ELEMENTARY REACTIONS IN GAS-PHASE SLOW COMBUSTION

By C. F. H. TIPPER, B.Sc., Ph.D.
(DEPARTMENT OF INORGANIC AND PHYSICAL CHEMISTRY, THE UNIVERSITY, LIVERPOOL)

Introduction

SINCE the beginning of this century the slow and the explosive reaction of oxygen with hydrocarbons and their simple derivatives have been the subject of a large number of investigations. There is now agreement on many aspects of such combustions; for instance that they are chain reactions involving atoms and free radicals; but the detailed mechanism is still somewhat controversial. This is scarcely surprising since these systems are generally very complex—as well as carbon monoxide, carbon dioxide, and water, various organic substances are formed some of which may oxidise or decompose under the conditions of the experiment. However, owing especially to work during the last ten years, it seems very likely that certain types of elementary reaction occur in all these systems, and it is proposed in this Review to consider the evidence which has led to such reactions' being suggested. The discussion will be limited to slow combustions, *i.e.*, those taking place at a measurable rate; the pressure of the reaction mixture is usually at or below atmospheric, and the working temperature range is in the region 100—500° c, depending on the fuel. Work on "hot" and "cool" flames, explosions, as well as oxidations of inorganic compounds, *e.g.*, hydrogen and carbon monoxide, will be considered if necessary.

Elementary reactions can be defined as those stages, of a simple order, which together make up an observed overall reaction, or in a more limited sense the term is used for those part-reactions which involve substances of a transitory nature such as atoms and free radicals.[1] For instance the accepted mechanism for the combustion of hydrogen includes the three elementary reactions

$$\cdot OH + H_2 \longrightarrow H_2O + H\cdot \quad (1)$$

$$H\cdot + O_2 \longrightarrow \cdot OH + O\cdot \quad (2)$$

$$\cdot O + H_2 \longrightarrow \cdot OH + H\cdot \quad (3)$$

In a book of great value to workers in the field of gaseous reactions Steacie has recently discussed elementary processes which may occur in the gas phase, including those involving oxygen, but his approach is different from that in this Review.

Historical

A short historical survey of the subject is necessary to provide a background for the later discussion.

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[1] Steacie, "Atomic and Free Radical Reactions", Reinhold Publishing Corporation, New York, 2nd edn., 1953.

Most of the products of combustion of hydrocarbons contain only one atom of oxygen, *e.g.*, CO, H_2O, $CH_3{\cdot}OH$, $CH_3{\cdot}CHO$, so that the mechanism must explain the mode of scission of the O–O link. Bone,[2] in order to explain the results of studies on the oxidation of the lower hydrocarbons (1902—1904), suggested that oxygen atoms were introduced between carbon and hydrogen atoms in the fuel molecule to give hydroxy-compounds, some of which were unstable; *e.g.*, for methane:

$$\begin{tikzcd}
CH_4 \arrow[r, "O"] & CH_3{\cdot}OH \arrow[r, "O"] & CH_2(OH)_2 \arrow[r, "O"] \arrow[d] & CH(OH)_3 \arrow[d] \\
CO + H_2O & {:}C(OH)_2 \arrow[l] & CH_2O + H_2O \arrow[l, "O"'] & CO_2 + H_2O + H_2
\end{tikzcd}$$

Callender,[3] however, in 1927 suggested that the first stage was the incorporation of the oxygen molecule as a whole in the hydrocarbon molecule, *e.g.*,

$$CH_4 + O_2 \longrightarrow CH_3{\cdot}O{\cdot}OH \quad . \quad . \quad . \quad . \qquad (4)$$

The peroxide was then supposed to react to give the final products.

During the development of the theory of chain reactions after 1928 it was realised that propagation steps were of two types, namely, non-branching, in which one chain carrier is destroyed and one formed, *e.g.*, reaction (1), and branching, in which the number of chain carriers is increased, *e.g.*, reactions (2) and (3). Gas-phase oxidation systems show all the characteristics of chain reactions. For instance, the quantum yield of the photo-oxidation of acetaldehyde is high;[4] the slow combustion of methane is sensitive to surface conditions and to the presence of inert gas;[5] that of propane is catalysed by azomethane[6] and that of di*iso*propyl ether is inhibited by aromatic amines;[7] and the dependence of the rate on the partial pressures of the reactants is often complex and there are abrupt transitions from slow reaction to explosion with small changes of conditions. Semenov[8] in 1930—1934 was able to explain the general course of most slow combustions, as shown by pressure–time curves at constant volume, by the following scheme:

$$\begin{tikzcd}
\text{Fuel} + O_2 \arrow[r] & \text{Intermediate (M)} \arrow[dl] \arrow[d] & \\
\text{Inert products} & \text{Branching} \arrow[r] & \text{Chain carriers}
\end{tikzcd}$$

The chain carriers can initiate the primary chain leading to the production of more M. The intermediate must be stable enough to build up to a pressure of several mm. Semenov called the branching degenerate or delayed in contrast to rapid branching by reactions such as (2) or (3).

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[2] See review by Bone, *Proc. Roy. Soc.*, 1932, *A*, **137**, 243.

[3] Callender, *Engineering*, 1927, **123**, 147, 182, 210.

[4] Carruthers and Norrish, *J.*, 1936, 1036.

[5] Hoare and Walsh, " Fifth Symposium on Combustion ", Reinhold Publishing Corporation, New York, 1955, p. 467.

[6] Scheer and Taylor, *J. Chem. Phys.*, 1952, **20**, 653.

[7] Chamberlain and Walsh, *Trans. Faraday Soc.*, 1949, **45**, 1032.

[8] Semenov, " Chemical Kinetics and Chain Reactions ", Oxford Univ. Press, 1935.

His analysis has been one of the most fruitful advances in the field, and his overall picture is generally accepted. It is agreed that the chain carriers are atoms and free radicals, but the identity of the intermediate M is still a matter of controversy. Norrish[9] suggests that the aldehydes formed lead to degenerate branching. Oxygen atoms are involved and his theory may be considered a development of Bone's, whereas Walsh, Hinshelwood, Ubbelohde, and others consider that below about 350° the important intermediates are hydroperoxides.[10] Certainly around 350° various peculiar phenomena, such as cool flames or negative temperature coefficients of the rate, are observed. It is probable that a partial change in mechanism occurs as the temperature is increased, and below about 350—400° is often called the " low " and above 350—400° the " high " temperature range for slow combustion.

Other features, such as the formation of olefins from saturated hydrocarbons, have come into prominence in recent years, but the respective rôles of aldehydes and peroxides continue to be studied. The mechanisms suggested usually include elementary reactions leading to the formation and disappearance of these substances.

Classification of evidence for suggested elementary reactions

The evidence for any elementary reaction falls into one or more of four categories.

(*a*) ***a-priori* Evidence.**—It has been suggested that the main types of elementary process are

(i) Reactions in which one chemical bond is broken or one formed, *e.g.*,

$$C_2H_6 \longrightarrow 2CH_3\cdot$$

(ii) Reactions in which one bond is broken and one formed, *e.g.*,

$$H\cdot + C_2H_6 \longrightarrow H_2 + C_2H_5\cdot$$

(iii) Rearrangement or decomposition of a radical, or addition of a radical to a molecule to give a larger radical, *e.g.*,

$$\cdot CH_2\cdot OH \longrightarrow CH_3O\cdot, \quad C_3H_7\cdot \rightleftharpoons CH_3\cdot + C_2H_4$$

(iv) Energy-transfer reactions.

However, when a radical possesses considerable excess of internal energy it may undergo reactions of a somewhat more complex nature. Also, more complicated bond rearrangements are quite probable if it is likely that the reaction suggested is heterogeneous. Since the concentration of free radicals in these systems is usually low relative to that of molecules, radical–radical reactions will be infrequent compared with radical–molecule reactions.

These ideas provide a general guide as to whether any reaction is intrinsically feasible. For instance it is unlikely that reaction (4) will take

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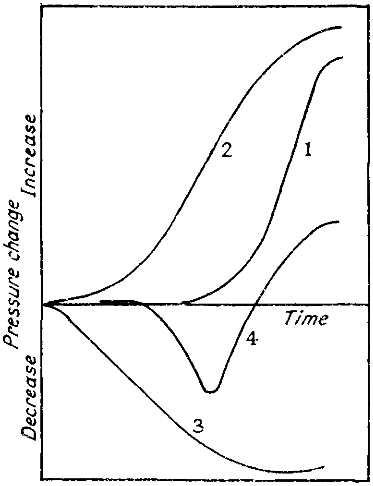
[9] Norrish, *Discuss. Faraday Soc.*, 1951, **10**, 269.

[10] *E.g.*, (*a*) Walsh, *Trans. Faraday Soc.*, 1946, **42**, 269 ; (*b*) Cullis and Hinshelwood, *Discuss. Faraday Soc.*, 1947, **2**, 117 ; (*c*) Small and Ubbelohde, *J. Appl. Chem.*, 1953, **3**, 193.

place in a single stage, and in fact three elementary steps, discussed later, are involved.



Typical pressure–time curves for slow-combustion reactions.

(*b*) **Evidence from Kinetic Measurements.**—The simplest method of following the course of a slow combustion is by measurements of pressure on the system confined in a quartz or Pyrex vessel at a constant volume and temperature (static method). Typical pressure–time curves are shown in the Figure. The usual type, 1, consists of a period of negligible pressure change (the induction period, τ) followed by acceleration to a maximum rate (ρ_{max}).[11] The acceleration is often exponential, *i.e.*, $\Delta p \propto \exp A't$, A' being the " net branching factor ". The rate then falls to zero. Some oxidations however commence at a measurable rate,[12] 2, while with others there is a pressure decrease initially,[13] 3, or, after the induction period,[14] 4. ρ_{max} is usually taken as the rate of reaction, but A' and τ both give a measure of this quantity. The variation of ρ_{max} and possibly A' and τ with temperature, reactant pressures, etc., has been studied for numerous slow combustions. It is essential to check the pressure–time curves against analytical data to find whether Δp really represents the extent of reaction.

The oxygen–fuel mixture can also be passed through a heated tube, and the amount of reaction determined for various flow times, pressures, etc. (flow method). It is possible though not always easy to obtain kinetic results in this way.

In many cases the results are not easily interpreted, but sometimes interesting information can be derived by setting up a reaction scheme

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[11] *E.g.*, McEwan and Tipper, *Proc. Roy. Soc.*, 1953, *A*, **216**, 280.

[12] *E.g.*, Bell and Tipper, *ibid.*, 1956, *A*, **238**, 256.

[13] *E.g.*, McDowell and Thomas, *J.*, 1949, 2208.

[14] *E.g.*, Bawn and Skirrow, " Fifth Symposium on Combustion ", Reinhold Publishing Corporation, New York, 1955, p. 521.

which leads to the correct kinetic relations and which also agrees with the other information (*e.g.*, analytical) about the oxidation (see the discussion of the methane–oxygen reaction by Lewis and Von Elbe [15]).

(*c*) **Evidence from the Products of the Oxidation.**—The scheme of elementary reactions suggested must obviously explain the formation of the various products. In fact the variation of the amounts of these with experimental conditions has supplied the main evidence for reactions discussed later. For example the hydrogen formed during the slow combustion of methanol increases with increase in the methanol–oxygen ratio.[12] This suggests that hydrogen atoms are present in the system and can react with oxygen or abstract hydrogen from the alcohol

$$H\cdot + CH_3\cdot OH \longrightarrow H_2 + \cdot CH_2\cdot OH$$

In the static method the reaction mixture is pumped from the vessel through traps cooled to appropriate temperatures after various times from the commencement of the oxidation under standard conditions, whilst in the flow method the products and unchanged reactants are merely passed from the heated tube through cooled traps. The latter method often enables relatively large amounts of unstable compounds formed to be obtained. The mixture can be roughly fractionated in the collecting traps, and the fractions are then analysed by any suitable method (*e.g.*, standard gas-analysis techniques, low-temperature distillation, gas-phase chromatography, volumetric or colorimetric analysis, mass-spectrometry, or infrared or ultraviolet spectroscopy).

(*d*) **Evidence from Specially Designed Experiments.**—Because of the complex nature of gas-phase oxidation systems some workers have tried to study atomic and free-radical reactions, which might be expected to occur in these systems, by designing special experiments. For example, by photolysing nitrous oxide in the presence of ethylene, Cvetanovic [16] has been able to investigate the reaction of oxygen atoms with the olefin. Transient intermediates can sometimes be identified in a mass-spectrometer or by spectroscopy. Unfortunately even such experiments cannot always give unambiguous information, as is well shown by work (discussed later) on the reaction of methyl radicals and oxygen.

Discussion of the various elementary processes usually involves correlating information, often indirect, from more than one source. For the occurrence of some reactions there is evidence from a large number of studies, and only selected references can be given.

Main types of elementary reaction

The reaction mechanisms suggested for the gas-phase oxidation of hydrocarbons and aldehydes are generally similar, and will be considered together. In fact, since aldehydes are formed and oxidised during hydrocarbon combustion the mechanisms may interact. The conditions under

[15] Lewis and Von Elbe, " Combustion, Flames and Explosions in Gases ", Academic Press, New York, 1951.

[16] Cvetanovic, *J. Chem. Phys.*, 1955, **23**, 1375.

which chain-crossing does and does not occur are discussed later. It is not possible to classify the elementary reactions completely logically, and it has been thought best to group together reactions of the individual molecules and radicals present or thought to be present in slow-combustion systems. Satterfield and Reid [17] have presented in diagrammatic form all the probable elementary reactions likely to occur in a typical gas-phase oxidation system (propane–oxygen), and readers may be interested to consult this in conjunction with the following seven sections.

1. Fuel Molecule + Oxygen.—It is necessary to assume that some reaction occurs whereby radicals are introduced into the oxidation system, and it is very unlikely that this is due to the thermal decomposition of some fuel molecules, since slow combustion takes place at temperatures well below the onset of " cracking ". However, traces of oxygen catalyse the pyrolysis of various compounds,[18, 19] and thus it appears that the primary initiation reaction is one between an oxygen and a fuel molecule. A kinetic study of the inhibition of the gas-phase oxidation of acetaldehyde by nitrogen dioxide at 100—150° indicates that initiation is a bimolecular reaction between acetaldehyde and oxygen.[20]

The state of the surface of the vessel has a marked effect on the slow combustion of many compounds. The induction period or the initial rate is especially sensitive to surface conditions and rigorous standardisation of experimental procedure is usually necessary to obtain consistent results.[11] Studies of the oxidations of propene and *iso*butane at 291° have shown that surface effects predominate during the induction period, τ.[21] Thus, although the overall process is undoubtedly complex during this period, the actual initiation is probably often at least partly heterogeneous. With many hydrocarbons the reaction must be relatively slow since τ is of the order of minutes, but with some other substances, *e.g.*, methanol, it is much more rapid since the oxidation commences at a measurable rate.[12]

The most likely primary initiation step is

$$RH + O_2 \longrightarrow R\cdot + HO_2\cdot \quad . \quad . \quad . \quad . \qquad (5)$$

$HO_2\cdot$ radicals have been detected mass-spectrometrically in several combustion systems,[22] although most are probably formed in other ways (section 4). R–H bond-dissociation energies vary from 102 kcal./mole (CH_3–H) to $\sim$78 kcal./mole (R·CO–H),[23] and Foner and Hudson [24] have determined $D(H{-}O_2)$ to be about 47 kcal./mole from the ionisation potential of $HO_2\cdot$ and the appearance potential of HO_2^+ from hydrogen peroxide. Reaction (5) is therefore endothermic by about 55 kcal./mole with methane and about 30 kcal./mole with the higher aldehydes. The activation energy

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[17] Satterfield and Reid, " Fifth Symposium on Combustion ", Reinhold Publishing Corporation, New York, 1955, p. 511.

[18] Niclause, Thesis, Nancy, 1953.

[19] Appleby, Avery, Meerbott, and Sartor, *J. Amer. Chem. Soc.*, 1953, **75**, 1809.

[20] McDowell and Thomas, *J.*, 1950, 1462.

[21] Ridge, *Trans. Faraday Soc.*, 1956, **52**, 858.

[22] *E.g.*, Eltenton, *J. Chem. Phys.*, 1947, **15**, 474.

[23] Cottrell, " The Strength of Chemical Bonds ", Butterworths, London, 1954.

[24] Foner and Hudson, *J. Chem. Phys.*, 1955, **23**, 1364.

in the gas phase would thus be very high. However, since the initiation reaction is very slow with many compounds even above 200—300° and may be heterogeneous, this is no reason for considering that reaction (5) would not occur.

It is possible to explain the kinetics and products of the oxygen-induced decomposition of *n*-butane,[19] formaldehyde,[25] and acetaldehyde [18] on the assumption that (5) is the initiation reaction. The aldehydes provide the best evidence since carbon monoxide, and hydrogen or methane, respectively, are formed in very high yield. Combe, Niclause, and Letort [26] have calculated that the activation energy of the initiation step with acetaldehyde is 23 ± 4 kcal./mole, which seems not unreasonable for the reaction

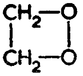
$$CH_3{\cdot}CHO + O_2 \longrightarrow CH_3{\cdot}CO + HO_2{\cdot}$$

With unsaturated hydrocarbons there is the possibility of addition to the double bond as well as hydrogen abstraction, since oxygen has some of the characteristics of a free radical. The endothermicities of reaction (5) are over 60 kcal./mole with ethylene and acetylene, and oxygen addition should thus be favoured especially if heterogeneous. Reactions (6*a*) and

$$C_2H_4 + O_2 \longrightarrow 2CH_2O \quad . \quad . \quad . \quad . \quad (6a)$$

$$C_2H_2 + O_2 \longrightarrow (CHO)_2 \quad . \quad . \quad . \quad . \quad (6b)$$

(6*b*) have been suggested ; [27, 28] presumably there are intermediate cyclic compounds, *e.g.*, (I). The aldehydes then oxidise, giving radicals. The first detectable product of the slow combustion of acetylene, which may commence with a fall in pressure, is glyoxal, and the walls of the vessel appear to be important in initiation.[28] Reaction (6*b*) must be relatively fast since there is a very short period of acceleration to the maximum rate. With higher olefins it is difficult to decide the relative importance of hydrogen abstraction and oxygen addition.



(I)

2. Fuel Molecule + Atom or Free Radical.—Since slow combustion is a chain process the fuel molecule must take part in a propagation reaction with one or more of the atoms or radicals, X, present in the system. With saturated aliphatic compounds, hydrogen abstraction almost certainly occurs

$$X{\cdot} + RH \longrightarrow XH + R{\cdot} \quad . \quad . \quad . \quad . \quad (7)$$

(*a*) X *is a hydrogen atom or a methyl radical.* Hydrogen, methane, and sometimes traces of higher paraffins are often products of slow combustion, the yields depending markedly on the temperature and relative concentrations of fuel and oxygen. With methanol at 440° the hydrogen present at the end of the reaction is reduced from 5·5 mm. to zero on raising the oxygen : methanol ratio from 1 : 1 to 2 : 1,[12] and with propane and *n*-butane in a flow system increase in the hydrocarbon : oxygen ratio increases the amount of methane formed.[17, 19] It is only towards the end of the

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[25] Style and Summers, *Trans. Faraday Soc.*, 1946, **42**, 388.

[26] Combe, Niclause, and Letort, *Rev. Inst. franc. Pétrole*, 1955, **10**, 786.

[27] Harding and Norrish, *Proc. Roy. Soc.*, 1952, *A*, **212**, 291.

[28] Steacie and McDonald, *J. Chem. Phys.*, 1936, **4**, 75.

oxidation of *iso*butane at 291° in a static system, when the oxygen has been nearly all consumed, that methane is produced.[29] These results suggest that hydrogen atoms and/or methyl radicals are present, and can either react with oxygen or abstract hydrogen from a fuel molecule. The hydrogen–oxygen reaction is retarded at just above the second explosion limit by ethane, propane, and formaldehyde, and this is probably due to reaction (7 ; $X=H$), the ethyl, propyl, or formyl radicals being unable to propagate the chain.[30]

The activation energies of hydrogen abstraction by hydrogen atoms and methyl radicals from numerous organic compounds in the gas phase have been determined (see Steacie[1] for discussion). They are low, <10—11 kcal./mole, and the steric factors are probably between 10^{-3} and 10^{-5}.

(*b*) X *is an oxygen atom.* Attempts to detect the presence of oxygen atoms in hydrocarbon flames by the addition of nitric oxide or sulphur dioxide have yielded negative results.[31, 32] Conditions in these experiments were different from those in normal slow combustions, however. Also if oxygen atoms are formed only in the branching reaction[9]

$$R{\cdot}CHO + O_2 \rightarrow R{\cdot}CO_3H \rightarrow R{\cdot}CO_2H + O{\cdot}$$

which is infrequent compared with the removal of aldehyde by radical attack, then their concentration would in any case be relatively small. Although there is no agreement on their rôle, if any, in the systems under consideration, work on the reaction of oxygen atoms, generated *in situ*, with saturated fuels will be briefly considered.

Steacie[1] has discussed the results of the reaction of products from a discharge through oxygen gas or water vapour with organic substances. For example the products with methane or ethane can be explained on the assumption that the initial process is (7 ; $R = CH_3$ or C_2H_5), E_7 being $\sim$8 kcal./mole with methane. More recently it has been found that oxygen atoms from the photolysis of nitrogen dioxide react with ethane above 100°,[33] and those from the mercury-photosensitised decomposition of nitrous oxide react with acetaldehyde at room temperature,[34] the activation energies being <10 and $\sim$3 kcal./mole respectively. Small amounts of added methane increase the rate of the carbon monoxide–oxygen reaction above the second limit, owing probably to the replacement of oxygen atoms by hydroxyl radicals by hydrogen abstraction from methane.[35]

Cottrell[23] has discussed the dissociation energy of the hydroxyl radical, and concludes that the best value is 108 ± 5 kcal./mole. This means that reaction (7 ; $X = O$) is roughly thermoneutral with methane and exothermic, up to about 25 kcal./mole (higher aldehydes), with other saturated fuels.

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[29] Batten, Gardner, and Ridge, *J.*, 1955, 3029.

[30] Baldwin, Corney, and Simmons, " Fifth Symposium on Combustion ", Reinhold Publishing Corporation, New York, 1955, p. 502.

[31] Gaydon, *Trans. Faraday Soc.*, 1946, **42**, 292.

[32] Whittingham, *ibid.*, 1948, **44**, 141.

[33] Rohr and Noyes, *Canad. J. Chem.*, 1955, **33**, 843.

[34] Cvetanovic, *ibid.*, 1956, **34**, 775.

[35] Hoare and Walsh, *Trans. Faraday Soc.*, 1954, **50**, 37.

(*c*) X *is a hydroxyl radical.* Hydroxyl radicals have been detected spectroscopically in hydrocarbon–oxygen flames,[36] and in the reaction of methyl radicals and oxygen by means of a mass-spectrometer.[37] Relatively large amounts of water are formed during slow combustions, and with many substances a large part is probably the result of the process

$$\cdot OH + RH \longrightarrow H_2O + R\cdot \quad . \quad . \quad . \quad . \quad (8)$$

Since D(H–OH) = 118 kcal./mole, this reaction is highly exothermic ; ΔH varies from -16 kcal./mole (methane) to -40 kcal./mole (higher aldehydes).

Stone and Taylor [38] have decomposed hydrogen peroxide vapour thermally and photolytically in a flow system in the presence of methane and ethane. The condensable products had a strong " organic " odour. Presumably the hydroxyl radicals formed abstracted hydrogen and the resulting methyl and ethyl radicals then reacted further. The reaction of hydrocarbons and aldehydes with the products of a discharge through water vapour, which include hydroxyl radicals, has been investigated. Avramenko and Lorentso [39] followed spectroscopically the rate of loss of hydroxyl radical, and claim to have obtained E_8 = 5·5, 0·5, and 4·0 kcal./mole with ethane, formaldehyde, and acetaldehyde respectively. It is doubtful, however, whether these values are very accurate.

(*d*) X *is the hydroperoxy-radical* (HO_2). There has been considerable controversy about the existence of hydroperoxy-radicals and their rôle in combustion. However, they have been detected mass-spectrometrically in the reactions $H + O_2$, $H_2 + O_2$, $Hg(CH_3)_2 + O_2$, and $CH_3\cdot + O_2$. Robertson [40] has calculated that about one in 10^5 collisions between a hydrogen atom and an oxygen molecule gives $HO_2\cdot$, and that the lifetime of the excited radicals is $\sim 5 \times 10^{-12}$ sec. at room temperature. Hoare and Walsh [41] have suggested that the marked retarding action of a PbO surface on the methane–oxygen reaction is due to efficient heterogeneous destruction of hydroperoxy-radicals, which are the main chain-propagating agents. Despite the difficulty of distinguishing between the various peroxidic substances formed during slow combustion (see Section 4), under certain conditions, *e.g.*, between 400° and 500° and in acid-washed or boric acid-coated vessels, it is now known that appreciable amounts of hydrogen peroxide are present in the oxidation products of methane,[42] methanol,[12] ethanol,[43] and propane.[17] It seems likely that hydroperoxy-radicals are present in these systems and that reaction (7 ; X = HO_2) occurs. The hydrogen peroxide probably decomposes on the surface, at least below 400—450°.[44]

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[36] Gaydon and Wolfhard, " Flames ", Chapman and Hall, London, 1953.
[37] Ingold and Bryce, *J. Chem. Phys.*, 1956, **24**, 360.
[38] Stone and Taylor, *ibid.*, 1952, **20**, 1339.
[39] Avramenko and Lorentso, *Doklady Akad. Nauk S.S.S.R.*, 1949, **67**, 867 ; **69**, 205.
[40] Robertson, *Discuss. Faraday Soc.*, 1954, **17**, 98.
[41] Hoare and Walsh, *Proc. Roy. Soc.*, 1952, *A*, **215**, 454.
[42] Egerton, Minkoff, and Salooja, *ibid.*, 1956, *A*, **235**, 158.
[43] Cullis and Newitt, *ibid.*, 1956, *A*, **237**, 530.
[44] Giguere and Lin, *Canad. J. Chem.*, 1957, **35**, 283 ; Satterfield and Stein, *J. Phys. Chem.*, 1957, **61**, 537.

$D(HO_2\text{–}H)$ can be calculated from the heats of formation of $HO_2\cdot$ and H_2O_2 to be 89 kcal./mole. Thus the hydrogen-abstraction reaction is endothermic with hydrocarbons (up to 13 kcal./mole with methane) but exothermic with aldehydes. It is therefore quite feasible thermochemically under the conditions where hydrogen peroxide is formed.

Steacie [1] has discussed work on the effect of hydrogen atoms from a discharge tube on hydrocarbon–oxygen mixtures. A rapid reaction occurs even at −183°, although in the absence of oxygen the hydrocarbon was not attacked. It appears that excited hydroperoxy-radicals are formed and react with the fuel. Norrish [9] considers that three-body collisions, $H\cdot + O_2 +$ molecule, are important, *e.g.*, in the oxidation of formaldehyde, but the overall reactions are virtually the same as if the radical were $HO_2\cdot$.

(*e*) X *is an alkoxy-* (RO) *or alkylperoxy-* (RO_2) *radical.* Hydrogen abstraction by these radicals will be discussed later.

Except in the simplest fuel molecules, methane and ethane, the hydrogen atoms are not all equivalent. It seems probable that, other things being equal, the weakest R–H bond will be broken in reaction (7). Steacie [1] concludes from the published data that C–H bond strengths decrease in the order primary $>$ secondary $>$ tertiary $\gg$ R·CO–H. The most weakly bound hydrogen atoms in olefins are those in the α-position with respect to the double bond. Carbon–hydrogen bonds in other compounds such as alcohols and amines appear to be attacked preferentially.[43, 45] The results of many oxidation studies, *e.g.*, of acetaldehyde and *iso*butane, suggest that the most weakly bound hydrogen atom is in fact removed.[26, 29] However, in the " high " temperature range small differences in bond strength will be less important, and Rust and Collamer [46] were able to explain the formation of some products of the oxidation of 2 : 2 : 4-trimethylpentane and 2 : 2-dimethylbutane at 450° only on the assumption that primary C–H bonds were attacked. Ubbelohde and his co-workers [47] have found that " large " paraffin molecules, *e.g.*, *n*-heptane, are " crumpled " in the gas phase, and thus with these molecules steric considerations may favour radical attack on primary C–H bonds.

Atoms and free radicals are known to add readily to olefins in the gas phase, and therefore this process may compete with hydrogen abstraction in the slow combustion of unsaturated compounds. Steacie [1] has discussed many typical reactions (*e.g.*, $H\cdot$ or $CH_3\cdot +$ olefins), but recent work has thrown more light on the addition reaction in systems containing oxygen. Cvetanovic [16] finds that oxygen atoms from the mercury-photosensitised decomposition of nitrous oxide react with ethylene 22 times as rapidly as with *n*-butane, the initial step being addition to the double bond, with an activation energy of ∼3 kcal./mole. The formation of ethylene oxide during the oxidation of ethylene [27] cannot be explained unless the C–H bonds are assumed to remain intact. Hydrocarbons containing more

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[45] Cullis and Willsher, *Proc. Roy. Soc.*, 1951, *A*, **209**, 218.

[46] Rust and Collamer, *J. Amer. Chem. Soc.*, 1954, **76**, 1055.

[47] *E.g.*, Ubbelohde, " Fifth Symposium on Combustion ", Reinhold Publishing Corporation, New York, 1955, p. 74.

than three carbon atoms have been found in the products of the slow combustion of ethylene and propene in a flow system,[48] and in a static system at below 300° the oxidations of but-2-ene and hex-1-ene commence with a marked pressure drop after the induction period, especially with high olefin : oxygen ratios.[14] Only a small part of this drop can be accounted for by hydroperoxide formation, and it seems likely that some polymerisation occurs by radical-addition reactions.

3. Reaction of Radicals formed from the Fuel Molecule.—(*a*) R *decomposes*. The higher alkyl radicals ($C_3H_7\cdot$ and above) are unstable above about 350°, and tend to split at a carbon–carbon bond giving a lower alkyl radical and an olefin (see Steacie [1] for discussion). For example [1, 49]

$$C_3H_7\cdot \longrightarrow CH_3\cdot + C_2H_4 \text{ ; } E \sim 26 \text{ kcal./mole} \quad . \quad . \quad (9)$$

$$\left.\begin{array}{lll} n\text{-}C_4H_9 & \longrightarrow & C_2H_5\cdot + C_2H_4 \\ iso\text{-}C_4H_9 & \longrightarrow & CH_3\cdot + C_3H_6 \end{array}\right\} ; \; E \sim 25 \text{ kcal./mole}$$

Olefins with a smaller number of carbon atoms than the parent molecule have been found in the products of the oxidation of many hydrocarbons, *e.g.*, propane,[17] *n*-butane,[19] 2 : 2 : 4-trimethylpentane,[46] and 2 : 2-dimethylbutane.[46] Only traces of hydrogen were detected, supporting the view that a C–H bond split is not favoured. With propane and butane, as far as can be judged from the results, the relative yields of the lower olefins appear to increase with increase of temperature and hydrocarbon : oxygen ratio. This suggests a competition between decomposition reactions and reactions of $C_3H_7\cdot$ or $C_4H_9\cdot$ with oxygen. Satterfield and Reid [50] have satisfactorily correlated numerous studies of the propane-oxygen reaction on the assumption, amongst others, that all the ethylene is formed by reaction (9). Relatively large amounts of carbon dioxide are produced during the oxidation of esters of the lower fatty acids at 280—425°, *e.g.*, with methyl formate, CO : CO_2 is 0·77 at 380°,[51] and some may well be formed by decomposition of the appropriate fuel radical, *e.g.*,

$$CH_3\cdot O\cdot OC\cdot \text{ or } \cdot CH_2\cdot O\cdot OCH \longrightarrow CH_3\cdot + CO_2$$

Carbonyl radicals (R′CO) from the aldehydes are generally less stable than alkyl radicals. Estimates of the activation energy of the decomposition (10), which may be pressure-dependent under certain conditions,[52, 53]

$$R'CO \longrightarrow R'\cdot + CO \quad . \quad . \quad . \quad . \quad (10)$$

have generally been derived from work on the photolysis of aldehydes. Steacie [1] concludes that the best values for E_{10} are 14—15 kcal./mole for formyl and 16 kcal./mole for acetyl, and that propionyl is less stable. Butadiene and toluene react rapidly in the gas phase with methyl radicals, giving less active radicals. The results of the photolysis of acetone in

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[48] Burgoyne and Cox, *J.*, 1953, 876.
[49] McNesby, Drew, and Gordon, *J. Chem. Phys.*, 1956, **24**, 1260.
[50] Satterfield and Reid, *J. Phys. Chem.*, 1955, **59**, 283.
[51] Parsons and Danby, *J.*, 1956, 1795.
[52] Dorman and Buchanan, *Austral. J. Chem.*, 1956, **9**, 30, 34.
[53] Hoare, *Trans. Faraday Soc.*, 1957, **53**, 791

the presence of the former compound suggest that E_{10} for acetyl is 13·5 kcal./mole [54] while from those on the pyrolysis in the presence of the latter Szwarc and Taylor [55] have calculated that $D(CH_3–CO)$ is about 17 kcal./mole. Thus a value of 16 ± 2 kcal./mole for E_{10} for acetyl seems reasonable. The relative yield of carbon monoxide formed in the oxidation of acetaldehyde and propionaldehyde above 100° increases with temperature and is larger with propionaldehyde.[56] It appears that carbon monoxide is produced by decomposition of carbonyl radicals, and that acetyl is more stable than propionyl. The fact that the rate of production of carbon monoxide during the photolysis of acetic anhydride increases with temperature, but remains constant with propionic anhydride, is in agreement with this,[57] but a recent study [58] of the photo-oxidation of diethyl ketone indicates that $E_{10}(R = C_2H_5) \geqslant 13 \pm 3–4$ kcal./mole, suggesting moderate stability for the propionyl radical. However, some recent work indicates that E_{10} for formyl is greater than that for acetyl. Reed [59] had deduced $D(H–CO) = 30{\cdot}4 \pm 2{\cdot}3$ kcal./mole from electron bombardment of formaldehyde ; photolysis of a mixture of CH_2O and CD_2O suggests a value of $\leqslant 27$,[60] and theoretical calculation gives 26 kcal./mole.[52]

Carbon monoxide is one of the main products of hydrocarbon slow combustion, and much if not all is probably formed from intermediate aldehydes by reaction (10), although

$$H\dot{C}O + O_2 \longrightarrow CO + HO_2\cdot$$

may well occur (see section 4*b*).

(*b*) R *adds to a double bond.* See previous section.

(*c*) R *adds to an oxygen molecule.* Since free radicals are known to combine readily it might be expected that the reaction

$$R\cdot + O_2 \longrightarrow RO_2{}^* \quad . \quad . \quad . \quad . \quad (11)$$

would occur on account of the properties of the oxygen molecule (section 2). The peroxy-radical would be formed in an excited state since it would carry away the energy released in the reaction. Studies of hydroperoxide formation in the oxidation of olefins in solution have shown that molecular oxygen is fixed in this way,[61] and it has been suggested by numerous workers that reaction (11) occurs in gas-phase slow combustion at least in the low-temperature range.

Ingold and Bryce [37] detected $CH_3{\cdot}O_2\cdot$ radicals among the products of the reaction of methyl radicals and oxygen by means of a mass-spectrometer ; this is the only direct evidence of the occurrence of reaction (11). However, the indirect evidence is also strong. The oxidation of acetalde-

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[54] Volman and Graven, *J. Chem. Phys.*, 1952, **20,** 919.
[55] Szwarc and Taylor, *ibid.*, 1955, **23,** 2310.
[56] Newitt and Baxt, *J.*, 1939, 1711.
[57] Ausloos, *Canad. J. Chem.*, 1956, **34,** 1709.
[58] Jolley, *J. Amer. Chem. Soc.*, 1957, **79,** 1537.
[59] Reed, *Trans. Faraday Soc.*, 1956, **52,** 1195.
[60] Klein and Schoen, *J. Chem. Phys.*, 1956, **24,** 1094.
[61] Bolland, *Quart. Rev.*, 1949, **3,** 1.

hyde in the gas-phase below 100° gives nearly quantitative yields of peracetic acid, suggesting that

$$CH_3{\cdot}CO{\cdot} + O_2 \longrightarrow CH_3{\cdot}CO_3{}^*$$

occurs, and is followed by hydrogen abstraction by peracetyl radicals.[13] The kinetics of the oxidation of propionaldehyde are very similar to those of acetaldehyde, indicating a similar mechanism.[26] The results of studies of the slow combustion of formaldehyde are more difficult to interpret, but it seems very likely that the formation of the performyl radical ($H{\cdot}CO_3$) does occur at least below 400° (see section 4*c*).

The evidence for the formation of hydroperoxides during the uncatalysed slow combustion of hydrocarbons [and thus for reaction (11 ; R = Alkyl)] will be discussed later. Very high yields of the appropriate hydroperoxides, isolated as such, have been obtained by the mercury-photosensitised oxidation of methane, ethane, and propane in flow systems at room temperature.[62, 63] Fok and Nalbandyan [63] were able to explain the kinetics of the oxidation of propane on the basis of a chain reaction involving reaction (11 ; $R = C_3H_7$) followed by hydrogen abstraction. In contrast, Watson and Darwent [64] have recently found that with ethane the rate at 40—200° was independent of pressure, composition, and temperature, and that the quantum yield was unity and independent of intensity. These results appear to eliminate the possibility of a chain process and so at present it is preferable to draw no conclusions as to the reactions of $R{\cdot}$ or $RO_2{\cdot}$ radicals from the work on these sensitised oxidations. However, the reaction of *iso*butane with oxygen catalysed by hydrogen bromide at 145°, which gives 75—85% of *tert.*-butyl hydroperoxide in a vessel coated with boric acid, is undoubtedly a chain process indicating that $(CH_3)_3C{\cdot}O_2{\cdot}$ radicals are formed.[65]

The first stages in the decomposition of di-*tert.*-butyl peroxide in the vapour phase at 120—160° are

$$(CH_3)_3C{\cdot}O{\cdot}O{\cdot}C(CH_3)_3 \longrightarrow 2(CH_3)_3CO{\cdot} \longrightarrow 2(CH_3)_2CO + 2CH_3{\cdot}$$

In the presence of oxygen no methane or ethane was detected, and therefore all the methyl radicals must react with oxygen. The final products show that $CH_3{\cdot}O_2{\cdot}$ radicals were probably formed.[66] The results of the photo-oxidation of methyl iodide,[67] ethyl iodide,[68] acetone,[69] diethyl ketone,[58, 70] diacetyl,[71] and azomethane [72] cannot be interpreted with any certainty. Discussion will be held over to the next section, but there is

[62] Gray, *J.*, 1952, 3150.

[63] Fok and Nalbandyan, *Doklady Akad. Nauk S.S.S.R.*, 1952, **85,** 1093 ; **86,** 589.

[64] Watson and Darwent, *J. Phys. Chem.*, 1957, **61,** 577.

[65] Rust and Vaughan, *Ind. Eng. Chem.*, 1949, **41,** 2595.

[66] Raley, Porter, Rust, and Vaughan, *J. Amer. Chem. Soc.*, 1951, **73,** 15.

[67] Bates and Spence, *ibid.*, 1931, **53,** 1689.

[68] Jones and Bates, *ibid.*, 1934, **56,** 2285.

[69] *E.g.*, (*a*) Marcotte and Noyes, *Discuss. Faraday Soc.*, 1951, **10,** 236 ; (*b*) Henty, *J. Amer. Chem. Soc.*, 1953, **75,** 5810 ; (*c*) Christie, *ibid.*, 1954, **76,** 1979.

[70] Finkelstein and Noyes, *Discuss. Faraday Soc.*, 1953, **14,** 76, 81.

[71] Taylor and Blacet, *Ind. Eng. Chem.*, 1956, **48,** 1505.

[72] Hoey and Kutschke, *Canad. J. Chem.*, 1955, **33,** 496.

considerable evidence for the occurrence of reaction (11) involving methyl and ethyl radicals in these systems.

The quantitative data on reaction (11) are collected in Table 1. For comparison it is assumed that E_{11} is zero and the steric factors (P) are listed.

TABLE 1

Method	Radical	P	Ref.
Mass-spectrometer	CH_3	10^{-3}—10^{-5}	37
Photolysis, $(CH_3)_2CO + O_2$	CH_3	$\leqslant 2 \times 10^{-4}$	69*a*
Photolysis, $(CH_3)_2N_2 + O_2$	CH_3	$\sim 10^{-2}$	72
Photolysis, $(C_2H_5)_2CO + O_2$	C_2H_5	$\leqslant 3 \times 10^{-5}$	70
Photolysis, $(C_2H_5)_2CO + O_2$	C_2H_5	$\sim 10^{-3}$	58
Effect of C_2H_6 on H_2–O_2 reaction	C_2H_5	$>8 \times 10^{-6}$	30
Analysis of data on C_3H_8–O_2 reaction (assuming P for $C_3H_7\cdot + O_2 \longrightarrow C_3H_6 + HO_2\cdot$ is unity) .	C_3H_7	$\sim 2{\cdot}5 \times 10^{-7}$	50

It appears that the steric factor decreases as the number of carbon atoms in the alkyl radical increases, but the results are not accurate enough to be certain that this trend is correct.

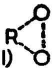
Very recently, Hoare and Walsh[72a] have found that, in the presence of acetone at 200°, reaction (11 ; R = CH_3) is actually of the third order :

$$CH_3\cdot + O_2 + M(\text{acetone}) \longrightarrow CH_3{\cdot}O_2 + M$$

and that on this basis results of other workers[37, 69a, 72] on the methyl–oxygen reaction can be correlated.

4. Reactions of the Excited Peroxy-radicals.—The probable reactions of $RO_2{}^*$ radicals represent one of the most important problems of slow-combustion studies.

(*a*) Since the peroxy-radicals are in an excited state it might be expected that the reverse reaction to (11) would occur readily. The low collision yields found for reaction (11) may point to a high probability for the dissociation. If, however, the peroxy-radical is of fairly complex structure, the lifetime may be relatively long, since the excess of energy would be spread over many degrees of vibrational freedom, and would not be freely available at the R–O_2 bond. Small and Ubbelohde[10] have suggested that the radical may exist in a loose ring form (II).



(II)

Hydrogen, which is known to be very effective in the collisional transfer of vibrational energy, is found to retard the oxidation of *n*-hexane at 250—300°.[73] Probably excited $C_6H_{13}O_2\cdot$ radicals are being rapidly deactivated and the unexcited radicals propagate the chain less readily. McDowell and Thomas[20] have found that small amounts of nitrogen dioxide catalyse the acetaldehyde–oxygen reaction. They suppose that this is due to the process

$$CH_3{\cdot}CO_3{}^* + NO_2 \longrightarrow CH_3{\cdot}CO_3\cdot + NO + O\cdot$$

followed by the rapid reaction (7 ; X = O, R = CH_3·CO).

[72a] Hoare and Walsh, *Trans. Faraday Soc.*, 1957, **53**, 1102.

[73] Small and Ubbelohde, *J.*, 1952, 4619.

(*b*) RO_2^* *decomposes.* When R is a hydrocarbon radical there is now strong evidence for the reaction (12*a*) or possibly (12*b*). It may well be

$$RO_2^* \longrightarrow \text{olefin} + HO_2\cdot \quad . \quad . \quad . \quad . \quad (12a)$$
$$RO_2^* + X \longrightarrow \text{olefin} + HO_2\cdot + X \quad . \quad . \quad . \quad (12b)$$
$$R\cdot + O_2 \longrightarrow \text{olefin} + HO_2\cdot \quad . \quad . \quad . \quad . \quad (12c)$$

that the reaction is actually (12*c*), the oxygen attacking a C–H bond, but it is preferable to discuss it here.

Ingold and Bryce [37] (see section 3*c*) detected methylene and hydroperoxy-radicals in the reaction of methyl radicals with oxygen at 1000°. These may have been formed by reactions (12 ; $R = CH_3$), but it seems likely that only at relatively high temperatures ($>600°$), if at all, is this reaction of importance in the oxidation of methane. The products of the slow combustion of higher hydrocarbons in the " high " temperature range may include olefins with the same number of carbon atoms as the original fuel, and with the appropriate surface conditions hydrogen peroxide is also a product.[17, 74] Satterfield and Reid [17] have investigated the rôle of propene in the oxidation of propane. The yields of propene and hydrogen peroxide per mole of propane consumed increased with temperature to a maximum at about 425° and then fell. In their correlation [50] of the data on propane combustion (section 3*a*) they assume that all the propene is formed by reactions (12 ; $R = C_3H_7$) and have calculated the activation energy to be 19 kcal./mole, E_{11} being assumed to be zero. Shtern [75] has deduced from Russian work on the slow combustion of propane that nearly all the propene comes from *iso*propyl radicals. Chain termination by alkyl radicals in the $H_2O_2C_2H_6$ or $-C_3H_8$ system is probably due to reactions (12 ; $R = C_2H_5$ or C_3H_7) since $HO_2\cdot$ radicals may be destroyed at the walls.[30] As the number of carbon atoms in the radical R increases reactions (12) will become progressively less important owing to the instability of the radical. With appropriate surface conditions acetaldehyde and hydrogen peroxide are formed quantitatively in ethanol oxidation at 270—370° during the induction period, strongly suggesting that reactions (12) and reaction (7 ; $X = HO_2$, $R = CH_3\cdot\dot{C}H\cdot OH$) are the chain-propagating steps.[43]

There have been many studies of systems in which the lower radicals are formed in the presence of oxygen, but it has not been possible to deduce unambiguously what are the modes of decomposition of the alkylperoxy-radicals. With methyl radicals the reaction most favoured has been

$$CH_3O_2^* \longrightarrow CH_2O\cdot + \cdot OH \quad . \quad . \quad . \quad . \quad (13)$$

Hydroxyl radicals have been detected in a mixture of methyl radicals and oxygen at 1000°,[37] and in acetone–oxygen and methyl iodide-oxygen mixtures undergoing flash photolysis,[76] but there is no indication of the method of formation. Formaldehyde is the only organic intermediate formed during oxidation of methane, at any rate above 400°.[42] It is also a product of the slow combustion of acetaldehyde above 200°,[56] where the acetyl radicals decompose rapidly, and of the photo-oxidation of acetone,[69]

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[74] Gray, *J.*, 1953, 741.

[75] Shtern, *Zhur. fiz. Khim.*, 1954, **28**, 613.

[76] Potter, *Discuss. Faraday Soc.* 1951, **10**, 326.

diacetyl,[71] and methyl iodide [67] below 200°. In these systems methyl radicals are undoubtedly formed in the initial steps. It seems quite probable from these and other results that at lower temperatures formaldehyde may be formed in other ways, *e.g.*, *via* $CH_3{\cdot}O{\cdot}OH$ or by radical–radical reactions in these systems, and it might be questioned whether the relatively simple radical $CH_3{\cdot}O_2{}^*$ would have a lifetime long enough for the bond rearrangements in reaction (13) to occur. Certainly more complex reactions such as

$$CH_3{\cdot} + O_2 \longrightarrow H\dot{C}O + H_2O$$

seem unlikely. However, since Egerton, Minkoff, and Salooja [42] were unable to detect any methyl hydroperoxide or methanol in the products of the slow combustion of methane above 400° despite a careful search, it is reasonable in the Reviewer's opinion to assume that methylperoxy-radicals react almost exclusively by reaction (13) in the "high" temperature range until definite evidence to the contrary is forthcoming.

Acetaldehyde is a major intermediate product of the oxidation of ethane, especially below 400°.[74, 77] It is also formed in relatively high yields during the photo-oxidation of diethyl ketone [58, 70] below 200°. The experimental evidence suggests that a reaction analogous to (13) may occur, *i.e.*,

$$C_2H_5{\cdot}O_2 \longrightarrow CH_3{\cdot}CHO + {\cdot}OH$$

It is probable that the formaldehyde and methanol produced during the ethane–oxygen and propionaldehyde–oxygen reactions are the result of the oxidation of acetaldehyde rather than of the decomposition

$$CH_3.CH_2.O_2 \longrightarrow CH_2O + CH_3{\cdot}O{\cdot}$$

followed by

$$CH_3{\cdot}O{\cdot} + RH \longrightarrow CH_3{\cdot}OH + R{\cdot}$$

Relatively large quantities of methanol and acetaldehyde are formed during the slow combustion of propane.[17, 78] Since above about 350° little hydroperoxide has been detected,[75] this suggests that

$$(CH_3)_2CH{\cdot}O{\cdot}O{\cdot} \longrightarrow CH_3{\cdot}CHO + CH_3{\cdot}O{\cdot}$$

occurs, followed by hydrogen abstraction by the methoxy-radicals. Traces of propionaldehyde are also formed,[78] probably from *n*-propylperoxy-radicals, *i.e.*,

$$CH_3{\cdot}CH_2{\cdot}CH_2{\cdot}O{\cdot}O \longrightarrow CH_3{\cdot}CH_2{\cdot}CHO + {\cdot}OH$$

The high ratio of acetaldehyde to propionaldehyde implies that the oxidation proceeds mainly through *iso*propyl radicals as expected (see section 2). Newitt and Schmidt [79] have investigated the effect of pressure on the oxidation. Surface effects were probably important since a steel vessel was used. Nevertheless, the fact that increase in pressure decreased the amount of methanol and aldehydes and increased the amount of *n*- and *iso*-propyl alcohol and acetone is simply accounted for on the assumption that the decomposition of propylperoxy-radicals was being replaced by the reactions

$$n\text{- or } iso\text{-}C_3H_7O_2{\cdot} + C_3H_8 \longrightarrow C_3H_7{\cdot} + n\text{- or } iso\text{-}C_3H_7{\cdot}O{\cdot}OH \longrightarrow n\text{- or } iso\text{-}C_3H_7{\cdot}OH,\ (CH_3)_2CO, \text{ etc.}$$

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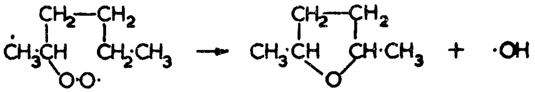
[77] Knox and Norrish, *Trans. Faraday Soc.*, 1954, **50,** 928.

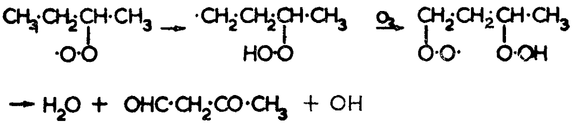
[78] *Idem, Proc. Roy. Soc.*, 1954, *A*, **221,** 151.

[79] Newitt and Schmidt, *J.*, 1937, 1665.

It is possible to explain the formation of various products, *e.g.*, aldehydes, ketones, and alcohols, of the slow combustion of higher hydrocarbons (RH) by postulating that relatively simple rearrangements of $RO_2\cdot$, $R'O_2\cdot$, $R''O_2$, etc., where R′, and R″, etc. are lower alkyl radicals from the decomposition of R.[46] Under conditions where little or no hydroperoxide can be detected it is preferable to do so. Minor products such as cyclic ethers, β-dicarbonyl compounds, and unsaturated aldehydes are also probably formed from alkylperoxy-radicals, *e.g.*,

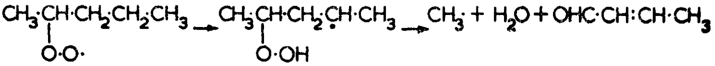


(cool flame of *n*-hexane [80])



$$CH_3\cdot CH_2\cdot\underset{\cdot O\cdot O}{CH}\cdot CH_3 \rightarrow \cdot CH_2\cdot CH_2\cdot\underset{HO\cdot O}{CH}\cdot CH_3 \xrightarrow{O_2} \underset{O\cdot O\cdot}{CH_2}\cdot CH_2\cdot\underset{O\cdot OH}{CH}\cdot CH_3 \rightarrow H_2O + OHC\cdot CH_2\cdot CO\cdot CH_3 + OH$$

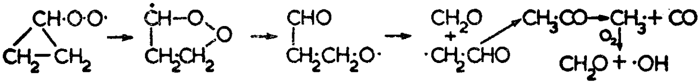
(preflame combustion of *n*-butane [81])



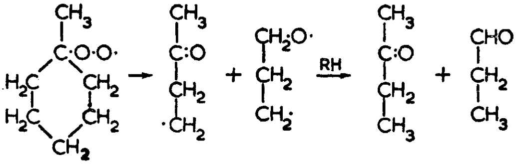
$$CH_3\cdot\underset{O\cdot O\cdot}{CH}\cdot CH_2\cdot CH_2\cdot CH_3 \rightarrow CH_3\cdot\underset{O\cdot OH}{CH}\cdot CH_2\cdot\dot{C}H\cdot CH_3 \rightarrow CH_3\cdot + H_2O + OHC\cdot CH{:}CH\cdot CH_3$$

(cool flame of *n*-pentane ;[82a] this is a slight modification of the authors' scheme)

The decomposition of peroxy-radicals derived from cyclic hydrocarbons will involve ring splitting. Formaldehyde is the intermediate responsible for degenerate branching in the slow combustion of *cyclo*propane at 380—430° and it has been suggested [83] that it is formed in the following way :



This does not involve the production of compounds such as ethylene which were not detected, but explains the formation of small amounts of methane. The lower aldehydes and ketones formed during the oxidation of methyl*cyclo*hexane at 380° [84] may come directly from $C_7H_{13}O_2{}^*$ radicals, *e.g.*,



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[80] Bailey and Norrish, *Proc. Roy. Soc.*, 1952, *A*, **212**, 311.

[81] Barusch, Neu, Payne, and Thomas, *Ind. Eng. Chem.*, 1951, **43**, 2766.

[82] (*a*) Malmberg, Smith, Bigler, and Bobbit, " Fifth Symposium on Combustion ", Reinhold Publishing Corporation, New York, 1955, p. 385 ; (*b*) McNevin, Urone, Omietanski, and Dunton, *ibid.*, p. 402.

[83] McEwan and Tipper, *Proc. Roy. Soc.*, 1953, *A*, **220**, 266.

[84] Garner, Long, and Temple, *Trans. Faraday Soc.*, 1953, **49**, 1193.

The ratio of carbon monoxide to dioxide in the oxidation products may be much less with *cyclo*pentane and methyl*cyclo*pentane at 400—450° than with paraffins under roughly the same conditions ($\sim 1{\cdot}5$ as compared with ~ 5).[85, 86] It seems probable that, while carbon dioxide is only formed by the oxidation of the aldehyde intermediate with the latter, with higher cyclic hydrocarbons the following type of reaction may occur:

cyclo-$C_5H_9{\cdot}O{\cdot}O{\cdot} \longrightarrow C_4H_9{\cdot} + CO_2$ (at least partly heterogeneous; Pyrex glass is effective but not boric acid [86])

The reaction

$$H{\cdot}CO{\cdot}O{\cdot}O{\cdot} \longrightarrow CO + HO_2{\cdot} \quad . \quad . \quad . \quad (14)$$

analogous to (12) has been suggested as a step in the thermal and photochemical oxidation of formaldehyde,[87] and the retarding effect of formaldehyde on the hydrogen-oxygen reaction [30] certainly points to the occurrence of (14) at least at "high" temperatures. By the use of carbon-14 Finkelstein and Noyes [70] showed that carbon dioxide was formed during the photolysis of diethyl ketone in the presence of oxygen by the oxidation of propionyl radicals,

$$C_2H_5{\cdot}CO_3{\cdot} \longrightarrow C_2H_5O{\cdot} + CO_2$$

Neiman and Feklisov [88] have suggested that the analogous reaction of acetyl radicals occurs during the oxidation of acetaldehyde. However, it is doubtful whether reactions such as the above play more than a minor rôle in hydrocarbon slow combustion.

(*c*) *Hydrogen abstraction by* RO_2^*. The reaction

$$CH_3{\cdot}CO_3^* + CH_3{\cdot}CHO \longrightarrow CH_3{\cdot}CO_3H + CH_3{\cdot}CO$$

must occur in the acetaldehyde-oxygen system to account for the yield of peracetic acid.[13, 26] The activation energy is 3·5 kcal./mole in the liquid phase with presumably unexcited radicals,[89] and thus is probably less in the gas phase. The retardation of the oxidation by the lower alcohols at 123·5° and by higher hydrocarbons at 150—250° has been studied.[90, 91] The increasing order of efficiency is that of decreasing C–H bond strength from primary to tertiary, suggesting that the effect is due to hydrogen abstraction by $CH_3{\cdot}CO_3^*$ from the additives giving radicals, *e.g.*, $CH_3{\cdot}\dot{C}H{\cdot}OH$, n-$C_7H_{15}{\cdot}$, which may not propagate the chain. Small amounts of performic acid have probably been detected in the products of the thermal and photo-oxidation of formaldehyde, and it is likely that HCO_3^* radicals may abstract hydrogen from formaldehyde, at any rate below 400° in these systems.[87, 92]

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[85] McGowan, Thesis, Liverpool, 1957.

[86] Burgoyne and Silk, *J.*, 1951, 572.

[87] Horner, Style, and Summers, *Trans. Faraday Soc.*, 1954, **50,** 1201; Scheer, "Fifth Symposium on Combustion", Reinhold Publishing Corporation, New York, 1955, p. 435.

[88] Neiman and Feklisov, *Doklady Akad. Nauk S.S.S.R.*, 1953, **90,** 583.

[89] Fillet, Niclause, and Letort, *J. Chim. phys.*, 1956, **53,** 8.

[90] Farmer and McDowell, *Trans. Faraday Soc.*, 1952, **46,** 624.

[91] Small and Ubbelohde, *J.*, 1950, 723; 1953, 637.

[92] Vanpée, *Bull. Soc. chim. belges*, 1953, **62,** 285.

The oxidation of hydrocarbons in solution proceeds *via* the formation of hydroperoxides by a chain reaction,[61] the propagation steps being (11)

$$RO_2\cdot + RH \longrightarrow RO{\cdot}OH + R\cdot \quad . \quad . \quad . \quad (15)$$

and (15). It has been known for a long time that peroxidic substances are often found in the products of normal slow combustion especially if the vessel surface has been pre-treated with acid or coated with boric acid. On the assumption that in the " low " temperature range these were hydroperoxides or their condensation products with aldehydes, it has been suggested that reaction (15), with excited $RO_2\cdot$, occurs in the gas phase,[10] other products and chain-branching being a consequence of peroxide breakdown.

Whereas there was no dark reaction between propane and oxygen in the presence of bromine at 210°, under the influence of ultraviolet light a decrease in pressure occurred accompanied by the formation of considerable amounts of $C_3H_7{\cdot}O{\cdot}OH$,[93] indicating that (15 ; $R = C_3H_7$) may occur. In the catalysed oxidation of *iso*butane,[65] however, *iso*-$C_4H_9O_2{}^*$ radicals abstract hydrogen from hydrogen bromide.

It has proved difficult to identify unambiguously the peroxides formed during non-catalytic slow combustion and to distinguish between hydrogen peroxide, hydroperoxides, and aldehyde peroxides, especially in mixtures of these substances, though recent studies have helped towards a solution of this problem.[94] Nevertheless, it now seems fairly certain that, in the " high " temperature range, any peroxide fraction recovered from the products consists of hydrogen peroxide and possibly aldehyde-H_2O_2 compounds.[12, 17, 42] Undoubtedly reaction (15) is not of major importance above 350—400°.

In the " low " temperature range the position is less clear. Ivanov[95] has isolated appreciable quantities of peroxides from the products of the oxidation of *cyclo*hexane in a flow system at 316°. He claims that the major portion is $C_7H_{14}O_7$, probably $C_6H_9(O{\cdot}OH)_2{\cdot}O{\cdot}O{\cdot}CH_2{\cdot}OH$. The ultraviolet spectrum of a reacting mixture of butane and oxygen at 270° shows some evidence of the presence of hydroperoxide,[96] and infrared analysis indicates that $(CH_3)_3C{\cdot}O{\cdot}O{\cdot}CH_2{\cdot}OH$ is a product of *iso*butane oxidation at the same temperature.[97] The condensable products of the slow combustion of *n*-heptane have been analysed for total peroxides iodometrically and for hydrogen peroxide by use of titanium sulphate, the difference being taken as organic peroxide,[98] and those of *iso*butane[29] and those from the cool flame of 2-methylpentane[82b] polarographically. Although the titanium sulphate method is uncertain in the presence of formaldehyde, the results do suggest that appreciable quantities of hydroperoxide are formed below

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[93] Sergeev and Shtern, *Doklady Akad. Nauk S.S.S.R.*, 1953, **91**, 1357.

[94] See refs., Bawn and Tipper, *Ann. Rep. Phys. Chem.*, 1956, **7**, 231.

[95] Ivanov, *Acta Physicochim., U.S.S.R.*, 1938, **9**, 421.

[96] Egerton and Young, *Trans. Faraday Soc.*, 1948, **44**, 750.

[97] Schubert and Pease, *J. Amer. Chem. Soc.*, 1956, **78**, 5553.

[98] Frank and Blackham, *Ind. Eng. Chem.*, 1954, **46**, 212; Pahnke, Cohen, and Sturgis, *ibid.*, p. 1024.

350°. In fact, with *n*-heptane Garner and Petty [99] have found that at 250° peroxides were the only detectable oxidation product, and these surely must have been $C_7H_{15}{\cdot}O{\cdot}OH$ or derived from it. 2 : 4 : 4-Trimethylpent-1-ene retards the oxidation below 350°, and the results [100] indicate that this is due to the reaction

$$C_7H_{15}{\cdot}O_2^* + C_8H_{16} \longrightarrow C_7H_{15}{\cdot}O{\cdot}OH + C_8H_{15} \text{ (inactive)}$$

The results of Newitt and Schmidt [79] suggest that hydroperoxide formation may occur in the propane–oxygen system at high pressures (see section 4*b*). With mixtures of oxygen and alkyl-*cyclo*pentanes or -*cyclo*hexanes (Me, Et, Pr, Bu^n), or ether in a static system below 250°, the pressure in the vessel decreases markedly at first and then rises.[101, 102] This decrease can only be the result of the formation of hydroperoxides, especially as with ether the peroxide is a maximum at the minimum of the pressure–time curve, and a coating of potassium chloride (known to decompose peroxides) on the walls eliminates the pressure drop.[102]

Although more work on this problem is obviously required, the weight of evidence does point to the importance of reaction (15) in the " low " temperature range. Comparison of the results for the higher paraffin–oxygen [98, 99] and acetaldehyde–oxygen–higher paraffin [91] systems indicates that RO_2^* radicals ($R = C_6H_{13}$, C_7H_{15}, etc.), present surely in both systems, react less readily with RH or $CH_3{\cdot}CHO$ than do $CH_3{\cdot}CO_3^*$ radicals.

(*d*) *Other reactions of* RO_2. Norrish and Taylor [103] consider that phenol may be formed in the oxidation of benzene at 650° directly from phenylperoxy-radicals by the reaction

$$C_6H_5{\cdot}O_2{\cdot} + C_6H_6 \longrightarrow C_6H_5{\cdot}OH + C_6H_5{\cdot}O{\cdot}$$

From a study of the catalysis by ozone of the slow combustion of the lower paraffins below 150°, Schubert and Pease [104] suggest that the reaction

$$RO_2{\cdot} + O_2 \longrightarrow RO{\cdot} + O_3$$

may be important in hydrocarbon oxidation.

5. Reactions of RO·OH.—(*a*) *Decomposition.* There is little direct information on the pyrolysis of alkyl hydroperoxides in the gas phase. Harris [105] found that in a flow system at 170—300° ethyl and *n*-propyl hydroperoxide underwent dehydration at the surface giving aldehydes. As flow rates in the mercury-photosensitised oxidations of methane, ethane, and propane (see section 3*c*) were reduced, the high yields of hydroperoxides decreased and formaldehyde, acetaldehyde, and propionaldehyde and acetone

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[99] Garner and Petty, *Trans. Faraday Soc.*, 1951, **47**, 877, 889.

[100] Garner, Long, and Webster, " Fifth Symposium on Combustion ", Reinhold Publishing Corporation, New York, 1955, p. 541.

[101] Lewin, *Bull. Soc. chim. belges*, 1933, **42**, 141.

[102] Lemay and Ouellet, *Canad. J. Chem.*, 1955, **33**, 1316.

[103] Norrish and Taylor, *Proc. Roy. Soc.*, 1956, *A*, **234**, 160.

[104] Schubert and Pease, *J. Chem. Phys.*, 1956, **24**, 919.

[105] Harris, *Proc. Roy. Soc.*, 1939, *A*, **173**, 126.

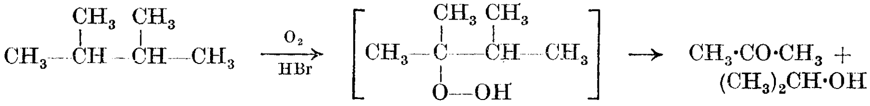
respectively were formed.[62, 63] The following heterogeneous reactions are therefore probable :

$$CH_3{\cdot}O{\cdot}OH \longrightarrow CH_2O + H_2O ; \quad C_2H_5{\cdot}O{\cdot}OH \longrightarrow CH_3{\cdot}CHO + H_2O ;$$
$$n\text{-}C_3H_7{\cdot}O{\cdot}OH \longrightarrow C_2H_5{\cdot}CHO + H_2O ;$$
$$iso\text{-}C_3H_7{\cdot}O{\cdot}OH \longrightarrow (CH_3)_2CO + H_2O \quad . \quad . \quad . \quad (16)$$

In an uncoated Pyrex vessel the products of the oxidation of *iso*butane, catalysed by hydrogen bromide, contained acetone and an alcohol but little *tert.*-butyl hydroperoxide (cf. section 3*c*).[65] The latter probably decomposed on the walls, *e.g.*,

$$(CH_3)_3C{\cdot}O{\cdot}OH \longrightarrow (CH_3)_2CO + CH_3{\cdot}OH$$

The products of the hydrogen bromide-catalysed oxidation of other hydrocarbons can be best accounted for by assuming that the appropriate hydroperoxides are first formed, but decompose rapidly.[65] For instance 2 : 3-dimethylbutane gives acetone and *iso*propyl alcohol, suggesting the processes



$$CH_3{-}\underset{}{\overset{CH_3}{\overset{|}{C}H}}{-}\overset{CH_3}{\overset{|}{C}H}{-}CH_3 \xrightarrow[HBr]{O_2} \left[CH_3{-}\underset{\underset{O-OH}{|}}{\overset{CH_3}{\overset{|}{C}}}{-}\overset{CH_3}{\overset{|}{C}H}{-}CH_3 \right] \longrightarrow CH_3{\cdot}CO{\cdot}CH_3 + (CH_3)_2CH{\cdot}OH$$

In neutral solvents of low dielectric constant, hydroperoxides may undergo fission at the O–O bond, *viz.*,

$$RO{\cdot}OH \longrightarrow RO{\cdot} + {\cdot}OH \quad . \quad . \quad . \quad . \quad (17)$$

the activation energies being between 30 and 40 kcal./mole.[106] It has been found that in carefully cleaned glass vessels the decomposition of hydrogen peroxide is homogeneous above 400—450°.[44] The kinetics depend on the conditions, but reaction (17 ; R = H) almost certainly occurs. This reaction probably accounts for some of the branching in methane–oxygen systems at 460—500°.[107] In the gas phase a homogeneous explosion of ethyl and *n*-propyl hydroperoxides may occur, presumably by a radical-chain mechanism. The initiation reaction might well be (17).[105] Fuel-rich acetaldehyde–oxygen mixtures at 250—350° give high yields of methanol.[108] At these temperatures acetyl radicals decompose rapidly, and some alcohol may be formed from methyl hydroperoxide by (17) followed by hydrogen abstraction by methoxy-radicals.

Many workers [10, 14] have assumed that reactions such as (16), non-branching, and (17), branching, occur in slow-combustion systems, but whether this assumption is reasonable depends on establishing the importance of reaction (15) in the particular system studied. The results of Newitt and Schmidt [79] with propane, discussed in sections 4*b* and 4*c*, imply that at high pressures, at which surface effects are less important,

$$n\text{- or } iso\text{-}C_3H_7{\cdot}O{\cdot}OH^{\cdot} \longrightarrow {\cdot}OH + n\text{- or } iso\text{-}C_3H_7O \xrightarrow{C_3H_8} n\text{- or } iso\text{-}C_3H_7{\cdot}OH$$

Obviously in those oxidations which commence with a pressure drop

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[106] Tobolsky and Mesrobian, " Organic Peroxides ", Interscience, New York, 1954.

[107] Egerton, Minkoff, and Salooja, *Combustion and Flame*, 1957, **1**, 25.

[108] Grumer, " Fifth Symposium on Combustion ", Reinhold Publishing Corporation, New York, 1955, p. 447.

(section 4*b*) the subsequent rise must be partly due to reactions of hydroperoxides, and the ketones and higher aldehydes, formed in *n*-heptane oxidation at 300°, are probably from the decomposition of the peroxide, which is the exclusive product[99] at 250°. Burgoyne and Silk[86] have found that with a 1 : 1 methyl*cyclo*pentane–oxygen mixture in a static system at 232° about 50% of the oxygen reacts without appreciable pressure change, the main organic products being aldehydes, ketones, acids, and peroxide. It seems likely that at least some of the carbonyl compounds were formed from $CH_3{\cdot}C_5H_8{\cdot}O{\cdot}OH$.

It has been suggested by Scheer[87] and by Vanpée[92] that performic acid, presumed to be an intermediate in formaldehyde oxidation (section 4*c*), decomposes heterogeneously by such reactions as

$$2H{\cdot}CO_3H \longrightarrow 2H_2O + 2CO + O_2 \quad . \quad . \quad . \quad . \quad (18)$$

or

$$2H{\cdot}CO_3H \longrightarrow 2H_2O + 2CO$$

Vanpée[92] has found that, with high formaldehyde-oxygen ratios, when all the oxygen has been consumed a second-order process occurs, and this may correspond to (18).

Considerable amounts of carbon dioxide are formed during the oxidation of acetaldehyde at 200—350°, but it is unlikely that the reaction

$$CH_3{\cdot}CO_3H \longrightarrow CH_3{\cdot}OH + CO_2$$

occurs to any great extent since the methanol–carbon dioxide ratio increases very rapidly with temperature.[56] The autocatalytic nature of the oxidation at lower temperatures is presumably due to the reaction of a small amount of the peracid produced giving radicals. Combe, Niclause, and Letort[26] have deduced that this process, which they consider to be

$$CH_3{\cdot}CO_3H + CH_3{\cdot}CHO \longrightarrow \text{free radicals} + ?$$

has an activation energy of 22 ± 4 kcal./mole. McDowell and Farmer[109] have explained the kinetics more simply on the assumption that a unimolecular decomposition (17 ; $R = CH_3{\cdot}CO$) occurs, and calculate that $k = 4 \times 10^{-3}$ sec.$^{-1}$ at 100°, a value which seems reasonable. Norrish,[9] however, takes the view that the branching reaction is

$$CH_3{\cdot}C(=O){-}O{-}O{-}H \longrightarrow CH_3{\cdot}C(=O){-}OH + O\cdot$$

(*b*) *Reaction with oxygen.* It has been suggested[110] that, in the presence of oxygen, hydroperoxides may be destroyed by reactions such as

$$RO{\cdot}OH + O_2 \longrightarrow {\cdot}OH + ?$$

(*c*) *Reaction with radicals.* Methyl and ethyl radicals from the decomposition of di-*tert.*-butyl and di-*tert.*-amyl peroxides in a flow system at 195° are found to abstract deuterium atoms from $(CH_3)_3C{\cdot}O{\cdot}OD$ giving $(CH_3)_3C{\cdot}O{\cdot}O{\cdot}$ radicals.[111]

6. Reactions of RO Radicals.—Gray[112] and Luft[113] have independently

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[109] McDowell and Farmer, "Fifth Symposium on Combustion", Reinhold Publishing Corporation, New York, 1955, p. 453.

[110] Malherbe and Walsh, *Trans. Faraday Soc.*, 1950, **46**, 824.

[111] Bell, Raley, Rust, Seubold, and Vaughan, *Discuss. Faraday Soc.*, 1951, **10**, 242.

[112] Gray, *Trans. Faraday Soc.*, 1956, **52**, 344.

[113] Luft, *Z. Electrochem.*, 1956, **60**, 94.

discussed the thermochemistry of alkoxy-radicals recently. Their calculated values of heats of formation and decomposition are collected and compared in Table 2.

TABLE 2

Radical	ΔH_f (kcal./mole)		Decomposition ΔH (kcal./mole)		
	Gray	Luft	Products	Gray	Luft
CH_3O	−0·5	2·5	$CH_2O + H\cdot$	25	20·2
C_2H_5O	−8·5	−3·5	$CH_3{\cdot}CHO + H\cdot$	21	16·8
			$CH_2O + CH_3\cdot$	13	7·5
n-C_3H_7O	−13	−9·5	$C_2H_5{\cdot}CHO + H\cdot$	19	—
			$CH_2O + C_2H_5\cdot$	10	—
iso-C_3H_7O	−18	−12·5	$(CH_3)_2CO + H\cdot$	18	16·1
			$CH_3{\cdot}CHO + CH_3\cdot$	12	5·5
n-C_4H_9O	−17	−15	$CH_2O + n\text{-}C_3H_7\cdot$	11	—
iso-C_4H_9O	−18	—	$CH_2O + iso\text{-}C_3H_7\cdot$	9	—
sec-C_4H_9O	−20	—	$CH_3{\cdot}CO{\cdot}C_2H_5 + H\cdot$	13	—
			$C_2H_5{\cdot}CHO + CH_3\cdot$	5	—
			$CH_3{\cdot}CHO + C_2H_5\cdot$	5	—
$tert.$-C_4H_9O	−25	−22	$CH_3{\cdot}CO{\cdot}CH_3 + CH_3\cdot$	5	6·6
$tert.$-$C_5H_{11}O$	−30	—	—	—	—

Although the absolute values of ΔH_f and of ΔH(decomp.) differ by a few kcal./mole the relative order is virtually the same.

(*a*) *Decomposition.* The stabilities of a series of alkoxyl radicals have been compared by decomposing alkyl *tert.*-butyl peroxides in the gas phase at 195° in the presence of excess of *cyclo*hexene as a hydrogen-atom donor.[111] The relative stability was defined as the ratio of moles of alcohol produced to moles of alcohol + moles of decomposition products, and the following results were obtained : CH_3O, 1·0 ; C_2H_5O, 0·86 ; n-C_4H_9O, 0·51 ; iso-C_3H_7O, 0·25 ; iso-C_4H_9O, 0·08 ; $tert.$-C_4H_9O, 0·08. ΔH(decomp.) can be considered as a theoretical measure of the stability of the radicals, and the experimental and theoretical orders of decreasing stability agree reasonably well, the assumptions involved being considered. The carbonyl products from the decomposition of alkyl nitrites at 230—240° in a stream of carbon dioxide have been identified.[114] The results show that the fission of alkoxy-radicals takes place at the carbon atom with the oxygen attached, the largest alkyl group splitting off most readily. This is in agreement with the calculated values of ΔH(decomp.). Volman and Graven [54] photolysed di-*tert.*-butyl peroxide in the presence of butadiene at 30—120° (cf. section 3*a*), and Birss, Danby, and Hinshelwood [115] decomposed the peroxide thermally in the presence of nitric oxide, an efficient inhibitor of free-radical reactions. The results suggested that the activation energy for the decomposition of $(CH_3)_3C{\cdot}O\cdot$ radicals was 11 ± 2 or 13 ± 2·4 kcal./mole, respectively, values somewhat higher than the calculated ΔH.

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[114] Adler, Pratt, and Gray, *Chem. and Ind.*, 1955, 1517.

[115] Birss, Danby, and Hinshelwood, *Proc. Roy. Soc.*, 1957, *A*, **239**, 154.

There is some evidence that the decomposition of alkoxy-radicals may occur in slow-combustion systems. Acetone is a product of *iso*butane oxidation, and with excess of hydrocarbon methane is formed when nearly all the oxygen is consumed.[29] This indicates that the reaction

$$(CH_3)_3C{\cdot}O{\cdot} \longrightarrow (CH_3)_2CO + CH_3{\cdot}$$

was probably occurring. It seems likely that some of the formaldehyde is formed during the oxidation of higher hydrocarbons in the "low" temperature range from appropriate alkoxyl radicals, rather than from the degradation of higher aldehydes, *e.g.*, with *n*-hexane and *n*-heptane.[10b] With the former the ratio $CH_2O : R'CHO$ does not vary greatly throughout the combustion. Neiman, Lukovnikov, and Feklisov [116] studied the slow combustion of hydrocarbons labelled with carbon-14 at 310—340°, and found that the formaldehyde came from any carbon atom, suggesting that the process

$$R''{\cdot}CH_2{\cdot}O{\cdot} \longrightarrow R''{\cdot} + CH_2O$$

takes place to some extent.

The products of the thermal decomposition of gaseous diacetyl peroxide in the presence of toluene at 90—250° were CO_2, C_2H_6, and a little CH_4.[117] The results were consistent with the presence of methyl radicals in the system, and thus the initial reaction

$$(CH_3{\cdot}CO_2)_2 \longrightarrow 2CH_3{\cdot}CO_2{\cdot}$$

was probably followed by

$$CH_3{\cdot}CO_2{\cdot} \longrightarrow CH_3{\cdot} + CO_2$$

The yield of carbon dioxide from the photolysis of acetic and propionic anhydride is constant from 30° to 195°, indicating that $CH_3{\cdot}CO_2{\cdot}$ and $C_2H_5{\cdot}CO_2{\cdot}$ radicals decompose very readily.[57] The decomposition of $RCO_2{\cdot}$ radicals may account for some at least of the appreciable quantities of carbon dioxide formed during the oxidation of hydrocarbons and aldehydes below 350°.

(*b*) *Hydrogen abstraction.* The mode of formation of alcohols during slow combustion has already been discussed (sections 4 and 5) in connection with other processes. The reaction

$$RO + R'H \longrightarrow ROH + R'{\cdot} \quad . \quad . \quad . \quad (19)$$

is probably of importance in many systems. The methanol isolated per mole of oxygen consumed was increased by addition of propene to a propane–oxygen mixture at 375° and 425°.[17] Since propene has an easily extractable hydrogen atom this supports the view that methanol was formed by reaction (19; $R = CH_3$, $R' = C_3H_7$, or $CH_2{\cdot}CH{:}CH_2$). The activation energy of (19) is probably low (<6 kcal./mole), since the results of a study of the decomposition of di-*tert.*-butyl peroxide in solution in 30 hydrocarbons indicated that the activation energy of hydrogen abstraction by $(CH_3)_3C{\cdot}O{\cdot}$ radicals was at least 7 kcal./mole less than that of radical decomposition.[118]

The products of slow combustion often include carboxylic acids so it is possible that hydrogen abstraction by $RCO_2{\cdot}$ radicals may occur, although

[116] Neiman, Lukovnikov, and Feklisov, *Zhur. obshchei Khim.*, 1955, **25**, 1317.
[117] Rembaum and Szwarc, *J. Amer. Chem. Soc.*, 1954, **76**, 5975.
[118] Brook, *Trans. Faraday Soc.*, 1957, **53**, 327.

Garner and Petty [99] consider that the acids formed during the oxidation of *n*-heptane are not derived from aldehydes. However, the carbon dioxide : acid ratio increases rapidly with temperature, *e.g.*, with $CH_3{\cdot}CHO$ and $C_2H_5{\cdot}CHO$ at 230° the ratio was 3·5 and 5·4 respectively, but no acids were produced at 350—400°.[56] These results certainly suggest that decomposition of $RCO_2{\cdot}$ is competing with hydrogen abstraction, and also that $CH_3{\cdot}CO_2{\cdot}$ is more stable than $C_2H_5{\cdot}CO_2{\cdot}$, which seems likely.

(*c*) *Reaction with oxygen.* Satterfield and Reid [17] have found that the yield of methanol per mole of oxygen consumed increased as the oxygen was used up during the reaction with propane. This implies that methoxy-radicals can react with oxygen as well as with propane. They consider that

$$CH_3{\cdot}O{\cdot} + O_2 \longrightarrow CO + H_2O + {\cdot}OH$$

occurs, but this process seems to be too complicated to take place in a single stage and possibly the products are $CH_2{:}O$ and $HO_2{\cdot}$ (cf. ref. 58).

7. Termination Reactions.—The variation of the overall rate of a chain reaction with concentration of reactants, etc., depends to a large extent on the termination reactions occurring, and thus these can often be deduced from the experimental kinetic relations. If the chains are long this is usually the only available method, since very small amounts of the products of these reactions will be formed. Several different radicals are present even in the simplest gas-phase oxidation system, and so the choice of termination steps is difficult and in many cases to some extent a matter of personal preference.

Change of the surface–volume ratio of the reaction vessel or a coating of various inorganic substances on the walls greatly affects the rate and sometimes the kinetics of the slow combustion of many compounds.[41, 119] This suggests that chain termination is heterogeneous, as does the accelerating effect of "inert" gases on the rate of methane and methanol oxidation.[12, 107] Norrish and Reagh [120] concluded from a study of the effect of vessel diameter on the slow combustion of lower hydrocarbons that destruction of chain carriers occurred on the walls at least to a considerable extent. However, with some substances (*e.g.*, *cyclo*pentane,[85] acetaldehyde [109]) or under certain conditions (*e.g.*, with n-C_7H_{16}–2 : 4 : 4-trimethylpent-1-ene–oxygen mixtures) [100] termination in the gas phase is more important.

The effect of surface on the oxidation of methane and *cyclo*propane is parallel to the effect on the hydrogen–oxygen reaction just above the second explosion limit, the order of decreasing rate being boric acid > acid-washed Pyrex or quartz > KCl > NaOH, PbO.[107, 119] This indicates that termination is by destruction of hydroperoxy-radicals, these being the only ones present unreactive enough to reach the walls.[41] For instance the following reactions have been suggested to obtain agreement with the experimental kinetics :

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[119] Broatch, McEwan, and Tipper, *Trans. Faraday Soc.*, 1954, **50**, 576.

[120] Norrish and Reagh, *Proc. Roy. Soc.*, 1940, *A*, **176**, 429.

$$\left.\begin{array}{lll} HO_2\cdot + O_2 & \longrightarrow & \text{inert products} \\ HO_2\cdot + C_3H_6 & \longrightarrow & \text{inert products} \end{array}\right\} \text{(\textit{cyclo}propane oxidation [83] at 380—430°)}$$

$$2HO_2\cdot \longrightarrow \text{inert products} \quad \text{(fuel-rich \textit{n}-butane–oxygen mixtures [19] at 486—528°)}$$

Vanpée[92] and Sheer[87] have suggested independently that chain termination in the thermal oxidation of formaldehyde at 330—400° involves $HCO_3\cdot$ radicals (see also sections *3c*, *4b*, 5), *viz.*,

$$\begin{array}{lll} HCO_3\cdot & \longrightarrow & \text{inert products (Vanpée)} \end{array}$$

$$\left.\begin{array}{lll} HCO_3\cdot + O_2 & \longrightarrow & CO + HO_2\cdot + O_2 \\ HCO_3\cdot + M & \longrightarrow & CO + HO_2\cdot + M \end{array}\right\}\text{(Sheer)} \quad . \quad . \quad (20)$$

Horner, Style, and Summers,[87] however, consider that in the photo-oxidation hydroperoxy-radicals are present and may react with formaldehyde or be destroyed on the walls. It certainly seems likely that $HO_2\cdot$ radicals would abstract hydrogen readily from formaldehyde above 300° (cf. section *2d*), and thus reaction (20) would be chain-propagating unless it was heterogeneous. The nature of the active centres responsible for propagation and termination in the thermal reaction then depends on the importance of reaction (14) in the system (see section *4b*).

It has been suggested that in the "low" temperature range reaction of peroxy-radicals may terminate the chain. For example the step

$$RCO_3\cdot + RCO_3\cdot \longrightarrow \text{inert products } [?\ (RCO)_2O_2 + O_2] \quad . \quad (21)$$

where $R = CH_3$ and C_2H_5 has been suggested by McDowell and Farmer[109] and Combe, Niclause, and Letort[26] in their discussions of the thermal and photo-oxidations of acetaldehyde and propionaldehyde below 150°. Radical-radical reactions are likely in the di-*tert.*-butyl peroxide–oxygen system (see section *3c*), since their concentration was relatively high. The formation of methanol, formaldehyde, etc., can best be explained by assuming that the reaction

$$2CH_3{\cdot}O_2\cdot \longrightarrow 2CH_3O + O_2$$

analogous to (21) occurs.[66] Hinshelwood and his co-workers[10b, 121] have explained the kinetics of the slow combustion of *n*-pentane, *n*-hexane, and butanone on the assumption that a termination step is

$$R\cdot + O_2 \longrightarrow \text{inert products}$$

Propene, but-2-ene, and hex-1-ene retard certain steps in their own oxidation.[14] This effect is probably due to reactions such as

$$RO_2\cdot + R'H \longrightarrow RO{\cdot}OH + R'\cdot \text{ (inert)}$$

(see section *4c*). The radical $R'\cdot$ from the olefins would be stabilised internally by resonance.

From this Review it will be realised that despite the large amount of work already done on slow combustion, the mechanisms of the oxidations are still not altogether clear, while for many of the elementary reactions which probably occur little is known of the activation energies and steric factors. Much remains for study in this interesting field.

The Reviewer thanks Professor C. E. H. Bawn, F.R.S., and Dr. G. Skirrow for helpful discussion.

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[121] Bardwell and Hinshelwood, *Proc. Roy. Soc.*, 1950, *A*, **201**, 26.