servations should permit one to decide whether the material which can be sedimented is truly insoluble, as micro-gel would be, or is undissolved associated material unconnected with the presence of branched and cross linked polymer.

It is known that undissolved or precipitated PAN contains crystalline regions, and the polymer is with difficulty soluble at room temperature. In fact rapid solution only occurs at elevated temperatures. If the polymer in solution forms associated clusters, the molecular weight of these clusters should vary with temperature and should re-form when the temperature is lowered. Light scattering at elevated temperatures or ultracentrifugation at elevated temperatures are possible methods of distinguishing between micro-gel and micro-crystalline regions. The latter procedure is the easier of the two and requires the assumption that the disassociated material will not sediment at high temperatures and will re-form when the polymer is dried. Distorted Zimm plots should persist after this treatment if they result from the presence of microcrystalline aggregates. Sample 11HF1 was ultracentrifuged at 90°, dried, redissolved, and the molecular weight was determined by light scattering. A distorted Zimm plot did not occur. The weight average molecular weight of another top fraction of sample 11H ultracentrifuged at room temperature was 341,000 with $(\eta) = 2.68$. The comparable data for a separate portion of this fraction ultracentrifuged at 90° was 297,000 and 2.71. Therefore, it is concluded that the material that is causing the difficulties probably is micro-gel and not associated clusters.

Distorted Zimm plots have been observed for every high molecular weight sample run to date. These include both high conversion copolymers and the first fraction of both a low and a high conversion homopolymer.

Possible Mechanisms of Branch and Gel Formation.—Ham[19] and Cleland and Stockmayer[3] have determined the chain transfer constant to monomers for polyacrylonitrile in dilute solution and come to the conclusion that little or no branching should occur at higher conversion.

The copolymer, of course, contains less than 10% vinyl acetate based on polymer content. Polyvinyl acetate is known to be branched easily. In fact, extreme care must be taken in the polymerization of vinyl acetate if linear molecules are desired. Thus, some branching might be expected in the copolymer as a result of the presence of vinyl acetate. However, PAN also shows the same behavior and therefore must itself contain micro-gel and therefore also be branched.

It is thus evident that the estimates of the severity of branching based on the literature data on the chain transfer constant cannot be correct. Even the PAN sample, which was prepared at 9% conversion, shows evidence for the presence of micro-gel and therefore must be branched.

The method of formation of micro-gel in PAN is not known, but some speculations may be presented. A multifunctional unit with a functionality greater than three will cause cross linking if present in polymerization or if it is formed sometime during the polymerization process.

By this mechanism it is possible that polymerization may proceed through a nitrile group. Although this process may not be energetically favorable, only one nitrile group out of 700 need enter the reaction to cause cross linking. The mechanism of branch formation by chain transfer is generally considered not to lead to gelation unless assisted by an independently occurring intermolecular reaction.[20]

Acknowledgments.—The author wishes to express his appreciation to Dr. Thomas W. DeWitt for many helpful discussions concerning this work, to Mr. Robert F. Crafts for making the measurements, to Dr. Lloyd T. Jenkins for preparing the polyacrylonitrile samples and to the Chemstrand Corporation for permission to publish this work.

DECATUR, ALABAMA

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[19] G. E. Ham, *J. Polymer Sci.*, **21**, 337 (1956).

[20] P. J. Flory, "Principles of Polymer Chemistry," Cornell University Press, Ithaca, N. Y., 1953.

[CONTRIBUTION FROM THE GENERAL ELECTRIC RESEARCH LABORATORY]

Radiation Chemistry of Organic Compounds. III. Branched Chain Alkanes

BY H. A. DEWHURST

RECEIVED JUNE 2, 1958

The yields of gas and liquid products, in the presence and absence of iodine, have been determined for the radiolysis (800 kvp. electrons) of the hexane isomers and a selected group of other branched alkanes. Infrared determination of the unsaturation showed that the kind of double bond formed was related to the hydrocarbon structure. The product distributions determined by gas chromatography reflect a marked structural effect in the radiolysis processes showing a preference for reactions adjacent to the branch site. The non-equivalence of radical fragments as determined by iodine scavenger suggests that simple C–C bond fission does not occur.

Introduction

Relatively little attention has been given to the effect of branching on the radiolysis of saturated aliphatic hydrocarbons. Schoepfle and Fellows[1] examined the gas products from three isomeric octanes and found that increased methyl substitution increased the methane yield and decreased the hydrogen yield. Schuler and co-workers,[2]

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[1] C. S. Schoepfle and C. H. Fellows, *Ind. Eng. Chem.*, **23**, 1396 (1931).

[2] E. N. Weber, P. F. Forsyth and R. H. Schuler, *Radiation Research* **3**, 68 (1955).

using iodine scavenger, concluded that the alkane liquids have about the same radical yield, independent of chain branching.

The present paper is concerned with the effect of structure on the total radiation chemistry of a series of isomeric hydrocarbons.

Experimental

Materials.—The hydrocarbons used were Phillips pure grade except for 2,2-dimethylbutane which was research grade and the 2-methylheptane which was a high purity API sample. The iodine was from Mallinckrodt.

Irradiation.—The samples were irradiated with 800 kvp. electrons from a resonant transformer unit. For the determination of gas products the liquid samples were thoroughly degassed and irradiated in thin window glass cells as previously described.[3]

For the determination of liquid products deaerated samples (2 g.) were irradiated under nitrogen (Linde-pure) in a shallow water-cooled, 2-inch diameter aluminum dish. The samples were irradiated uniformly at a dose rate of 8.0 $\times 10^{20}$ e.v./g./min. as previously described.[3] Saturated iodine solutions were deaerated with nitrogen and irradiated under nitrogen in the water-cooled aluminum dish. A few small crystals of iodine were placed in the irradiation cell, equipped with a magnetic stirrer, to ensure iodine saturation.

Analytical.—The methods used for the analyses of gas and liquid products have been described.[3] Differential infrared spectroscopy was used to obtain a more precise measurement of the unsaturation. The vapor fractometer column was didecyl phthalate and was calibrated for retention time and area per cent. with known solutions.

Results and Discussion

Gas Formation.—The yields of hydrogen and methane from the isomeric hexanes and a selected group of heptanes and octanes are given in Table I. The hexanes show a regular decrease in the hydrogen yield with increase in methyl substitution. Although the methane yield increased with methyl substitution, a simple correlation with the number of methyl groups present was not observed. The *gem*-dimethyl structure (2,2-dimethyl substituted) gave the highest methane yield. It is noteworthy that for the branched hydrocarbons the methane yield shows a qualitative correlation with the relative mass spectral abundance of the ion corresponding to the parent ion minus mass 15 shown in Table I.

TABLE I

HYDROGEN AND METHANE YIELDS FOR BRANCHED CHAIN ALKANES

Energy absorbed = 5 $\times 10^{20}$ e.v.

Alkane	*G*, molecules/ 100 e.v. H_2	CH_4	Mass spectrometer $C^+_{\text{parent-methyl}}$
n-Hexane[a]	5.0	0.2	5
2-Methylpentane	4.0	.5	27
3-Methylpentane	3.4	.2	5
2,3-Dimethylbutane	2.9	.5	15
2,2-Dimethylbutane	2.0	1.2	72
n-Heptane[a]	4.7	0.09	1.9
2,4-Dimethylpentane	4.9	0.2	17.2
n-Octane[a]	4.8	0.08	0.07
2-Methylheptane	5.2	.4	12.4
2,2,4-Trimethylpentane	3.0	.7	4.7

[a] H. A. Dewhurst, ref. 3.

Infrared Results.—Some typical results for the formation of unsaturation as a function of the energy absorbed are shown in Fig. 1 for 2-methylpentane. From plots such as this, initial *G* (unsaturation) values were obtained and are shown in Table II for a number of branched chain hydrocarbons. The *n*-alkanes form mainly *trans*-vinylene double bonds[3] whereas the branched hydrocarbons form mainly vinylidene[4] and vinyl unsaturation. These results demonstrate that the type of double bond formed can be directly related to the hydrocarbon structure. The G_t value for total unsaturation was approximately the same for all the alkanes studied. Comparison of the unsaturation from 2-methylpentane and 2-methylheptane illustrates the effect of increasing the hydrocarbon tail; a decrease in vinylidene unsaturation was observed with a corresponding increase in the *trans*-vinylene unsaturation. In this case the kind and amount of unsaturation formed shows, to a first approximation, a direct correlation with the number of CH_2 and CH_3 groups in the hydrocarbon.

TABLE II

UNSATURATION FROM BRANCHED CHAIN ALKANES

Alkane	*G*, molecules/100 e.v. *trans*	Vinyl	Vinylidene	G_t
n-Hexane[a]	1.2	0.3	0	1.5
2-Methylpentane	0.4	.3	0.9	1.6
3-Methylpentane	0	.8	.1	0.9
2,3-Dimethylbutane	0	0	1.4	1.4
2,2-Dimethylbutane	0	0.15	1.2	1.3
n-Heptane[a]	1.3	0.2	0	
2,4-Dimethylpentane	0	0	1.0	1.0
n-Octane[a]	1.4	0.3	0	
2-Methylheptane	0.7	.4	0.5	1.6

[a] H. A. Dewhurst, ref. 3.

Infrared measurements were of value in determining the reactivity of the different branched structures. The results of these measurements are shown in Table III. Comparison of 2-methylpentane with 2-methylheptane shows that the addition of 2 CH_2 groups decreased the reaction at the branch-site by one half in agreement with the observed effect on the unsaturation. The reactivities of 2,2-, 2,3- and 2,4-dimethyl structures were approximately the same and were about twice the reactivity of the isopropyl and internal methyl structures in 2-methylpentane and 3-methylpentane, respectively. It is of interest therefore to note the

TABLE III

G-VALUES FOR REACTION OF BRANCHED STRUCTURES

Structure	*G*, molecules/100 e.v. Isopropyl 1170 cm.$^{-1}$	*gem*-Dimethyl 925 cm.$^{-1}$	Internal methyl, 1152 cm.$^{-1}$
2-Methylpentane	3.4	..	..
3-Methylpentane	..	..	3.7
2,2-Dimethylbutane	..	6.5	..
2,3-Dimethylbutane	6.5	..	..
2,4-Dimethylpentane	7.0	..	..
2-Methylheptane	1.8	..	..

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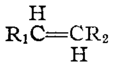
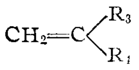
(3) H. A. Dewhurst, *J. Phys. Chem.*, **61**, 1466 (1957).

(4) *trans*-Vinylene structure 

$R_1\overset{H}{C}{=}\underset{H}{C}R_2$

Vinylidene structure 

$CH_2{=}C\begin{smallmatrix}R_3\\R_4\end{smallmatrix}$

approximate constancy of the reactivity per branch for the hexane isomers.

Gas Chromatography.—It has been shown[3] that the product distribution from *n*-alkane liquids can be classified conveniently into three groups, namely, low molecular weight (C_l), intermediate molecular weight (C_i) and dimer (C_d) products. Such a classification, useful also for the branched chain alkanes, is shown in Table IV for the major products from the isomeric hexanes.

The low molecular weight group consists mainly of products that result from reaction adjacent to the branch. For example, the major C_l products from 2-methylpentane were C_3 and C_5 hydrocarbons while the major products from 3-methylpentane were C_2 and C_4 hydrocarbons. Similarly large yields of C_2 and C_4 products were obtained from 2,2-dimethylbutane while 2,3-dimethylbutane formed mainly C_3 product. The yield of C_5 hydrocarbon bears approximately the same relationship to the hydrocarbon structure as shown by the methane yield (Table I).

If it is assumed that the C_i products are formed by recombination of parent and fragment radicals, then the C_i products observed (Table IV) show a preference for fragment radicals that result from C–C bond fission adjacent to the branch site. For example, 2-methylpentane did not form any appreciable amounts of C_8 and C_{10} products, instead a large yield of C_9 product was formed. Although a large number of C_i products were obtained from 2,2-dimethylbutane, the C_8 and C_{10} products were in greater amounts corresponding to a preferred cleavage into C_2 and C_4 fragments.

TABLE IV

GAS CHROMATOGRAPHY RESULTS FOR IRRADIATED ISOMERIC HEXANES

Energy absorbed = 2.9×10^{21} e.v./g.

	G, molecules/100 e.v.		
Alkane	C_l	C_i	C_d
n-Hexane[a]	$C_2 = 0.6$	$C_7 = 0.2$	
	$C_3 = .45$	$C_8 = .4$	
	$C_4 = .5$	$C_9 = .6$	
	$C_5 = .2$	$C_{10} = .4$	$C_{12} = 2.0$
2-Methylpentane	$C_3 \sim 1.6$	$C_6 + C_7 = 1.6$	
	$C_5 = 0.7$	$C_9 = 1.8$	
			$C_{12} = 1.3$
3-Methylpentane	$C_4 \sim 2.4$	$C_7 = 0.5$	
	$C_5 = 0.3$	$C_8 = 1.1$	
		$C_{10} = 0.7$	$C_{12} = 1.0$
2,2-Dimethylbutane	$C_2 \sim 1.5$		
	$C_4 \sim 2.4$	$C_7 = 0.7$	
	$C_5 = 1.2$	$C_8 = .75$	
		$C_9 = .2$	
		$C_{10} = .4$	
		$C_{11} + C_{12} = 0.6$	
2,3-Dimethylbutane	$C_3 \sim 1.2$	$C_7 = 0.4$	
	$C_4 = 0.1$	$C_8 = 0.3$	
	$C_5 = 0.6$	$C_9 = 2.4$	$C_{12} = 0.9$

[a] H. A. Dewhurst, *J. Phys. Chem.*, **62**, 15 (1958).

The formation of C_{12} hydrocarbon was observed for all the isomeric hexanes. A precise determination of the C_{12} yield from 2,2-dimethylbutane was not possible because of the strong overlap of the product peaks on the chromatogram. In all cases the dimer yield was less for the branched than for the straight chain hexane. It is probable that the parent radical form 2-methylpentane, 3-methylpentane and 2,3-dimethylbutane results from loss of the tertiary H-atom. This could be shown by a complete determination of the dimer structure.

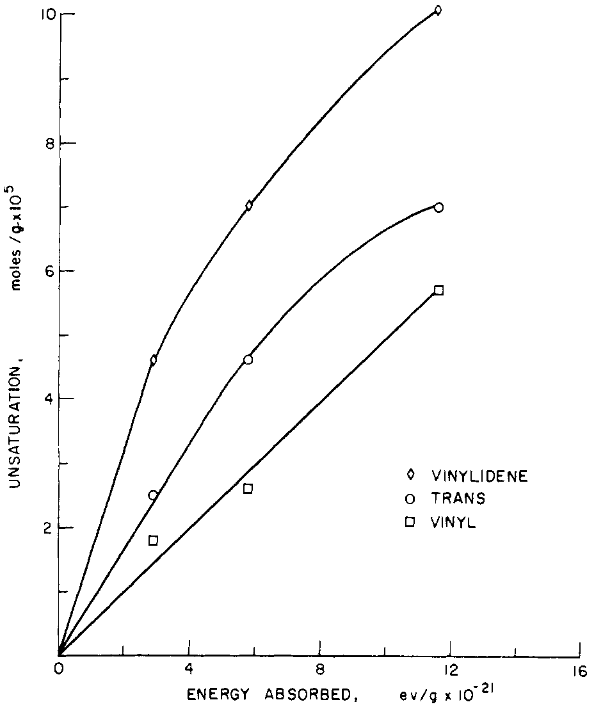


Fig. 1.—Unsaturation as a function of energy absorbed from radiolysis of 2-methylpentane.

Effect of Iodine.—The alkyl iodide yields from saturated iodine solutions of some of the isomeric hexanes were determined by gas chromatography and are given in Table V. In spite of complications at high iodine concentrations Schuler and McCauley[5] have shown that for liquid butane the complications apparently do not affect the alkyl iodide yields. If the same is true of the isomeric hexanes then the alkyl iodide distribution can be taken as representing the radical distribution.

TABLE V

ALKYL IODIDE YIELDS FROM ISOMERIC HEXANES SATURATED WITH IODINE

Energy absorbed = 2.9×10^{21} e.v./g.

	G, molecules/100 e.v.					
Hydrocarbon	CH_3I	C_2H_5I	C_3H_7I	C_4H_9I	$C_5H_{11}I$	$C_6H_{13}I$
n-Hexane[a]	0.1	0.4	0.7	0.3	<0.1	3.3
2-Methylpentane	..	2.6	1.0	<0.1	0.7	1.6
3-Methylpentane	..	1.6	<0.1	0.7	<0.1	1.7
2,2-Dimethylbutane	2.1	0.6	<0.1	?	0.2	1.2

[a] Footnote *a* of Table IV.

The methyl iodide yields from 2- and 3-methylpentane were not determined because of incomplete

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(5) C. E. McCauley and R. H. Schuler, THIS JOURNAL, **79**, 4008 (1957).

resolution by the gas chromatography column used. In most cases the structure of the C_5 and C_6 iodides was not determined; however, from the position of these products on the gas chromatogram an indication of the structure could be obtained. *t*-Butyl iodide could not be determined because of its easy decomposition at elevated temperatures. In all cases, 2,2-dimethylbutane a possible exception, the presence of iodine eliminated both the C_i and C_d products. The effect of iodine on the C_1 products is less certain because of volatility losses. It was noted, however, that iodine decreased the methane yield from 2,2-dimethylbutane by only one-half.

The iodide products from *n*-hexane consisted mainly of the *n*-alkyl type with the exception of the C_6 iodide which was 20% *n*-hexyl and 80% *sec*-hexyl. In general the iodide products from the branched isomers, apart from methyl and ethyl iodide, did not contain any appreciable quantities of *n*-alkyl iodides. The total alkyl iodide yield from the hexanes was approximately the same as that reported for liquid butane.[5]

A surprisingly large yield of ethyl iodide was obtained from 2-methylpentane while only a negligible amount of C_4 iodide was observed. The C_3 iodide was entirely isopropyl showing that a simple C–C bond fission at the branch site does not occur since this would lead to equal amounts of isopropyl and *n*-propyl iodides. The distribution of alkyl iodide products from 3-methylpentane was in qualitative accord with the C_i product distribution shown in Table IV. The C_4 iodide product was entirely *sec*-butyl. The non-equivalence of the methyl iodide and pentyl iodide yields again showed that simple C–C bond fission into radicals does not occur.

Conclusion.—The products observed from the branched alkanes show, in most cases, a preference for C–C bond fission at points adjacent to the branch site. Qualitatively, similar behavior can be seen in the mass spectral fragmentation patterns. However, two important differences should be noted. The mass spectra of 3-methylpentane and 2,2-dimethylbutane show very large rearrangement peaks. There was no evidence that such rearrangement processes were important for the radiolysis of the liquids. It may well be that this kind of rearrangement process is quenched in the condensed phase but might be observed in vapor phase radiolysis. The second important difference was noted in the abundance of the parent fragment. The parent ion peaks in the mass spectra of the branched hydrocarbons are exceedingly small whereas in the liquid radiolysis the parent fragment is a major component of the total product observed. This difference undoubtedly reflects the effect of state on the abundance of the parent fragment.

The observed non-equivalence of radical fragments in many cases suggests that simple C–C bond fission does not occur. It is evident that conventional free radical chemistry does not apply insofar as the fragmentation processes are concerned. It may be that ion-molecule reactions, which could generate free radicals in non-equivlaent amounts, play an important role even in the condensed phase. Similar reactions involving the interaction of excited molecules could also be written to give a non-equivalence of radicals.

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SCHENECTADY, NEW YORK

[CONTRIBUTION FROM THE DIVISION OF PHYSICAL CHEMISTRY, UNIVERSITY OF MINNESOTA, INSTITUTE OF TECHNOLOGY]

Some Properties of the Ground Triplet State of Chlorophyll and Related Compounds[1]

BY ROBERT LIVINGSTON AND EIJI FUJIMORI

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The absorption spectra of the lowest triplet states of certain polyatomic molecules were measured by the use of the flash photolytic-flash photographic technic. The compounds studied included chlorophylls-*a* and -*b*, pheophytins-*a* and -*b*, Zn-chlorophyll-*a*, several porphyrins and Mg-phthalocyanine. In general, these spectra resemble those which have been published for the triplet states of the chlorophylls. The principal absorption maxima of the ground state do not appear in the absorption of the triplet state and are replaced by a broad absorption, having a maximum on the long wave length side of the Soret band and gradually decreasing toward the red. No transients were detectable for copper or iron substituted porphyrins or for Cu-chlorophyll-*a*, presumably due to the short lives of the triplet states of these molecules.

A long-lived excited state, presumably the lowest triplet state, plays an important role[2a] in the photochemical reactions of dyes and pigments. The development of the flash photolytic technique[2b] has made possible the direct study of some properties of the triplet states of these molecules. The present results were obtained with a flash-photolytic, flash-spectrographic apparatus, patterned on that of Porter and Windsor.[3] While this method is well adapted to the measurement of the wave lengths of absorption maxima, it yields only semi-quantitative values of the extinction coefficients of broad, relatively structureless absorption curves which are characteristic of the triplets of chlorins and porphyrins. A few qualitative observations of the half-lives of certain compounds are included in this report. The results of detailed kinetic studies of the decay of the chlorophyll triplet, which were ob-

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(1) This work was supported by a grant from the National Science Foundation (NSF-G 1449) for which the authors are grateful.

(2) (a) E. Rabinowitch, "Photosynthesis," Interscience Publishers, New York, N. Y., pp. 484–547 and 1507–1528; (b) G. Porter, *Proc. Roy. Soc.* (*London*), **A200**, 284 (1950).

(3) G. Porter and M. Windsor, *Disc. Faraday Soc.*, **17**, 178 (1954).