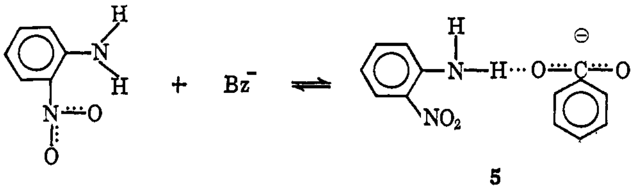
the activity of B may be less than the concentration, (2) part of B may be self-associated, (3) the value of $pK^d_{IH^+}$ may decrease as a consequence of change of the solvent character, and (4) there may be some hydrogen bonding of $(H_2O)_3H^+$ or $(ROH)_2H^+$ to AN. For these reasons the values of $K^f_{(H_2O)_4H^+}$ and $K^f_{(ROH)_3H^+}$ reported in Table IV may be smaller than the true values.

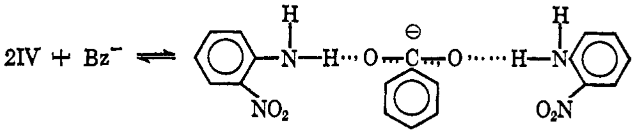
The basicity of water in AN is considerably less (Table IV) than that of acetamide, which has a $pK^d_{BH^+}$ of 6.0. Evidently acetamide is not formed under our experimental conditions because the decrease of H_s^+ would have been considerably greater than that plotted in Figure 4.

Quite generally the expression for basic strength can be quite ambiguous and may depend on experimental conditions, even in a given solvent. In acetonitrile the value of y is a better expression of basic strength than $K^f_{B_nH^+}$ even though y varies with concentration of B (Figure 3). For example, in 0.01 *M* solution y of *t*-butyl alcohol is some 10 times greater than that of water, but in 1 *M* solution y is about the same. Also in dimethyl sulfoxide water acts like a fairly strong base, $K^f_{H_3O^+}$ being 0.45.[24] On the other hand, in AN DMSO is a much stronger base than water, $K^f_{H^+DMSO}$ being 6.3×10^5 [25] as compared to $K^f_{H_3O^+} = 1.4 \times 10^2$.

o-Nitroaniline in its reactions with the benzoate ion behaves as a weak hydrogen-bond donor, the hydrogen-bond-donating properties possibly being weakened by intramolecular hydrogen bonding in structure **4**.



4 **5**



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Both in water and AN *m*-nitroaniline is a stronger base than the *ortho* isomer, the difference in their $pK^d_{BH^+}$ in AN being 7.6 (present paper) − 4.85 = 2.75 units, the same difference as in water.[26]

Although *o*-nitroaniline is a much stronger base than AN, water, and methanol, and therefore a much stronger hydrogen-bond acceptor than AN, no evidence has been obtained that it breaks the hydrogen bond between the donor water and the acceptor AN.

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The Radiolysis of Liquid *n*-Pentane

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Abstract: The radiation-induced decomposition of liquid *n*-pentane was studied as a function of temperature and total dose. Effects of olefins, oxygen, and nitrous oxide on product formation were also investigated. At room temperature, rupture between a primary and a secondary carbon atom occurs with a *G* value of 0.3 and between two secondary carbon atoms with a *G* value of 1.2. The total yield of C–C rupture was found to be temperature dependent, with *G* values of 1.7, 1.5, and 1.0 at temperatures of 95, 20, and −116°, respectively. Unsaturated products with six to ten C atoms, formed at low doses, are suggested to result from reactions within the spurs. Isomerization of radicals, though occurring, is relatively unimportant. Effects of an increase in radiation dose are attributed to the accumulation of olefins in the irradiated liquid. It is concluded that these olefins not only scavenge radicals and atoms, but that they are also involved in other processes. Similarly, the reduction in hydrogen yield in the presence of pentene is only partly due to scavenging of H atoms. Positive ions probably contribute to polymer formation in these solutions. Effects of oxygen and of nitrous oxide indicate that saturated products are mainly formed in reactions involving free radicals, whereas a considerable fraction of C_2–C_4 olefins are produced by molecular elimination. Positive ions are among the intermediates in the formation of these olefins.

The radiolysis of liquid *n*-pentane has been the subject of a number of investigations.[2–7] However, no complete product analysis has been reported at low radiation dose. Moreover, reported *G* values vary considerably. In this paper, results obtained in the radiolysis of liquid *n*-pentane, including the effects of temperature and radiation dose, are discussed. Experiments were also carried out in the presence of olefins and scavengers for radicals and electrons, notably oxygen and nitrous oxide.[8–12]

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Table I. Columns Used for Gas Chromatographic Separations

Separated products	Wt % stationary phase on Embacel	Column length, m	Column temp, °C
H_2, N_2, CH_4	Molecular sieve, 5 Å	4	Room temperature
C_1–C_5	25% *n*-hexadecane	6	30
C_5–C_7	25% dimethyl sulfolane	13	40
C_7–C_{10}	25% squalane and 30%	4	Various temp
	o-tritolyl phosphate	2	Various temp
$>C_7$	10% silicon grease	6	Various temp
$C_5H_{10}O$, $C_5H_{11}OH$	20% polyglycol 4000	4	140
C_6–C_{10}	10% silicon gum SE 30 and	2	100
	squalane (capillary column)	100	Various temp

Table II. Product Yields (*G* Values) in Irradiated *n*-Pentane

	Cobalt-60 γ						3-MeV X	3-MeV e^-	2-MeV e^-	30-keV e^-
	Dose, Mrads									
	0.8	10.5	27	36	48	60	38	105	25 and 100	0.3–23
	a	*a*	*a*	*b*	*b*	*b*	*c*	*c*	*d*	*e*
H_2	5.1	4.4	3.7	4.17	3.71	3.5	4.1		4.20	4.98
CH_4	0.26	0.24	0.26	0.22	0.22	0.24			0.22	0.12
C_2H_4	0.37	0.25	0.14		0.65	0.59			0.36	0.28
C_2H_6	0.61	0.60	0.55						0.27	0.26
C_3H_6	0.35	0.25	0.16	0.09	0.09	0.10			0.29	0.19
C_3H_8	0.58	0.60	0.55	0.59	0.58	0.61			0.33	0.25
C_4H_8-1	0.08	0.05	0.04	0.02	0.02	0.03			0.06	
C_4H_8-2	0.02			0.05	0.04	0.02				
n-C_4H_{10}	0.10	0.10	0.10	0.12	0.13	0.13			0.09	
C_5H_{10}-1	1.00	0.73			1.02	1.14	0.47		0.71	
trans-C_5H_{10}-2	1.23	1.12					1.00			
cis-C_5H_{10}-2	0.53	0.52					0.37			
C_6H_{14}	0.05			0.13	0.07	0.40		0.14	0.17	
C_7H_{16}	0.20			0.32	0.23	0.26	0.47	0.33	0.86	
C_8H_{18}	0.22			0.23	0.19	0.23	0.43	0.28	0.79	
C_9H_{20}	0.06			0.07	0.06	0.04	0.05	0.05	0.21	
$C_{10}H_{22}$	1.44	1.00	0.9	1.31	1.16	1.04	1.45	0.80	2.68	

[a] This work. [b] Reference 4. [c] Reference 3. [d] Reference 2b. [e] Reference 7.

Experimental Section

Pentane (Fluka purum, ≥99 mole %) was treated with concentrated sulfuric acid to remove traces of unsaturated hydrocarbons, then washed, dried, and distilled from sodium in a 17-plate column. Oxygen (purity, ≥99.9%) was used as such. Nitrous oxide (≥98%), containing nitrogen as the main impurity, was passed through a trap at −100°, followed by degassing at −196°. Ethylene (Fluka purum, containing 0.02 mole % ethane) and pentene-2 (Fluka purum, ≥99 mole %) were used as such. Carbon-14 labeled pentene-1 (Philips-Duphar) was purified by gas–liquid chromatography.

Solutions of these additives in *n*-pentane were made up volumetrically. Degassing, by repeated cycles of freezing, pumping, and thawing, was followed by irradiation with cobalt-60 γ rays. For low-temperature irradiations, the Pyrex cells were placed in dewar vessels filled with either melting ice (0°), melting diethyl ether (−116°), melting 2-butanol (−125°), a mixture of ice and NaCl (−21°), solid CO_2 (−78°), or liquid N_2 (−196°). Energy absorption was measured with a ferrous sulfate dosimeter, using for $G(Fe^{3+})$ a value of 15.6. Appropriate corrections were made for differences in electron densities of the absorbing compounds. The dose rate was approximately 0.1 Mrad/hr (10^{17} eV/(g min)). Pure *n*-pentane was irradiated with doses varying from 0.06 to 36 Mrads. In the presence of additives, the dose was 1 Mrad, unless stated otherwise.

All products except hydrogen and nitrogen were analyzed gas chromatographically, using a flame ionization detector. Nitrogen, formed in the presence of N_2O, was measured with a thermal conductivity detector, together with hydrogen and methane, after collecting these products at −196° and gas chromatographic separation. A number of columns were used for the various separations. Relevant data are given in Table I.

Peak areas of products were compared with those obtained from standard solutions of the various compounds in *n*-pentane after subjecting these solutions to the same treatments as the irradiated samples. No standards were available for some of the C_6–C_{10} isomers. In that case, the sensitivity of detection of isomers with an equal number of carbon atoms was assumed to be equal. These products could be identified with a high degree of certainty by estimating their boiling points from gas chromatographic data, using the capillary column. All analytical procedures used in this investigation have been checked with solutions containing known amounts of products.

In some experiments hydrogen and methane were collected at −196° and measured volumetrically. The methane fraction was determined gas chromatographically. In other experiments the yields of C_1–C_4 hydrocarbons and of pentene-1 were determined by gas chromatographic analysis of the vapor obtained by evaporating irradiated samples into a large evacuated volume. Pentenes and products with more than five carbon atoms were measured by injecting liquid samples of various size into the gas chromatograph. The pentene isomers were analyzed on the dimethyl sulfolane column. The various isomers with six to ten carbon atoms were first separated from pentane and lower hydrocarbons on a silicon gum column, then collected at −196°, and analyzed by means of a capillary column. The yield of H_2O, which is formed in the presence of N_2O, was measured by means of two experiments which were identical with the exception that in one experiment the inner wall of the irradiation vessel was covered with a sodium mirror. The observed increase in the H_2 yield is assumed to be due to H_2O reacting with excess sodium, as the sodium mirror did not affect the hydrogen yield in the absence of N_2O. Additional products, formed in the presence of O_2, were analyzed on a column containing polyglycol (Table I). One product peak coincided with pentanone-2 and pentanone-3. Two other peaks, with retention volumes slightly less than for pentanol-1, probably represented pentanol-2 and pentanol-3. Peak areas were compared with areas from standard solutions of pentanone-3 in *n*-pentane. The sensitivities of detection were assumed to be equal.

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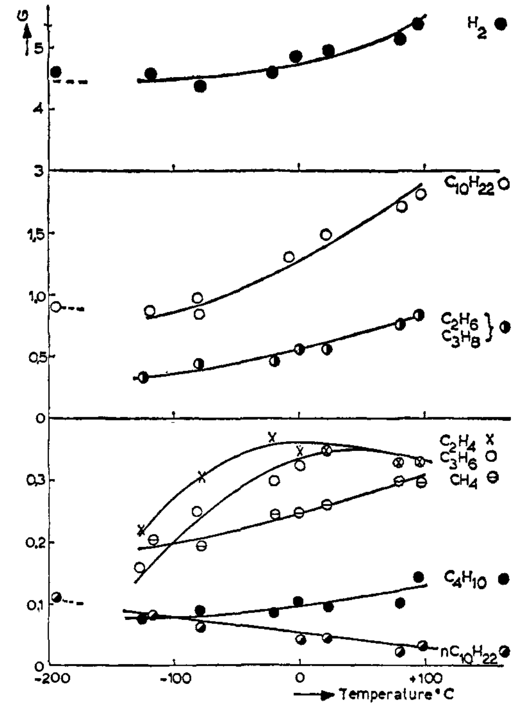

Figure 1. Temperature dependence of product yields.

Some irradiated samples were hydrogenated at room temperature, using platinum oxide as a catalyst, in order to determine any formation of unsaturated products with six to ten carbon atoms. In other experiments, the total yield of unsaturated products was determined by bromination in the dark. The irradiated sample was transferred quantitatively into a bromine solution of known concentration in carbon tetrachloride. Excess bromine was determined by shaking the solution with an aqueous potassium iodide solution, followed by titration of the iodide with a solution of sodium thiosulfate.

Information regarding the formation of polymer (products with ten or more carbon atoms) in irradiated solutions of pentene-1-^{14}C in *n*-pentane was obtained as follows. After irradiation, *n*-decane and *n*-pentane were added to the solutions, followed by slow evaporation of the more volatile compounds. Addition of *n*-pentane followed by evaporation was repeated until all the pentene was removed. The major fraction of the polymer remained in the irradiation vessel. The activity of a fraction of this residue was compared with the specific activity of the pentene-1, by liquid scintillation counting.

Results

Effects of Temperature and Dose. Product yields are shown in Table II and the isomer distributions of intermediate products and dimers in Table III. These data were obtained at room temperature.

In Table II, the observed *G* values are compared with results reported in the literature. At a low irradiation dose (0.06 Mrad) *G* values of 5.30 and 1.48 were observed for H_2 and $C_{10}H_{22}$. Some unsaturated compounds were formed among the intermediate products and dimers. Approximate *G* values of 0.03, 0.01, and 0.15 were obtained for the octenes, nonenes, and decenes, respectively. These *G* values remained constant when the dose was varied from 1 to 2 Mrads. No products with more than ten carbon atoms could be detected at low dose. It has already been mentioned that considerable differences exist between reported yields from irradiated liquid *n*-pentane. However, most *G* values observed in the earlier investigations were obtained at high doses where secondary effects are important. Our hydrogen yield of 5.3, obtained at a dose of 0.06 Mrad, agrees fairly well with *G* values of 4.98 and 5.04 as reported by Claes and Rzad[7] and by Schuler and Kuntz,[6] respectively. The latter authors reported a methane yield of 0.25, which is consistent with our results. It should be noted that the material balance of our results at low conversion is excellent; all products with their respective *G* values give rise to an observed C:H ratio equal to 4.9:12. At higher total dose our *G* values agree fairly well with those obtained by Sutherland and Allen,[4] as can be seen from Table II.

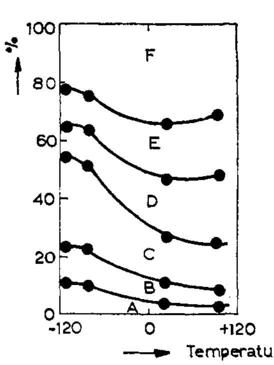

Figure 2. Isomer ratios for decanes as a function of temperature: (A) *n*-decane, (B) 3-ethyloctane, (C) 4-methylnonane, (D) 3-ethyl-4-methylheptane, (E) 3,4-diethylhexane, (F) 4,5-dimethyloctane.

Table III. Composition of Intermediate Products and Dimers

Product	Rel contribution, %
3-Methylpentane	19
2-Methylpentane	39
n-Hexane	42
3-Ethylpentane	24
3-Methylhexane	54
n-Heptane	22
3-Ethylhexane	24
4-Methylheptane	55
n-Octane	21
Isononanes	~85
n-Nonane	~15
4,5-Dimethyloctane	36
3,4-Diethylhexane	19
3-Ethyl-4-methylheptane	20
4-Methylnonane	15
3-Ethyloctane	7
n-Decane	3

The effect of temperature on the yields of a number of products (dose *ca.* 1 Mrad) was also investigated, and results are shown in Figures 1–3. Many *G* values were found to decrease with decreasing temperature. However, the yield of *n*-decane increased while the yields of the pentenes and also of the butenes were hardly affected. It was also observed that a change in temperature had but a small effect on the total yield of intermediate products (products with six to nine carbon atoms). However, isomer ratios of intermediate products and also of dimers change considerably with temperature as is shown in Figures 2 and 3. From Figure 3 it is also evident that isomer ratios for heptanes and octanes are similar within experimental error. The yields of products which may be formed in reactions involving 1-pentyl radicals (*n*-C_7, *n*-C_8, *n*-C_{10}, 3-ethyl-C_8,

Table IV. Product Yields in Irradiated *n*-Pentane in the Presence of N_2O and O_2

N_2O, mole %	O_2, mole %	G values												
		H_2	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	C_4H_8-1	C_4H_{10}	C_5H_{10}-1	*trans*-C_5H_{10}-2	*cis*-C_5H_{10}-2	$>C_{10}$	N_2
...	...	5.1	0.25	0.35	0.60	0.35	0.60	0.08	0.10	1.00	1.23	0.53	1.4	...
0.6	...	3.5	0.21	0.20	0.43	0.22	0.47	0.06	0.10	...	...	...	2.4	3.2
1.1	...	3.4	0.20	0.19	0.42	0.21	0.45	0.05	0.10	1.64	1.51	0.50	2.4	3.6
...	0.2	3.9	0.09	0.32	0.23	0.30	0.26	0.08	0.07	...	...	...		...
...	0.4	3.7	0.07	0.31	0.23	0.29	0.25	0.07	0.06	0.41	0.64	0.36	0.21	...
...	0.8	...	...	...	...	...	...	...	...	0.44	0.61	0.33	...	...
0.6	0.5	2.7	0.08	0.24	0.20	0.22	0.23	0.06	0.05	0.84	0.61	0.24	0.21	3.3
1.2	1.4	...	...	...	...	...	...	...	...	0.80	0.65	0.25	...	...

and 4-methyl-C_9) show a relative increase with decreasing temperature.

The dose dependence of the yields of a number of products is shown in Figure 4. Products with more than ten carbon atoms were observed at higher doses, their dose dependence being typical for secondary products.

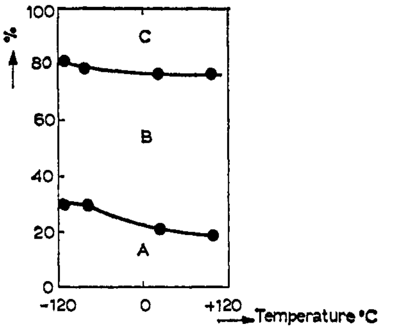

Figure 3. Isomer ratios for heptanes and octanes as a function of temperature: (A) *n*-heptane or *n*-octane, (B) 3-methylhexane or 4-methylheptane, (C) 3-ethylpentane or 3-ethylhexane.

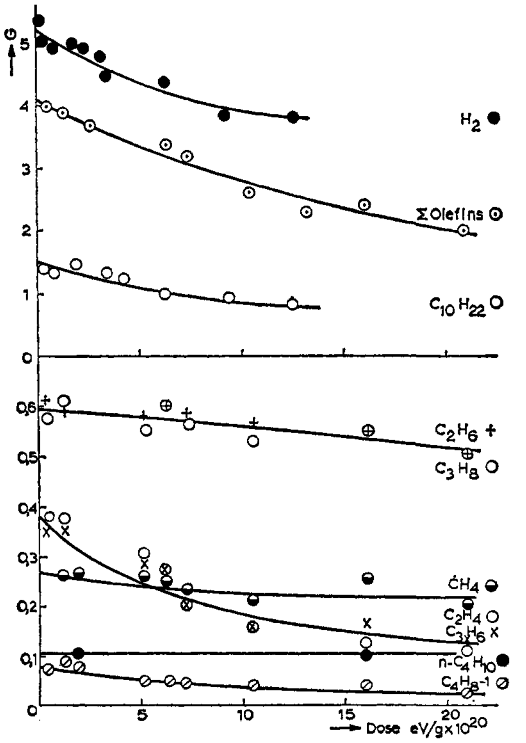

Figure 4. Dose dependence of product yields.

Effects of Additives. Experimental results obtained in the presence of various additives are shown in Figures 5 and 6 and in Tables IV–VI. In addition, the following information was obtained.

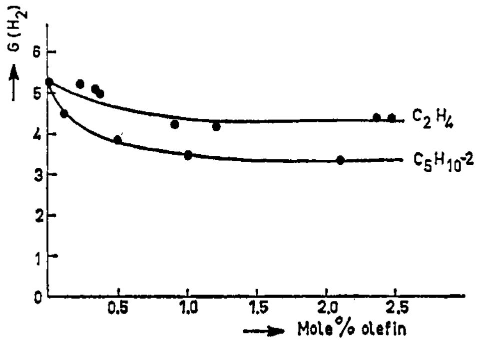

Figure 5. Hydrogen yields in the presence of ethylene and pentene-2.

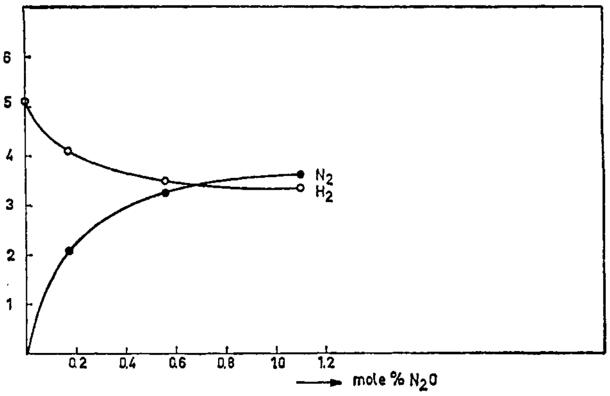

Figure 6. Yields of hydrogen and nitrogen in the presence of N_2O.

Polymer (products with ten or more C atoms) is formed in irradiated solutions of 1.1 mole % pentene-1 in *n*-pentane. Using ^{14}C-labeled pentene and a total dose of 3.5×10^{20} eV/g, a *G* value of about 6 was found for pentene-1 included in the polymer. This *G* value was reduced to *ca.* 3 in the presence of oxygen. When both O_2 and NH_3 were added, a further reduction was observed at a G value < 1.

A 70% reduction was observed in the yields of C_6–C_9 hydrocarbons when oxygen was present, whereas these yields were reduced by 10% in solutions containing nitrous oxide. Isomer ratios, *n*-heptane:3-ethylpentane:3-methylhexane, were similar to those reported in Table VI for *n*-octane:3-ethylhexane:4-methylheptane.

Table V. Isomer Distributions of Dimers (%)

	C_5H_{12} + O_2	C_5H_{12} + N_2O	C_5H_{12} + O_2 + N_2O
n-Decane	13	3	13
3-Ethyloctane	15	9	16
4-Methylnonane	30	15	29
3-Ethyl-4-methylheptane	13	20	13
3,4-Diethylhexane	11	19	11
4,5-Dimethyloctane	18	34	18

Table VI. Isomer Distributions of Octanes (%)

	C_5H_{12} + O_2	C_5H_{12} + N_2O	C_5H_{12} + O_2 + N_2O
n-Octane	35	22	35
3-Ethylhexane	21	24	21
4-Methylheptane	44	54	44

Pentanols and pentanones are formed in the presence of oxygen with a total *G* value of about 3.6. When both oxygen and nitrous oxide are present, this value increases to *ca.* 5.6. Water is produced with a *G* value of about 2 in solutions containing N_2O. Oxygen was not observed as a product in these solutions.

Discussion

Experiments at Low Conversions. All the products listed in Tables II and III can be formed in reactions involving radicals, produced by rupture of one C–C or C–H bond in *n*-pentane.[13] Rearrangement of these radicals, which may initially be formed in excited states, would have resulted in the formation of more isomers in the C_6–C_9 range. Some unidentified saturated products have actually been observed among the intermediate products, their *G* values being relatively small. This suggests that radical isomerizations may occur but are not very important. Similar conclusions have been reported in the literature.[14,15]

The formation at low dose of unsaturated products with eight, nine, and ten carbon atoms is probably the result of reactions involving pentenyl radicals. These radicals were observed by Holroyd and Klein[15] in irradiated liquid *n*-pentane. They may be formed in reactions involving pentene molecules. At low doses these reactions probably occur within the spurs where high local concentrations of reacting species exist.

The *G* value for rupture of carbon–carbon bonds can be calculated, using the following equation

$$G(\text{C–C rupture}) = [\textstyle\sum G(C_1\text{–}C_4) + \sum G(C_6\text{–}C_9)]/2$$

A value of 1.5 is obtained at a dose of 0.8 Mrad. Similar calculations show that rupture between a primary and a secondary carbon atom occurs with an approximate *G* value of 0.3, whereas rupture between two secondary carbon atoms has a yield of 1.2.

The relative yields of the various radicals in the irradiated solution cannot be calculated accurately from the isomer distribution of the C_6–C_9 hydrocarbons, even if it is assumed that these intermediate products are solely formed in reactions between C_5 and C_1 to C_4 radicals. For such a calculation the ratios of rate constants for disproportionation and combination reactions between the various radicals should be known. However, neglecting differences in these ratios for the reactions involved, the following approximate radical distributions are obtained.[16] $CH_3{:}C_2H_5{:}C_3H_7{:}C_4H_9$ = 1:5:5:1 and $1\text{-}C_5H_{11}{:}2\text{-}C_5H_{11}{:}3\text{-}C_5H_{11}$ = 2:5:2. These calculated ratios agree fairly well with the ratios $CH_3{:}C_2H_5{:}C_3H_7{:}C_4H_9$ = 1.0:5.1:4.0:0.7 and $1\text{-}C_5H_{11}{:}2\text{-}C_5H_{11}{:}3\text{-}C_5H_{11}$ = 1.0:2.2:1.1, as reported by Holroyd and Klein.[15]

Effects of Temperature on Product Yields. The results given in Figure 1 show that a change in temperature considerably affects product yields. When the temperature is decreased, the contribution of reactions with relatively high activation energies will be reduced and cage effects will also become increasingly important.

Hydrogen is (partly) formed in reactions between hydrogen atoms and pentane molecules.

$$H\cdot + C_5H_{12} \longrightarrow H_2 + C_5H_{11} \qquad (1)$$

The contribution of thermal hydrogen atoms reacting according to reaction 1 will decrease with decreasing temperature. Other processes, such as reactions between atoms and radicals, may become more important.

$$H\cdot + C_5H_{11}\cdot \longrightarrow C_5H_{12} \qquad (2)$$

$$H\cdot + C_5H_{11}\cdot \longrightarrow H_2 + C_5H_{10} \qquad (3)$$

This will result in a decrease in hydrogen formation, as was indeed observed (Figure 1).

Alkyl radicals are formed by rupture of a C–C bond in pentane. Their yields will decrease with decreasing temperature as a result of the cage effect. This is confirmed by calculated *G* values for C–C rupture of 1.7, 1.5, and 1.0 at 95°, room temperature, and −116°, respectively. Moreover, the contribution of H-atom abstraction by these radicals from the solvent will also decrease, because of the required activation energy. These effects can account for the observed reduction in the yields of saturated C_1–C_4 hydrocarbons with decreasing temperature, as these products are mainly formed in reactions involving alkyl radicals. This will be discussed in a subsequent section. The diminishing contribution at low temperature of H-atom abstraction from the solvent will also result in decreased yields of pentyl radicals, and consequently in reduced dimer formation. The decrease in total dimer yield is accompanied by an increase in *n*-decane formation, as is shown in Figure 1. It can be attributed to a relative increase in the contribution of *n*-pentyl radicals to dimer formation. Such an interpretation is consistent with observed changes in the isomer ratios of intermediate products and dimers as a function of temperature (Figures 2 and 3). This relative increase in the yield of *n*-pentyl radicals may be due to a decreasing contribution at low temperature of reactions 4a and 4b.

$$1\text{-}C_5H_{11}\cdot + C_5H_{12} \longrightarrow 2\text{-}C_5H_{11}\cdot + C_5H_{12} \qquad (4a)$$

$$1\text{-}C_5H_{11}\cdot + C_5H_{12} \longrightarrow 3\text{-}C_5H_{11}\cdot + C_5H_{12} \qquad (4b)$$

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(13) This statement is not meant to suggest that such reactions are actually involved in the formation of all these products. It will indeed be shown that a number of products are formed in reactions not involving free radicals.

(14) H. Widmer and T. Gaümann, *Helv. Chim. Acta*, **46**, 944 (1963).

(15) R. A. Holroyd and G. W. Klein, *J. Am. Chem. Soc.*, **84**, 4000 (1962).

(16) The yield of *n*-hexane was not used in these calculations. The relatively large contribution of this product to the total yield of the hexanes suggests that it is not only formed in reactions between CH_3 and $n\text{-}C_5H_{11}$ radicals, but also by combinations between other fragment radicals.

Similar reactions, causing a change in identity of radicals in solution, have also been proposed in other hydrocarbons.[17,18]

Pentenes are partly formed in disproportionation reactions between $C_5H_{11}\cdot$ and other radicals. The observed decrease in dimer yield at low temperature is not accompanied by a similar reduction in pentene formation. Various effects of temperature on pentene formation can be proposed, to account qualitatively for this observation. At low temperature there is a relative increase in H atoms and C_1–C_4 radicals reacting with pentyl radicals instead of reacting with pentane molecules (reactions 4–7). This may at least partly compensate for the expected decrease in pentene formation.[19]

$$R\cdot + C_5H_{12} \longrightarrow RH + C_5H_{11}\cdot \tag{4}$$

$$R\cdot + C_5H_{11}\cdot \longrightarrow C_5H_{10} + RH \tag{5}$$

$$R\cdot + C_5H_{11}\cdot \longrightarrow C_5H_{12} + \text{olefin} \tag{6}$$

$$R\cdot + C_5H_{11}\cdot \longrightarrow R\text{-}C_5H_{11} \tag{7}$$

Moreover, the ratio of rate constants of reactions 5 and 7, k_5/k_7, may increase with decreasing temperature, causing a relative increase in the yield of pentene. Such changes in the ratios of rate constants for disproportionation and combination reactions have been reported in the literature.[20–22] This may also contribute to the observed decrease in the yield of dimers at low temperatures.

Effect of Radiation Dose. Figure 4 shows that an increase in radiation dose has a marked effect on the yields of several products. Also the material balance, which was good at low conversions, becomes worse with increasing dose. This suggests that other (secondary) products are formed. New products with more than ten carbon atoms were indeed observed at these high doses.

The influence of total dose on product formation can at least partly be attributed to the accumulation of olefins in the irradiated solutions. These olefins may react with various intermediates such as radicals, ions, and exited molecules.[23] The following reactions between radicals and pentene, which is the major unsaturated product in irradiated *n*-pentane, will be considered

$$R\cdot + C_5H_{10} \longrightarrow RH + C_5H_9\cdot \tag{8}$$

$$R\cdot + C_5H_{10} \longrightarrow R\text{-}C_5H_{10}\cdot \tag{9}$$

where $R\cdot$ represents an alkyl radical or a hydrogen atom. Similar reactions may occur with other product olefins.[24] These reactions and the subsequent reactions of product radicals can qualitatively account for the observed effects, notably for the considerable decrease in the yields of the various olefins.

However, the yields of saturated products with one to four carbon atoms, which are mainly formed in reactions involving free radicals, as follows from their yields in the presence of oxygen, are only slightly affected by an increase in dose from 0.8 to 36 Mrads. This indicates that, for the radicals involved, reaction 9 does not compete efficiently with reactions 4 and 8. In that case, a small effect of total dose on hydrogen formation might also be expected, if only reactions 8 and 9 were competing with reaction 1. The experimental results, notably the small decrease in saturated C_1–C_4 products and the more pronounced reduction in $G(H_2)$ with increasing dose, suggest that other processes also contribute. This is consistent with our results in the presence of ethylene and of pentene.

Effects of Olefins. Figure 5 shows that the hydrogen yield is reduced in the presence of ethylene and of pentene-2. With the latter additive the reduction is more pronounced. Scavenging of H atoms by these olefins according to reactions similar to 8 and 9 may occur. However, such a mechanism cannot account for the stronger decrease in $G(H_2)$ when pentene-2 is added, since H atoms react with ethylene almost exclusively by addition to the double bond,[25] whereas with pentene both addition and abstraction reactions are important. Hence, other processes must contribute to the decrease in $G(H_2)$ when pentene-2 is added. Apparently, these processes do not occur, or are much less important, in the presence of ethylene. Reactions of excited molecules and ions with pentene, including energy-transfer processes, may be involved. These reactions may also, at least partly, account for the observed decrease in the total concentration of olefins, when relatively concentrated solutions of pentene-2 (*ca.* 2 mole %) are irradiated. The results are similar to those reported for solutions of cyclohexene in cyclohexane.[26]

Polymer formation, observed in the presence of pentene-1, is reduced by O_2. This reduction is more pronounced when both O_2 and NH_3 are present. The effect of O_2 suggests that part but not all of the polymer is formed by free radical reactions. The observed additional reduction in the presence of NH_3, which is a scavenger of positive ions, suggests that ionic species may be involved in these condensation reactions.

Effects of Oxygen. It is generally assumed that the major effect of oxygen on product formation is due to scavenging of free radicals and atoms, and our experiment results are interpreted accordingly.

The considerable reduction in the yields of saturated products (Table IV) indicates that they are mainly formed in processes involving free radicals. Residual yields in the presence of oxygen may either be the result of reactions within the spurs, where high local radical concentrations exist, or they may be due to molecular elimination reactions, for example, from excited molecules. The following reactions are considered.

$$C_5H_{12}^* \longrightarrow C_5H_{10} + H_2 \tag{10}$$

$$C_5H_{12}^* \longrightarrow C_5H_{11}\cdot + H\cdot \tag{11}$$

$$C_5H_{12}^* \longrightarrow CH_4 + C_4H_8 \tag{12}$$

$$C_5H_{12}^* \longrightarrow (CH_3\cdot + C_4H_9\cdot) \tag{13}$$

$$(CH_3\cdot + C_4H_9\cdot) \longrightarrow CH_4 + C_4H_8 \tag{14}$$

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(17) G. A. Muccini and R. H. Schuler, *J. Phys. Chem.*, **64**, 1435 (1960).

(18) P. J. Dyne and J. Denhartog, *Can. J. Chem.*, **41**, 1794 (1963).

(19) However, the total yield of C_1–C_4 radicals decreases with temperature as a result of the cage effect.

(20) M. Matsuoka, P. S. Dixon, A. P. Stefani, and M. Szwarc, *Proc. Chem. Soc.*, 304 (1962).

(21) P. S. Dixon, A. P. Stefani, and M. Szwarc, *J. Am. Chem. Soc.*, **85**, 2551 (1963).

(22) P. S. Dixon, A. P. Stefani, and M. Szwarc, *ibid.*, **85**, 3344 (1963).

(23) W. A. Cramer and G. J. Piet, *Trans. Faraday Soc.*, **63**, 1402 (1967).

(24) With ethylene reaction 8 is not important.[25]

(25) R. A. Holroyd, *J. Phys. Chem.*, 70, 1341 (1966).

(26) P. J. Dyne and J. W. Fletcher, *Can. J. Chem.*, **38**, 851 (1960).

$$(CH_3\cdot + C_4H_9\cdot) \longrightarrow CH_3\cdot + C_4H_9\cdot \tag{15}$$

$$C_5H_{12}^* \longrightarrow C_2H_4 + C_3H_8 \tag{16}$$

$$C_5H_{12}^* \longrightarrow C_2H_6 + C_3H_6 \tag{17}$$

$$C_5H_{12}^* \longrightarrow (C_2H_5\cdot + C_3H_7\cdot) \tag{18}$$

$$(C_2H_5\cdot + C_3H_7\cdot) \longrightarrow C_2H_6 + C_3H_6 \tag{19}$$

$$(C_2H_5\cdot + C_3H_7\cdot) \longrightarrow C_2H_4 + C_3H_8 \tag{20}$$

$$(C_2H_5\cdot + C_3H_7\cdot) \longrightarrow C_2H_5\cdot + C_3H_7\cdot \tag{21}$$

The parentheses indicate that sibling radicals are present within the liquid cage in which they are initially formed. Alkyl radicals, escaping from the spurs, react with solvent molecules or with other radicals (most probably pentyl radicals), if radical scavengers are not present.

$$R\cdot + C_5H_{12} \longrightarrow RH + C_5H_{11}\cdot \tag{4}$$

$$R\cdot + C_5H_{11}\cdot \longrightarrow R\text{-}C_5H_{11} \tag{7}$$

$$R\cdot + C_5H_{11}\cdot \longrightarrow \text{disproportionation reactions} \tag{5,6}$$

The observed residual yields in the presence of oxygen are approximately equal for CH_4 and C_4H_8, for C_2H_4 and C_3H_8, and for C_2H_6 and C_3H_6. This is consistent with reactions 14, 19, and 20, between sibling radicals within the liquid cage, but also with molecular elimination according to reactions 12, 16, and 17. The formation, in the presence of excess oxygen, of products with six to ten carbon atoms suggests that reaction 7 also occurs within the spurs.

A change in isomer ratios of intermediate products and dimers is observed in the presence of oxygen. The results show a smaller decrease in the yields of products derived from *n*-pentyl radicals (Tables V and VI). Similar changes, observed with decreasing temperature, were attributed to a decreased contribution of reactions 4a and 4b at lower temperatures. These reactions can also account for the effect of oxygen on these isomer ratios. In the presence of oxygen, residual yields of the C_6–C_{10} products are due to reactions within the spurs. Apparently, reactions 4a and 4b cannot compete effectively with reaction 7 under the conditions existing in the spurs (high local radical concentrations), and no change in identity of radicals will occur.

The yields of olefins with two to four carbon atoms are much less affected by oxygen (Table IV). Hence, the major fraction of these products have no free radicals as precursors. The observed effect may be due to interference with reaction 6. On the other hand, the yields of various pentene isomers are considerably reduced in the presence of oxygen. Probably part of the pentene formation proceeds according to reaction 5. Scavenging of radicals by oxygen will reduce the pentene yield and may lead to oxygenated products. Pentanols and pentanones were observed with a total *G* value of *ca.* 3.6. Reactions 10 and 5, the latter within spurs, may both contribute to the residual pentene yield in the presence of excess oxygen.

The hydrogen yield is reduced to a value of 3.7 in the presence of O_2. This might be attributed to reaction 22 competing with 1.

$$H\cdot + O_2 \longrightarrow HO_2 \tag{22}$$

$$H\cdot + C_5H_{12} \longrightarrow H_2 + C_5H_{11}\cdot \tag{1}$$

Other processes, such as quenching of excited molecules or scavenging of electrons by oxygen may also contribute to the observed reduction in product yields. The latter process is known to occur in aqueous systems.[27] It is not possible from our experimental results to distinguish between these various mechanisms.

Effects of N_2O and $N_2O + O_2$. Nitrous oxide reacts reacts with electrons.[8–12,28,29]

$$N_2O + e^- \longrightarrow N_2 + O^- \tag{23}$$

Nitrogen formation in the presence of N_2O is not affected by addition of oxygen, as is shown in Table I. This either suggests that O_2 does not compete with N_2O for electrons or that O_2^- transfers its electron to N_2O.

Reaction 23 competes with

$$C_5H_{12}^+ + e^- \longrightarrow C_5H_{12}^* \longrightarrow \text{products} \tag{24}$$

In addition, the following reactions should be considered.[30]

$$C_5H_{12}^+ + O^- \longrightarrow C_5H_{11}\cdot + OH\cdot \tag{25}$$

$$OH\cdot + C_5H_{12} \longrightarrow H_2O + C_5H_{11}\cdot \tag{26}$$

Similar reactions have been proposed in cyclohexane.

The formation of saturated intermediate products is reduced by N_2O by approximately 10%. This can be attributed to decreased C_1–C_4 radical formation, probably as a result of competing reactions 23 and 24. However, a decrease in the formation of these radicals by *ca.* 10% cannot fully account for the observed reduction in saturated C_1–C_4 hydrocarbon yields. Especially the yields of C_2H_6 and C_3H_8 are more strongly affected, and effects of N_2O on molecular elimination reactions such as 12, 16, and 17 may also contribute.

As was mentioned before, C_2–C_4 olefins may predominantly be formed either in reactions 14, 19, and 20, between sibling radicals within the liquid cage, or in molecular elimination processes, but no distinction between the two mechanisms could be made. However, our results in the presence of N_2O show a considerable decrease in the yields of these olefins. Since N_2O has a small effect on C_1–C_4 radical formation, the results indicate that a large fraction of the C_2–C_4 olefins is the result of molecular elimination reactions. It is also evident that positive ions are intermediates in these processes.

Molecular elimination of olefins does not proceed solely according to reactions 12, 16, and 17. This follows from the observation that, in O_2-containing solutions, the residual yields of C_2H_4 and C_3H_6 are further reduced upon N_2O addition, whereas the yields of C_3H_8 and C_2H_6 are hardly affected.

Dimers are formed according to reaction 7a. The

$$C_5H_{11}\cdot + C_5H_{11}\cdot \longrightarrow C_{10}H_{22} \tag{7a}$$

dimer yield increases when N_2O is present but the isomer distribution remains the same (Tables IV and V). These results suggest that additional dimer formation proceeds by a mechanism similar to that in pure *n*-pentane. This is consistent with the observation that, in the presence of O_2, the dimer yield is reduced to the same value, whether N_2O is present or not, and also with increasing yields of pentanols and pentanones

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(27) S. Gordon, E. J. Hart, M. S. Matheson, J. Rabani, and J. K. Thomas, *Discussions Faraday Soc.*, **36**, 193 (1963).

(28) W. V. Sherman, *Nature*, **210**, 1285 (1966).

(29) L. A. Rajbenbach, *J. Am. Chem. Soc.*, **88**, 4275 (1966).

(30) Instead of, or in addition to, reactions 25 and 26, a reaction sequence $O^- + C_5H_{12} \rightarrow OH^- + C_5H_{11}\cdot$ and $OH^- + C_5H_{12}^+ \rightarrow H_2O + C_5H_{11}\cdot$ may also occur.

when N_2O is added to a solution of O_2 in *n*-pentane prior to irradiation.

Increased pentyl radical formation in the presence of N_2O will result in enhanced yields of pentenes, formed according to reaction 5. Moreover, pentene formation in nonradical processes, for example, reaction 10, is also affected by N_2O. This is evident from the observed decrease in *cis*-pentene-2 yield when N_2O is added to solutions of oxygen in *n*-pentane, as shown in Table IV. The observed increase in pentene-1 formation when N_2O is added to these solutions cannot be due to the formation of free pentyl radicals in reactions 25 and 26. However, it can be explained by reaction 25, if the radicals formed in this reaction have a finite probability of reacting with each other within the liquid cage to form pentene and H_2O. The formation of H_2O, with a *G* value of about 2, has been observed in the presence of N_2O.

Hydrogen formation is reduced when N_2O is added to *n*-pentane. This decrease is smaller than the yield of N_2, which is formed simultaneously, as is shown in Figure 6. Similar observations were made in the radiolysis of solutions of N_2O in cyclohexane.[9,11] It may indicate that dissociative electron capture (reaction 23) is a more efficient process than hydrogen formation following parent ion–electron recombination.[31] It may also be partly due to additional modes of decomposition of N_2O.

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(31) This interpretation is consistent with observed increases in hydrogen yield when HI or HCl is added to cyclohexane: P. J. Horner and A. J. Swallow, *J. Phys. Chem.*, **65**, 953 (1961); J. R. Nash and W. H. Hamill, *ibid.*, **66**, 1097 (1962).

A Nuclear Magnetic Resonance Study of Steric Effects in the 2-Butenes[1]

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Abstract: The 60-Mcps proton nmr spectra of *cis*- and *trans*-2-butene are reported and analyzed. A semiempirical method has been used to construct a potential energy surface representing the steric interaction between the methyl groups of the *cis* isomer, and this surface has been used to interpret the vicinal coupling constants. It is found that the barrier restricting rotation about the carbon–carbon single bonds is not of the simple threefold type, and that the preferred conformation is skewed from that in which a methyl proton eclipses the carbon–carbon double bond. The values of the *trans* and *gauche* vicinal couplings determined in this study, $J_t = 10.0 \pm 1.0$ cps and $J_g = 3.7 \pm 0.2$ cps, are in good agreement with those reported by other workers.

In a former paper,[3] we reported on a nuclear magnetic resonance study of steric effects in *cis*- and *trans*-1,4-dichloro-2-butenes. It was found in that case that the analysis was complicated by inseparable contributions from both skewing and population effects, so that only a lower limit to the magnitude of the steric interaction was inferred.[4] The parent compounds, *i.e.*, *cis*- and *trans*-2-butene, present no such complicating factors, however. Thus, it is possible in this case to identify changes in the nmr parameters directly with skewing effects, which have their origin in the strains produced by intramolecular steric interactions. We report the result of our study of *cis*- and *trans*-2-butene in the present paper.

As in our former work, so in this case also we rely upon the marked angular dependence of the proton–proton vicinal couplings across carbon–carbon single bonds to interpret the effect. Of course, rapid rotation of the methyl groups about the carbon–carbon single bonds is to be expected, and the observed coupling is interpreted as a rotational average. The average is weighted by the relative stability of the various configurations, however, so that, if a skewing does take place, a different rotational average should be observed.

There is good reason to believe that in the *trans* isomer the preferred orientation of the methyl group is that for which one of the protons is *trans* to an adjacent vinyl proton.[3,5] The fact that a rather strong steric interaction is to be expected if such an orientation persisted in the *cis* isomer can be appreciated by observing the model of Figure 1, which is constructed to scale for the experimentally observed[6] (although perhaps not quanti-

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(1) Based in part on work performed under the auspices of the U. S. Atomic Energy Commission.

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(3) H. G. Hecht and B. L. Victor, *J. Am. Chem. Soc.*, **89**, 2532 (1967).

(4) In ref 3, an error was made in defining the equilibrium. The correct expression should be $\Delta F = -RT \ln [p_I/(1 - 2p_I)]$ which leads to $\Delta H_{trans} = -650$ cal/mole and $\Delta H_{cis} \rightarrow -\infty$. Thus, no limit at all can properly be established. We wish to thank S. S. Butcher for calling this error to our attention in a private communication.

(5) M. Barfield and D. M. Grant, *J. Am. Chem. Soc.*, **85**, 1899 (1963); H. J. M. Bowen, A. Gilchrist, and L. E. Sutton, *Trans. Faraday Soc.*, **51**, 1341 (1955); A. A. Bothner-By and H. Günther, *Discussions Faraday Soc.*, 34, 127 (1962); D. R. Herschbach and L. C. Krisher, *J. Chem. Phys.*, **28**, 728 (1958).

(6) L. O. Brockway and P. C. Cross, *J. Am. Chem. Soc.*, **58**, 2407 (1936).