

NRC Publications Archive Archives des publications du CNRC

Thermal decomposition products of polyisobutylene Tsuchiya, Y.; Sumi, K.

This publication could be one of several versions: author's original, accepted manuscript or the publisher's version. /
La version de cette publication peut être l'une des suivantes : la version prépublication de l'auteur, la version
acceptée du manuscrit ou la version de l'éditeur.

For the publisher's version, please access the DOI link below. / Pour consulter la version de l'éditeur, utilisez le lien
DOI ci-dessous.

Publisher's version / Version de l'éditeur:

<https://doi.org/10.4224/40001513>

*Research Paper (National Research Council of Canada. Division of Building
Research); no. DBR-RP-408, 1969-08-01*

NRC Publications Archive Record / Notice des Archives des publications du CNRC :

<https://nrc-publications.canada.ca/eng/view/object/?id=7b492443-74ad-4afa-a21e-bc2d649934dc>

<https://publications-cnrc.canada.ca/fra/voir/objet/?id=7b492443-74ad-4afa-a21e-bc2d649934dc>

Access and use of this website and the material on it are subject to the Terms and Conditions set forth at

<https://nrc-publications.canada.ca/eng/copyright>

READ THESE TERMS AND CONDITIONS CAREFULLY BEFORE USING THIS WEBSITE.

L'accès à ce site Web et l'utilisation de son contenu sont assujettis aux conditions présentées dans le site

<https://publications-cnrc.canada.ca/fra/droits>

LISEZ CES CONDITIONS ATTENTIVEMENT AVANT D'UTILISER CE SITE WEB.

Questions? Contact the NRC Publications Archive team at

PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca. If you wish to email the authors directly, please see the
first page of the publication for their contact information.

Vous avez des questions? Nous pouvons vous aider. Pour communiquer directement avec un auteur, consultez la
première page de la revue dans laquelle son article a été publié afin de trouver ses coordonnées. Si vous n'arrivez
pas à les repérer, communiquez avec nous à PublicationsArchive-ArchivesPublications@nrc-cnrc.gc.ca.

Ser
TH1
N21r2
no. 408
c. 2

BLDG

840
ANALYZED

NATIONAL RESEARCH COUNCIL OF CANADA
CONSEIL NATIONAL DE RECHERCHES DU CANADA

THERMAL DECOMPOSITION PRODUCTS
OF POLYISOBUTYLENE

BY

YOSHIO TSUCHIYA AND KIKUO SUMI

43083

REPRINTED FROM
JOURNAL OF POLYMER SCIENCE: PART A - 1
VOL. 7, 1969
P. 813 - 826

RESEARCH PAPER NO. 408
OF THE
DIVISION OF BUILDING RESEARCH

BUILDING RESEARCH
- LIBRARY -

SEP 4 1969

NATIONAL RESEARCH COUNCIL

OTTAWA

PRICE 25 CENTS

AUGUST 1969

NRC 10895

LES PRODUITS DE LA PYROLYSE DU POLYISOBUTYLENE

SOMMAIRE

Les auteurs ont soumis du polyisobutylène à une pyrolyse sous vide à 325°, 345° et 365°C, et ont recueilli les produits volatils à l'aide d'azote liquide. Ils ont analysé par chromatographie en phase gazeuse les carbures d'hydrogène produits de C_1 à C_{24} . Ils étudient la formation des principaux produits par la voie des radicaux libres. Les transferts intramoléculaires de radicaux peuvent rendre compte de la production des substances de fragmentation de la molécule, y compris les dimères, les trimères, les tétramères, etc., de l'isobutylène.

CISTI / ICIST



3 1809 00211 1984

ANALYZED

Thermal Decomposition Products of Polyisobutylene

YOSHIO TSUCHIYA and KIKUO SUMI, *Division of Building Research,
National Research Council of Canada, Ottawa, Canada*

Synopsis

Polyisobutylene was decomposed at 325, 345, and 365°C under vacuum, and the volatile products were trapped by using liquid nitrogen. The products, C₁-C₂₄ hydrocarbons, were analyzed by gas chromatography. The formation of the main products is discussed on the basis of a free-radical mechanism. Intramolecular radical transfer can account for the production of most fragments including dimers, trimers, tetramers, and so on, of isobutylene.

A knowledge of decomposition products is necessary in understanding the mechanism of thermal decomposition of polymers. Published information on the decomposition products of polyisobutylene is very scarce. Straus and Madorsky¹ used mass spectrometry for the analysis of decomposition products of this polymer: the major products having up to six carbons were analyzed, but isomers were not separated. van Schooten and Evenhuis² used gas chromatography. They simplified the analysis by hydrogenating all the olefins to paraffins, and then presented data on the combined amounts.

The purpose of this investigation was to obtain more complete information on the volatile thermal decomposition products of polyisobutylene in order to elucidate the mechanism of decomposition of this polymer.

EXPERIMENTAL

Material

A commercial grade of polyisobutylene having a viscosity-average molecular weight of 90 000 was purified by dissolving it in benzene, precipitating it with acetone, and then washing it with methanol. The residual methanol was removed by drying under vacuum. These operations were carried out in the dark in a nitrogen atmosphere in order to prevent oxidation.

Thermal Decomposition

The apparatus for the thermal decomposition of polyisobutylene was similar to that used by Madorsky and Straus.³ A sample weighing 0.5 g

TABLE I
Gas Chromatographic Conditions

Con- dition	Type of column	Stationary phase	Carrier gas	Detector	Temperature
1	Packed, 6 ft, $\frac{1}{8}$ in. od	60-80 mesh silica gel de- activated with 4% silicone oil DC 200	Helium, 20 psi	Flame ionization	Programmed: 10°C/min from 60 to 200°C
2	Support coated open tubular 100 ft, 0.02 in. id	Squalane	Helium, 5 psi	"	Isothermal: -17, 0, 50, 100, and 150°C Programmed: 6°C/min from 60 to 150°C
3	Open tubular 150 ft, 0.02 in. id	Apiezon L	Helium, 20 psi	"	Isothermal: 100 and 180°C Programmed: 10°C/min from 60 to 250°C

was placed in a small Pyrex tube connected to a liquid nitrogen trap and a vacuum pump. After the system was flushed with helium and evacuated to 1×10^{-3} mm Hg, the vacuum line to the pump was closed, and an electric furnace provided with wheels was moved quickly along steel tracks to position the sample in the hot zone. The sample was decomposed for 20 min at 325, 345, or 365°C.

Most of the volatile decomposition products were collected in a liquid nitrogen trap; some condensed inside the cooler parts of the pyrolysis tube and the tube leading to the trap. By removing the liquid nitrogen, the fraction volatile at room temperature was transferred from the trap into a gas-sampling bottle of known volume. The condensates in the tubes and trap were washed with a predetermined amount of benzene, which was known from preliminary experiments to be a minor component of the decomposition products. The benzene extract and the fraction volatile at room temperature were analyzed separately; then combined amounts of each product were obtained.

Analysis

The chromatographic conditions used to analyze the decomposition products are presented in Table I. The identification of peaks was carried out as described below.

Lower Hydrocarbons from C₁ to C₅. Gas-solid chromatography (condition 1) and gas-liquid chromatography (condition 2) were used; retentions of the peaks were compared with those of known compounds.

Hydrocarbons from C₄ to C₂₄. Gas-liquid chromatography (conditions 2 and 3) was used along with the following: (a) subtraction technique to remove unsaturated hydrocarbons from a mixture of products to facilitate identification of some of the peaks⁴; (b) comparison of retention indices with those of known compounds with the use of *n*-alkanes as standards; (c) hydrogenation of alkenes followed by identification of resulting alkanes; and (d) the linear relationship between boiling point and retention index.

RESULTS AND DISCUSSION

Analysis of Products

Data obtained from chromatograms of decomposition products of polyisobutylene pyrolyzed at 365°C are presented in Figure 1. The relative areas of peaks found at different retention indices for both pyrolysis products and hydrogenated pyrolysis products, are shown along with the names of compounds that were identified. Six peaks that had retention indices between 100 and 600 were identified without difficulty. Seven of the eleven peaks with indices between 600 and 800 were also identified, but with more effort. For example, the identification of peaks P₁₁ and P₁₂, of Figure 1 was carried out as follows. The subtraction technique showed

TABLE II
Identification of Peaks having Retention Indices between 600 and 800 with Squalane

Peak	Retention index obtained ^a	Saturated (S) or unsaturated (U)	Assigned formula	Retention index of assigned compound ^b	Boiling point of assigned compound, °C ^c	Location of peak after hydrogenation same as
a	630.3	S	$ \begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{CH}-\text{CH}_2-\text{CH}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} $	630	80.5	a
b	638.5	U	$ \begin{array}{c} \text{CH}_2=\text{C}-\text{CH}_2-\text{CH}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} $	637.5	81.6	a
c d	640.7 687.6	U U	$ \begin{array}{c} \text{CH}_3-\text{C}=\text{CH}-\text{CH}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} $	641	83.3 —	a ?
e	690.9	S	$ \begin{array}{c} \text{CH}_3-\text{CH}-\text{CH}_2-\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array} $	690	99.2	e

g	705.5	U	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	704	101.4	e
h	755.1	U	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}=\text{CH}-\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	715	104.9	e
i	762.8	U				
j	773.6	S	$\begin{array}{c} \text{CH}_3 \quad \text{CH}_3 \\ \quad \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	—	122.3	j
k	794.2	U	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{CH}_2-\text{C}-\text{CH}_3 \\ \quad \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$	—	—	— ^d

^a Liquid phase; squalane, 50°C; $b = 0.415$.^b Literature values.⁶Data of Ferris.⁵

^d Two peaks were obtained.

Two peaks were obtained by pyrolysis, retention times were 1.29 and 1.43. The former is due to 2,3-dimethylhexane.

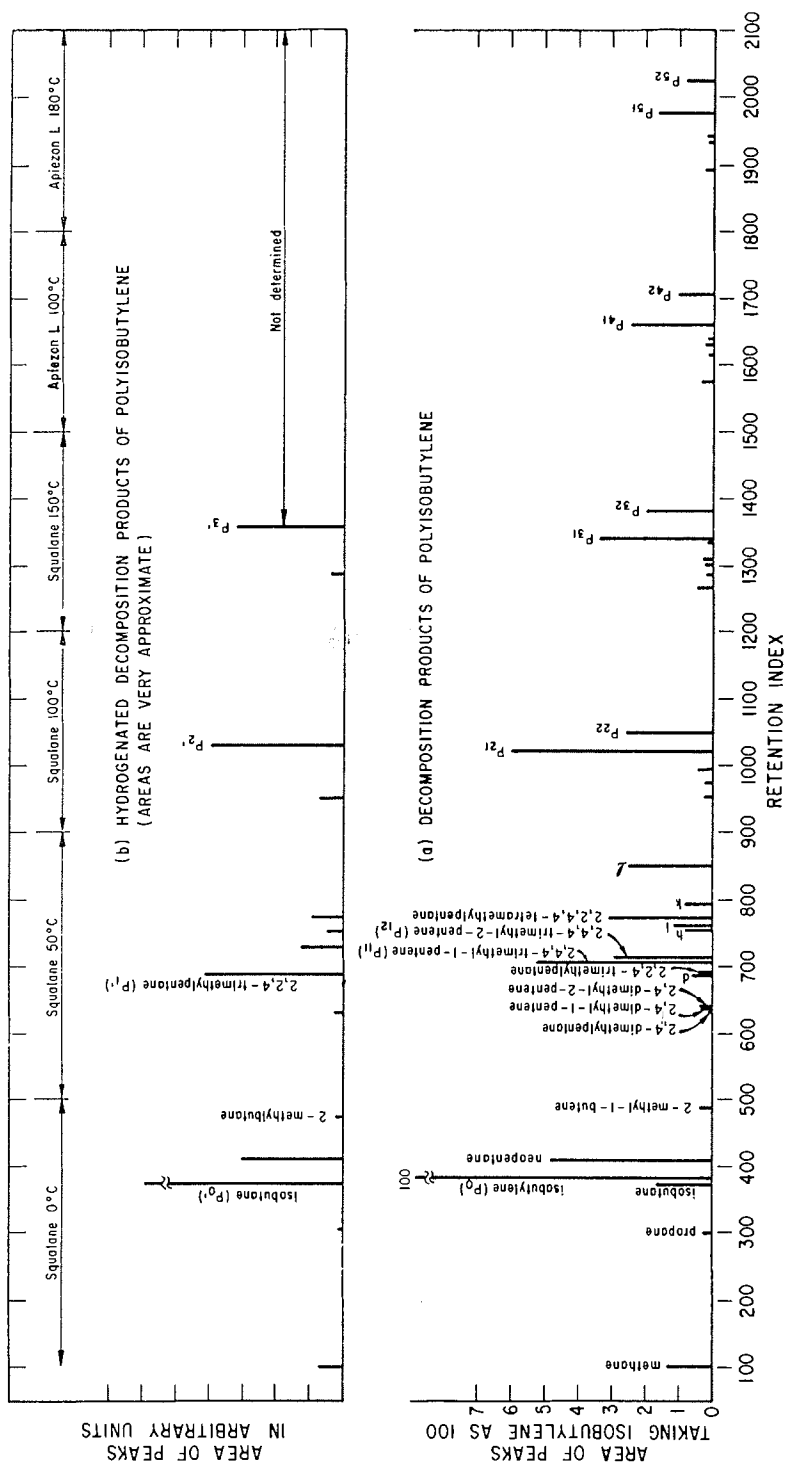


Fig. 1. Area of peaks vs. retention index.

that these two peaks were caused by unsaturated hydrocarbons. Hydrogenation of these products followed by analysis showed that they combined to form a single peak P_1' , indicating that they have the same carbon skeleton. Boiling point data of alkanes, cyclanes, and aromatics⁵ were examined to find compounds that have an estimated retention index close to that of P_1' . Two such compounds were 1,1-dimethylcyclopentane and 2,2,4-trimethylpentane. The former could have been formed by hydrogenation of three different cycloalkenes, none of which had an estimated retention index similar to those of P_{11} or P_{12} . The latter has two unsaturated forms, 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene. Their estimated retention indices agreed with those of P_{11} and P_{12} . In addition, the retention index of a pure sample of 2,2,4-trimethylpentane agreed with that of P_1' . Similar methods were used to identify other peaks with retention indices between 600 and 800. These results are presented in Table II.

In Figure 1 a pattern consisting of groups of peaks is noted. Peaks P_0 , P_{11} , P_{21} , P_{31} , P_{41} , and P_{51} are uniformly spaced; peaks P_0 , P_{12} , P_{22} , P_{32} , P_{42} , and P_{52} are also uniformly spaced, suggesting that they form two homologous series. The hydrogenated peaks P_0' , P_1' , P_2' , and P_3' form another series. Peaks P_{n1} and P_{n2} (where $n = 1, 2, \dots$) resulted from unsaturated compounds and had the same carbon skeleton as P_n' . Peak P_0 was identified as isobutylene and P_{11} and P_{12} as 2,4,4-trimethyl-1-pentene and 2,4,4-trimethyl-2-pentene (dimers of isobutylene), respectively. The above knowledge and consideration of the mechanism of decomposition suggest that P_{21} and P_{22} are the trimers 2,4,4,6,6-pentamethyl-1-heptene and -2-heptene, P_{31} and P_{32} are the tetramers, and so on. Unfortunately, data on retention indices and boiling points of these compounds were not available for positive identification of trimers, tetramers and pentamers. The retention indices and estimated boiling points of prominent peaks are given in Table III, along with boiling points of branched alkenes having the same number of carbon atoms as the trimers, tetramers, and pentamers. The similarity of boiling points is considered to be supporting evidence for the identification of these peaks. The boiling point of peak P_2' (which was considered to be due to 2,2,4,4,6-pentamethylheptane) obtained from boiling point-retention index relation was 184°C. As the boiling point of this compound could not be found in the literature, it was computed by using an empirical method to determine the physical properties of hydrocarbons.⁷ These properties are determined from the next lower paraffins from which they can be derived by substitution of a methyl group for a hydrogen atom. The boiling point of this compound, derived from that of 2,2,4,4-tetramethyl heptane, was 184.3°C.

The three largest hydrogenated pyrolysis products were isobutane, 2,2,4-trimethylpentane, and 2,2,4,4,6-pentamethylheptane. This finding agrees with experimental results that have been reported earlier.²

The main volatile decomposition products of polyisobutylene obtained at the three different pyrolysis temperatures are presented in Table IV.

TABLE III
Retention Indices and Boiling Points of Oligomers of Isobutylene

	Retention index	Chromatographic data	Estimated boiling point, °C	Similar compound	Boiling point, °C
Monomer; isobutylene (2-methylpropene)	387	Squalane, 0°C	-6.90 ^a		
Dimer; 2,4,4-trimethyl-1-pentene	703.7	Squalane, 50°C	101.44 ^a		
Dimer; 2,4,4-trimethyl-2-pentene	715.2	"	104.91 ^a		
Trimer; 2,4,4,6,6-pentamethyl-1-heptene	1023	Squalane, 100°C	182	Triisobutylene (mixed trimers)	179-181 ^b
Trimer; 2,4,4,6,6-pentamethyl-2-heptene	1051	"	188	2,2,3,5,5-Pentamethyl-3-heptene	178
Tetramer; 2,4,4,6,6,8,8-heptamethyl-1-nonene	1340	Squalane, 150°C	245	2,7-Dimethyl-3,6-diisopropyl-4-octene	247
Tetramer; 2,4,4,6,6,8,8-heptamethyl-2-nonene	1378	"	252		
Pentamer; 2,4,4,6,6,8,8,10,10-nonamethyl-1-undecene	1660	Apiezon L, 100°C	299	2,2,4,7,10,12,12-Heptamethyl-6-tridecene	290
Pentamer; 2,4,4,6,6,8,8,10,10-nonamethyl-2-undecene	1707	"	306		
Hexamer; 2,4,4,6,6,8,8,10,10,12,12-undecamethyl-1-tridecene	1975	Apiezon L, 180°C	342		
Hexamer; 2,4,4,6,6,8,8,10,10,12,12-undecamethyl-2-tridecene	2022	"	348		

^a Literature value.⁴

^b Literature value.⁸

TABLE IV
Thermal Decomposition Products of Polyisobutylene on Pyrolysis at Various Temperatures T

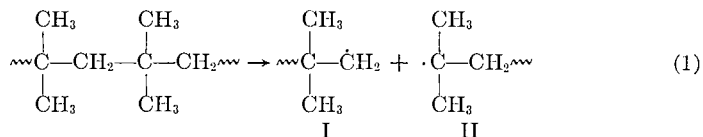
	$T = 325^{\circ}\text{C}$		$T = 345^{\circ}\text{C}$		$T = 365^{\circ}\text{C}$	
	Polymer, wt-%	Volatiles, mole-% ^a	Polymer, wt-%	Volatiles, mole-% ^a	Polymer, wt-%	Volatiles, mole-% ^a
Methane	0.104	13.6	0.22	5.9	0.47	3.9
Propane	0.006	0.29	0.0019	0.19	0.078	0.24
Isobutane	0.044	1.59	0.18	1.37	0.58	1.35
Isobutylene	1.72	64.3	10.2	78.9	33.9	81.6
Neopentane	0.36	10.3	0.79	4.7	1.64	3.1
2-Methyl-1-butene	0.006	0.19	0.043	0.27	0.136	0.26
2,4-Dimethylpentane	0.0003	0.006	0.004	0.017	0.030	0.040
2,4-Dimethyl-1-pentene	0.0010	0.021	0.018	0.077	0.113	0.16
2,4-Dimethyl-2-pentene	0.0010	0.021	0.018	0.077	0.128	0.18
Peak d	0.0011	0.023	0.025	0.11	0.195	0.27
2,2,4-Trimethylpentane	0.0011	0.021	0.018	0.069	0.117	0.14
2,4,4-Trimethyl-1-pentene	0.086	1.61	0.49	1.91	1.77	2.13
2,4,4-Trimethyl-2-pentene	0.063	1.12	0.31	1.18	1.01	1.21
Peak h	0.006	0.12	0.062	0.24	0.27	0.33
Peak i	0.008	0.15	0.078	0.30	0.41	0.49
2,2,4,4-Tetramethylpentane	0.071	1.17	0.39	1.31	1.07	1.12
Peak k	0.011	0.18	0.082	0.28	0.29	0.31
Peak l	0.012	0.20	0.13	0.45	0.84	0.89
2,4,4,6-Pentamethyl-1-heptene	0.26	3.20	0.75	1.94	2.06	1.65
2,4,4,6-Pentamethyl-2-heptene	0.10	1.23	0.27	0.69	0.77	0.61
Total volatiles analyzed (100 - Residue), wt-%	2.8 4.9		14.1 15.7		45.9 46.8	

^a Molecular weights of unidentified compounds were estimated from their retention indices.

Mechanism of Thermal Decomposition

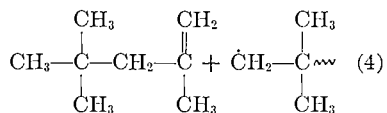
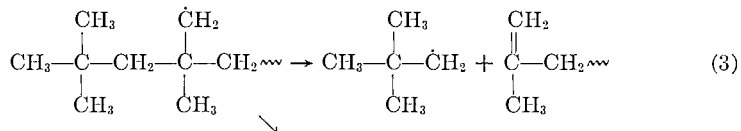
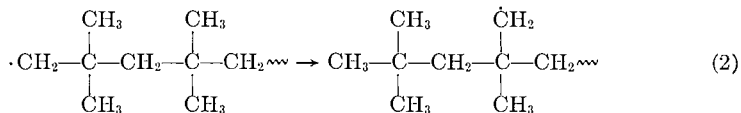
In a previous paper, the formation of volatile thermal decomposition products of polyethylene was discussed on the basis of a free-radical mechanism.⁴ The formation of the decomposition products of polyisobutylene will be examined on the same basis. A possible reaction scheme is given below.

Initiation. Random scission of polymer chain should produce two different types of macroradicals, one of which is primary (I), and the other, tertiary (II).

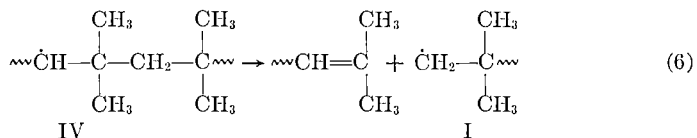
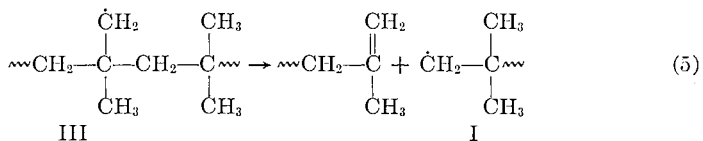


Propagation. Both types of radicals produced by initiation could produce the monomer, isobutylene.

Intramolecular Radical Transfer, Followed by Decomposition. The propagation reactions must compete with intra- and intermolecular radical transfer reactions. A radical produced by initiation or decomposition can be transferred to another carbon in the same chain, which then decomposes to form an alkane radical and an alkene, e.g.,



Intermolecular Radical Transfer, Followed by Decomposition. When intermolecular radical transfer takes place, two types of macroradicals,



IV

TABLE V
Volatile Decomposition Products of Polyisobutylene Resulting from Intramolecular Radical Transfer at 365°C

Transfer to:	Primary or secondary	Alkene	Alkane
Starting from primary radical (I)			
3rd carbon	Secondary	2,4,4-Trimethyl-2-pentene (P ₁₂), 1.21	Methane, (3.9) ^a
Methyl group attached to 4th carbon	Primary	2,4,4-Trimethyl-1-pentene (P ₁₁), 2.13	2,2-Dimethylpropane (neopentane), (3.1)
5th carbon	Secondary	2,4,4,6,6-Pentamethyl-2-heptene, (P ₂₂) 0.61	2,2-Dimethylpropane
Methyl group attached to 6th carbon	Primary	2,4,4,6,6-Pentamethyl-1-heptene, (P ₂₁) 1.65	2,2,4,4-Tetramethylpentane, (1.12)
7th carbon	Secondary	2,4,4,6,6,8,8-Heptamethyl-2- nonene, (P ₃₂) 0.43	2,2,4,4-Tetramethylpentane
Starting from tertiary radical (II)			
2nd carbon	Secondary	2,4-Dimethyl-2-pentene, 0.18	Methane
Methyl group attached to 3rd carbon	Primary	2,4-Dimethyl-1-pentene, 0.16	2-Methylpropane (isobutane), (1.35)
4th carbon	Secondary	2,4,4,6-Tetramethyl-2-heptene, not determined	2-Methylpropane
Methyl group attached to 5th carbon	Primary	2,4,4,6-Tetramethyl-1-heptene, not determined	2,2,4-Trimethylpentane, (0.14)
6th carbon	Secondary	2,4,4,6,6,8-Hexamethyl-2-nonene, not determined	2,2,4-Trimethylpentane

^a Methane could be produced following radical transfer to any primary or secondary carbon of polyisobutylene.

III and IV, are produced. Decomposition of these radicals results in the formation of primary macroradicals (I).

Termination. The termination reactions could proceed by the combination of two radicals or by disproportionation, which results in the formation of an alkane and an alkene. As both reactions involve two radicals, the amount of products formed by termination in the present experiments is considered small.

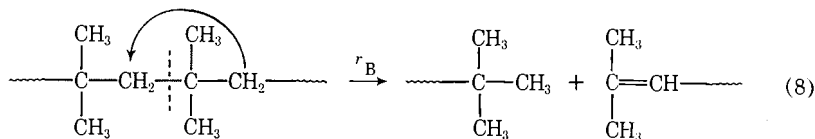
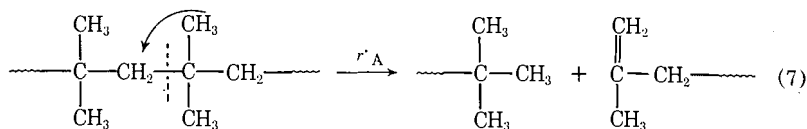
The formation of the main volatile decomposition products of polyisobutylene can be explained by two competing reactions; propagation, and intramolecular radical transfer and subsequent decomposition. The proportion of monomer in the volatile products depends on the relative rates of these two reactions. A proportionately larger amount of monomer was produced in the decomposition of polyisobutylene as compared with that of polyethylene,⁴ indicating that intramolecular radical transfer is relatively more difficult in the decomposition of polyisobutylene. Three out of four hydrogen atoms of this polymer are primary, which require higher activation energy for transfer than secondary hydrogen; and also secondary hydrogen is sterically obstructed by the two methyl groups attached to every other carbon atom of the polymer chain. Thus, propagation reaction predominates over transfer reactions resulting in the production of large amounts of monomer.

The formation of different volatile decomposition products of polyisobutylene as a result of intramolecular radical transfer is presented in Table V. This mechanism can account for the formation of all the main volatile products except for the monomer isobutylene. The amounts of each substance produced at a pyrolysis temperature of 365°C are shown in terms of mole per cent of volatiles. The amounts of products that could be accounted for by more than one reaction are given in parentheses. The volatile products formed as a result of intramolecular transfer from primary radicals (I) were much greater than from tertiary radicals (II). This difference is probably due to the greater availability of primary radicals (I) as a result of intermolecular transfer by reactions (5) and (6), and the relative instability of primary radicals (I) which causes them to favor transfer.

The presence of a pattern consisting of pairs of peaks, P_{n1} and P_{n2} (where $n = 1, 2, \dots$), in Figure 1 can also be explained by intramolecular radical transfer followed by decomposition. P_{n1} is 1-alkene produced by transfer to primary carbon and P_{n2} is 2-alkene produced by transfer to secondary carbon. The mole ratio of P_{n1} to $P_{(n+1)2}$ depends on the relative ease of radical transfer to primary carbon and to secondary carbon. The experimental findings for this ratio were in the range of 2.9–3.8. The theoretical value of this ratio was found to be 1.24, by: (a) assuming the difference in activation energy between transfer to primary carbon and secondary carbon to be 2000 cal., (b) considering the number of transferable hydrogen atoms to be 6 for primary carbon and 2 for secondary carbon, and (c) taking into account the number of possible β -scissions following trans-

fer, i.e., 3 for primary and 6 for secondary carbon. The discrepancy between the theoretical value and the experimental values indicates that less radical transfer to secondary carbon took place than suggested by this theory. This was probably due to the steric hindrance caused by the presence of methyl groups.

The experimental data were also examined on the basis of another mechanism that has been considered by a number of investigators. Repeated random splitting of a polymer chain resulting in simultaneous saturation and unsaturation is shown in eqs. (7) and (8).



Reaction (7) should produce a saturated end and a 1-alkene end, and reaction (8) should produce a saturated end and a 2-alkene end. Combination of these four ends with four other ends produced in the same way should result in six different types of compounds: one alkane, two alkenes (1-alkene and 2-alkene), and three alkadienes. If the reaction rate $r_A = r_B$, equal amounts of 1-alkene, 2-alkene, and alkane should be produced. If $r_A > r_B$, the three largest products in decreasing order should be 1-alkene, alkane, 2-alkene; if $r_A < r_B$, the order should be 2-alkene, alkane, 1-alkene. The experimental findings were in conflict with the above mechanism; large amounts of 1-alkene and 2-alkene were produced, but only small amounts of alkane.

CONCLUSIONS

The formation of thermal decomposition products of polyisobutylene has been explained on the basis of a free radical mechanism in which intramolecular radical transfer is assumed to play an important role. The amount of products formed following radical transfer to primary carbon atoms was much greater than that from transfer to secondary carbon atoms. This difference suggests that transfer to secondary carbon is obstructed by the methyl groups attached to every other carbon atom of the polymer chain. For the same reason, propagation reaction predominates over intramolecular radical transfer reactions, yielding a large amount of monomer. The formation of dimers, trimers, tetramers, and so on found in the decomposition products can be explained by intramolecular radical transfer reactions.

This paper is a contribution of the Division of Building Research of the National Research Council of Canada and is published with the approval of the Director of the Division.

References

1. S. Straus and S. L. Madorsky, *J. Res. Nat. Bur. Stand.*, **66**, 401 (1962).
2. J. van Schooten and J. K. Evenhuis, *Polymer*, **6**, 343 (1965).
3. S. L. Madorsky and S. Straus, *J. Res. Nat. Bur. Stand.*, **63A**, 261 (1959).
4. Y. Tsuchiya and K. Sumi, *J. Polym. Sci.*, in press.
5. S. W. Ferris, *Handbook of Hydrocarbons*, Academic Press, New York (1959).
6. D. A. Tourres, *J. Gas Chromatog.*, **5**, 35 (1967).
7. A. W. Francis, *Ind. Eng. Chem.*, **35**, 442 (1943).
8. *Handbook of Chemistry and Physics*, Chem. Rubber Publishing Co., Cleveland, 48th ed., 1967, p. C-508.

Received January 15, 1968

Revised March 18, 1968