[CONTRIBUTION FROM THE PITTSBURGH EXPERIMENT STATION, U. S. BUREAU OF MINES, AND THE COAL RESEARCH LABORATORY, CARNEGIE INSTITUTE OF TECHNOLOGY]

The Combustion of Paraffin Hydrocarbons[1]

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Norrish[4] has proposed a chain mechanism of the oxidation of hydrocarbons which describes the slow and explosive reaction of methane in agreement with a number of observations; it does not describe the phenomenon of the low-temperature explosion peninsula and other associated effects ("cool" flames, maximum in the reaction rate found in the neighborhood of 350° for all paraffin hydrocarbons above methane); it also does not explain the formation of methyl alcohol in large quantities in the oxidation of rich mixtures of propane[5] at low temperatures, a fact which, according to Pease. can best be explained by a chain mechanism involving monovalent (alkyl and alkoxyl) radicals. Pease's mechanism applies exclusively to this observation and does not describe the experimental facts accounted for by Norrish's scheme. A more extensive mechanism was proposed by Ubbelohde[6] but was not treated kinetically.

In the present paper a mechanism of the oxidation of paraffin hydrocarbons is proposed which is believed to allow a more comprehensive interpretation of chemical and kinetic facts.

Chemistry of the Oxidation

It is generally recognized that the oxidation of hydrocarbons passes through the aldehyde stage to the ultimate products carbon monoxide, carbon dioxide and water. Since aldehyde added in small amounts to a hydrocarbon-oxygen mixture very markedly decreases the induction period,[7] the latter is interpreted as the period during which the aldehyde gradually accumulates.[4,8] Its presence appears to be necessary for the creation of chain centers responsible for the subsequent chain reactions in the gas phase. Thus, the chemistry of hydrocarbon and aldehyde oxidation being intimately related, it is advantageous to consider first the aldehyde oxidation.

Oxidation of Aldehydes.—Two oxidation reactions of aldehydes have been reported.

One is a catalytic surface reaction[9] which is particularly pronounced at low temperatures (not much above room temperature) but decreases toward higher temperatures. This reaction passes through a peracid stage to carbon dioxide as the chief oxide of carbon, the process being strongly accelerated by coating the surface with potassium chloride.[9b]

The other reaction is a gas-phase reaction unquestionably of the chain type;[9,10] it proceeds through a step-wise degradation to lower aldehydes[10a] by the intermediate formation of peracids,[9,10d] carbon monoxide being the only oxide of carbon formed. Formaldehyde cannot degrade further but is oxidized to carbon monoxide and water. The chain character of the gas-phase reaction is demonstrated by the inhibitory action of packing the vessel and by the large quantum yield in the photochemical oxidation of acetaldehyde.[11]

The primary products in the photochemical reaction consist largely of monovalent radicals arising from the photodissociation[12]

$$CH_3CHO + h\nu = CH_3 + HCO \qquad (1)$$

In the absence of oxygen this would be followed by[12a]

$$CH_3 + CH_3CHO = CH_4 + CH_3CO \qquad (2)$$

In the presence of oxygen it is plausible that O_2 adds directly to the CH_3CO forming a peroxidic radical. This radical is assumed to react further with acetaldehyde in a manner analogous to reaction (2). Since the only radicals regenerated

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(4) Norrish, *Proc. Roy. Soc.* (London), **A150**, 36 (1935).

(5) (a) Pease, THIS JOURNAL, **57**, 2296 (1935); (b) also, Pease and Munro, *ibid.*, **56**, 2034 (1934).

(6) Ubbelohde, *Proc. Roy. Soc.* (London), **A152**, 354 (1935).

(7) (a) Bone and Hill, *ibid.*, **A129**, 434 (1930); (b) Bone and Allum, *ibid.*, **A134**, 578 (1931); (c) Steacie and Plewes, *ibid.*, **A146**, 583 (1934).

(8) Bone and Gardner, *ibid.*, **A154**, 297 (1936).

(9) (a) Hatcher, Steacie and Howland, *Can. J. Research*, **7**, 149 (1932); (b) Pease, THIS JOURNAL, **55**, 2753 (1933).

(10) (a) Pope, Dykstra and Edgar, *ibid.*, **51**, 1875 (1929); (b) Fort and Hinshelwood, *Proc. Roy. Soc.* (London), **A129**, 284 (1930); (c) Askey, THIS JOURNAL, **52**, 974 (1930); (d) Bodenstein, *Z. physik. Chem.*, **B12**, 151 (1931).

(11) Bowen and Tietz, *J. Chem. Soc.*, 234 (1930); *cf.* Carruthers and Norrish, *ibid.*, 1036 (1936).

(12) (a) Leermakers, THIS JOURNAL, **56**, 1537 (1934); (b) Blacet, and Roof, *ibid.*, **58**, 278 (1936); (c) Rollefson, *J. Phys. Chem.*, **41**, 259 (1937).

are CH_3CO and $CH_3CO(OO)$ the chain would then be carried on essentially by the reactions

$$CH_3CO(OO) + CH_3CHO = CH_3CO + CH_3CO(OOH) \qquad (3)$$

$$CH_3CO + O_2 = CH_3CO(OO) \qquad (4)$$

At low temperatures the reaction stops at the peracid stage, the latter compound being formed in large amounts. If it is now assumed that chains are broken in the gas phase by

$$2CH_3CO(OO) = CH_3COOOOCCH_3 + O_2 \qquad (5)$$

a kinetic consideration shows that the reaction rate should be proportional to the square root of the light intensity and to the first power of the aldehyde concentration but independent of the oxygen concentration, as is found experimentally.[11]

At higher temperatures the reaction does not stop at the peracid stage and is assumed to lead to degradation reactions in rapid succession. This may be represented by

$$\begin{array}{r} RCH_2CO \xrightarrow{O_2} CO + H_2O + RCO \xrightarrow{O_2} \ldots.\ CO + H_2O + CH_3CO \\ \downarrow O_2 \quad (6) \\ HCHO^* + CO + OH \end{array}$$

It is not entirely justified to exclude the formation of intermediate aldehydes as has been done here. However, intermediate aldehyde stages seem to be traversed rapidly to formaldehyde. The approximate formulation (6) possesses kinetic advantages. The formation of formaldehyde in the last step of reaction (6) is accompanied by the evolution of approximately 110 kcal. which is adequate to excite the observed luminescence ("cool" flames).[6]

Comparison of the chain length in thermal decomposition and oxidation of aldehydes shows that the latter is far more rapid than the former.[10a,11,13]

Chain Mechanism in Hydrocarbon Oxidation.—Once aldehyde has been formed by some mechanism which will be discussed later, it partly oxidizes catalytically to peracid, the latter being destroyed to form carbon dioxide or, as may be supposed, sometimes dissociating into two monovalent radicals, a fraction of which enters the gas phase to give rise to chains. The carbon dioxide-forming reaction being catalyzed by potassium chloride, the production of chain carriers and therefore the rate of hydrocarbon oxidation should be slowed down in a potassium chloride-coated vessel as is found experimentally.[14]

The mechanism for the oxidation of methane exclusive of branching reactions may be visualized as follows:

Chain initiation

$$HCHO + O_2 \xrightarrow{\text{Surface}} HCO(OOH) \xrightarrow{\text{Surface}} HCOO + OH \qquad \text{I}$$

Methane oxidation chain

$$OH + CH_4 = CH_3 + H_2O \qquad \text{II}$$
$$CH_3 + O_2 = HCHO + OH \qquad \text{III}$$

Aldehyde oxidation chain

$$OH + HCHO = HCO + H_2O \qquad \text{IV}$$
$$HCO + O_2 = HO_2 + CO \qquad \text{V}$$
$$HO_2 + HCHO = CO + H_2O + OH \qquad \text{VI}$$

Chain breaking

$$OH \xrightarrow{\text{Surface}} \text{destruction} \qquad \text{VII}$$

Direct association of oxygen in reaction V in binary collisions would seem to be very improbable. Reaction VI conforms to the fact that the ultimate products of the chain oxidation of formaldehyde in the gas phase are carbon monoxide and water.[10b]

While most of the formaldehyde is oxidized in the gas phase, some of it diffuses to the wall and reacts there to form more radicals according to (I). Many of these radicals remain adsorbed on the wall and eventually recombine to form saturated products. Some diffuse into the gas phase and generate new reaction chains. Thus. the process accelerates slowly from an unnoticeable to a measurable reaction during which the formaldehyde increases to a concentration easily detectable analytically.[15] In agreement with this are the experiments of Bone and Gardner,[8] who found a pronounced auto-accelerating curve for the increase of formaldehyde concentration with time.[16]

For the oxidation of higher hydrocarbons the mechanism is analogous. The radical CH_3 now becomes RCH_2, etc. Such large radicals presumably can add O_2 directly in a binary collision forming RCH_2OO, thus allowing an explanation of the formation of methyl alcohol in mixtures

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(13) Sickman and Allen, THIS JOURNAL, **56**, 1251 (1934). See also Fletcher, *Proc. Roy. Soc.* (London), **A146**, 357 (1934).

(14) (a) Pease and Chesebro, *Proc. Nat. Acad. Sci.*, **14**, 472 (1928); (b) Pease, THIS JOURNAL, **51**, 1839 (1929); (c) Taylor and Riblett, *J. Phys. Chem.*, **35**, 2667 (1931).

(15) Bone and Wheeler, *J. Chem. Soc.*, **81**, 535 (1902), and many other investigators since.

(16) The exponential character of the curve does not seem to justify the opinion of these authors "that the formation of formaldehyde probably did not begin until after half way through the induction period."

containing a large excess of hydrocarbon. On analogy with Pease's[5a] mechanism we may write

$$RCH_2CH_2 + O_2 = RCH_2CH_2OO \longrightarrow RCHO + CH_3O \quad (7)$$

$$CH_3O + RCH_2CH_3 = CH_3OH + RCH_2CH_2 \quad (8)$$

The decomposition of the alkyl peroxide radical is in agreement with the similar behavior of saturated alkyl peroxides.[17] Now, the experimental data show that less alcohol is formed as the oxygen content of the mixture is increased[5a] and that finally the alcohol yield becomes negligible. Thus, in mixtures of 1 part of octane with 11 to 13 parts of oxygen, no alcohols are found.[10a] This fact may be accounted for by the destruction of methoxyl according to

$$CH_3O + O_2 = CO + H_2O + OH \quad (9)$$

It is evident that in very rich mixtures methyl alcohol and aldehydes should appear in approximately equal amounts, a fact borne out by experiment.[5a]

A further refinement of the proposed mechanism and enhancement of its chemical plausibility is obtained from experiments on the slow oxidation of rich mixtures of methane and ethane at high pressures.[18] In the case of methane, methyl alcohol is formed, the yield increasing with decrease in the oxygen content. It is only in mixtures containing a few per cent. of oxygen that the yield becomes large. The other products are carbon monoxide, carbon dioxide and water and a small amount of formaldehyde. In the case of ethane, both ethyl and methyl alcohols appear besides carbon monoxide, carbon dioxide and water. There are appreciable amounts of acetaldehyde, acetic acid and also methane. Increasing the oxygen content causes a decrease in the yields of the oxygenated organic compounds, but it is noted that the ethyl alcohol yield decreases very much more than the methyl alcohol.[18d]

To harmonize these facts, the following reaction will be assumed

$$CH_3 + O_2 + CH_4 = CH_3OOH + CH_3 \quad (10)$$

This reaction is favored by high pressures and rich mixtures. Concerning a direct proof of methyl peroxide formation, it is noted that this substance, as indeed others representative of this group, is highly unstable[17] and that there is no hope of isolating it from the reacting mixture, as has indeed been the experience.[7a,b,15,18b,c,d]

Methyl peroxide possesses a strong tendency to condense with aldehydes. With formaldehyde, oxydimethyl peroxide, $CH_3OOCH_2(OH)$, is formed.[17] The latter compound seems to possess a particular ability to dissociate at the peroxidic bond. This is evident by comparison of its behavior with that of the related compound dioxydimethyl peroxide, $CH_2(OH)O-OCH_2(OH)$, in alkaline solution. The latter decomposes into molecular hydrogen and formic acid* and the former partly into atomic hydrogen[17] and formic acid, indicating that the oxydimethyl peroxide undergoes primary dissociation into the radicals CH_3O and $CH_2(OH)O$.

It may be assumed, therefore, that in the high-pressure oxidation of methane, methyl peroxide and formaldehyde condense to oxydimethyl peroxide, which decomposes into radicals. A methyl alcohol chain then becomes possible involving reactions 8 (the hydrocarbon being methane), 10 and the last discussed condensation–dissociation reaction. The products carbon monoxide and formaldehyde would arise from reactions 9 and III. The mechanism thus accounts for the decreasing yield of methyl alcohol with increasing oxygen content. For the formation of carbon dioxide it is possible to propose other reactions such as the heterogeneous decomposition of oxydimethyl peroxide.[17]

If the same scheme is applied to the high-pressure oxidation of ethane, that is, starting correspondingly with ethyl peroxide and acetaldehyde, it is evident that methyl alcohol should appear as an oxidation product instead of water. The experimental facts concerning the total yields of oxygenated compounds and the ratio of the methyl and ethyl alcohol yields are also readily accounted for. Acetic acid probably arises from another decomposition reaction of oxydiethyl peroxide yielding also ethyl alcohol. Methane may arise from a side reaction conceivably involving the destruction of acetaldehyde.

It may be assumed that alkyl peroxide radicals condense similarly with aldehydes and dissociate at the peroxidic bond as postulated above. This would constitute a branching reaction (to be called peroxide branching) since two new free

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(17) Rieche, "Alkylperoxide und Ozonide," Steinkopff, Dresden, 1931.

(18) (a) Yoshikawa, *Bull. Inst. Phys. Chem. Res.* (Tokyo), **10**, 305 (1931); see *Abs. Sci. Papers Inst. Phys. Chem. Res.*, **16**, 1931; (b) Newitt and Haffner, *Proc. Roy. Soc.* (London), **A134**, 591 (1931); (c) Newitt and Bloch, *ibid.*, **A140**, 426 (1933); (d) Newitt and Szego, *ibid.*, **A147**, 555 (1934).

* See Rieche and Meister's [*Ber.*, **68B**, 1465 (1935)] mechanism of the decomposition of oxymethyl peroxide.

valences are thus created. Evidently the probability of this reaction would depend on the lifetime of the R-OO radical (reaction 7) and thus is favored by lower temperatures. This would explain the pronounced reactivity[14a,19] and explosivity[20] particularly of normal paraffins in the neighborhood of 350°, and the accompanying phenomenon of "cool" flames[10a,14a,20,21] (see Fig. 1). If the hydrocarbon contains side groups then, as first pointed out by Pope, Dykstra and Edgar,[22] the degradation reaction 6 on reaching the tertiary carbon atom would leave a ketone instead of an aldehyde. The ketone cannot be expected to undergo condensation with peroxide and thus the fact can be explained that isoparaffins exhibit the low temperature phenomena to a lesser and lesser degree as the structure of the molecule is more condensed.[20b,22]

The radicals arising from the peroxide branching reaction are expected to oxidize further. Judging from the reaction energy involved in the oxidation, other bonds may be broken and assuming OH to be the favored radical, as many as five OH may result.

If one assumes with Norrish that the explosion at higher temperatures is predominantly of the branched chain type, another branching reaction with a positive temperature coefficient must be advanced. Expressions suitable for the description of explosion limits and other facts are obtained by assuming that branching occurs in ternary collisions of the radical HO_2 with aldehyde and oxygen. The reaction may be supposed to involve the primary oxidation of the aldehyde to peracid and subsequent dissociation of the latter. From an energy point of view the reaction is plausible. It will be referred to as the peracid branching reaction. Altogether three free valences appear, yielding on further oxidation three OH. The reaction may be written

Peracid branching

$$HO_2 + O_2 + HCHO \text{ or } RCHO \longrightarrow 3OH \qquad \text{VIII}$$

In order to account for the influence of mixture composition on the ignition temperature, a reaction competing with reaction V will be assumed, namely

Formaldehyde condensation

$$HCO + HCHO \longrightarrow (CH(OH)CHO) \xrightarrow{O_2} 2CO + H_2O + OH \qquad \text{IX}$$

That such an assumption is not improbable, particularly if one of the reactants is a radical, is shown by the fact that condensation products of formaldehyde, polyoxymethylenes, are known, which at 240° in the gas phase retain molecular weights amounting to 6 to 8 fold HCHO.[23]

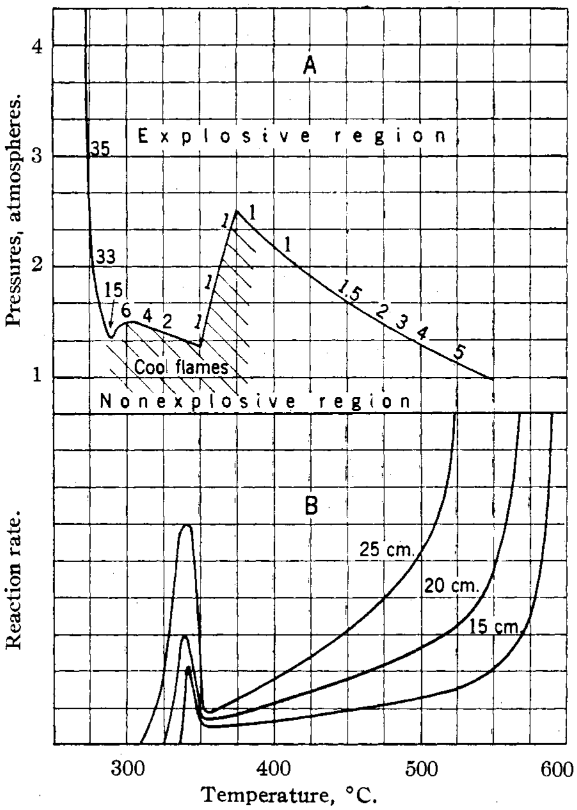

Fig. 1.—*Curve A:* Ignition region of 3.1% hexane in air mixture. Region of "cool flames" marked by shaded area. Induction periods in seconds indicated by numbers along curve (Townend, Cohen and Mandlekar reference 20b). *Curve B:* Reaction rates of 11.1% pentane in oxygen mixture at different pressures (Neumann and Aivazov reference 19a).

No crucial experiments seem to be available to rule out the possibility that methane explosions are thermal in nature in which case the peracid branching reaction VII could be dispensed with. However, the branched chain theory is adequate to describe the experimental results cited below.

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(19) (a) Neumann and Aivazov, *Nature*, **135**, 655 (1935); (b) Beatty and Edgar, THIS JOURNAL, **56**, 102 (1934).

(20) (a) Townend and Mandlekar, *Proc. Roy. Soc.* (London), **A141**, 484 (1933); *ibid.*, **A143**, 168 (1933); (b) Townend, Cohen and Mandlekar, *ibid.*, **A146**, 113 (1934); (c) Townend ,and Chamberlain, *ibid.*, **A154**, 95 (1936); (d) see also Prettre, Dumanois and Lafitte, *Compt. rend.*, **191**, 329 (1930).

(21) Emeléus, *J. Chem. Soc.*, 1733 (1929); Prettre, *Bull. soc. chim.*, **51**, 1132 (1932); Beatty and Edgar, THIS JOURNAL, **56**, 112 (1934).

(22) Pope, Dykstra and Edgar, *ibid.*, **51**, 2203 (1929).

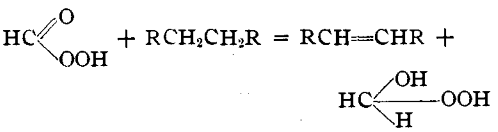
(23) Beilstein "Handbuch der organischen Chemie," 4th edition, Vol. I, 1918, p. 568.

Primary Reactions.—For the kinetic treatment, the only specific assumption concerning the primary reaction between hydrocarbon and oxygen that need be made is that it is, as mentioned above, an aldehyde producing reaction. It is difficult to obtain experimental facts pertaining to this reaction because it is obscured by the ensuing chain reaction. However, it appears to the authors that the most probable assumption is a catalytic reaction. If, for example, a mixture of methane and oxygen is passed through a porous porcelain filter at atmospheric pressure and 440°, formaldehyde and some methyl alcohol are found.[24] The presence of the latter substance is explained readily on the basis of catalytic combination of methane and oxygen to methyl peroxide, which subsequently reacts as explained under high pressure oxidation.

A possibility for a direct gas-phase reaction with oxygen, at least for higher paraffins, is suggested by Stephens'[25a] experiments on the oxidation of alkyl-substituted benzenes. That higher paraffin hydrocarbons react with oxygen at temperatures as low as 130° to form explosive peroxides among other products, is well known.[25b]

At very high temperatures one may also consider the primary reaction to involve atoms or radicals originating from thermal dissociation.

Secondary Reactions.—Before leaving the chemical part of this paper, attention may be called to the fact that there are a number of secondary reactions of the non-chain type. Some of those which lead to oxygen-ring compounds have been studied by Ubbelohde.[26] A particularly common type is one that gives rise to the simultaneous appearance of olefins and oxyalkyl peroxides.[5b] This reaction can best be understood as the interaction of a newly formed peracid molecule with a hydrocarbon molecule.



$$\mathrm{HC}{\overset{\displaystyle O}{\underset{\displaystyle OOH}{<}}} + \mathrm{RCH_2CH_2R} = \mathrm{RCH{=\!=}CHR} + \mathrm{HC}{\overset{\displaystyle OH}{\underset{\displaystyle H}{\text{———}}}}\mathrm{OOH} \qquad (11)$$

Mono-oxyalkyl peroxides are surprisingly non-explosive,[17] which accounts for the fact that they can be isolated at the high temperatures of the oxidation. They have been observed in the oxidation of hydrocarbons from ethane[7a] upward only, which is understandable in view of the fact that peracid cannot react with methane, as in reaction 11. By condensation with aldehydes they give rise to more complicated products.[27]

Kinetics of the Oxidation

Methane.—In the following, the symbols k_1, k_2, etc., are the velocity coefficients for the corresponding reactions in the mechanism I to IX. Concentrations in the gas phase are indicated by brackets. By assuming weak adsorption the rate of reaction I becomes on the basis of the Langmuir isotherm

$$(k_1/d)\ [\mathrm{HCHO}][\mathrm{O_2}] \qquad (12)$$

where d is diameter of the vessel.

It has been shown[28] that for the case of chain initiation at the wall the following equation obtain

$$\frac{2\lambda}{\epsilon r}\ \gamma m_0 + \alpha\bar{n} = \frac{\pi^2 D}{r^2}\ \bar{n} \qquad (13)$$

$\bar{n}$ is the average concentration of chain carriers, λ is the mean free path, r the radius of a spherical reaction vessel, ϵ the chain breaking efficiency of the wall, γ the ratio of surface to volume of the vessel, m_0 the rate of chain initiation per unit surface, α the velocity coefficient of chain branching and D the diffusion coefficient. This equation is a good approximation of the exact diffusion equation for the steady state and for the usual case that $\lambda/\epsilon r \ll 1$.[28]

π^2D/r^2 will be replaced by $k_7/[M]d^2$ and $2\lambda/\epsilon r$ will be replaced by $k/[M]d$ where $[M]$ is the total concentration.

The concentration of formaldehyde in the gas phase reaches a maximum determined from the relative rates of aldehyde forming and destroying reactions. It is given by

$$[\mathrm{HCHO}]_{\mathrm{max.}} = \frac{k_2}{2k_4}\ [\mathrm{CH_4}] \qquad (14)$$

From equation (13) and the reaction mechanism I to IX

$$\frac{kk_1}{[\mathrm{M}]d^2}\ [\mathrm{HCHO}]_{\mathrm{max.}}[\mathrm{O_2}] + \frac{k_4k_5k_8[\mathrm{HCHO}]_{\mathrm{max.}}[\mathrm{O_2}]^2}{k_6(k_5[\mathrm{O_2}] + k_9[\mathrm{HCHO}]_{\mathrm{max.}})}\ [\mathrm{OH}] = \frac{k_7}{[M]d^2}\ [\mathrm{OH}] \qquad (15)$$

whence, for $k_9[\mathrm{HCHO}]_{\mathrm{max.}} \ll k_5[\mathrm{O_2}]$, the rate of methane oxidation for the steady state is given by

$$-\frac{\mathrm{d}[\mathrm{CH_4}]}{\mathrm{d}t} = \frac{k_1k_2{}^2k}{2k_4}\ \frac{[\mathrm{CH_4}]^2[\mathrm{O_2}]}{k_7 - (k_2k_8/2k_6)[\mathrm{CH_4}][\mathrm{O_2}][M]d^2} \qquad (16)$$

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[24] Newitt and Gardner, *Proc. Roy. Soc.* (London), **A154** 329 (1936).

[25] (a) Stephens, This Journal, **50**, 2523 (1928); (b) Grün, *Ber.*, **53**, 987 (1920).

[26] Ubbelohde, *Proc. Roy. Soc.* (London), **A152**, 378 (1935).

[27] This accounts for the peroxides isolated by Mondain-Monval, and Quanquin [*Ann. Chim.*, **15**, 309 (1931)] and others.

[28] Von Elbe and Lewis, This Journal, **59**, 970 (1937).

Equation (16) shows that if the negative term in the denominator is small compared with k_7 the rate should be independent of the diameter of the vessel. This has been reported[29] for ethane–oxygen mixtures at low pressures (a few mm.) and at about 600° in silica vessels etched with hydrofluoric acid, the latter apparently having the effect of producing a surface of more or less uniform and also enhanced catalytic activity.[29,30] It appears that under these conditions the negative term, which is strongly dependent on pressure, is small. On the other hand, experiments on methane at 650° and at much higher pressures (atmospheric) show a decrease of the reaction rate on decreasing the dimensions of the vessel (packing).[14a] This is consistent with equation (16).

If, in a given vessel at constant temperature and pressure, the mixture composition is changed, equation (16) indicates a maximum reaction rate for a mixture containing between 50 and 66.7% methane in oxygen, the former percentage corresponding to a minimum of the denominator and the latter percentage to a maximum of the numerator. At atmospheric pressure and 447°, Bone and Allum[7b] found that a mixture containing 66.7% methane reacts faster than mixtures containing 50 or 75% methane. Intermediate points were not recorded.

Equation (16) shows that the reaction rate depends on a power of the methane concentration exceeding 2 and on a power of the oxygen concentration exceeding 1, depending on the magnitude of the negative term in the denominator compared with k_7. This is borne out by the experiments of Fort and Hinshelwood[10b] at 467° and pressures ranging from 300 to 600 mm.

The nature of the surface enters into the coefficients k_1 and k. Since the surface is likely to undergo imperceptible changes during the reaction, the rate should be erratic and unpredictable as is the general experience in untreated vessels.[31]

Concerning the explosive reaction it would be inconsistent to follow Semenoff's[32] suggestion of "degenerate" explosions for hydrocarbons since his suggestion becomes plausible only if an active intermediate of long lifetime were formed, reacting independently of the main chain reaction. No compelling reason for the suggestion is seen in the apparently continuous acceleration of the rate curves up to the inflection point since the steady-state treatment given in this paper would give the same type of curve on considering the consumption of the reactants. The condition for explosion is found to be

$$\frac{k_4k_5k_8[O_2]^2[HCHO]_{\text{max.}}}{k_6(k_5[O_2] + k_9[HCHO]_{\text{max.}})} = k_7/[M]d^2 \qquad (17)$$

It may be surmised that the actually observed explosion limit is somewhat affected by the rate of heat liberation, that is, the reaction rate. This would explain why the explosion limits depend somewhat upon the nature of the surface[20c,33] which enters into the coefficients k and k_1.

The sum of the energies of activation of reactions II and VIII is most probably larger than the energy of activation of reaction VI; the sum of the energies of reactions II and IX is larger than the sum for reactions IV and V. $[M]$ is equal to the sum of the concentrations $[CH_4] + [O_2] + [X]$, where $[X]$ is the concentration of any foreign gas. Combining equations (14) and (17) and substituting temperature functions, one obtains

$$([CH_4] + [O_2] + [X])\frac{[CH_4][O_2]^2}{[O_2] + K'e^{-A'/T}[CH_4]} = \frac{K}{d^2}e^{A/T} \qquad (18)$$

The ignition temperature should increase with decreasing vessel dimensions. This has been confirmed by experiments at 1 atmosphere pressure.[33,34]

Equation (18) reduces approximately to

$$\log P = (A/T) + B \qquad (19)$$

A and B being constants; the experimental curves have often been expressed by equations of this type.[14c,31]

If foreign gas, such as argon, is added to the mixture without affecting the concentrations of CH_4 and O_2 (that is, total pressure is increased), the ignition temperature should decrease. This has been found experimentally.[35] If part of the combustible mixture is replaced by foreign gas leaving the sum of the concentrations the same, the ignition temperature should increase. This also has been observed.[36] Moreover, if helium is substituted for argon, the ignition temperature is higher,[36] corresponding to the larger

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[29] Sadownikow, *Phys. Z.* (U. S. S. R.), **4**, 735 (1933).

[30] Kowalsky, Sadownikow and Tschirkow, *ibid.*, **1**, 451 (1932).

[31] Sagulin, *Z. physik. Chem.*, **B1**, 275 (1928); compare reference 14c with Neumann and Serbinow, *Phys. Z.* (U. S. S. R.), **1**, 536 (1932).

[32] N. Semenoff, "Chemical Kinetics and Chain Reactions," Oxford University Press, Oxford, Eng., 1934.

[33] Mason and Wheeler, *J. Chem. Soc.*, 2079 (1922).

[34] Taffanel and Floch, *Compt. rend.*, **157**, 469 (1913).

[35] Neumann and Serbinow, *Phys. Z.* (U. S. S. R.), **4**, 433 (1933).

[36] Naylor and Wheeler, *J. Chem. Soc.*, 2456 (1931).

value of the diffusion coefficient which enters into k_7 and, therefore, K.

If the ratio of methane to oxygen is changed, leaving the sum of the concentrations constant, the ignition temperature should pass through a minimum for a mixture ratio $CH_4:O_2 < 1:1$. Only if the term $K'e^{-A'/T}[CH_4]$ in the denominator of (18) were negligible would this minimum occur at a ratio 1:1. The larger this term is the more the minimum is shifted to leaner mixtures. Since the term becomes larger toward higher temperatures, mixtures diluted with foreign gas should exhibit a shift of the minimum ignition temperature to smaller ratios of $CH_4:O_2$ than is found in the undiluted mixture. In fact, at 1 atmosphere total pressure the minimum ignition temperature for undiluted mixtures has been found at a ratio of about 1:2, whereas using argon as diluent (O_2:A the same as $O_2:N_2$ in air) the minimum is at a ratio 1:3.6.[36] If the ignition temperature is increased still further by replacing argon by helium, the minimum is at a ratio 1:4.[36]

If the size of the vessel is decreased, thus increasing the ignition temperature, the minimum again shifts toward leaner mixtures.[36]

If the total pressure is increased, thus lowering the ignition temperature, the minimum shifts toward richer mixtures.[20c]

According to equation (17), it should be possible to induce explosions by the addition of formaldehyde in excess of $[HCHO]_{max}$. Smaller amounts should not lower the ignition temperature although they should decrease the induction period. Actually, formaldehyde added in amounts of 1 to 2% substantially lowers the ignition temperature;[20c] in amounts of about 0.027% practically no lowering is observed, but the induction period is markedly shortened.[36] That $[HCHO]_{max.}$ is smaller than 1% appears from the fact that in the non-explosive oxidation of CH_4, formaldehyde is found only in traces.[7b]

Higher Hydrocarbons.—The mechanism of the oxidation of higher hydrocarbons consists of the following reactions and the former reactions IV to IX.

Initiation

$$RCHO + O_2 \xrightarrow{\text{surface}} RCO(OOH) \xrightarrow{\text{surface}} RCOO + OH \qquad \text{I}$$

Hydrocarbon oxidation chain

$$OH + RCH_3 = RCH_2 + H_2O \qquad \text{II}$$

$$RCH_2 + O_2 = RCH_2OO \qquad \text{III}$$

$$RCH_2OO = R'CHO + CH_3O \xrightarrow{O_2} CO + H_2O + OH \qquad \text{X}$$

Peroxide branching

$$RCH_2OO + RCHO = (RCH_2O - OC(OH)R) \xrightarrow{O_2} 5OH \qquad \text{XI}$$

Degradation reaction

$$RCHO + OH = H_2O + RCO \xrightarrow{O_2} CO + H_2O + R'CO \xrightarrow{O_2} \ldots$$

$$CO + H_2O + CH_3CO \xrightarrow{O_2} HCHO^* + CO + OH \qquad \text{XII}$$

The condition for explosion is now found to be

$$\underbrace{\frac{k_2k_{11}}{k_{10}}[RCH_3][Ad]_{max.}}_{\text{Peroxide branching}} + \underbrace{\frac{k_4k_5k_8[O_2]^2[Ad]_{max.}}{k_6(k_5[O_2] + k_9[HCHO]_{max.})}}_{\text{Peracid branching}} = k_7/[M]d^2 \qquad (20)$$

where $[Ad]_{max.}$ is now the total maximum aldehyde concentration and equals

$$[Ad]_{max.} = \left(\frac{2k_4}{k_{12}} - 1\right)[HCHO]_{max.} = \frac{k_2}{2k_4}\left(\frac{2k_4}{k_{12}} - 1\right)[RCH_3] \qquad (21)$$

As before, the nature of the surface has been found to influence somewhat the explosion limits.[14c,20]

Since the peracid branching term is small at low temperatures and moderate pressures, the peroxide branching term must be large in order to fulfill the explosive condition (20). Since the radical R-OO is considered to have a long lifetime at low temperatures, the peroxide branching term is largely dominated by reaction X and is proportional to $Te^{A/T}[RCH_3]^2$. This term increases with decreasing temperature, tending toward infinity, thus accounting for the pronounced explosivity toward lower temperatures. The reason the reaction becomes non-explosive again at still lower temperature may be due to the greater stability toward oxidation of the condensation product in reaction XI and a gas phase chain breaking process involving the combination of two R-OO radicals. That the reaction becomes non-explosive at low pressures can be seen from equation (20). Thus, in a qualitative way, the peninsula shape of the explosion region and the maximum in the reaction rate may be accounted for.

It is reasonable to assume that the activation energies of the reactions in question are more or less independent of the length of the paraffin molecule so that the temperature limit of the peninsula is approximately the same for all higher paraffins.

Equation (20) in combination with (21) shows that for richer mixtures the explosion limit should be shifted toward lower pressures, which has been observed.[20] Decreasing the vessel diameter narrows the explosion region;[14c,20] if this is carried to the extreme by packing, the reaction, explosive or non-explosive, is entirely suppressed.[14a] Since, due to the intensity of peroxide branching, the concentration of excited formaldehyde becomes rather high, it is understandable that the luminescence should become pronounced ("cool" flames). Simultaneously the induction periods become very short[20] (see Fig. 1). If aldehyde is added to the mixture, branching becomes large immediately. In ethane, where the peninsula is weakly developed, addition of 1 to 2% of acetaldehyde brings out the peninsula phenomenon sharply and reduces the induction period prior to explosion from hours to seconds.[20c]

If the aldehyde added exceeds $[\mathrm{Ad}]_{\mathrm{max.}}$, the explosion region should widen progressively with increasing amounts. Also, the nature of the aldehyde should make little difference. These facts have been observed.[20]

If the energy of activation of reaction II exceeds that of reaction IV the value of $[\mathrm{Ad}]_{\mathrm{max.}}$ should increase toward higher temperatures. This explains the decreased effect of aldehyde on the position of the explosion limits toward higher temperatures.[20,37]

At higher temperatures the peracid branching term becomes predominant, and the ignition characteristics of higher hydrocarbons approach those of methane. The limits are generally lower, which is consistent with the larger $[\mathrm{Ad}]_{\mathrm{max.}}$ as compared with $[\mathrm{HCHO}]_{\mathrm{max.}}$ Comparing the explosion regions of methane[20c] and also isobutane[20b] with those of normal paraffins, it may be estimated that peroxide branching predominates up to about 400° whereas peracid branching predominates above about 500°.

That addition of foreign gas without altering the concentrations of the reactants produces the same effect as it does in methane, namely, lowers the ignition temperature, is shown in hexane–air and hexane–oxygen explosions.[20b] Likewise, if a part of the mixture is replaced by foreign gas, the ignition temperature is increased.[20b]

Experiments are available on the effect of mixture composition on the minimum ignition pressure in the region of predominant peracid branching as defined above. According to equation (20) toward lower temperatures the minimum should again shift from a mixture ratio of less than 1:1 to 1:1. At about 680° a minimum ignition pressure was found for a pentane–oxygen mixture having a ratio about 1:2.[31] At a considerably lower temperature, 480–520°, a minimum was found for an ethane–oxygen mixture having a ratio 1:1.[14c]

Studies of reaction rates are not apt to lead to simple relationships since branching of one type or another appears over the whole temperature range. As long as peroxide branching is predominant the equation for the reaction rate (same as equation (16) with peroxide branching term replacing peracid branching term) indicates that the most reactive mixture should be far on the rich side, >2:1. Measurements show that the rate is still increasing for a 2:1 mixture.[7a]

Summary

It is pointed out that there are certain shortcomings in existing theories which are overcome in the proposed theory. The concept of chain initiation *via* aldehyde is seen to require discussion of aldehyde oxidation. A chain mechanism consistent with experimental facts and chemical plausibility is described. The chain mechanisms of aldehyde and hydrocarbon oxidation are linked to each other and combined with a modified form of Pease's mechanism for higher hydrocarbons. Plausible relations between the high pressure oxidation of methane and ethane and the chemistry of peroxides are discussed. From this, a branching reaction involving alkyl peroxides and aldehydes which is operative predominantly at low temperatures is shown to be plausible chemically. It is called "peroxide branching" to distinguish it from "peracid branching" operative predominantly at high temperatures. The mechanisms of primary aldehyde forming reactions and secondary non-chain reactions are discussed. It is shown that kinetic facts concerning the slow reaction and explosion limits of methane are consistent with the scheme; that certain phenomena exhibited by higher hydrocarbons at relatively low temperatures (ex-

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(37) This also explains why in ethane–oxygen mixtures, Bone and Hill[7a] observed an explosion induced by 1% acetaldehyde, whereas Steacie and Plewes[7c] did not. The former worked at 316° and the latter at 452° (*cf.* Townend and Chamberlain).[20c]

plosion peninsula, maximum in the reaction rate, "cool" flames) can be described by peroxide branching; and that peracid branching can describe the explosion limits of higher hydrocarbons at high temperatures.

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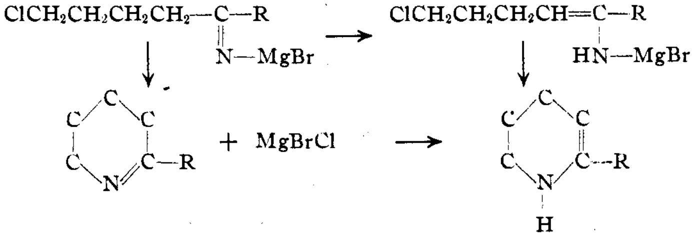
[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE]

Synthesis of Some New Alpha-Substituted Tetrahydropyridines and Piperidines[1]

BY RICHARD SALATHIEL, J. MARVIN BURCH AND R. M. HIXON

A general method for the preparation of α-substituted tetrahydropyridines has been developed, a preliminary report of which was presented by Starr and Hixon,[2] who reported the preparation of α-phenyltetrahydropyridine. This preparation followed the general plan of the method used by Craig, Bulbrook and Hixon,[3] who reported the preparation of α-substituted pyrrolines by a modification of Cloke's reaction.[4] This paper extends this synthesis to the preparation of other compounds in this series, and to the preparation of the corresponding piperidines.

The reactions involved are first the reaction of a Grignard reagent with δ-chlorovaleronitrile to form the mixed magnesium bromide salt of a δ-chlorobutylketimine, $Cl(CH_2)_4CM + RMgBr \longrightarrow ClCH_2CH_2CH_2CH_2—CR{=}NMgBr$, and second the closing of the ring which is accomplished by replacing the ether in the reaction mixture with xylene and raising the temperature. Expressing this reaction by equations completely analogous to those proposed by Craig, Bulbrook and Hixon,[3] two possible mechanisms are shown.



Experimental Part

δ-Chlorovaleronitrile, b. p. 118–121° (25 mm.), was prepared as described by Starr and Hixon.[2]

α-Phenyltetrahydropyridine.—A Grignard reagent was prepared from 4.86 g. of magnesium, 34.5 g. of bromobenzene and 160 cc. of ether. A solution of 23.5 g. of δ-chlorovaleronitrile in 25 cc. of ether was added dropwise, as the reaction mixture was stirred and refluxed. The addition product, a heavy viscous colorless liquid, separated from the solvent. The ether was removed by distillation from an oil-bath, the volume in the flask being kept constant by the addition of xylene. When the temperature in the flask reached 130–135°, the liquid addition product quickly changed to a solid, semi-crystalline, yellow mass. Heating just sufficient to reflux the xylene was continued for an hour. The material was cooled and hydrolyzed, using 130 cc. of hydrochloric acid (sp. gr. 1.10). The xylene layer was separated and extracted again with hydrochloric acid. The acid solution was extracted with 20 cc. of petroleum ether to remove residual xylene, then made strongly basic with sodium hydroxide and extracted with ether. The ether extract was dried and fractionated. There was collected at 142–150° (20 mm.) 21 g. of a nearly colorless oil, which turns brown quickly on exposure to air. The yield is 66% of the theoretical.

The hydrochloride, precipitated from aqueous acetone, melted at 86–87° as reported by Gabriel[5] but when dried in a current of warm air the melting point becomes 152–153°. Other derivatives, the picrate, m. p. 181.5°, and the mercuric chloride–hydrochloride double salt, m. p. 165–166°, were prepared.

α-(*p*-Chlorophenyl)-tetrahydropyridine.—A Grignard reagent prepared from 2.43 g. of magnesium, 21.1 g. of *p*-chlorobromobenzene and 125 cc. of ether, was added to a solution of 11.8 g. of δ-chlorovaleronitrile. A procedure similar to that for α-phenyltetrahydropyridine yielded 9.5 g. of a colorless base boiling at 165° (13 mm.) which crystallized in the receiver, m. p. 54°. The yield is 49% of the theoretical.

A picrate, m. p. 177–178°, was crystallized from an alcohol solution. A mercuric chloride–hydrochloride double salt, m. p. 133–135°, a chloroplatinate, m. p. 192°, and a hydrochloride, m. p. 215–217°, were prepared from aqueous solutions.

Anal. Calcd. for $C_{11}H_{12}ClN{\cdot}HCl$: N, 6.09. Found: N, 6.19, 6.15.

α-(*p*-Tolyl)-tetrahydropyridine.—A Grignard reagent prepared from 2.5 g. of magnesium turnings, 21 g. of *p*-bromotoluene and 120 cc. of ether was treated with 11.7 g. of δ-chlorovaleronitrile. The product was obtained by a procedure similar to that for α-phenyltetrahydropyridine. The major portion of the 9 g. of the product distilled over at 145° (13 mm.). The yield is 52% of the theoretical.

The following derivatives were prepared: chloroplati-

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[1] Supported in part by grants from the Rockefeller Fluid Research Fund and from the Industrial Science Research Funds of the Iowa State College.

(2) Starr and Hixon, THIS JOURNAL, **56**, 1595 (1934).

(3) Craig, Bulbrook and Hixon, *ibid.*, **53**, 1831 (1931).

(4) Cloke, *ibid.*, **51**, 1174 (1929).

(5) Gabriel, *Ber.*, **41**, 2012 (1908).