THE MECHANISM OF THE COMBUSTION OF HYDROCARBONS[1]

GUENTHER VON ELBE

Coal Research Laboratory, Carnegie Institute of Technology, Pittsburgh, Pennsylvania

AND

BERNARD LEWIS

Explosives Division, Pittsburgh Experiment Station, U. S. Bureau of Mines, Pittsburgh, Pennsylvania

Received July 17, 1937

The purpose of this paper is to present a critical comparison of recent theories suggested by Norrish and Foord (6), Ubbelohde (13), Jost and coworkers (4), Pease (7), Semenoff (12), and von Elbe and Lewis (14) for the mechanism of the combustion of hydrocarbons. The subject may be divided into the chemical mechanism and the kinetics of the oxidation. A detailed description will not be presented, the object being to discuss viewpoints on subjects touched on by several authors.

THE CHEMICAL MECHANISM

The unbranched-chain reaction

It is generally agreed that the oxidation of hydrocarbons occurs by a chain mechanism and that aldehydes appear as intermediates. Both Ubbelohde and von Elbe and Lewis formulate the chain reaction on the basis of evidence obtained in the oxidation of aldehydes. The latter reaction is also of the chain type, and it is reasonable to assume that both the above chain reactions are interdependent. Ubbelohde follows Bäckstrom's (1) mechanism by which the aldehyde oxidation chain is initiated by the formation of a radical RCO which then reacts according to the scheme:

$$\mathrm{RCO} \xrightarrow{O_2} \mathrm{RCO(OO)} \xrightarrow{\mathrm{RCHO}} \mathrm{RCO(OOH)} + \mathrm{RCO} \qquad (1)$$

According to Ubbelohde, in the presence of a paraffin hydrocarbon

$$\mathrm{RCO(OO)} + \mathrm{RCH_3} \rightarrow \mathrm{RCO(OOH)} + \mathrm{RCH_2} \xrightarrow{O_2}$$

$$\mathrm{RCH_2OO} \xrightarrow{\mathrm{RCH_3}} \mathrm{RCH_2OOH} + \mathrm{RCH_2} \qquad (2)$$

[1] Published by permission of the Director, U. S. Bureau of Mines, and Director, Coal Research Laboratory, Carnegie Institute of Technology. (Not subject to copyright.)

The alkyl peroxide undergoes decomposition

$$RCH_2OOH \rightarrow RCHO + H_2O \qquad (3)$$

a reaction of which the peroxide radical may also be capable, to give either aldehyde and OH or aldehyde radical and H_2O. Such suggestions are also advanced by Jost and coworkers. For the formation of the main oxide of carbon, namely carbon monoxide, Ubbelohde, as well as Jost, proposes the subsequent decomposition of the aldehyde formed in reaction 3, or of the aldehyde radical formed in reaction 1, leaving the saturated hydrocarbon or hydrocarbon radical, respectively. As a side reaction, Ubbelohde proposes the occasional transformation of the hydrocarbon radical into olefin and hydrogen atom; this, however, is a strongly endothermic process. Having shown experimentally the formation of oxygen ring compounds in the higher paraffin series, he arrives at a simple mechanism for such ring formation from peroxide radicals. Furthermore, the formation of alcohols at high pressures is accounted for by the interaction of two peroxide radicals to yield two molecules of alcohol and O_2.

von Elbe and Lewis arrive at Bäckstrom's mechanism (reaction 1) from the following independent evidence. In the photochemical decomposition of aldehydes, monovalent radicals are formed; in the photoöxidation of aldehydes higher than formaldehyde, peracids are formed by a chain mechanism. These two facts alone make reaction 1 the only plausible one, and in addition this mechanism correctly describes the dependence of the yield on light intensity and concentrations of reactants. According to von Elbe and Lewis, the decomposition of aldehydes or their radicals into carbon monoxide and hydrocarbon or radical is not plausible. This is shown particularly by the experiments of Pope, Dykstra, and Edgar (8) on the thermal decomposition of aldehydes. However, it is very plausible that the peracid or its radical should decompose at the high temperature, for example, according to the scheme:

$$RCH_2CO(OO) \begin{cases} \nearrow RCHO + CO + OH & (4a) \\ \searrow RCO + CO + H_2O & (4b) \end{cases}$$

This would agree with Pope, Dykstra, and Edgar's overall "degradation" reaction which in normal paraffins ultimately leads to formaldehydes and which in iso-paraffins is interrupted at the ketone stage (9). Various possibilities of this interruption have been discussed by Jost.

For the oxidation of an alkyl radical, Pease proposed the following chain instead of the second and third steps in reaction 2,

$$RCH_2CH_2 \xrightarrow{O_2} RCHO + CH_3O \xrightarrow{RCH_2CH_3} CH_3OH + RCH_2CH_2 \qquad (5)$$

since he observed the formation of large amounts of methyl alcohol at moderate temperatures in rich mixtures of propane and oxygen. In order to reconcile this mechanism with the probable appearance of alkyl peroxides as proposed by Ubbelohde, which is made plausible by the appearance of a low-temperature branching reaction (see below), and with the absence of methyl alcohol in lean mixtures of propane and oxygen, von Elbe and Lewis introduced the following modification of reaction 5:

$$RCH_2CH_3 \xrightarrow{O_2} RCH_2CH_2OO \rightarrow RCHO + CH_3O \begin{cases} \xrightarrow{RCH_2CH_3} CH_3OH + RCH_2CH_2 \\ \xrightarrow{O_2} CO + H_2O + OH \end{cases} \quad (6)$$

If the alkyl radical is CH_3, a direct association with O_2 is very improbable, as is indicated by the work of Kimball (5). This also applies to the formaldehyde radical HCO. Therefore, for ordinary pressures, von Elbe and Lewis postulate

$$CH_3 + O_2 \rightarrow HCHO + OH \quad (7)$$

$$HCO + O_2 \rightarrow CO + HO_2 \quad (8)$$

HO_2 reacting according to

$$HO_2 + HCHO \rightarrow CO + H_2O + OH \quad (9)$$

In the oxidation of rich mixtures of methane at high pressures CH_3OO may be formed in three-body collisions and give rise to methyl alcohol by various reactions, involving presumably the primary condensation of methyl peroxide or its radical with formaldehyde, followed by dissociation at the peroxidic bond. This corresponds to the peroxide studies of Rieche and coworkers (10). This hypothesis proves to be fruitful in accounting not only for the experimental facts connected with the high-pressure oxidation of methane and ethane, but also for the low-temperature branching of higher paraffins (see below). In particular, in the high-pressure reaction the effect of mixture composition on the alcohol yields is explained by the susceptibility to oxidation of the alkoxyl radical as in reaction 6. The suggestions of Jost and coworkers concerning alcohol formation at high pressures are not far removed from the above: A ternary collision between alkyl radical, O_2, and hydrocarbon molecule is postulated to lead either immediately to alcohol and alkoxyl or to alkyl peroxide and

an alkyl radical, the peroxide to dissociate into OH and alkoxyl, the latter giving rise to alcohol.

Norrish's chain mechanism is based entirely on the alternate appearance of oxygen atoms and alkylene radicals which, for methane, he writes

$$O + CH_4 \rightarrow CH_2 + H_2O \quad (10)$$

$$CH_2 + O_2 \rightarrow HCHO + O \quad (11)$$

and for formaldehyde oxidation as an unspecified chain mechanism involving oxygen atoms. At high pressure, oxygen atoms are assumed to combine with hydrocarbons in a three-body collision to form alcohols. The reaction constitutes a chain-breaking process in the gas phase which is of the first order with respect to the chain carrier. A similar chain-breaking process with monovalent radicals is impossible. A number of objections to the oxygen atom mechanism have been advanced by Ubbelohde, Jost, and von Elbe and Lewis, among which two may be mentioned here. If oxygen atoms are introduced into hydrocarbons at room temperatures, emission of the band spectra of C_2, CH, and OH occurs; that is, radicals appear possessing a different number of free valences than the oxygen atom. In the slow oxidation of methane these spectra are not emitted. Instead there is the fluorescence spectrum that has been found to arise from excited formaldehyde. If oxygen atoms were participating in the mechanism, the absence of bands of C_2, CH, and OH would be difficult to explain. A second objection is that a reaction between an oxygen atom or a bivalent radical with a saturated molecule can easily be conceived as leading to two monovalent radicals which should exhibit the properties of chain carriers. The reverse process—namely, the formation of bivalent from monovalent radicals—would require the reaction of two monovalent radicals, which would be a very rare event in view of their low concentration.

The view is generally accepted that at ordinary pressures chains are broken principally at the wall.

Chain branching

The low-temperature reactivity and explosivity of higher hydrocarbons can be explained by assuming a branching reaction with an optimum probability in a certain temperature range. Ubbelohde suggests branching to occur on collision of an energy-rich peroxide with hydrocarbon to yield water, alkyl radicals, and alkoxyl radicals or to occur in a triple collision between two hydrocarbon molecules and a peroxide radical to yield two alkyl and one alkoxyl radicals. Assuming the lifetime of the peroxide molecule or its radical to be limited by the decomposition reaction (3) and to be shorter the higher the temperature, branching is favored at

lower temperatures. Essentially the same idea is proposed by Jost. On the other hand, von Elbe and Lewis propose a branching reaction which had already successfully accounted for the alcohol yields in the high-pressure reactions and was supported by the chemistry of peroxides. According to this, the breaking of the peroxidic bond is sensitized by the condensation of the peroxide or its radical with aldehyde. This branching mechanism accounts for the influence of aldehyde on the low-temperature explosion peninsula, which is not described by the alternative branching mechanisms of Ubbelohde and Jost. The branching probability is largely determined by the lifetime of the peroxide radical, which is governed by a decomposition reaction analogous to reaction 3. The absence of a low-temperature explosion peninsula in methane is easily understood by the inability of methyl radicals to form methyl peroxide radicals except in triple collisions. The gradual disappearance of the low-temperature explosion peninsula in higher paraffins having more condensed structures is again connected with their decreasing ability to form aldehydes.

The oxygen atom mechanism of Norrish apparently does not admit a similar set of plausible competing reactions.

The explosion limit of methane and the high-temperature explosion limits of higher hydrocarbons can be explained, according to von Elbe and Lewis, by another branching reaction:

$$HO_2 + HCHO + O_2 \rightarrow 3OH + CO_2$$

or (12)

$$HO_2 + C_nH_{2n+1}CHO + O_2 \rightarrow 3OH + CO_2 + \cdots n(CO + H_2O)$$

competing with a reaction involving primary formaldehyde condensation, namely,

$$HCO + HCHO \rightarrow (CH(OH)CHO) \xrightarrow{O_2} 2CO + H_2O + OH \quad (13)$$

The necessity for introducing reactions of this kind depends on whether one considers the high-temperature explosion to be of the thermal or branched-chain type. This will be discussed below.

KINETICS

The steady-state rate

Detailed kinetic treatments are to be found in the work of Norrish and Foord, which is confined to methane, and in the work of von Elbe and Lewis. Both treatments are based on the production of chain carriers by aldehyde, assumed to be a homogeneous reaction by Norrish and Foord and a heterogeneous reaction by von Elbe and Lewis, and the destruction and production of aldehyde by chain mechanisms. Since in von Elbe and

Lewis' treatment the concentration of formaldehyde at the surface is assumed to be proportional to the gas-phase concentration, both mechanisms are kinetically equivalent, except for the homogeneous alcohol-forming chain-breaking reaction of Norrish and the branching reactions of von Elbe and Lewis. For the case of negligible branching and neglecting the alcohol-forming reaction, the steady-state rate following the establishment of the maximum aldehyde concentration is in both cases proportional to the square of the hydrocarbon concentration and the first power of the oxygen concentration. If aldehyde forms chain carriers in the gas phase, then for a chain-breaking efficiency of the wall that is large compared with the ratio of the mean free path to vessel diameter, the reaction rate is proportional to the total pressure and the proportionality factor in the rate equation is independent of the nature of the surface (15). If the chain-breaking efficiency is small compared with the above ratio, the rate becomes inversely proportional to the chain-breaking efficiency, but the additional pressure factor in the rate equation disappears (15). In the first of the above cases the rate is proportional to the square of the diameter and in the second case to the first power of the diameter.

If aldehyde forms chain carriers at the wall, no additional pressure factor enters into the rate equation, and the proportionality factor always depends on the nature of the surface (15). As long as branching is negligible the rate is independent of diameter.

The pronounced effect of surface on the rate rules out the first case under the formation of chain carriers from aldehyde in the gas phase. Concerning the second case, it is not very probable that vessels having walls of extremely low chain-breaking efficiencies should have been used by all investigators. According to the theory, a decision between the second and third cases (formation of chain carriers from aldehyde at the wall) should be possible by investigating the diameter dependence of the rate. In ethane–oxygen mixtures at low pressures (a few centimeters of mercury) and at about 600°C. in silica vessels etched with hydrofluoric acid, the rate has been found to be independent of diameter (11). The experiments were well reproducible, pointing to the conclusion that etching produces a more or less uniform and stable surface. In unetched vessels the results were erratic. Norrish and Foord investigated the effect of diameter on the rate in untreated cylindrical Pyrex vessels at 530°C. in the pressure range 150 to 300 mm. of mercury. They find a mild diameter dependence between diameters of 7.5 mm. to 37.5 mm., although for small vessels they find a sharp drop in the rate. Before any conclusions are drawn from these results, the influence of pressure should be mentioned.

At a constant total pressure of about 1 atm. and at 447°C., Bone and

Allum (2) found that a mixture containing 66.7 per cent of methane in oxygen reacted faster than mixtures containing 50 or 75 per cent of methane. At 467°C. and at pressures ranging from 300 to 600 mm., Fort and Hinshelwood (3) found the rate to depend on a power of the methane concentration exceeding 2 and a power of the oxygen concentration exceeding 1. At 480°C. and presumably up to atmospheric pressure, Norrish and Foord found approximate proportionality of the rate to the product $(CH_4)^2P$ at constant oxygen pressure and to the product $(O_2)P$ at constant methane pressure. They also added nitrogen to 250 mm. of methane and 100 mm. of oxygen up to a total pressure of about 800 mm. and found approximate proportionality of the rate to total pressure.

Of these results, those of Bone and Allum are most readily interpreted by the fact that the product $(CH_4)^2(O_2)$ reaches a maximum at 66.7 per cent methane. The other observations on the influence of total pressure are predicted neither by case 2 nor by case 3 unless one grants that the chain-breaking efficiency of the wall is inversely proportional to the pressure. This is not inconceivable if one considers the possible influence of adsorbed gas layers on the wall. It is also possible that aldehyde produces chain carriers both by a heterogeneous and by a homogeneous reaction with oxygen, the former predominating at lower pressures and the latter at higher pressures. One would then expect some intermediate case between 1 and 3, thus allowing for the influence of the nature of the surface, the diameter dependence, and the pressure factor.

There is still one other possibility which was specifically considered by von Elbe and Lewis (14), that is, case 3 obtains and chain branching is not negligible. The branching term would introduce a diameter dependence and a pressure factor of variable orders depending on the relative magnitudes of the chain-breaking and chain-branching rates. Experiments have not been sufficiently extensive to rule out the necessity for such flexibility.

Norrish and Foord do not fully apply the diffusion theory, in that they assume the rate of chain breaking always to be proportional to a factor S/Pd, S being the surface activity per unit area, P the total pressure, and d the diameter of the vessel. Therefore they have not fully treated the complex problem of accounting simultaneously for the influence of pressure, diameter, and nature of the surface. Strictly within their own picture, the chain-breaking rate should be proportional to $1/Pd^2$ for efficiencies large compared to the ratio of the mean path to diameter and proportional to S/d for efficiencies small compared to this ratio. In the former, the influence of the nature of the surface would have had to be sacrificed and a fairly powerful diameter dependence introduced; in the latter, the pressure factor would have had to be sacrificed.

The explosive reaction

In the treatments of Norrish and Foord and of von Elbe and Lewis aldehyde is both created and destroyed by chain carriers. The rate of production of formaldehyde is at first a very slow process, because the concentration of chain carriers is very small. Its rate of destruction is still smaller, because the aldehyde concentration is also very small. Assuming that the production of new chain carriers by aldehyde is a rare event, one can appreciate the rather long induction periods during which the aldehyde concentration increases, until finally it becomes comparable in magnitude to the concentration of hydrocarbon (of the order of 1 per cent) and the rates of formation and destruction of aldehyde approach equality. The reaction rate then reaches its steady-state value. Norrish and Foord believe that explosion occurs if this maximum rate is sufficiently fast to destroy the thermal equilibrium. They link their theory to the Semenoff theory of "degenerate" branching (12). The latter author's views, however, differ from those of Norrish and Foord and of von Elbe and Lewis in that the intermediate product, which presumably must be identified with aldehyde, is oxidized to the final products independently, that is, without reacting with a chain carrier. Thus, if the concentrations of the reactants, hydrocarbon and oxygen, remained constant, there would be a steady accumulation of the intermediate product and consequently a continuous acceleration of the reaction rate due to production of new chain carriers by aldehyde. The rate would never reach a steady state and only exhaustion of the reactants would slow it down. From a chemical point of view, this course of the reaction is hardly conceivable, because it is known that aldehyde is oxidized by a chain reaction. Semenoff's support for his argument, namely, that the inflection point in the rate curve occurs at a high percentage of the total reaction, is not borne out by the experiments of Norrish and Foord. It should also be mentioned that without prejudicing the steady-state theory, a constant reaction rate cannot actually be observed during the course of the reaction because the effect of exhaustion of the reactants should occur early, so that the non-explosive reaction will always consist of a period of acceleration followed by a period of deceleration.

There remains the question whether the explosion is of the thermal type (Norrish and Foord) or of the branched-chain type (von Elbe and Lewis). There are no certain simple criteria to decide this question. Only the upper explosion limits of such mixtures as hydrogen or carbon monoxide and oxygen can be ascribed, with some assurance, to chain branching. In the present case, thermal and branched-chain theories both demand a continuous acceleration of the reaction on approaching the explosion limit by the change of any experimental variable. It is not justifiable to give

preference to either theory from observations of this type, unless the observations can be made accurately and quantitatively and compared with a quantitative theory. Neither theory nor experimental technique has developed to this stage.

Norrish and Foord base their preference for the thermal character of the explosion on their observation that the induction periods, measured in the non-explosive region up to maximum reaction rate and in the explosive region up to ignition, lie on a continuous curve when plotted against total pressure. However, this result is also consistent with the branched-chain theory.

Although the reaction rate depends rather strongly on the nature of the surface, the branched-chain theory (15) demands that the explosion limit be relatively unaffected by the nature of the surface unless the chain-breaking efficiency is small compared with the ratio of the mean free path to vessel diameter. Actually, the limit is found to be influenced somewhat by the nature of the surface. Assuming that the chain-breaking efficiency is large compared with the above-mentioned ratio, this does not rule out the possibility that the limit is essentially governed by a chain-branching mechanism and that it is lowered somewhat by a thermal factor which enters in by virtue of the acceleration of the reaction rate near the limit.

von Elbe and Lewis base their preference for the branched-chain theory of the explosion on the effect of mixture composition on ignition temperature. Whereas the maximum reaction is at a mixture composition of about 66.7 per cent methane in oxygen, the minimum ignition temperature has been found for a mixture containing about 33 per cent methane. Judging from the change of the product $(CH_4)^2(O_2)$ and the change in thermal conductivity of the mixtures, this shift of optimum composition appears entirely too large to be accounted for by the thermal theory in connection with the proposed chain mechanism of the slow reaction, and to require the introduction of an additional mechanism which is readily conceived of as a branching mechanism. The argument is strengthened still further by the effect on the minimum ignition temperature of substituting helium for argon as diluent in methane–oxygen mixtures. Keeping the total pressure constant one would expect, on the basis of the purely thermal theory, the minimum ignition temperature in helium mixtures to shift to a larger ratio of methane to oxygen as compared to argon mixtures, because the larger heat conductivity of the former mixtures would require a faster reaction to destroy the thermal equilibrium. Actually the reverse is true, the minimum ignition temperature in helium mixtures being shifted toward smaller ratios. The branched-chain mechanism as proposed by von Elbe and Lewis accounts for these and related facts.

SUMMARY

Recent theories of hydrocarbon oxidation have been critically compared. The evidence favors monovalent radical chains. The assumption of intermediate formation of peroxides and of sensitization of peroxide dissociation by condensation with aldehyde proves to be fruitful in explaining varied phenomena, such as the low-temperature reactivity of higher hydrocarbons and the high-pressure oxidation of methane and ethane. The implications of the chain theory in interpreting the experimental results have been discussed. The necessity of revising Norrish and Foord's steady-state treatment has been pointed out. The question of thermal versus branched-chain explosions in methane remains open, with some experimental evidence favoring the latter.

REFERENCES

(1) BÄCKSTROM: Z. physik. Chem. **B25,** 99 (1934).
(2) BONE AND ALLUM: Proc. Roy. Soc. (London) **A134,** 578 (1931).
(3) FORT AND HINSHELWOOD: Proc. Roy. Soc. (London) **A129,** 284 (1930).
(4) JOST, VON MÜFFLING, AND ROHRMANN: Z. Elektrochem. **42,** 488 (1936).
(5) KIMBALL: J. Chem. Phys. **5,** 310 (1937); cf. KASSEL: J. Chem. Phys. **5,** 922 (1937).
(6) NORRISH AND FOORD: Proc. Roy. Soc. (London) **A157,** 503 (1936); cf. NORRISH: Proc. Roy. Soc. (London) **A150,** 36 (1935).
(7) PEASE: J. Am. Chem. Soc. **57,** 2296 (1935).
(8) POPE, DYKSTRA, AND EDGAR: J. Am. Chem. Soc. **51,** 1875 (1929).
(9) POPE, DYKSTRA, AND EDGAR: J. Am. Chem. Soc. **51,** 2203 (1929).
(10) RIECHE: Alkylperoxyde und Ozonide. Steinkopff, Dresden (1931).
(11) SADOWNIKOW: J. Phys. Chem. (U. S. S. R.) **4,** 735 (1933).
(12) SEMENOFF: Chemical Kinetics and Chain Reactions. Oxford (1935).
(13) UBBELOHDE: Proc. Roy. Soc. (London) **A152,** 354 (1935); Z. Elektrochem. **42,** 468 (1936).
(14) VON ELBE AND LEWIS: J. Am. Chem. Soc. **59,** 976 (1937).
(15) VON ELBE AND LEWIS: J. Am. Chem. Soc. **59,** 970 (1937).

DISCUSSION[2]

HAROLD A. BEATTY (Ethyl Gasoline Corporation, Detroit, Michigan): The pioneer work of Pope, Dykstra, and Edgar (J. Am. Chem. Soc. **51,** 2203 (1929)) on the slow oxidation of branched-chain octanes suggested that a step-wise degradation of the longest straight chain takes place until a secondary carbon atom is reached, at which point a stable ketone is formed. This suggestion has been more or less accepted as a specific fact by subsequent investigators, without its having been put to experimental proof. Actually, the results of some previously unpublished work by the author in 1931 on the slow oxidation of 2,5-dimethylhexane indicate that the overall reaction is by no means as simple as was originally suggested.

[2] Received September 25, 1937.

Using the conventional flow method (Beatty and Edgar: J. Am. Chem. Soc. **56,** 102 (1934)) it was found that the oxidation of this octane in air starts at a low temperature, 235°C. At 346°C. the reaction is very fast, the temperature near the inlet being 74°C. above that of the thermally uniform portion of the furnace, 272°C., and it may safely be assumed that 75 to 100 per cent of the hydrocarbon is partially oxidized. Holding this temperature constant, 17.40 g. of the hydrocarbon was oxidized in 635 min. at a molal oxygen/fuel ratio of 9.6.

Analysis of the gaseous products uncondensed at −78°C. gave, per mole of hydrocarbon input, 2.30 moles of oxygen used, and 0.73 mole of carbon monoxide, 0.10 mole of carbon dioxide, and 0.08 mole of unsaturated gas (probably ethylene) formed. The liquid condensate weighed 23.44 g., giving a total recovery of 99.9 per cent. It contained, per mole of hydrocarbon input, 1.80 moles of water and about 0.2 mole of acid, principally formic acid. So far this is in fairly good agreement with the suggested mechanism of oxidation to 5-methylhexanone-2.

However, the aqueous condensate, d = 1.05, weighed 11.4 g. of which only 40 per cent was water; aldehyde and acetone were present in quantity. The upper layer, d = 0.84, weighing but 12.0 g., had a boiling range from below 90°C. to above 155°C. The fraction boiling below 100°C., 3.6 g., gave a strong test with Schiff's reagent, and yielded a *p*-nitrophenylhydrazone melting at 142.5–143.5°C., with a molecular weight of about 200 to 225, apparently not a single compound. The fraction boiling from 115°C. to 155°C., 3.1 g., gave negative tests with sodium, sodium bisulfite, and semicarbazide, and a trace of oil with *p*-nitrophenylhydrazine; certainly none of the expected ketone was present.

This analysis is admittedly far from complete, but it serves its purpose to the extent of showing definitely that a certain amount of extensive degradation or rupture of the carbon chain takes place, and that no 5-methylhexanone-2 appears in the products. It seems, therefore, that while the original suggestion is probably valid in principle, it cannot be accepted literally or specifically, and each individual branched-chain hydrocarbon will have to be considered, to a certain extent, as an isolated problem.