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Decompositions of Di-*t*-Alkyl Peroxides. II. Reactions of the Resultant Free Radicals

BY FREDERICK F. RUST, FRANK H. SEUBOLD AND WILLIAM E. VAUGHAN

In the previous paper[1] evidence was presented that free methyl radicals derived from decomposing di-*t*-butyl peroxide reacted with and converted a part of the acetone—also a product of the decomposition—to methyl ethyl ketone and higher ketones. The inclusion of other compounds with the decomposing di-*t*-butyl and di-*t*-amyl peroxides has now made possible a study of other gas phase reactions of free methyl and free ethyl in the temperature region of 200–235°. Although possibilities for organic syntheses will suggest themselves—such as the addition of two methyl or ethyl groups to a double bond or the replacement of hydrogen atoms by methyls, it is not the intent of the present paper to present optimum conditions for such syntheses. Instead, it is hoped that the present study will demonstrate the usefulness of the di-*t*-alkyl peroxides as tools in the study of free radical phenomena. The fate of the various peroxide-derived free radicals in different hydrocarbon atmospheres is revealed by the components which have been separated from fairly complex reaction mixtures.

Thus, the abstraction of a hydrogen atom from a molecule by methyl and the combination of the resulting radical with another methyl is shown by the formation of ethylbenzene from toluene and triptane from 2,3-dimethylbutane.

$$(CH_3)_3COOC(CH_3)_3 \longrightarrow [2(CH_3)_3CO—] \longrightarrow 2CH_3 + 2CH_3COCH_3 \quad (1)$$

$$RH + CH_3 \longrightarrow CH_4 + R \quad (2)$$

$$R + CH_3 \longrightarrow RCH_3 \quad (3)$$

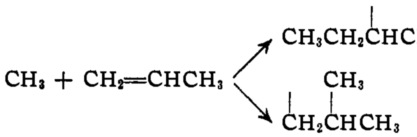
When olefins become the objects of radical attack the transformations are more complex, but the results are in general agreement with current concepts of chain initiation, transfer, and termination in polymerization reactions. Thus, as suggested by other workers,[2] *methyl addition to ethylene* gives a propyl radical which adds to other ethylene molecules unless or until the chain is terminated by collision with another methyl.

$$CH_3 + nC_2H_4 \longrightarrow CH_3(C_2H_4)_n \quad (4)$$

$$CH_3(C_2H_4)_n + CH_3 \longrightarrow CH_3(C_2H_4)_nCH_3 \quad (5)$$

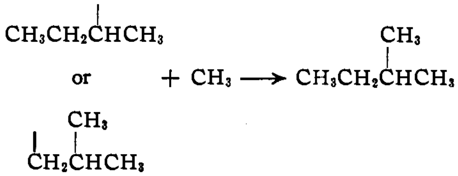
At these low temperatures, however, the polymerization is relatively uncomplicated by disproportionation reactions. *n*-Butane, *n*-hexane and *n*-octane were isolated and no odd carbon-numbered hydrocarbons or unsaturates were found.

The reaction of *methyl and propylene* has been more extensively studied. Addition of free methyl to the double bond



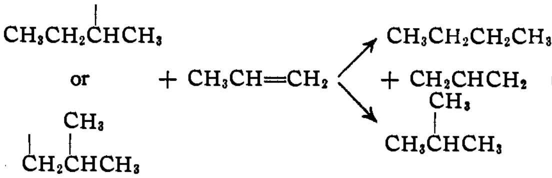
$$CH_3 + CH_2{=}CHCH_3 \begin{array}{l} \nearrow CH_3CH_2\overset{|}{C}HCH_3 \\ \searrow \overset{|}{C}H_2\overset{CH_3}{\overset{|}{C}}HCH_3 \end{array} \quad (6)$$

is followed either by (a) combination with another methyl to give isopentane



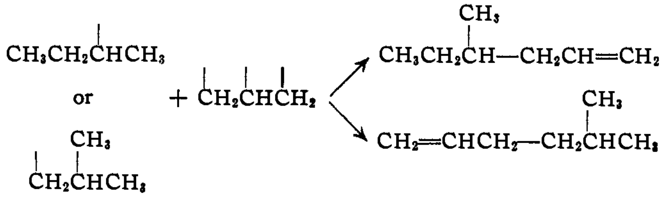
$$\begin{array}{c} CH_3CH_2\overset{|}{C}HCH_3 \\ \text{or} \\ \overset{|}{C}H_2\overset{CH_3}{\overset{|}{C}}HCH_3 \end{array} + CH_3 \longrightarrow CH_3CH_2\overset{CH_3}{\overset{|}{C}}HCH_3 \quad (7)$$

(b) abstraction of a hydrogen atom from propylene to yield butanes



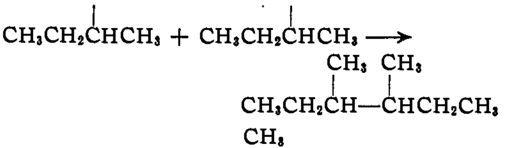
$$\begin{array}{c} CH_3CH_2\overset{|}{C}HCH_3 \\ \text{or} \\ \overset{|}{C}H_2\overset{CH_3}{\overset{|}{C}}HCH_3 \end{array} + CH_3CH{=}CH_2 \begin{array}{l} \nearrow CH_3CH_2CH_2CH_3 \\ \quad + CH_2CHCH_2 \\ \searrow CH_3\overset{CH_3}{\overset{|}{C}}HCH_3 \end{array} \quad (8)$$

(c) combination with allyl to form a heptene

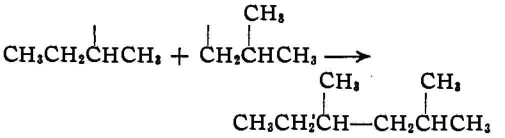


$$\begin{array}{c} CH_3CH_2\overset{|}{C}HCH_3 \\ \text{or} \\ \overset{|}{C}H_2\overset{CH_3}{\overset{|}{C}}HCH_3 \end{array} + \overset{|}{C}H_2\overset{|}{C}H\overset{|}{C}H_2 \begin{array}{l} \nearrow CH_3CH_2\overset{CH_3}{\overset{|}{C}}H—CH_2CH{=}CH_2 \\ \searrow CH_2{=}CHCH_2—CH_2\overset{CH_3}{\overset{|}{C}}HCH_3 \end{array} \quad (9)$$

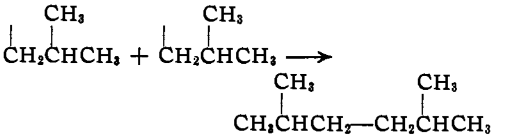
(d) addition to other radicals to form, for example, octanes



$$CH_3CH_2\overset{|}{C}HCH_3 + CH_3CH_2\overset{|}{C}HCH_3 \longrightarrow CH_3CH_2\overset{CH_3}{\overset{|}{C}}H—\overset{CH_3}{\overset{|}{C}}HCH_2CH_3 \quad 10)$$



$$CH_3CH_2\overset{|}{C}HCH_3 + \overset{|}{C}H_2\overset{CH_3}{\overset{|}{C}}HCH_3 \longrightarrow CH_3CH_2\overset{CH_3}{\overset{|}{C}}H—CH_2\overset{CH_3}{\overset{|}{C}}HCH_3 \quad (11)$$



$$\overset{|}{C}H_2\overset{CH_3}{\overset{|}{C}}HCH_3 + \overset{|}{C}H_2\overset{CH_3}{\overset{|}{C}}HCH_3 \longrightarrow CH_3\overset{CH_3}{\overset{|}{C}}HCH_2—CH_2\overset{CH_3}{\overset{|}{C}}HCH_3 \quad (12)$$

(e) addition to propylene in a manner analogous

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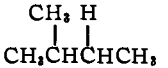
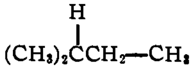
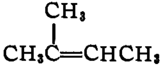
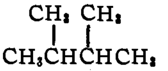
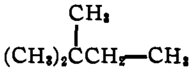
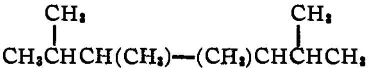
[1] Raley, Rust and Vaughan, THIS JOURNAL, 70, 88 (1948).

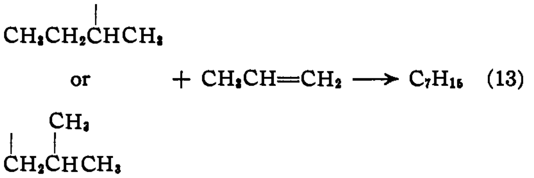
[2] Steacie, "Atomic and Free Radical Reactions," Reinhold Publishing Corp., 1946.

TABLE I

ISOLATED PRODUCTS FROM REACTION OF METHYL WITH 2-BUTENE AND ISOBUTENE, 235°

Products from 2-butene	Products from isobutene	Mechanism of formation, equation
 $CH_3\overset{CH_3}{\overset{\vert}{C}}H\overset{H}{\overset{\vert}{C}}HCH_3$	 $(CH_3)_2\overset{H}{\overset{\vert}{C}}CH_2—CH_3$	6 and 8
$CH_3—CH_2CH{=}CHCH_3$	$CH_2{=}C(CH_3)CH_2—CH_3$	14 and 15
 $CH_3\overset{CH_3}{\overset{\vert}{C}}{=}CHCH_3$	$(CH_3)_2C{=}CH—CH_3$	14 and 15
 $CH_3\overset{CH_3}{\overset{\vert}{C}}H\overset{CH_3}{\overset{\vert}{C}}HCH_3$	 $(CH_3)_2\overset{CH_3}{\overset{\vert}{C}}CH_2—CH_3$	6 and 7
Nonenes	Nonenes	6 and 9
 $CH_3\overset{CH_3}{\overset{\vert}{C}}HCH(CH_3)—(CH_3)CH\overset{CH_3}{\overset{\vert}{C}}HCH_3$	Decanes	6 and 10
Higher boiling	Higher boiling	....

to the addition of methyl with eventual formation of octanes and higher products



$$CH_3CH_2\overset{\vert}{C}HCH_3 \text{ or } \overset{CH_3}{\overset{\vert}{C}}H_2\overset{\vert}{C}HCH_3 + CH_3CH{=}CH_2 \longrightarrow C_7H_{16} \quad (13)$$

When methyl abstracts a hydrogen atom from propylene

$$CH_3 + CH_3CH{=}CH_2 \longrightarrow CH_4 + CH_2CHCH_2 \quad (14)$$

the resulting allyl can be found in the C_7 olefin (equation 9) or as butene.

$$CH_3 + CH_2CHCH_2 \longrightarrow CH_3CH_2CH{=}CH_2 \quad (15)$$

Each of these hydrocarbons has been identified in the reaction products and, perhaps equally important, no others of different carbon structure have been found.

Evidence for initial addition of methyl to either end of the propylene double bond is indicated by the presence of both normal and isobutane among the reaction products (equation 8). That ethyl behaves similarly is shown by isolation of *n*- and isopentane from the reaction of propylene and di-*t*-amyl peroxide (*cf.* Beeck and Rust[3]).

One unexplained phenomenon is the shift in the double bond of the olefinic products which probably occurs at the time of formation. Thus, both 1- and 2-butene are found and, although a terminal double bond would be predicted for the heptenes, actually a shift to an internal position has occurred in a part of the product. The expected carbon structure is, however, borne out by infrared analysis of the hydrogenated C_7 fraction.

The attack of methyl on 2-butene or isobutylene gives the products which would be predicted from the analogous reactions of methyl with propylene. These products are listed in Table I, together with references to the equations representing the mode of formation of the analogous compounds derived from propylene. Thus, 2,3-dimethylbutane which is derived by dimethylation of the double bond of 2-butene is analogous to isopentane which is formed by dimethylation of the propylene double bond. The mechanism is illustrated by equations 6 and 7. The exaggerated bonds shown in the table are the ones newly formed as a consequence of radical attack.

When di-*t*-amyl peroxide is decomposed at 235°, the products prove that ethyl radicals are released and when propylene is mixed with the decomposing peroxide, the expected compounds are formed. 3-Methylhexane, from the addition of two ethyl groups to the double bond; iso- and normal pentane, from internal and external addition, respectively, of ethyl radical to the double bonds (equation 6 and 8); and straight chain pentenes, from the replacement of a hydrogen atom by an ethyl group (equation 14 and 15), have all been isolated.

Effect of Surface

Extensive investigation by previous workers[2] has provided ample evidence for the combination of methyl radicals at the wall. So important is this wall effect that virtually no olefin could be involved in reactions with methyl if 15-mm. Pyrex tubing were used as the reactor. Successful results were obtained in 70-mm.-tubes. The obvious implication is that methyl addition to double bonds and methane formation by hydrogen abstraction are largely gas phase reactions. The conditions of combination for larger radicals are not suggested by the present work.

Materials and Procedure

The ethylene was a product of the Ohio Chemical Company and assayed 99.5%. Propylene was prepared by dehydration of isopropyl alcohol and, after being purified by distillation, analyzed 98.2%, the remainder being air and saturates. The 2-butene was analyzed by infrared absorption to be as follows: 1-butene, 5.5%; 2-butene, 94.2%; butadiene, 0.2%; and *n*-butane, 0.1%. The isobutene was a refinery product which analyzed 99.7%. The liquid hydrocarbons were all carefully distilled and checked for purity by refractive indices.

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(3) Beeck and Rust, *J. Chem. Phys.*, **9**, 480 (1941).

The di-*t*-butyl and di-*t*-amyl peroxides were synthesized in accordance with the procedures given by Vaughan and Rust.[4] The di-*t*-butyl peroxide had an index n^{20}_{D} 1.3890 and was 98+% pure. The di-*t*-amyl peroxide distilled at 54.5–55° at 17–18 mm.; its refractive index was n^{20}_{D} 1.4083.

In general, experiments were conducted by metering the gaseous hydrocarbons or carrier nitrogen through flowmeters and the liquid peroxide through a rotameter. The peroxide was vaporized and mixed with the gaseous materials in a glass tubular coil surrounded usually by boiling water. The reaction mixture then passed directly into the top of the reactor tube (1250 cc., 70 mm. i.d.), which was heated by a thermostated oil-bath. The liquid product was collected in a water wash-bottle and an ice-cooled trap while the effluent gas was passed into an aspirator bottle. The gases and vapors were analyzed by low temperature distillation except where otherwise specified.

Experimental

Toluene and Di-*t*-butyl Peroxide. 2,3-Dimethylbutane and Di-*t*-butyl Peroxide.—Mixtures of hydrocarbon and peroxide in a molar ratio of 2:1 were metered into the reaction system at a rate calculated to give a total vapor flow of 300 cc./minute[5] N.T.P. Carrier nitrogen (50 cc./minute) was added. The reaction temperature was 235°.

From toluene, ethylbenzene (b. p. 136°, n^{20}_{D} 1.4937) was produced in a 6.25% yield based on the input peroxide. Higher boiling product, 50% greater in amount than the ethylbenzene, was also collected; this material had a molecular weight of 199 which compares with 182 for diphenylethane.

Under comparable conditions triptane was produced from the dimethylbutane in a yield of 7.7%. The analysis of the triptane fraction was made by infrared absorption. Higher boiling products in comparable volume were not investigated.

Ethylene and Di-*t*-butyl Peroxide.—Experiments were carried out as follows: A mixture of ethylene plus peroxide was introduced at a rate of 200 cc./min. vapor volume into a Pyrex tube heated to 225 or 235°. Ratios of ethylene to peroxide between 1:1 and 9:1 were used. The data are given in Table II.

TABLE II

REACTION OF DI-*t*-BUTYL PEROXIDE AND ETHYLENE

Temp., °C.	210	225	225	225	225	235
Ratio C_2H_4:peroxide	1:1	1:1	2:1	4:1	9:1	9:1
% Peroxide reacted	56.8	89.6	94.2	80.4	59.2	63.5
% Reacted peroxide converted to						
Ethane	66.9	82.3	68.2	62.1	40.7	61.6
n-Butane	9.7	6.8	14.2	15.1	28.8	13.6
n-Hexane	4.4	1.6	4.6	13.4	10.2	16.0
n-Octane	...	...	...	...	...	4.0

In every case higher boiling products were produced but the amounts were too small to permit identification. The hexane had a boiling point of 69° and n^{20}_{D} 1.3750 (lit.[6] 68.7° and 1.3750). Respective values for the octane isolated are b. p. 124.2° and n^{20}_{D} 1.3986 (lit., 125.6° and 1.3976). The above estimates of conversions are based on the actual amounts of materials isolated and on the amount of decomposed peroxide as given by the ketone formed. Unreacted peroxide in the high boiling fractions was removed by boiling with concentrated hydrogen iodide in acetic acid; the resulting iodine was destroyed with thiosulfate solution and the alkyl iodides with alcoholic potassium hydroxide. The residue was then washed and fractionated.

Propylene and Di-*t*-butyl Peroxide.—Propylene and di-*t*-butyl peroxide vapor reacted at 235° with input flow rates of propylene and peroxide of 200 cc./min. and 100 cc./min. The effluent vapors, after passing through a water bubbler and ice-cooled trap, were collected in an aspirator bottle and later fractionated by low temperature distillation. The gaseous fractions were analyzed subsequently in an Orsat-type apparatus with the exception of the C_4 cut which was analyzed by infrared spectrophotometry. The composition of these light fractions is shown in Table III.

TABLE III

Product	Per cent.
Propylene	60.6
Methane	13.7
Ethane	9.8
Isopentane	6.3
n-Butane	2.4
1-Butene	2.0
2-Butene	0.8
Isobutane	0.4
Others	4.0

The liquid product was washed with water and hydroxylamine to remove as much ketone as possible and then fractionated. Besides the low boiling cuts (C_5) this distillation showed fractions in the C_7, C_8 and C_9 ranges and a very substantial amount of still higher boiling material. The 107 to 113.5° cut after washing with concentrated sulfuric acid and distilling, had a refractive index of n^{20}_{D} 1.3970. According to infrared analysis this fraction was *ca.* 95% 2,4-dimethylhexane, and 5% 2,5-dimethylhexane. These two octanes have reported boiling points of 109.8 and 109.3° and indices n^{20}_{D} 1.3958 and 1.3929, respectively. The 113.5 to 119.5° fraction had an index n^{20}_{D} 1.4044 before and after washing with concentrated sulfuric acid. Infrared analysis showed it to be 98% 3,4-dimethylhexane (lit. b. p. 117.85°, n^{20}_{D} 1.40436). The next higher fraction boiling around 135° appears to be a nonane, but has not been identified. Figure 1 is a line diagram of the infrared absorption spectra of the heptene and octane fractions.

In order to determine the carbon skeleton of the small heptene fraction, propylene and peroxide were passed through the reactor at 235° for twenty-five hours. The resulting product, after being washed free of acetone, was hydrogenated at 80° in isopropyl alcohol with Ruffert nickel. The product was filtered, water-washed, dried

TABLE IV

YIELD OF HIGHER HYDROCARBONS DERIVED FROM PROPYLENE (BASED ON INPUT PEROXIDE)

Product	Per cent.
n-Butane	4.5
1- and 2-butene	5.0
Isobutane	<1.0
Isopentane	20.0
Heptenes	0.5
3,4-Dimethyloctane	2.0
2,4-Dimethyloctane	1.5
2,5-Dimethyloctane	<0.1

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[4] Vaughan and Rust, U. S. Patent 2,403,771.

[5] Hereinafter, "cc./min." means cc. vapor/minute N.T.P.

[6] The literature values for the physical constants for the hydrocarbons cited herein are taken from M. P. Doss, "Physical Constants of the Principal Hydrocarbons," The Texas Company, New York, N. Y., 1942.

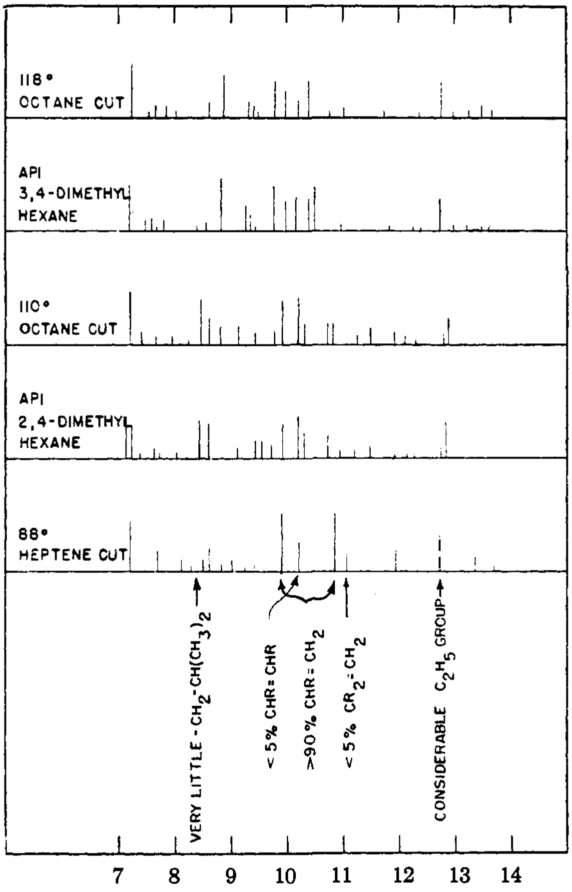

Fig. 1.—Infrared spectra of di-*t*-butyl peroxide–propylene reaction products.

and fractionated. The heptane fraction was separated and by infrared analysis was found to be 85–95% 3-methylhexane and 5–15% 2-methylhexane. The yields of some products are given in Table IV.

2-Butene and Di-*t*-butyl Peroxide.—Di-*t*-butyl peroxide (100 cc./min.) and 2-butene (200 cc./min.) were mixed and passed into the reactor at 235°. Analysis of the effluent gaseous products gave

	Per cent.
Butenes	60.0
Methane	17.5
Ethane	9.3
Pentenes	4.2
Isopentane	1.2
Other	7.8

The fraction containing dimethylbutane was washed with water and concentrated sulfuric acid to remove acetone and olefins. The material was then distilled and found to have an index n^{20}D 1.3750 and a boiling point of 58.2° (lit., 1.3749 and 57.99°). The dibromide derivative was prepared (2,3-dibromo-2,3-dimethylbutane); this had a melting point of 163–164°, and a mixed melting point of 163.5–164.0°.

The higher boiling product was carefully water-washed and then steam distilled. The hydrocarbons were separated from the water in the distillate and refractionated. The material that boiled between 128 and 142° had a molecular weight (by vapor density) of 122.6 to 122.7, and a molecular weight on the basis of bromine number of 126; the molecular weight of nonene is 126. A narrow boiling fraction between 153.5 and 155.0° had a molecular weight of 139, while the theoretical value for decane is 142. Based on the probable reaction mechanism this decane must be the heretofore unreported 2,3,4,5-tetramethylhexane. The boiling point, as given by the distillation flat, was 155° and the index, n^{20}D, 1.426. A substantial amount of still higher boiling material remained. The yields are given in Table V.

TABLE V

YIELD OF HIGHER HYDROCARBONS DERIVED FROM 2-BUTENE (BASED ON INPUT PEROXIDE)

Product	Per cent.
Pentenes	10.0
Isopentane	3.5
Dimethylbutane	8.0
Nonenes	2.0
Decane	1.5

Isobutene and Di-*t*-butyl Peroxide.—Isobutene (200 cc./min.) and di-*t*-butyl peroxide (100 cc./min.) were passed into the reactor at 235°. The reaction products were analyzed essentially as described for propylene and 2-butene. Dimethylation of the double bond gives neohexane. The boiling point of the isolated fraction was 49–50° and its index n^{20}D 1.3686 (lit., 49.7° and 1.3686, respectively). However, the principal products are *t*-amylenes. The predicted compound would be $CH_2{=}\overset{\overset{CH_3}{|}}{C}CH_2{-}CH_3$ but the usual accompanying isomerization, in this case to trimethylethylene, seems to be rapid. Infrared analysis of the amylene fraction shows 60% 2-methyl-1-butene and 40% trimethylethylene. Isopentane is formed in an appreciable quantity (n^{20}D 1.3530, b. p. 28.0°; lit., n^{20}D 1.3540, b. p. 27.9°).

The low temperature distillation of the gaseous effluent gave results as follows

	Per cent.
Isobutene	56.0
Methane	21.3
Ethane	8.0
t-Pentenes	5.1
Isopentane	4.7
Others	4.9

A fraction boiling in the nonene range, 128–136°, had a molecular weight of 121.5 and bromine number of 115.5; for nonene the molecular weight and theoretical bromine number are both 126.

A fraction distilling between 162 and 172° was found to have a molecular weight of 141 and a bromine number of 2.6, which compares well with 142 and zero for decane. By analogy with propylene the decanes expected and probably present are 2,2,4,4-, 2,2,5,5- and 3,3,4,4-tetramethylhexanes. Inclusion of additional isobutene units in the reaction chain gives higher molecular weight hydrocarbons. Yields are shown in Table VI.

TABLE VI

YIELD OF HIGHER HYDROCARBONS DERIVED FROM ISOBUTENE (BASED ON INPUT PEROXIDE)

Product	Per cent.
t-Amylenes	8.5
Isopentane	7.5
Neohexane	6.0
Nonenes	2.0
Decanes	2.0

Propylene and Di-*t*-amyl Peroxide.—Propylene 200 cc./min. and di-*t*-amyl peroxide vapor 100 cc./min. were passed through the reactor at 235°. The effluent gaseous products of the reaction were found to be as follows

	Per cent.
Propylene	61.3
n-Butane	17.3
Ethane	8.5
Ethylene	2.0
Propane	2.0
Straight chain pentenes	1.3
n-Pentane	1.1
Methane	0.9
Isopentane	0.7
Others	4.9

The liquid products collected were water-washed and fractionated. Cut I (20–54°) was water-washed to remove some acetone and analyzed by infrared absorption. Its hydrocarbon composition was 50% isopentane, 25% *n*-pentane, 10% 1-pentene and 5% each of 2-pentene, 2-methyl-1-butene and 2-methyl-2-butene. The 54–57° fraction was almost entirely acetone, and the very small amount of water-insoluble organic material (b. p. 70–71°) was not analyzed further. A small intermediate fraction (57–91°) was washed with hydroxylamine hydrochloride solution and dried; infrared analysis showed 5% of a 1-olefin, 60% 3-methylhexane and 30% 2-methylhexane. The remaining 5% was ketone which was not completely removed by water-washing. Cut IV (b. p. 91–94) was washed with concentrated sulfuric acid with virtually no change in volume or the refractive index of 1.3890. Infrared analysis identified the material as 3-methylhexane and a vapor density measurement gave the molecular weight as 100 (theory 100.2). The decane fraction (153–161°) after being washed with concentrated sulfuric acid and $6\ N$ sodium hydroxide analyzed as follows: carbon 84.4%, hydrogen 15.4%, mol. wt. 149; calcd., 84.5, 15.5 and 142, respectively.

TABLE VII

YIELD OF HIGHER HYDROCARBONS DERIVED FROM PROPYLENE (BASED ON DI-*t*-AMYL PEROXIDE)

Product	Per cent.
Amylenes	2.7
n-Pentane	2.5
Isopentane	1.6
3-Methylhexane	8.0
Nonenes and decanes	3.0

Acknowledgment.—The authors are indebted to the members of the Spectroscopic Department of This Company, and in particular to Dr. R. S. Rasmussen, for the infrared analyses.

Summary

1. The di-*t*-alkyl peroxides are especially useful tools for the study of free radical processes.

2. Some of the products from the interaction of free methyl and ethyl with various saturated and unsaturated hydrocarbons have been isolated and identified. Mechanisms of formation of these compounds are suggested.

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[7] Original manuscript received September 26, 1946.

[CONTRIBUTION FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY OF THE IOWA STATE COLLEGE]

The Structures of the Carbides, Nitrides and Oxides of Uranium[1]

BY R. E. RUNDLE, N. C. BAENZIGER, A. S. WILSON AND R. A. McDONALD

Introduction

The systems uranium–carbon, uranium–nitrogen and uranium–oxygen have been given thorough X-ray study in the course of work carried out for the Metallurgical Project. In this paper this work will be summarized rather briefly, giving pertinent structural information and necessary details concerning the methods used in carrying out the work.

In general, little discussion of the structures will be presented here. The nature of the metal-like monocarbide, mononitride and monoxide are discussed elsewhere along with other similar compounds.[2] Since the structures of nearly all the phases examined have been simple, parameterless structures of types described thoroughly in "Strukturbericht," it has seemed unnecessary to present lengthy accounts of the structural determinations, together with tables of calculated and observed intensities. In every case not otherwise indicated a careful comparison of observed and calculated intensities for the assigned structure has been made.

Though this paper is intended primarily as a summary of X-ray structures, many of the compounds whose structures are reported here were discovered and their compositions first obtained either solely by X-ray study or jointly with chemical investigations. It seems well to point out, therefore, that X-ray study of the carbides, nitrides and oxides of uranium has required extensive revision of formulas in these systems. The monocarbide and the mononitride were discovered, with chemical and metallographic aid, by X-ray diffraction; the monoxide was found solely by X-ray diffraction. Not a single nitride of uranium had been assigned a correct formula before these X-ray studies were made.[3] Even among the higher oxides new phases were found, and the relationships among the higher oxides

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[1] Paper No. 7 of the Institute for Atomic Research. Work done under contract W-7405 eng-92, Manhattan Project, U. S. Corps of Engineers. F. H. Spedding, Project Director. A review of this work will be published in Div. VIII, Manhattan Project Technical Series.

[2] R. Rundle, "A New Interpretation of Interstitial Compounds," submitted for publication in *Acta Crystallographica*.

[3] Gmelin's "Handbuch der anorganischen Chemie," system Number 55, Verlag Chemie, Berlin, 1936, p. 107 ff.