 | 72 ,, | 37·4 | 45·6 | 1·1 | 8·6 |

Continued heating above the point of minimum pressure is accompanied by a sharp rise in pressure due to rapid oxidation of products formed during the fall of pressure, after which the curve proceeds almost in accordance with the gas laws. A significant feature of this portion of the curves is that they are comparable with those of the paraffin series, especially as regards the influence of oxygen content, which produces a proportionate increase of pressure after the period of decomposition is complete (Brunner and Rideal, *loc.*

*cit.*, p. 1165). This similarity is more evident when the initial oxidation products are compared, for both in the oxidation of amylene and in the induction period of *n*-hexane these contain high percentages of aldehydes, acids, and polymerised products prior to the rapid rise in pressure. A further noteworthy point concerning the curves for high concentrations of amylene is that after the temperature of minimum pressure is passed, the rise is comparatively small, and the final portion of the curve proceeds according to the gas laws but at a lower level than the initial line, thus denoting the presence of fewer molecules than in the original mixture. Therefore, whatever products may be formed during the initial slow oxidation and fall of pressure, they are comparatively stable, and if all the oxygen has been removed during their formation they undergo little decomposition at slightly higher temperatures. It is unlikely that these compounds are peroxides, which on account of their instability would readily decompose with a much greater increase of pressure, and yield oxides of carbon. In the presence of excess of oxygen these initial products are rapidly oxidised at or above a certain critical temperature which is characterised by a minimum point in the curves, and the extent of oxidation is dependent on the amount of available oxygen (see Table I). These suggestions receive confirmation from chemical analysis. In the case of rich amylene mixtures the final products were mostly high-boiling liquids which included aldehydes, and the total amount of carbon monoxide and dioxide was small, whereas the final products with a high oxygen content contained a very much higher percentage of these oxides.

It is very significant that the products of the above mixtures, especially when the amylene ratio is large, are identical with those obtained by the slow decomposition of amylene peroxide, and it was thought at first that the contraction in the curves was due to rapid peroxide formation. An experiment was stopped at this juncture, and the bulb cooled first in air and then in cold water, the peroxides being subsequently estimated by liberation of iodine from acidified potassium iodide solution and titration with $N/100$-sodium thiosulphate. Although iodine was assuredly set free, the amounts were equivalent to only about 5—10% of the peroxides demanded by the drop in pressure.

The following interpretation of the above facts is suggested. At low temperatures, amylene combines with oxygen to form peroxides which may either dissociate or decompose to aldehydes, etc., but at these temperatures dissociation preponderates. The rate of formation of peroxides is accelerated by rise in temperature, but this may lead to an increase in the amount of peroxides being decomposed to aldehydes, etc., which polymerise, and so account for the fall in pressure. At a critical temperature, denoted by the minimum point of depression in the curves, there are sufficient unstable products present to set up chain reactions giving rise to rapid oxidation. Peroxides may decompose rapidly to aldehydes, etc., which, in the presence of excess oxygen and the energy of this reaction, may be oxidised to oxides of carbon and water.

The induction period of Brunner and Rideal (*loc. cit.*) may possibly be accounted for by assuming a slow primary dehydrogenation for *n*-hexane at 210°, followed by peroxidation of the unsaturated hydrocarbons produced. These peroxides may decompose in the manner suggested for amylene or accelerate the formation of unsaturated hydrocarbons (*loc. cit.*), and so increase the peroxide concentration until a limiting value is reached, whereupon the decomposition is attended with rapid oxidation in the presence of excess oxygen. For this reaction to proceed, a temperature of 210° is adequate, since it has been found by the author that the initial slow oxidation of hexylene commences at about 200°.

The oxidation of amylene has also been carried out to show the following influences.

*Pressure.*—A 100 c.c. cylindrical bulb (having a larger ratio of surface to volume than the 225 c.c. bulb) was used with a contained mixture of approximate composition $C_5H_{10} + O_2$, but successive mixtures were subjected to increasing initial pressure, with the following results :

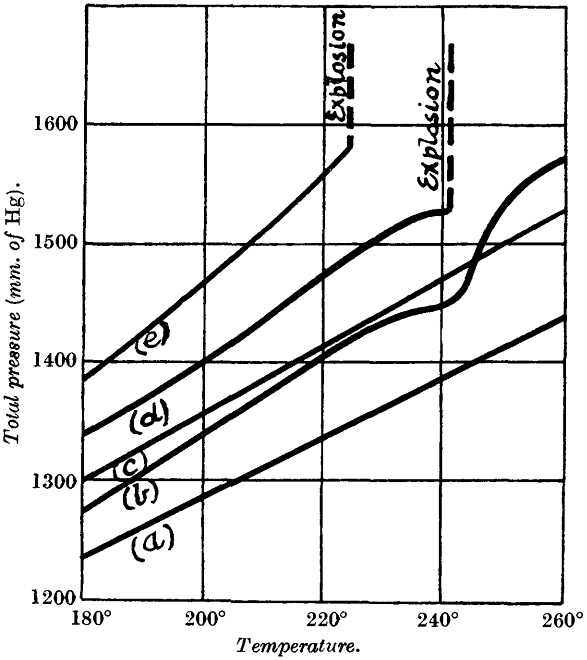
| Pressure (cms.) at 200°. | Result. |
|---|---|
| 139·5 | Curve similar to those in Fig. 1. |
| 179·5 | A slight drop in the curve at 220° ; at 239°, violent oxidation with evolution of gas at great pressure. |
| 275·8 | Explosion at 238°. |

*Catalysts.*—The typical oxidation curves above are only obtained in the absence of water, but the result of the addition of a material quantity is seen in curve (*b*) (Fig. 2). The function of the water is probably to destroy any peroxides formed, which would account for the pressure curve being much in excess of that of the theoretical gas curve (*a*).

Inhibitors of oxidation, such as lead tetraethyl, aniline, and quinol, were found to possess the usual effect of minimising the reaction at the critical point. In curve (*c*), Fig. 2, the effect of the addition of 0·5% of lead tetraethyl is shown. This negative catalyst almost eliminates the contraction part of the curve, and there is apparently very little change up to 260°. An analysis of the gases after cooling gave $CO_2$, 4·6; CO, 3·8%—evidence that a slow chemical action had been proceeding.

Brunner and Rideal have demonstrated that increase in active surface is an important factor in autoxidation, and that two effects were to be noted : (i) catalysts such as powdered glass and pumice increase the rate of peroxide formation, (ii) charcoal catalytically destroys peroxides. Accordingly, 1 g. of powdered pumice was heated at about the same rate as in previous experiments in a 50% amylene mixture; the curve obtained (*d*, Fig. 2) indicates progressively higher pressures than the amylene–nitrogen curve, and this must be attributed to increase in velocity of oxidation due to increased surface, and this in turn may be accounted for by accelerated peroxide formation. At 234° there is a slight depression; this was followed by a violent detonation at 240°, which broke the bulb and caused deposition of carbon. It is noteworthy that the temperature of explosion coincides with the minimum point in the curve of a similar mixture with pumice absent, above which temperature rapid oxidation occurs.

FIG. 2.



A mixture of amylene and oxygen can likewise be made to detonate in the presence of carbon. Curve (*e*), Fig. 2, illustrates the pressure changes on heating a 50% mixture with 1 g. of decolorising charcoal. The slope of the curve is even more pronounced than in the case of pumice, and this is probably due to the more rapid decomposition of peroxides formed with greater velocity on the surface of the charcoal. At 222° the mixture exploded, and with greater violence than in the case of pumice. This may have an important bearing on the question of detonation in internal-combustion engines, in which deposited carbon promotes pinking. A paper will be published in the near future on detonation by the above method.

## *Summary.*

It is suggested that the second step in the combustion of a paraffin hydrocarbon is the oxidation of the primarily formed unsaturated compound to peroxide which decomposes readily, giving rise to further products (presumably aldehydes, etc.), which, in the presence of oxygen, are further oxidised to carbon monoxide and dioxide and water, owing to energy of the decomposing peroxide molecules communicated to the newly formed aldehydes, etc. Under certain conditions this action may proceed with explosive violence.

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