CXLVIII.—*On the Oxidation of* n-*Hexane.*

By Max Brunner and Eric Keightley Rideal.

There is now increasing evidence that peroxides are formed during combustion of saturated hydrocarbons and play an important part in the process of detonation. A number of views have been expressed as to the nature and mechanism of their formation. According to Grün (*Ber.*, 1920, **53**, 987) a primary energy-rich " moloxide " results from the interaction of molecular oxygen with a hydrocarbon so activated as to possess a nascent double bond in which, however, the terminal carbon atom does not take part. The moloxide can under certain unspecified conditions give rise to explosion, or it can rapidly lose energy and become converted into a normal and more stable peroxide, a modification of the well-known earlier views of Traube, Manchot, and Bach.

Callendar (*Engineering*, 1927, **123**, 147, 182, 210) considers that molecular oxygen reacts directly with the hydrocarbon to form an alkyl or dialkyl peroxide, and Bennett and Mardles (J., 1927, 3155) likewise support the view that the primary product of interaction is a peroxide. On the other hand, Bone considers that combustion of these compounds involves hydroxylation rather than peroxide formation, and Lewis (J., 1927, 1555) believes that the primary reaction consists of a dehydrogenation yielding an unsaturated hydrocarbon and hydrogen; the latter is preferentially burnt, but the former might form peroxides by addition.

The autoxidation of benzaldehyde involves the primary formation of a moloxide, benzaldehyde peroxide; this in turn is converted into perbenzoic acid, which can react with benzaldehyde. It has been shown (Rideal, *Rapport du Conseil de Chimie Solvay*, 1925, p. 586; Reiff, *J. Amer. Chem. Soc.*, 1926, **48**, 2893; Brunner, *Helv. Chim. Acta*, 1927, **10**, 707) that the formation of the peroxide is primarily a surface action and that the subsequent reactions of the peroxide can continue in the homogeneous phase. The investigations of Bäckstrom (*Medd. K. Vetenskapsakad. Nobel-Inst.*, 1927; *J. Amer. Chem. Soc.*, 1927, **49**, 1460), however, led him to the conclusion that the oxidation of benzaldehyde was an example of the chain mechanism of the type first postulated by Christiansen and Kramers (*J. Physical Chem.*, 1924, **28**, 145). It was suggested by one of us (E. K. R.) that the discrepancy between the two conclusions could be reconciled on the assumption that chain reactions only commence in these autoxidative processes when the *peroxide* concentration, produced initially at surfaces, rises to certain critical values. In support of this view, it was urged that, in the autoxidation of benzaldehyde with relatively inactive or poisoned catalysts, a period of induction is always observed. During this period of induction the peroxide content of the solution gradually rises, and almost abruptly the reaction acquires an enormous increase in velocity. It is possible that the cause of chain formation when the peroxide concentration has risen to a critical value is purely thermal (the temperature coefficient is about 2·4 for a rise of 10°), but several arguments can be advanced in favour of the alternative view of a true chain of excitation by collision between *peroxide* molecules.

In this paper the behaviour of hexane is compared and contrasted with that of benzaldehyde. Owing to the return of one of us (M. B.) to Switzerland, the comparison has not been pursued in detail, but some of the results obtained differ so markedly from those of other investigators that it was thought desirable to place them on record.

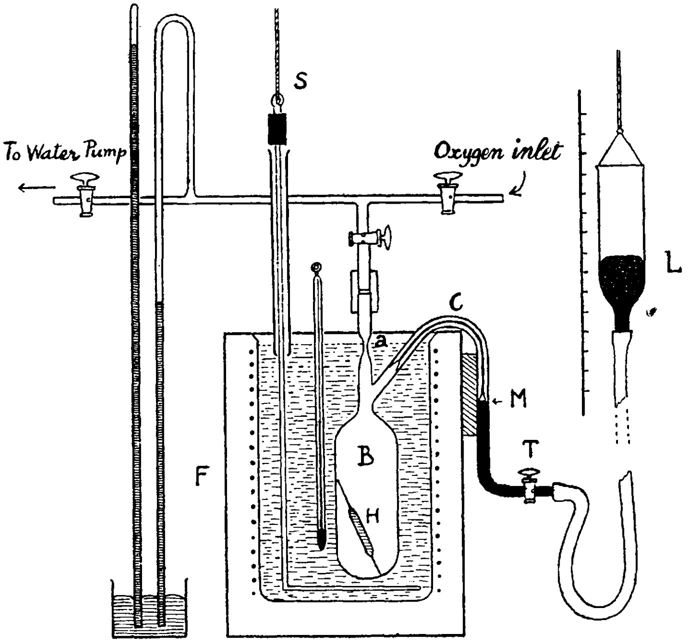
It seemed probable that the process of oxidation of hexane would be similar to that of benzaldehyde, *viz.*, one of autoxidation involving the primary formation of a moloxide by addition of molecular oxygen, which is probably a surface action, followed by a conversion of the moloxide into a peroxide which can react with hexane either in the gas phase or at surfaces. When, however, the concentration of the peroxide in the gas phase rises to certain critical values, this gives rise to a chain mechanism for combustion. According to the experiments of Callendar (*loc. cit.*), the normal saturated hydrocarbons possess characteristic temperatures of initial combustion (T.I.C.), the value of which is, however, affected by the composition of the gas mixture. Callendar finds the T.I.C. for hexane to be 205° in a 33% hexane–air mixture, rising to 390° in a 1·9% mixture. Lewis noted similar critical temperatures, that for hexane being at 232°; he termed these "critical inflexion temperatures" (C.I.T.). He also stated that the value was somewhat affected by the size of the vessel or the presence of platinum; that rapid heating gave a less steep inflexion in the pressure–temperature curves; that a large proportion of hexane lowered the C.I.T. as well as the T.I.C. (Callendar); and finally, that the presence of a small quantity of water was necessary, as in the case of the autoxidation of benzaldehyde (*loc. cit.*).

Repetition of these experiments under various conditions led us to the conclusion that hexane possessed no such critical temperature, and that before a period of rapid combustion takes place at any temperature it is necessary to keep the hexane–air mixture at that temperature for a certain period of time; in fact, the autoxidation process of hexane is similar to that of benzaldehyde, in that there is an apparent period of induction, which is capable of variation. During this period of induction, which is affected by temperature, peroxide formation, decomposition, and reaction with hexane likewise occur, the peroxide content rising until the period of rapid combustion commences. The period of induction is also affected by inhibitors, such as aniline, as well as by surface catalysts like pumice.

EXPERIMENTAL.

n-Hexane was purified by repeated treatment with concentrated sulphuric acid, 20% oleum, and caustic soda, the fraction distilling from sodium at 68·99—69·06° (corr.) being employed. Oxygen from a cylinder was dried over phosphoric anhydride and purified from carbon dioxide.

FIG. 1.



The reaction vessel (Fig. 1) consisted of a Pyrex bulb, *B*, connected by capillary tube, *C*, to the mercury manometer, *L*. A small sealed bulb, *H*, containing a known weight of hexane, was introduced and the bulb, *B*, was evacuated, filled with oxygen to the desired pressure, and sealed off at *a*. The small bulb, *H*, was broken by agitation, and the reaction vessel then placed in an electrically heated and well-stirred oil-bath, *F*. The mercury level in *L* was maintained at a definite mark, *M*, in the capillary tube close to its entrance to the reaction vessel.

Condensation of hexane in the capillary was readily prevented by occasional warming. The temperature of the oil-bath could be maintained by electrical relay to within 0·1°. At the completion of the reaction, the vessel *B* was removed from the oil-bath, cooled in a mixture of ice and salt, and the final pressure determined at a definite temperature. The reaction vessel was connected to a mercury-filled gas burette, and a fraction of the gas drawn into the burette. The gas analysis comprised determinations of oxygen, carbon dioxide and monoxide, and unsaturated hydrocarbons, and in a few cases the residual gas was analysed by combustion over copper oxide in a quartz capillary. Before each experiment the vessel *B* was thoroughly cleaned with hot chromic acid, washed with water, and dried.

Fig. 2.

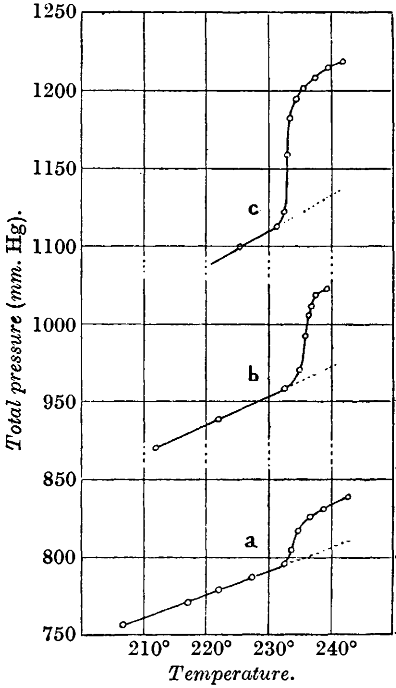
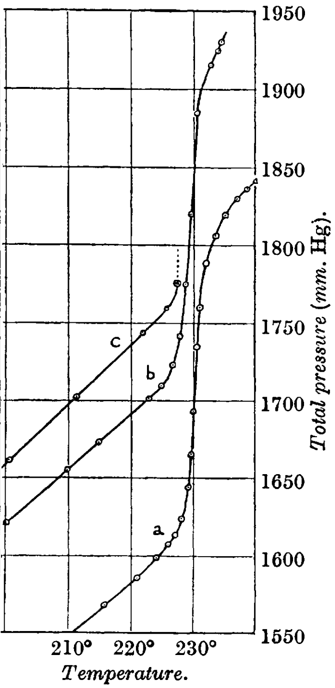
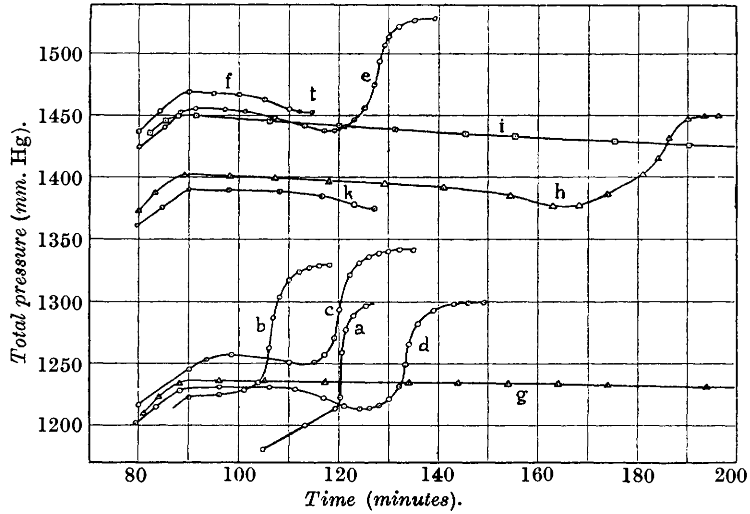


Fig. 3.



In Figs. 2 and 3 are shown the results obtained on heating hexane–oxygen mixtures in the manner described; the apparent C.I.T. is noted at 232°. With increasing proportion of oxygen there is likewise an increase in the total pressure after the period of rapid combustion has taken place (*i.e.*, at the apparent C.I.T.), and from the following table it will be seen that this increase is almost proportional to the oxygen content of the gas until the hexane content has fallen to 31·7% (Fig. 3, *c*), where the reaction becomes explosive, chemiluminescence occurs, and large quantities of soot are deposited. Owing to the explosive nature of this reaction, the analytical figures are only approximate, but the quantities of unsaturated hydrocarbons formed (which resembled isoprene in odour) show a marked increase with increasing pressure. It is significant that the transition from the small increase of pressures observed with hexane-rich mixtures to the explosive mixture (*ca.* $C_6H_{14} + 2O_2$) is gradual, both the temperature and the initial slope of the pressure curves being identical (see Fig. 3, *b* and *c*).

FIG. 4.



				Gas analysis, %.			
Curve.	Hexane, % by vol.	% Increase in pressure at the C.I.T. (= *b*).	$\frac{\% O_2}{b}$.	CO_2.	Unsaturated hydrocarbons.	CO.	O_2.
Fig. 2, *a*	77·9	3·39	6·5				
b	63·3	5·53	6·6				
c	50·8	7·28	6·7	28·04	0·23	27·73	
Fig. 3, *a*	35·7	12·0	5·3				
b	33·7	11·7	5·7	38·04	1·13	29·76	0·36
c	31·7	Explosion		7·01	3·61	26·65	2·5

In Fig. 4 are shown the curves obtained on heating hexane–oxygen mixtures to definite temperatures and maintaining them at these temperatures until the sudden pressure increase was noted. The experimental conditions and results were as follows :

Curve.	Hexane, % by vol.	Final temp. of oil-bath.	Apparent period of induction (mins.).	Remarks.
a	50·8	232°	Nil	Experimental conditions as realised by Lewis and in the former series.
b	45·7	220	7	
c	45·2	215	17	
d	46·1	210	37	Final pressure increase = 86 mm.
e	43·8	210	30	Showing the influence of pressure on shortening the period of induction.
f	43·9	210	—	Stopped for analysis at *t*, see curve.
g	46·0	210	232	With 2·0 mg. of aniline; final pressure increase only 31 mm.
h	44·0	210	76	With 0·25—0·3 mg. aniline; final pressure increase = 73 mm.

The existence of a period of induction is clearly observed. Although in all cases the initial heating of the oil-bath to the desired temperature occupied some 90 minutes, the error introduced by this procedure must be small, since, owing to the apparently large temperature coefficient of the reaction shortening the period of induction, this period would probably be of the order of 100 minutes at 200°. In Curve *a* the induction period is telescoped into the period of initial combustion, as in the experiments of Lewis and those described in the previous section. The induction period is also shortened by an increase in the total pressure of the reactants, *e.g.*, in experiments *d* and *e* the induction period has been reduced from 37 to 30 mins., *i.e.*, in the ratio of 1·23 to 1, by an increase in the total pressure from 1230 mm. to 1450 mm. with hexane contents of 43·8% and 46·1%, respectively; the oxygen pressures thus stand in the ratio of 815 to 664 mm., *i.e.*, 1·22 to 1. The rate of the reaction which governs the induction period is thus determined by the oxygen pressure over these ranges of pressure and temperature.

This period of induction is very similar to that observed in the autoxidation of benzaldehyde, in that it is sensitive to temperature changes and greatly affected by small quantities of inhibitors (*g*, *h*). For instance, 0·25 mg. of aniline (*h*) produces an induction period of 76 mins. for the reaction at 210°, whereas in the autoxidation of benzaldehyde at 20°, 0·20 mg. of iodine produces an induction period of 40 mins. (Brunner, *loc. cit.*, p. 722). With 2·0 mg. of aniline under the same conditions (*g*) the induction period is lengthened to 232 mins. At the end of this period the rapid reaction set in, but this proceeded more slowly, taking 70 mins. and giving a pressure increase of only 31 mm. Without any inhibitor the induction period is 37 mins., the main reaction taking 21 mins., with a pressure increase of 86 mm.

It seemed probable that during the period of induction the formation of a hexane moloxide, and thus of a peroxide, was taking place in a manner analogous to the benzaldehyde reaction. It is noted that during the period of induction at constant temperature there is always a small but definite fall in pressure, usually some 15 mm. Whilst the formation of the moloxide and of the peroxide would be accompanied by a fall in pressure, the possibility of the formation of polymerised products of unsaturated hydrocarbons, or of non-volatile oxidation products, renders the observation less significant. An analysis was accordingly carried out on a mixture just before the increase in pressure had commenced. At the point corresponding to *t* (Curve *f*), the bulb was removed, cooled to 0° in ice, and opened under an acid solution of potassium iodide; after thorough agitation the peroxide was determined by titration of the liberated iodine with *N*/100-sodium thiosulphate. The original weight of hexane was 0·101 g. with an oxygen pressure of 400 mm. at 14·3° in a bulb of 57·6 c.c.; the weight of peroxide obtained, calculated on the formula $C_6H_{14}O_2$, was 0·0032 g., or nearly 3·2% of the original hexane. That this figure does not represent the total formation of peroxide during the period of induction, but that some peroxide had already reacted with hexane to produce oxidation products, was confirmed by another analysis on a 44·3% hexane mixture after a period of induction of 35 mins. at 210° (Curve *k*). The analysis showed 13·02% CO_2, 1·23% unsaturated compounds, 68·1% O_2, and 6·8% CO, and the gas also contained some 3% of nitrogen from the original oxygen and a small quantity of hydrogen and hydrocarbon vapour. It is clear that at least 30% of the original oxygen had been consumed during this period of induction. At the moment of the commencement of the period of rapid combustion there is 0·0032 g. of peroxide present in the vessel, which is equivalent to a gas pressure of 14·17 mm. at 210°. Taking the molecular weight of the peroxide as 118 and the molecular radius as 5×10^{-8} cm., we obtain for the mean time interval between collisions of peroxide molecules a value of $1{\cdot}10 \times 10^{-8}$ sec., which is comparable with that obtained for excited molecules. Such a period is therefore in agreement with the conception of a chain mechanism of excitation of peroxide molecules.

If the active surface in a process of autoxidation be increased, in the case of benzaldehyde oxidation two effects are to be observed. (1) Certain catalysts, such as glass powder and pumice, increase the rate of peroxide formation; these shorten the period of induction and increase the rate of maximum oxygen uptake. (2) Others, like charcoal, catalytically destroy the peroxide and thus decrease the rate of oxidation.

With powdered pumice (1 g.) present in a 43·8% hexane–oxygen mixture at 210°, Curve *i* was obtained. Even after 325 mins. there was no period of rapid oxidation, although a total pressure fall of 57 mm. was observed. At the end of this period analysis of the gas revealed the pressure of 57·19% CO_2, 0·69% unsaturated compounds, 13·56% O_2, and 16·3% CO. It is clear that combustion is taking place but at a slow rate—a phenomenon similar to that observed with charcoal in the autoxidation of benzaldehyde.

Furthermore, it is clear that the slow combustion differs from the rapid in that there is not an increase but a slight decrease in pressure—an indication that aldehydes and acids as well as polymerised products are formed in quantities sufficient to nullify any increase in pressure caused by the interaction of the hexane peroxide with hexane to produce carbon dioxide and water. It seems probable that during this period of slow reaction a number of chemical reactions involving peroxide molecules are taking place, and the identification of small quantities of products isolated affords some slight experimental evidence for the following:

(1) Decomposition to aldehyde and water, followed by partial further oxidation and condensation of the aldehyde produced.

(2) Reaction with hexane to produce unsaturated hydrocarbon and water. The unsaturated hydrocarbons produced undergo polymerisation or further oxidation.

During the period of rapid combustion, the chain-excited peroxide molecules react and act as centres of activation for normal hexane molecules, which then undergo direct combustion. The importance of peroxides in these secondary reactions has been emphasised by Egerton (*Nature*, 1928, **121**, 10).

The necessity for the preliminary formation of a high concentration of reaction centres for the propagation of a chain reaction does not appear to be confined to oxidation of benzaldehyde and saturated hydrocarbons, for similar conclusions can be drawn from the observations of Chariton and Walta (*Z. Physik*, 1926, **39**, 547) on the oxidation of phosphorus vapour, and from the numerous interactions between the alkali metals and substances such as pentachloroethane and bromoform (Staudinger, *Z. angew. Chem.*, 1925, **38**, 578).

Summary.

The process of oxidation of *n*-hexane has been shown to bear a striking similarity to the autoxidation of benzaldehyde. The temperature of initial combustion has been shown not to be a characteristic of the hydrocarbon, for rapid combustion will set in after a period of induction at lower temperatures. During this period of induction slow autoxidation proceeds together with the formation of peroxides. The period of induction at constant temperature is greatly affected by the oxygen pressure and by the presence of inhibitors, such as aniline, or of surface catalysts, such as pumice. The temperature coefficients of the reactions proceeding in the induction period are high.

The suggestion is made that the reactions involve the formation at catalytic surfaces of an active moloxide, which is subsequently converted into a more stable peroxide. The peroxide can react either in the gas phase or at the surface, but when the peroxide concentration reaches a critical value, chain propagation ensues, causing excitation and combustion of molecules coming into contact with the reaction centres of the chain.

THE LABORATORY OF PHYSICAL CHEMISTRY,
CAMBRIDGE.
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