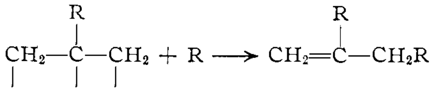
and the olefins, which are formed in substantial quantity, of



$$CH_2{-}\overset{R}{C}{-}CH_2 + R \longrightarrow CH_2{=}\overset{R}{C}{-}CH_2R$$

1-butene from propylene by way of allyl and methyl is an example of the foregoing.

At a temperature of 630° the hydrogen peroxide–propylene reaction is noticeably productive of C_3H_4 (allene). Inasmuch as radical–radical association reactions are important paths to some end products, it is not unreasonable to ascribe other compounds, *e.g.*, allene, to radical–radical disproportionations.

$$CH_2{-}CH{-}CH_2 + R \longrightarrow CH_2{=}C{=}CH_2 + RH$$

The importance of allyl radical reactions in the case of propylene is demonstrated by the fact that 55 and 70% of the reacted propylene at 530 and 630°, respectively, yields products traceable to allyl radical precursors. Products which stem from initial abstraction of vinylic hydrogen atoms are evident, particularly in the case of ethylene and in the higher temperature region.

$$CH_2{=}CH_2 + OH \longrightarrow CH_2{=}CH{-} + H_2O$$

$$2CH_2{=}CH{-} \longrightarrow CH_2{=}CH{-}CH{=}CH_2$$

$$CH_2{=}CH{-} \longrightarrow CH{\equiv}CH + H$$

Although vinyl radicals can be postulated as intermediates in other reactions, butadiene and acetylene seem to be devoid of reasonable alternate antecedents. A significant yield of acetylene (5.4%) from propylene seems likewise to be a result of vinyl hydrogen removal.

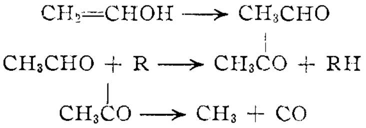
$$CH_3CH{=}CH_2 + OH \longrightarrow CH_3CH{=}CH{-} + H_2O$$

$$CH_3CH{=}CH{-} \longrightarrow CH_3 + CH{\equiv}CH$$

Addition of a hydroxy radical to the double bond must be the single most important reaction with ethylene even at 525° and must be progressively less important with propylene and isobutylene. The resultant hydroxyalkyl radicals can be stabilized as alcohols by hydrogen capture, but evidently the more usual evolution of hydroxyalkyl leads to eventual fragmentation of the molecule. Methane, carbon monoxide and formaldehyde are important products of the hydrogen peroxide–ethylene experiments and in the propylene studies these plus, in particular, ethylene must be accounted for. The initial hydroxyethyl radical which seems to be a step in the breakdown of ethylene, shows little evidence of instability and, in fact, rather limited reaction opportunities. The complete absence of hydrogen at 435° precludes a β-scission of a carbon–hydrogen bond so that it can only be concluded that hydroxyethyl is a hydrogen donor. That some donor of considerable efficiency is present can be deduced from the important yields of ethane. The reaction steps suggested then become

$$-CH_2CH_2OH + X \longrightarrow CH_2{=}CHOH + XH$$

X = olefin or radical



$$CH_2{=}CHOH \longrightarrow CH_3CHO$$

$$CH_3CHO + R \longrightarrow CH_3CO + RH$$

$$CH_3CO \longrightarrow CH_3 + CO$$

At 435° acetaldehyde is a significant product and its decomposition to methyl and carbon monoxide frequently has been demonstrated.[7] Thus, this course of fragmentation for ethylene—and for propylene—seems reasonable.

The production of hydrocarbons of higher carbon number is surely a consequence of radical addition to olefin double bonds. Indicative of the number of processes yet to be explored is the analysis of a broad product fraction boiling from 15 to 57°—identified among the products as C_5's. The C_5 hydrocarbons in the fraction were identified as pentanes 2.9%, amylenes 32.2%, pentadienes 32.8%, cyclopentane 2.5%, cyclopentene 13.2% and cyclopentadiene 2.1%.

[7] E. W. R. Steacie, "Atomic and Free Radical Reactions," Vol. 1, 2nd Ed., Reinhold Publishing Co., New York, N. Y., 1954, p. 206.

EMERYVILLE, CALIF.

[CONTRIBUTION FROM THE SHELL DEVELOPMENT COMPANY]

Intramolecular Oxidation. The Autoxidation of Some Dimethylalkanes

BY FREDERICK F. RUST

RECEIVED MARCH 2, 1957

The products from the liquid phase, non-catalytic oxidations of 2,3-dimethylpentane (I), 2,4-dimethylpentane (II), 2,5-dimethylhexane (III) and 2,6-dimethylheptane (IV) have been identified and related to one facet of the mechanism of hydrocarbon oxidation. In the cases of II and III, the 2,4- and 2,5-dihydroperoxides, respectively, were made in extraordinarily high yields despite the fact that less than 10% of the hydrocarbons reacted. The results show that intramolecular peroxy radical attack is highly efficient at the β-position, somewhat less so at the γ-position and apparently of little or no significance at either the α- or Δ-positions. The efficiency of intramolecular oxidation appears to be favored by attachment of the peroxy radical to a tertiary carbon atom.

Introduction

Although the oxidation of aliphatic hydrocarbons is conventionally represented as an intermolecular process of the type

$$RO_2 + RH \longrightarrow RO_2H + R$$

$$R + O_2 \longrightarrow RO_2$$

increasing evidence indicates that an oxidation chain does not necessarily propagate from molecule to molecule, but, depending on conditions, can propagate from one point to another within the molecule. The formation of β-dicarbonyl compounds and oxirane rings in the gas phase oxidation of pentane,[1] hexane[2] and 2,2,4-trimethylpentane[3] and the production of a 2,5-dihydroperoxide from the cobalt catalyzed liquid phase oxidation of 2,5-dimethylhexane[4] have been interpreted on this basis.

The present study covers the liquid phase noncatalytic oxidation of hydrocarbons of the general structure $C-\overset{C}{\overset{|}{C}}-(C)_x-\overset{C}{\overset{|}{C}}-C$, where x was varied from 0 to 3. From the reaction products of this series of hydrocarbons can be deduced some of the characteristics of intramolecular oxidation.

Materials

The 2,3- and 2,4-dimethylpentanes were obtained from Phillips Chemical Company. The first was the technical grade, 95+%, which was further fractionated. A center cut was collected at 89.0–89.5°; $n^{20}D$ 1.3917. The 2,4-dimethylpentane was research grade and used without further treatment (b.p. 80.6°, $n^{20}D$ 1.3811). The 2,5-dimethylhexane was prepared by a Grignard coupling reaction with methallyl chloride followed by separation and hydrogenation of the dimethallyl. The product used distilled at 108.6–109.6°; $n^{20}D$ 1.3928. 2,6-Dimethylheptane was obtained by dehydrating diisobutylcarbinol over alumina at 390° and then hydrogenating the resulting olefin. A fraction, 133.5–135.2°, $n^{20}D$ 1.4013, was oxidized.

Experimental

The hydrocarbons were oxidized in a closed system comprised of a Pyrex reactor, an all-glass pump, a hydraulically pressured steel oxygen reservoir fitted with a sight gage, and Dry Ice-cooled traps in the system immediately following the reactor and the reservoir. Oxygen at 35 p.s.i.g. was circulated through the hydrocarbon at 115–120°. The oxygen consumption was measured at constant pressure by following the rising water level in the calibrated reservoir.

The peroxide in the product was determined iodimetrically by reduction with acidified (acetic acid) potassium iodide in isopropyl alcohol solution under reflux for five minutes.

The hydrocarbon charge was usually 400 cc. of which from 5–8% was oxidized and in general the product was concentrated to *ca.* 70 cc. by flashing off the unreacted hydrocarbon. If necessary, pressure was reduced during concentration to keep the kettle temperature below 60° in order to minimize peroxide breakdown. The concentrate was diluted to *ca.* 300 cc. with isopropyl alcohol and reduced with hydrogen and platinum oxide catalyst. The products were then separated by fractional distillation. Where small amounts of product were to be analyzed, separation was effected on a Piros–Glover spinning band micro-still. Significant departures from this procedure are discussed under the individual hydrocarbons.

In most cases the oxidation product had two phases, but after topping off the traces of water and a substantial fraction of the unreacted hydrocarbon under reduced pressure, a single phase usually was obtained. In the case of 2,5-dimethylhexane the dihydroperoxide is a crystalline solid which readily can be separated by filtration.

Results

2,3-Dimethylpentane.—The autoxidation of this hydrocarbon resulted in a 52.5% yield of peroxide based upon consumed oxygen—the lowest for the four hydrocarbons investigated. Following the removal of the hydrocarbon, water and the low boiling scission products, an analysis of the residue for total oxygen and peroxide oxygen showed 0.340 g. atom of combined oxygen of which 0.214 was in peroxide groups. The remainder, 0.126 g. atom, is essentially carbonyl and hydroxyl and, as such, is assumed to have its genesis in a radical–oxygen association. This remainder, therefore, requires 0.126 g. mole of oxygen for its formation or 0.252 g. atom. This, with the peroxide oxygen, gives a total of 0.466 g. atom of oxygen required to form the high boiling products. The difference between this value and the 0.27 mole of oxygen reacted (0.54 g. atom) is 0.08 g. atom. This last figure indicates the magnitude of the scission reactions and other losses. Small amounts of acetone and methyl ethyl ketone are produced.

A peroxide concentrate was obtained in sufficient quantity for distillation in a falling-film molecular still by combining the products of two runs. Four fractions totalling 40.2 g. were collected.

Fraction no.	Grams	% C	% H	% O (diff.)	Empirical formula	% Peroxide (ROOH)
I	4.0	65.1	12.2	22.7	$C_7H_{15.8}O_{1.83}$	63.7[a]
II	32.5	63.4	11.8	24.8	$C_7H_{15.7}O_{2.02}$	73.4[a]
III	2.0	58.7	10.4	30.9	$C_7H_{14.9}O_{2.76}$	55.0[b]
IV	1.7	57.4	10.0	32.6	$C_7H_{14.7}O_{3.0}$	55.7[b]

[a] Calculated as $C_7H_{16}O_2$. [b] Calculated as $C_7H_{14}O_3$.

2,3-Dimethyl-2-(and-3)-hydroperoxypentane, which is a principal component, has 63.6% carbon, 12.1% hydrogen. Fraction II which accounts for more than 80% of the total, shows an average of two oxygen atoms per molecule although only 73.4% of all molecules contain a peroxide group. Infrared inspection shows a significant amount of carbonyl. When the peroxide groups are hydrogenated to hydroxyls, a carbonyl analysis indicates that at least 16% of this product has two oxygen atoms per molecule and evidently is largely 4-hydroxy-3,4-dimethyl-2-pentanone because as indicated by a very low periodate value the ketone and hydroxyl groups are for the most part non-adjacent.

2,4-Dimethylpentane.—The oxidation of 2,4-dimethylpentane is the least complicated of any in this series. Under comparable conditions this hydrocarbon takes up oxygen to give an 89% peroxide yield. Hydrogenation of the peroxide concentrate gives 2,4-dimethyl-2,4-pentanediol in 95% yield based on the input oxygen. The remainder is accounted for by 2,4-dimethyl-2-pentanol; 2,4-dihydroperoxy-2,4-dimethylpentane crystallized from the sirupy product after standing for about a week.

2,5-Dimethylhexane.—The cobalt stearate catalyzed oxidation of 2,5-dimethylhexane is computed from the data of Wibaut and Strang[4] to give 2,5-dihydroperoxy-2,5-dimethylhexane in 15% yield. In the non-catalytic autoxidation system discussed here total peroxide was produced in 83% yield and the crystalline diperoxide was filtered from the hydrocarbon in 50% yield—based on consumed oxygen. The remaining peroxidic product was concentrated by distilling off unoxidized hydrocarbon under reduced pressure and then hydrogenated in 2-propanol solution at not above 50° with platinum oxide catalyst. The 2,5-dimethyl-2-hexanol was isolated by distillation. The high boiling residue amounting to 20% mole of the product had an empirical formula, based on carbon and hydrogen

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[1] M. R. Barusch, J. T. Neu, J. Q. Payne and J. R. Thomas, *Ind. Eng. Chem.*, **43**, 2766 (1951).

[2] H. C. Bailey and R. G. W. Norrish, *Proc. Roy. Soc. (London)*, **212**, 311 (1952).

[3] D. O. Collamer and F. F. Rust, THIS JOURNAL, **76**, 1055 (1954).

[4] J. P. Wibaut and S. Strang, *Koninkl. Ned. Akad. Wetenschap. Proc. B*, **54**, 231 (1951).

analyses, of $C_8H_{16.8}O_{2.9}$. A small amount of crystalline material was separated from this residue which showed a strong test for ketone and gave a carbon–hydrogen analysis in agreement with a 40–60 molar mixture of 2,5-dimethyl-2,5-hexanediol and 2,5-dimethyl-3-keto-2,5-hexanediol.

When about 30% of the hydrocarbon charge was oxidized and the volatile components removed at 70° under vacuum pump pressure a clear peroxidic residue was obtained. This was run through a falling film molecular still at 56°. The distillate was treated with 30% sodium hydroxide, the solid precipitate filtered off, dissolved in a minimum of water and the pure peroxide released by bubbling carbon dioxide into the solution. This peroxide layer was extracted with an isopentane–ether mixture and the mixed solvent then removed under vacuum. Upon standing for a week the somewhat viscous peroxide crystallized. Carbon and hydrogen analyses (59.0% C and 11.0% H) and mol. weight of 159, computed from peroxide determination, showed it to be 2,5-dimethyl-5-hydroperoxy-2-hexanol (theory 59.3% C; 11.1% H; mol. wt. 162). Reduction in 2-propanol with hydrogen and platinum oxide catalyst gave 2,5-dimethyl-2,5-hexanediol (m.p. and mixed m.p. 87.5°). The diperoxide obtained at low levels of hydrocarbon conversion is apparently partially reduced or becomes difficult to recover as the oxidation proceeds.

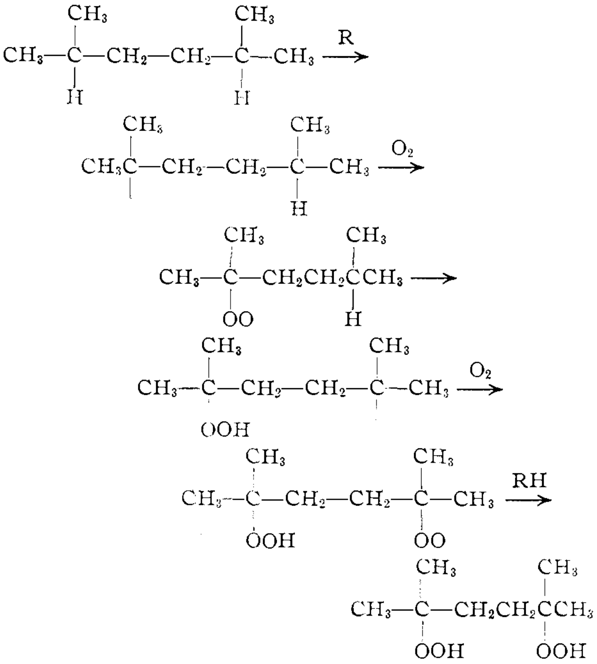
2,6-Dimethylheptane.—In contrast to the oxidations of 2,4-dimethylpentane and 2,5-dimethylhexane, the oxidation of 2,6-dimethylheptane is far less clear cut. The evidence is strong, however, that intramolecular oxidation is an important determinant. Under conditions where not more than 8% of the 2.25 mole input hydrocarbon was oxidized, there was isolated from the hydrogenated product 0.038 mole of 2,6-dimethyl 2-heptanol and 0.087 mole of higher boiling products with an empirical formula $C_9H_{19.1}O_{2.4}$. Of the total combined oxygen in this mixture only 10% was associated with ester and acid groups which would be a consequence of carbon skeleton cleavage reactions. Calculating on the basis that one oxygen molecule was required to place one atom of oxygen in the final reduced product an approximate oxygen balance can be struck.

From 2,6-dimethyl, 2-heptanol	0.038 mole O_2
From $C_9H_{19.1}O_{2.4}$ (0.087 × 2.4)	0.209 mole O_2
	0.247 mole O_2
Total oxygen consumed	0.273 mole

Efforts were made to isolate 2,6-dimethyl-2,6-heptanediol and although fractions were isolated which showed the correct carbon and hydrogen analyses, these results were inadequate because the product was a thick clear liquid rather than crystals of the 2,6-diol (m.p. 76°). In one experiment crystals were collected from an unhydrogenated concentrate which had both peroxide and carbonyl groups and an empirical formula of $C_9H_{18}O_4$ (% carbon 57.2; % hydrogen 9.5; theory 56.8% and 9.5%). The structure $(CH_3)_2COOHCH_2COCH_2COH(CH_3)_2$ is proposed.

Discussion

As pointed out by Wibaut and Strang the liquid phase oxidation of 2,5-dimethylhexane can best be interpreted by an intramolecular attack of the initially formed tertiary peroxy radical upon the remaining tertiary hydrogen atom followed by formation of a second peroxy group.



The crystalline diperoxide was the same as that first prepared by Tannenberger[5] from the glycol and hydrogen peroxide.

This study has sought to arrive at some assessment of the importance of intramolecular oxidation to liquid hydrocarbon systems and accordingly has concerned itself with autoxidation rather than the cobalt-catalyzed reactions which are less favorable to peroxide preservation.

By selecting a series of hydrocarbons in which the reactive tertiary hydrogen atoms are separated by interposing up to three methylene groups, it has been possible to estimate the preferred positions of intramolecular oxidative attack. By far the most favored pattern of reaction involves attack of the peroxy radical in the β-position. This is exemplified by the oxidation of 2,4-dimethylpentane which resulted in about 90% of the product being substituted by oxygen in both the 2- and 4-positions. This preparation of a β-diperoxide by autoxidation is believed to be novel, although this compound has been prepared recently from hydrogen peroxide and the glycol by Criegee and Paulig.[6]

The oxidation of 2,5-dimethylhexane, which gives high yields of the 2,5-diperoxide demonstrates that intramolecular attack in the γ-position by the peroxy radical is the next most favored possibility.

In the case of 2,6-dimethylheptane such a preponderant fraction of the oxygen consumed was involved in the production of polyoxygenated products that it seems improbable that these products could have been formed by other than an intramolecular mechanism similar to that discussed for the other dimethylalkanes. However, the case for Δ-attack by a peroxy radical was not conclusively re-

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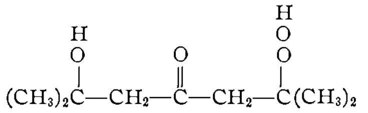
[5] R. Tannenberger, Doctoral Dissertation, Karlsruhe, 1945.

[6] R. Criegee and G. Paulig, *Chem. Ber.*, **88**, 72 (1955).

solved. Thus, despite the apparent inability of a peroxy radical in the 2-position to remove a hydrogen atom in the 6-position—at least with any facility—there is considerable indication that removal of hydrogen from the 4- and 5-positions is occurring with considerable regularity. In this connection the tentative identification of a crystalline compound



$$(CH_3)_2C(OH)-CH_2-C(=O)-CH_2-C(OOH)(CH_3)_2$$

suggests the possibility of a "zipper" effect in the oxidation of certain linear hydrocarbons. The amount of this compound was, however, too small to suggest that such an effect would be important in any but special situations.

When 2,3-dimethylpentane is oxidized and the peroxides reduced, 2,3-dimethyl-2-(and 3)-pentanol are the principal and almost equally important products. It is significant that 3,4-dimethyl-2-pentanone-4-ol, which is the only reduction product which would be expected by a β-oxidation mechanism, is the most important of the remaining products retaining the original carbon skeleton. α-Attack by a peroxy radical seems to be of no significance.

In view of the foregoing results it seems reasonable to relate much of the formation of keto-acids, lactones, etc., in conventional paraffin oxidation to intramolecular chain propagation. However, no such extensive intramolecular reaction has been observed in the oxidation of the normal paraffins as was found for these branch chain hydrocarbons. Therefore, it is concluded that the well recognized effect of a gem-dimethyl grouping[7] in favoring ring closures is important here in intramolecular attack by peroxy groups.

Acknowledgment.—The author wishes to acknowledge particularly helpful discussions with Drs. H. E. De La Mare and D. E. Winkler.

(7) P. D. Bartlett, *J. Chem. Ed.*, **30**, 27 (1953).

EMERYVILLE, CALIF.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF PENNSYLVANIA]

Free Radicals from the Heterogeneous Decomposition of Butane[1]

BY SYDNEY W. FLEMING AND K. A. KRIEGER

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A method which provides information about the nature of certain adsorbed intermediates is described. Essentially the method consists in observing the decomposition of a hydrocarbon (butane) into free radicals on a heated wire acting as a catalyst. The reaction is carried out at pressures of 1–2 μ in a vessel whose walls are coated with radioactive iodine. The alkyl iodides formed are separated and their activities measured. Catalyst temperatures ranged from 305 to 1490°. Both aluminum (oxide) and tungsten catalysts produce free radicals ranging in complexity from methyl to *sec*-butyl. The radicals formed depend upon the catalyst used and on the temperature. Platinum produces no free radicals under these conditions.

Introduction

A major problem in catalysis is that of discovering the nature of the intermediates whose formation is critical in determining the course of the reaction. In the case of heterogeneous catalysis the methods of studying the intermediates are especially limited, owing to the necessary presence of a catalyst, most often a solid, on whose surface the critical intermediate is formed, and which greatly interferes with the usual methods of observation. In seeking a solution to this difficulty some success has been attained by the use of infrared spectroscopy, which, in suitable circumstances, is able to detect alterations in chemical bonds attendant on adsorption.

The present paper is an attempt, along quite different lines, to approach the observation of adsorbed intermediates. Unfortunately, the method is not quite direct, as the description will show, but it does apparently succeed at least in detecting certain immediate products of desorption, before their nature has been changed by subsequent reaction.

The results reported here are limited to a single reactant and three catalysts, and it is difficult with these limited data to make with certainty any very broad generalizations. The collection of future data, with more varied reactants and catalysts, is expected to remedy this defect. Additional work utilizing this method is in progress in this Laboratory, but this report is made now in the hope that others may find the technique useful.

Experimental

Briefly, the method involves production of free radicals by decomposition of butane on catalysts in the form of metal wires and trapping of the free radicals released by the catalyst into the vapor phase by means of a radioactive iodine mirror, followed by fractional distillation and determination of the activities of individual fractions. These activities give the relative quantities of the alkyl iodides formed from the original free radicals trapped by the mirror.

Apparatus.—The experimental apparatus, shown in Fig. 1, consisted of a reaction chamber, L, with a wire catalyst suspended in the center and equipped with electrical connections for heating the wire. Associated apparatus was provided for metering butane into the reaction chamber at the very low rates required. The mirror was formed on the walls of the reaction vessel, and in order for free radicals formed on the wire to reach the wall without suffering collision with butane molecules, the butane pressure was kept between 1 and 2 μ, giving a mean free path on the order of the tube diameter of 5 cm.

During each run the vessel containing the iodine mirror was maintained at Dry Ice temperature. At the end of each run the reaction vessel was warmed to room temperature to allow the product along with the excess free iodine to dis-

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[1] Based on a thesis submitted to the University of Pennsylvania, 1954 in partial fulfillment of the requirements for the degree of Doctor of Philosophy.