147. *Crossed Reaction Chains in Oxidation by Molecular Oxygen. Part I. Oxidation of Hydrocarbons in Aldehyde–Air Mixtures.*

By N. J. H. Small and A. R. Ubbelohde.

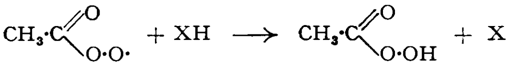
One theory of hydrocarbon oxidation assumes that the reaction chain

$$R + O_2 \longrightarrow RO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$RO_2 + RH \longrightarrow RO\cdot OH + R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

is closely similar whether R is an alkyl radical in the oxidation of hydrocarbons, or an acyl radical in the oxidation of aldehydes.

To test how far the oxidation chains for these two molecular species can in fact " cross," small proportions of paraffins, olefins, benzene, and hydrogen have been added to an acetaldehyde–air mixture undergoing vigorous oxidation around 150—200°. These added molecules were found either to be substantially inert, or to act as inhibitors for the oxidation of the acetaldehyde.

The conclusion is that the oxidation chains of the hydrocarbon tested cannot " cross " freely with those for acetaldehyde, at the temperature of the experiment. When the added molecules act as inhibitors for the oxidation of acetaldehyde, they may do so by donation of hydrogen atoms to the peroxide radicals :



$$CH_3\cdot C\begin{smallmatrix}/\!\!/O\\ \diagdown O\cdot O\cdot\end{smallmatrix} + XH \longrightarrow CH_3\cdot C\begin{smallmatrix}/\!\!/O\\ \diagdown O\cdot OH\end{smallmatrix} + X$$

but the resulting X radicals do not themselves continue long oxidation chains under the conditions used. The inhibiting action of hydrogen may also be caused by its deactivating " energy chains " by facilitating the exchange of vibrational energy.

The close relation between the oxidation mechanism of gaseous aldehydes and that of gaseous paraffins has been noted by various authors, and has been used to elucidate some of the steps in hydrocarbon oxidation (Ubbelohde, *Proc. Roy. Soc.*, *A*, 1935, **152**, 354, 378 ; Lewis and Von Elbe, " Flames, Combustion and Explosions of Gases," Cambridge, 1938).

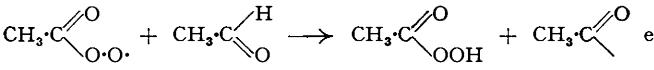
One of the outstanding difficulties in substantiating the details of a scheme of oxidation for gaseous hydrocarbons is that the minimum temperature at which reaction can conveniently be observed at ordinary pressures is around 250°. At this temperature, labile reaction products such as hydroperoxides, whose constitution is particularly significant, are frequently too short-lived for identification except by special techniques (Egerton, Llewellyn Smith, and Ubbelohde, *Phil. Trans.*, 1935, **234**, 433; Ubbelohde, Drinkwater, and Egerton, *Proc. Roy. Soc.*, 1936, **153**, No. 878, 103). The guiding idea in the researches to be described is to discover which of the numerous reaction steps in the oxidation of hydrocarbons imposes the use of temperatures as high as 250°. In particular, the aim was to investigate how far the reaction rate was controlled by the postulated initial attack on the hydrocarbon

$$X + RH \longrightarrow XH + R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (A)$$

where X may be any third body; in the main oxidation chain X is a peroxide radical (cf. Ubbelohde *et al.*, *locc. cit.*), *i.e.*,

$$R + O_2 \longrightarrow RO_2 \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$
$$RO_2 + RH \longrightarrow RO\cdot OH + R \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The experimental principle employed was to bombard the RH molecule with a large number of aldehyde peroxide radicals, at a temperature where the reaction



$$CH_3\cdot C\begin{smallmatrix}/\!\!/O\\ \diagdown O\cdot O\cdot\end{smallmatrix} + CH_3\cdot C\begin{smallmatrix}/H\\ \diagdown\!\!\diagdown O\end{smallmatrix} \longrightarrow CH_3\cdot C\begin{smallmatrix}/\!\!/O\\ \diagdown OOH\end{smallmatrix} + CH_3\cdot C\begin{smallmatrix}/\!\!/O\\ \diagdown\end{smallmatrix} \text{ etc.} \quad . \quad . \quad . \quad (3)$$

is proceeding freely, and to investigate :

(*a*) Whether the result of the attack was to start *hydrocarbon* oxidation chains according to (1) and (2) above;

(*b*) Failing the establishment of such chains, whether there was any evidence for the formation of alkyl radicals under the initial bombardment of hydrocarbon by aldehyde peroxide radicals, according to reaction (*A*), but without extensive sequences of (1) and (2); and

(*c*) Failing either (*a*) or (*b*), whether there was any evidence of chemical crossing of reaction chains at the temperature of the experiment.

Possibility (*a*) would have the great practical advantage of permitting the controlled oxidation of hydrocarbons in the vapour phase at much lower temperatures than usual; this could lead to interesting and valuable oxidation intermediates.

Possibility (*b*) would be of very considerable theoretical interest, as indicating new facts about the kinetic characteristics of the oxidation steps for paraffins. The yields of interesting oxidation intermediates would, however, be much smaller since proportionally many fewer paraffin molecules would enter into reaction for each R radical formed according to (*A*).

Finally, possibility (*c*) would imply the need for very considerable activation energy, even for reaction (*A*).

As is discussed below, the main conclusion was that none of the hydrogen compounds so far exposed to bombardment by acetaldehyde peroxide radicals appears to undergo reaction according to (*a*). Heptane, hydrogen, and hex-1-ene give definite evidence of following course (*b*). This has theoretical as well as practical implications which are further detailed below.

EXPERIMENTAL.

Experimental Procedure.—The main lines of experimental procedure can be summarised by reference to Fig. 1. *A*—*B* is a Pyrex reaction tube, 50 cm. long, of internal diameter 4·5 cm., wound with nichrome wire and lagging, and heated electrically so as to maintain the gas flowing through it at any temperature up to approx. 360°. At the inner ends of *a*, *b*, *c*, broken glass fragments and glass wool serve to produce turbulence so as to mix the gas streams. Normally one of these is pure nitrogen charged to a calculated partial pressure with acetaldehyde vapour. A second is air, which could be used to carry the XH molecules if these were required in the oxidation. The total flow in mols./sec. was not appreciably affected when the second stream was carrying molecules of a compound XH (see Table I). For mixing in hydrogen or additional nitrogen (Table I *b*), a third stream was introduced as indicated in Fig. 1 (*c*).

TABLE I.

Mixture.	$CH_3{\cdot}CHO$.	XH.	O_2.	N_2.	Total rate of flow.	Temp. of steep rise of oxidation rate.
a, $CH_3{\cdot}CHO$/(ref. O_2/N_2 mixture) ...	0·267	—	0·0937	0·803	1·164	150°
b, ,, + N_2 *	0·267	0·142 *	0·0937	0·803	1·306	190
c, ,, + C_6H_6	0·267	0·0982	0·0937	0·803	1·262	190
d, ,, + C_6H_{14}	0·267	0·142	0·0937	0·803	1·306	190
e, ,, + C_7H_{16}	0·267	0·100	0·0937	0·803	1·264	200
f, ,, + H_2	0·267	0·150	0·0937	0·803	1·314	210
g, ,, + unsaturated	0·267	0·125	0·0937	0·803	1·289	*ca.* 200

* Additional N_2 in this mixture matches approx. the amount of XH in mixtures *c* to *g*.
Figures are in 10^{-3} g.-mols./sec.

By this means a mixture of acetaldehyde and (nitrogen + XH) in approximately constant molar proportions flowed through the reaction tube at constant velocity. The aim was to maintain substantially constant conditions for the aldehyde oxidation, except in so far as these were modified by the crossing of the aldehyde reaction chains with any reactions involving XH.

At *B* the condensing system was maintained at the temperature of liquid oxygen, the cold finger shown in Fig. 1 being cooled by means of carbon dioxide and alcohol. As required, this condensation vessel could be rapidly interchanged with similar vessels, so as to permit collection of a series of samples without any interruption in the reaction flow. The products were allowed to melt and were analysed as described below.

The reactions and the melting of the reaction products were carried out behind protective screens, since when oxidation is extensive very considerable yields of peroxide might be formed. Actually only mild ignitions were observed from time to time when combustion was in progress.

A cross piece fitted with quartz windows was also provided in the reaction system near *A*. This was for use in experiments on photochemical initiation described in subsequent publications, but will not be referred to again in the present paper.

Experimental Details.—Gases were taken from cylinders of compressed air and nitrogen at rates controlled by capillary flow meters with mercury manometers. Stream (*a*) (approx. 10 c.c./sec.) was nitrogen saturated at 0° with acetaldehyde vapour and shielded from strong light. Stream (*b*) consisted of air normally saturated with various molecules XH by maintaining the appropriate liquid in a pair of carburettors at the calculated temperatures. A third stream (*c*) was used for the compositions (*b*) and (*f*) in Table I. This gave approximately constant composition, as is shown in Table I.

Details of the carburettors are illustrated in Fig. 2. Tests showed that with carburettors in series no increase in their number beyond two further increased the content of the gas in aldehyde or in XH, *i.e.*, saturation was effectively attained.

Temperature control in the baths around the carburettors was by an immersion heater regulated by a Sunvic control.

Materials.—Acetaldehyde. This was prepared by distilling paraldehyde with dilute sulphuric acid as required, using a current of nitrogen to protect it from oxidation.

Benzene, f. p. 5·48°. This was prepared by repeated crystallisation of " AnalaR " benzene, thiophen-free. It was used with the carburettor vessel at 50·5° to give a partial pressure of 280 mm.

n-*Heptane.* This was prepared by fractionating commercial heptane and collecting the cut of b. p. 95·5—97°. Before fractionation unsaturated hydrocarbons were carefully removed on account of their suspected action as inhibitors. The crude heptane was stored over fuming oleum for about a week with occasional shaking. It was then repeatedly washed with strong potassium hydroxide solution and then with water, and dried (Na_2SO_4) for 24 hours. Carburettors at 68° gave $p = 280$ mm.

n-*Hexane.* This was prepared in the same way as *n*-heptane. The final cut had b. p. 67·5—68·5°. Both fractionations were carried out in nitrogen. Carburettors at 41° gave a partial pressure of 280 mm.

n-*Hex*-1-*ene.* This was prepared by dehydrating *n*-hexyl alcohol by the procedure recommended in *Org. Synth.*, Vol. I, p. 421. The fraction of commercial *n*-hexyl alcohol, b. p. 155·2—156·0°, was dehydrated with 50% aqueous sulphuric acid, and the hydrocarbon was repeatedly washed with concentrated sodium hydroxide solution and then refluxed for 24 hours with two successive batches of 20% aqueous sodium hydroxide solution to remove any trace of sulphur compounds.

Final drying (Na_2SO_4) and fractionation through a column gave a cut of b. p. 61—64°. No trace of sulphur compounds was detected in the product. This material was mixed with twice its volume of *n*-hexane and used with carburettors at 41° to give $p = 280$ mm.

FIG. 1.

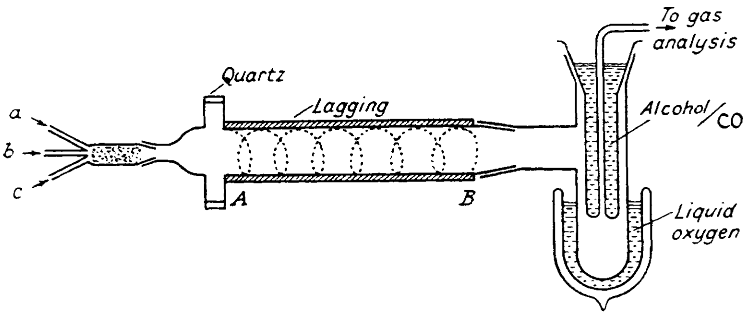
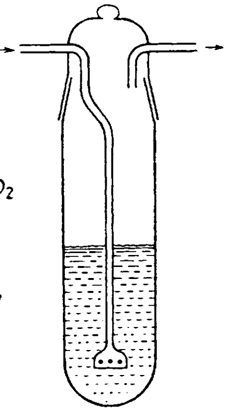


FIG. 2.



Combustion apparatus and vapourisers.

Hydrogen. Taken from cylinders, this was used without further purification. Its rate of flow was determined by a separate flowmeter and was adjusted to a value such that the amount of hydrogen passing through the combustion tube was comparable to the concentration of molecules XH used in previous experiments.

Preparation of the Reaction Vessel.—Before each run, the reaction vessel was cleaned with hot nitrating acid at about 80°, then with abundant distilled water, and finally dried with filtered air. The temperature was measured by a thermometer reading to 360° ± 0·5° and wholly encased in a Pyrex tube which was likewise cleaned with nitrating acid etc. before each run. The degree of reproducibility thus achieved was good, as can be inferred, for example, from the results on the oxidation of pure acetaldehyde (Figs. 3 and 4).

Collection and Analysis of Products.—Only summarised results will be given in the present paper.

The amounts of acetaldehyde, XH, and oxygen used in a run were determined by analysis and checked from the amounts remaining in the calibrated carburettors and the volumes of gases used. The gases flowing past the cooled surfaces were normally stripped of all except permanent gases and possibly some carbon dioxide. Completeness of condensation was verified, for example, by the obtaining of negative tests for acetaldehyde and formaldehyde during the progress of a run. When the percentage content of carbon dioxide was required, samples of exit gases were collected without the condensing system in place. Exit gases were analysed by a " fountain " gas-analysis apparatus which need not be detailed here.

The treatment of the melted condensate was as follows : As a precautionary measure, 25 c.c. of distilled water were first added, to dilute any peroxides formed. When hydrocarbon had been added the condensate separated into two layers. The hydrocarbon layer was shaken 4—5 times with water, and the washings were added to the aqueous layer. The whole aqueous product was made up as a standard solution which could be titrated for peroxide, acid, and aldehyde content (see below).

In the case of *n*-heptane, recovered hydrocarbon, after being scrubbed with water, was carefully fractionated to obtain a preliminary idea of the fate of the molecules of XH which had reacted. Not more than 1% of the *n*-heptane had given rise to oxidation products of comparable molecular weight.

More detailed investigation of what happens to those molecules of XH which are attacked whilst passing through the reacting aldehyde–oxygen system requires special techniques, in view of the small amounts involved. This is being described in subsequent papers.

Fine needle-like crystals were also isolated from the residues of fractionation. Qualitative tests showed this to be a polymerisation product of acetaldehyde. That it is probably metaldehyde seems to be confirmed (i) by m. p. *ca.* 125° and (ii) by the fact that heating them with a drop of dilute acid yielded acetaldehyde.

The aqueous layer contained unchanged acetaldehyde, formaldehyde, peroxides, and acids (chiefly acetic and peracetic).

FIG. 3.

Effect of aldehyde/O_2/N_2 ratio on the critical oxidation temperature of acetaldehyde.

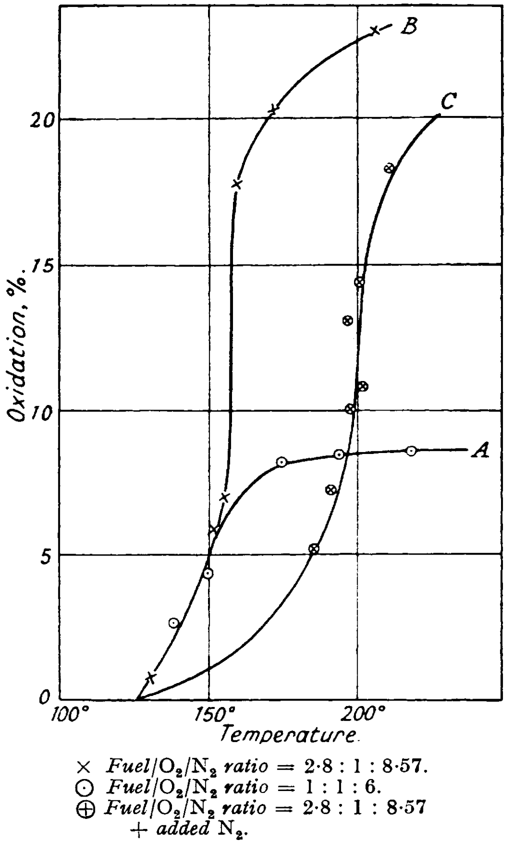
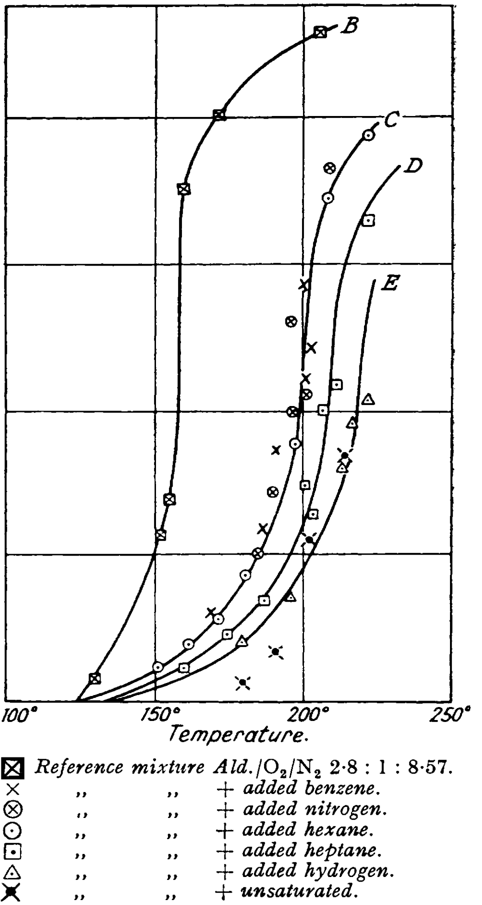


FIG. 4.

Effect of added molecules on the critical oxidation temperature of an aldehyde/O_2/N_2 mixture 2·8 : 1 : 8·57.



The peroxides were determined by filling conical flasks, containing aliquot portions of the scrubbing water with carbon dioxide, adding potassium iodide and dilute sulphuric acid, and allowing reaction to proceed for 2 minutes before titration with standard sodium thiosulphate solution. Prompt analysis of the peroxides was necessary after the melting of the condensate, since the concentration of peroxides in the scrubbing liquor decayed to one-half in *ca.* 15 minutes. This decay could be delayed by addition of free acid to the scrubbing water. In the experimental results given below, the data for peroxides were generally obtained within 2—3 minutes of melting of the condensate. They are believed to be fairly close to the initial concentrations present, unless the decay on condensation or on melting is much more rapid than the average estimated for the samples made up.

Acids formed were titrated with N-sodium hydroxide (phenolphthalein).

The total aldehyde content was analysed by means of sodium sulphite (cf. Walker, " Formaldehyde," 1944, p. 257) using thymolphthalein as indicator and titrating the alkali produced with N-sulphuric acid.

Where required, formaldehyde was determined separately by the method used by Egerton, Smith, and Ubbelohde (*loc. cit.*). Addition of an equal volume of 10% sulphuric acid to the test solution suppresses the reaction of the higher aldehydes with Schiff's reagent and makes it specific for the determination of formaldehyde. The acetaldehyde which is present in appreciably greater amounts gives an immediate colour, but this fades in ½ hour, whereas that due to formaldehyde does not fade in 12 hours.

During the analysis the purple tint due to the formaldehyde present was compared colorimetrically with that produced by a standard solution, and the result is included in the table below.

Results.—(a) *Oxidation of pure* n-*heptane and pure* n-*hexane.* In confirmation of previous results, experiments which need not be recorded in detail showed that when various mixtures of these paraffins with oxygen and nitrogen in proportions similar to those in Table I were passed through the apparatus without acetaldehyde, the minimum temperature at which appreciable oxidation could be detected under the most favourable conditions was 250°. Products included peroxides and much formaldehyde.

(b) *Formation of acids and peroxides.* With acetaldehyde mixtures, the dominant reaction either alone or in the presence of XH was in all cases the oxidation of the acetaldehyde. Curves in Figs. 3 and 4 show plots of the aldehyde oxidised to peroxide and acid. The sum of the g.-equivs. of these two constituents produced under different conditions is expressed as a percentage of the acetaldehyde originally present in the reaction mixture. Smooth plots are obtained with a steep rise at a critical temperature which depends on the mixture used and on any inhibiting effects due to XH. For convenience these temperatures are listed in the last column of Table I.

(c) *Other oxidation products of acetaldehyde.* Representative gas analyses are given in Table II. It will be observed that at the temperature of the experiment both carbon monoxide and dioxide are detectable in the exit gases, the former in greater quantity. Other oxidation products of higher molecular weight are referred to above.

TABLE II.

Representative gas analysis (reaction tube, 200°. Mixture I*a*).

Material.	Supplied.	Recovered.	Material.	Supplied.	Recovered.
Acetaldehyde	1·23 g.-equiv.	0·155 g.-equivs.	Formaldehyde	—	0·022 g.-equivs.
Oxygen	0·241 g.-equivs.	0·029 g.-mols.	Peroxide	—	0·085 ,,
CO_2	—	0·0156 ,,	Acid	—	0·135 ,,
CO	—	0·029 ,,			

(d) *Oxidation of heptaldehyde by acetyl peroxide radicals.* As an addition to determination of the effect of added molecules on acetaldehyde oxidation (Table I), heptaldehyde was introduced into an aldehyde oxidation at 200° (carburettors at 104°). About half of it could be recovered under these conditions, the remainder being apparently oxidised. If the formation of the corresponding aldehyde is an early step in hydrocarbon combustion, then the observations in the previous paragraph suggest that, when the paraffin reacts, the corresponding aldehyde should be recoverable A preliminary fractionation of *n*-heptane collected after passage through the oxidising aldehyde system gave no evidence of heptaldehyde formation. Further comment is reserved until larger quantities can be investigated.

DISCUSSION.

(1) *Characteristics of the Oxidation of Acetaldehyde.*—In accordance with the results of other workers (cf. McDowell and Thomas, *J.*, 1949, 2208, for recent references) curves *A* and *B* of Fig. 3 confirm that the oxidation of acetaldehyde proceeds at markedly lower temperatures and more rapidly for a fuel–air mixture of 2·8 : 1 than of 1 : 1. The yields of acid and peroxide (calculated as acetic and peracetic acids) correspond with about 20% of the aldehyde actually consumed in passage through the reaction tube. Gas analysis (cf. Table II) shows the presence of some carbon monoxide and dioxide, as well as giving information on the amount of oxygen consumed. Although the oxygen is all accounted for, it is not clear what happens to the unrecovered acetaldehyde. Some of it polymerises to a rubber-like polymer which can be depolymerised on storage or boiling with water.

(2) *Effect of Hydrocarbons on the Oxidation of Acetaldehyde.*—From Fig. 4 and Table I, it is evident that the added hydrocarbon XH inhibits the oxidation of acetaldehyde, when XH is hydrogen, hexene, or heptane.

The order of increasing collision diameters (Table III) does not suggest any explanation of this inhibition in terms of a simple dilution effect.

TABLE III.

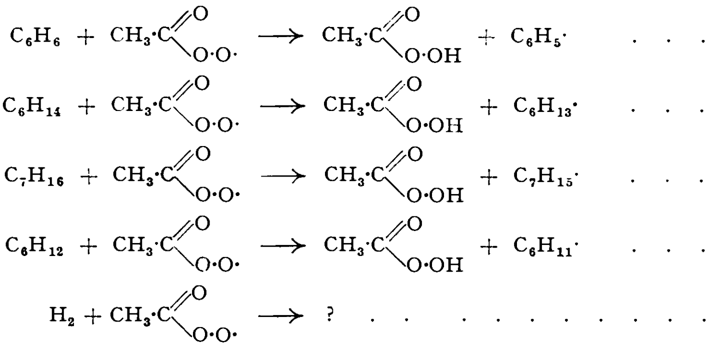
Molecule	C_6H_6.	N_2.	H_2.	C_6H_{14}.	C_7H_{16}.
Collision diameter, A.	4·66	3·18	2·40	5·18	5·8

Cf. Schuil, *Phil. Mag.*, 1939, **28**, 683.

When inhibition is observed it could in principle arise either by energy degradation on collision between the inhibitor and the activated chain carriers, or by chemical reaction between the inhibitor and the chain carrier. The possibility of energy degradation is discussed under

(3), but in the authors' opinion the inhibition can most readily be interpreted on the theory that acetyl peroxide radicals have a finite probability of removing hydrogen from each of the molecules XH, but with varying effectiveness. An order of increasing ease of removal would be as in *A* (i) to *A* (v) below.

From Fig. 4 it appears that the molecules nitrogen, benzene, and hexane behave substantially in the same way and may be presumed to be inert on collision with acetyl peroxide radicals. However the fact that heptane and hexene both have marked inhibitory effects could be reconciled with the apparent inertness of hexane and benzene if the probability of removal of hydrogen in the reactions *A* (i) and *A* (ii) is markedly less than that in *A* (iii) and *A* (iv). Comparatively small differences in activation energy would suffice to give this effect. For example, if the activation for *A* (ii) were 6 kcals. greater than for *A* (iii), and the temperature-independent terms in the velocity equation were the same, the rate of *A* (ii) would be one-thousandth of the rate of *A* (iii) at 460° K.



$$C_6H_6 + CH_3{\cdot}C\begin{smallmatrix}{/\!\!/}O\\ \diagdown O{\cdot}O{\cdot}\end{smallmatrix} \longrightarrow CH_3{\cdot}C\begin{smallmatrix}{/\!\!/}O\\ \diagdown O{\cdot}OH\end{smallmatrix} + C_6H_5{\cdot} \quad . \; . \; . \quad A(\mathrm{i})$$

$$C_6H_{14} + CH_3{\cdot}C\begin{smallmatrix}{/\!\!/}O\\ \diagdown O{\cdot}O{\cdot}\end{smallmatrix} \longrightarrow CH_3{\cdot}C\begin{smallmatrix}{/\!\!/}O\\ \diagdown O{\cdot}OH\end{smallmatrix} + C_6H_{13}{\cdot} \quad . \; . \; . \quad A(\mathrm{ii})$$

$$C_7H_{16} + CH_3{\cdot}C\begin{smallmatrix}{/\!\!/}O\\ \diagdown O{\cdot}O{\cdot}\end{smallmatrix} \longrightarrow CH_3{\cdot}C\begin{smallmatrix}{/\!\!/}O\\ \diagdown O{\cdot}OH\end{smallmatrix} + C_7H_{15}{\cdot} \quad . \; . \; . \quad A(\mathrm{iii})$$

$$C_6H_{12} + CH_3{\cdot}C\begin{smallmatrix}{/\!\!/}O\\ \diagdown O{\cdot}O{\cdot}\end{smallmatrix} \longrightarrow CH_3{\cdot}C\begin{smallmatrix}{/\!\!/}O\\ \diagdown O{\cdot}OH\end{smallmatrix} + C_6H_{11}{\cdot} \quad . \; . \; . \quad A(\mathrm{iv})$$

$$H_2 + CH_3{\cdot}C\begin{smallmatrix}{/\!\!/}O\\ \diagdown O{\cdot}O{\cdot}\end{smallmatrix} \longrightarrow \; ? \quad . \; . \; . \; . \; . \; . \; . \; . \; . \; . \quad A(\mathrm{v})$$

The hypothesis is that, when the reactions occur, the oxidation is inhibited because the new radicals produced fail to prolong the chains. As the temperature is raised oxidation proceeds once more, so that the inhibition is compensated. In principle this could happen either by further oxidation of aldehyde or by more important contributions to the overall oxidation from (1) and (2). So far as it has been possible to examine the condensates it seems unlikely that extensive chain oxidation of any of the hydrocarbons occurs, even at the critical reaction temperatures listed in Table I. The inference is that even when alkyl radicals are produced by reaction (*A*) it requires a higher temperature before chain oxidation of the hydrocarbon will occur at all freely. Thus *either* step (1) *or* step (2) must have an activation energy which requires the temperature of 250° before a pure paraffin will be oxidised at all freely.

What actually happens to the hydrocarbon radicals in the present set-up is still under investigation, but clearly they do not start the long oxidation chains which apply at 250° or above. It is significant that *A* (iv) occurs much more readily than *A* (ii), presumably owing to the smaller activation required to remove hydrogen atoms from the α-position relative to a double bond in an olefin, compared with the activation to remove hydrogen atoms from a paraffin (cf. Farmer, *Trans. Faraday Soc.*, 1942, **38**, 348).

(3) *Inhibition of Acetaldehyde Oxidation by Molecular Hydrogen.*—This striking effect may be akin to the inhibition of oxidation of pentane by molecular hydrogen in the region 260—280° (Prettre, *Compt. rend.*, 1936, **203**, 619. Jost (" Explosion and Combustion Processes in Gases," McGraw-Hill, 1946) has attributed this effect of hydrogen to its catalytic influence on the reaction walls. An alternative explanation may well be that energy chain transfers are important in these oxidations (Ubbelohde, *Proc. Roy. Soc.*, 1935, *A*, **152**, 369). The well known effect of hydrogen in degrading the vibrational energy by collision with carbon dioxide molecules (cf. the review in *Reports Progr. Physics*, 1948, **12**, 264) may be paralleled by its effect in degrading the vibrational energy of chain carriers before these have time to continue the succeeding links in the chain.

A third possible explanation would be that the acyl peroxide radicals use up both hydrogen atoms on collision, so that the chain is not propagated in the usual way.

QUEENS UNIVERSITY, BELFAST. [*Received, November* 10*th*, 1949.]