sible effects.

ently protects cyclohexane to some extent against primary decomposition as evidenced by effect on hydrogen yields. However, the picture is by no means simple for hot hydrogen atoms produced in a primary chemical act may react with either species present and produce changes not characteristic of the liquid state. In particular, it is difficult to understand absence of ethane from the products of the mixture. Thus, the ionization transfer picture is consistent with a portion of the results obtained in this case but, of itself, does not explain all of them. Much more extensive study of vapor mixtures would be required for unravelment of all pos-

5. Conclusion

Radiolysis of the hydrocarbon mixtures studied yields products not predictable on the basis of a simple law of averages. An ionization transfer mechanism is consistent with all the effects observed but if this hypothesis is adopted it is evident that excitation transfer also plays an important role in establishment of ultimate products in a liquid mixture. The latter effect is most clearly seen in the case of the cyclohexene-benzene mixture, in which the former component has the higher excitation potential and the ionization potentials are nearly the same. Acknowledgment.—The authors are greatly indebted to Professor J. L. Magee and Doctors J. C. Devins and E. J. Y. Scott for suggestions and frequent discussion in regard to this work.

REMARKS

H. LINSHITZ (Syracuse University): Manion and Burton have shown that the presence of unsaturated molecules in irradiated hydrocarbon mixtures markedly decreases the yield of decomposition products. In this connection, I would like to point out that these unsaturated molecules are uniquely well suited for dissipation of the available energy, through the charge transfer process discussed by Magee.

According to this view, the degree of protection afforded by a given molecule should depend not only on the probability of a charge transfer reaction between it and the original ion but also on the nature of the excited states formed by combination of the new ion and an electron. In general, the reaction between odd ions and electrons may be expected to lead with high probability to triplet states which are not readily excited optically. In the particular case of unsaturated molecules the low-lying triplet states are stable, and the energy may thus readily be dissipated through normal quenching processes, without decomposition. On the other hand, formation of triplet states in saturated molecules should lead to considerable bond rupture, as is observed. The effectiveness of benzene as a protective agent compared with, say, cyclohexene may be due partly to its large crosssection for charge transfer (connected with the availability of charge over the whole molecule) and partly to the low energy of its deepest-lying triplet state. One may venture to predict that molecules like anthracene, with especially low-lying triplets and extensive charge distributions, would be even more effective than benzene.

DETECTION AND IDENTIFICATION OF FREE RADICALS IN THE RADIOLYSIS OF ALKANES AND ALKYL IODIDES¹⁻³

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The use of iodine having a high specific activity in I^{131} has been applied to the detection and identification of free radicals formed in the radiolysis of alkyl iodides and alkanes. The fragmentation patterns observed were reliable to approximately $\pm 5\%$ and several tests of the identity of the fractions were successful. Fragmentation patterns have been obtained for the normal alkyl iodides methyl through butyl in both liquid and vapor states. In these cases the bond most frequently ruptured appeared to be the C–I bond. Radiolysis of the normal alkanes through pentane, plus neopentane, showed some complementary relationships to mass spectra of these compounds. Some possible reaction mechanisms are discussed.

Introduction

Free radicals undoubtedly occur as important intermediates in the decomposition of hydrocarbons and their derivatives produced by ionizing radiations. Recent discussions of the primary processes of radiation decomposition⁴⁻⁶ indicate a variety of ways in which they may be formed. The initial interaction of the ionizing radiation (electrons or Xradiation) produces both excitation and ionization. Dissociation into free radicals is a highly probable consequence of excitation and a similar dissociation

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(2) Work supported in part by the Atomic Energy Commission under Contract At(11-1)-38.

(3) Presented at the Symposium on Radiation Chemistry, 119th ACS Meeting, Cleveland, Ohio, April 8-12, 1951.

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(6) J. L. Magee and M. Burton, J. Am. Chem. Soc., 72, 1965 (1950); 73, 523 (1951). process may be expected of the ions. Subsequent ion neutralization also yields excited molecules and again dissociation into free radicals is a highly probable process. These possibilities may be summarized as

$$\begin{array}{c} \swarrow^{A} \searrow \\ A' \longleftarrow A^{+} + e \\ \downarrow (1) \qquad \downarrow (2) \\ R_{1} + R_{2} \qquad R_{3}^{+} + R_{4} \end{array}$$

Fluorescence, ultimate molecule formation, collisional deactivation and other processes also occur but here we have mentioned only the main paths of free radical formation.

Process 1 may be considered a photochemical decomposition, although the fact that ionizing radiations are used in this work indicates that we shall be dealing with highly excited molecular energy states and probably a considerable variety of these. Process 2 can be studied by consideration of mass spectrographic data. It is well known that the mass spectra of alkanes and their derivatives show many mass peaks for molecule and radical ions of smaller mass than the parent ion.^{7,8} This attests to the importance of process 2 although the mass spectrometer detects the ion, whereas we shall be concerned with the complementary radical. Analogies between the results of this study and those of photochemistry and mass spectrometry may be expected.

The detection and identification of free radicals in photochemical processes has been a subject of much concern. Methods which may be regarded as precursors of the present one include: the use of metal mirrors by Paneth and Hofeditz⁹ and later by Rice, et al.¹⁰; the use of lead mirrors containing radioactive lead by Leighton and Mortenson¹¹; the use of carbon tetraiodide mirrors by Simons and Dull¹²; the use of molecular iodine mirrors by Belchetz and Rideal¹³; and the use of iodine vapor by Gorin.¹⁴ Hamill and Schuler¹⁵ used molecular io-dine containing I^{131} (β^- , $t_{1/2} = 8$ days) to measure the rate of reaction of alkyl radicals with molecular iodine in the photolysis and radiolysis of alkyl iodides. This method was later extended by Williams and Hamill¹⁶ to systems in which complex mixtures of radicals were produced by radiolysis and photolysis. Durham, Martin and Sutton¹⁷ have applied the same technique to the detection of methyl and propyl radicals in the sodium flame reaction with propyl halide.

The present work continues the investigation of the nature and relative amounts of some free radicals formed by ionizing radiations from alkanes and alkyl iodides. The systems studied contain the alkane or alkyl iodide as liquids or gases plus a small concentration (mole fraction $ca. 10^{-8}$) of molecular iodine. As a first approximation the presence of iodine is neglected in the primary processes and radicals are presumed to form through reactions such as 1 and 2, above. Some secondary reactions of these radicals which might be considered are

$$R_1 + R_2 \longrightarrow R_1 R_2 \tag{3}$$

$$R_1 + R_3 H \longrightarrow R_1 H + R_3$$
 (4)

$$R_1 + I_2 \longrightarrow R_1 I + I \tag{5}$$

At moderate reaction rates, the radical concentration will be so small as to make the rate of reaction 3 negligible in comparison to 4 or 5. Reaction 4 has an activation energy of 10–15 kcal., while reaction 5 has a very small activation energy, probably around 1 kcal. Therefore, at the temperatures (ca. 25°)

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and relative concentrations used in this work, reaction 5 is taken to be the fate of substantially all *thermal* free radicals produced. Reactions such as 4 may yet play some part in the radiation decomposition, but if so they represent the reaction of excited or "hot" radicals, formed with excess internal or translational energy in reactions such as 1 and 2. The alkyl iodides, although formed in micromolar quantities, will contain a high specific activity of I^{131} . Addition of appropriate inactive alkyl iodide carriers to the reaction products, followed by fractional distillation and radioactivity determinations permits estimation of the relative free radical yields.

Experimental

Milligram quantities of iodine containing approximately ten microcuries of I^{131} ¹⁸ were prepared by oxidation of dry potassium iodide with dry potassium dichromate at elevated temperatures in vacuum. The iodine sample was distilled into a small break-off tube for later introduction into the reaction system.

The alkyl iodides used as target materials and as distillation carriers were purified by fractional distillation in a glasspacked Todd column 1.5×100 cm. at a reflux rate of 300 ml. per hour and a reflux ratio of 40:1. A middle cut from each distillation was retained, dried over phosphorus pentoxide and stored in a dark vessel. Samples for radiolysis were further subjected to bulb-to-bulb distillation in vacuum to ensure removal of dissolved gases. Alkanes used for radiolysis were of research grade and were further distilled in the vacuum line only to remove dissolved gases. The radiolysis of liquid alkyl jodides was performed on 5-

The radiolysis of liquid alkyl iodides was performed on 5cc. samples containing approximately 1 mg. of dissolved iodine. Both components were introduced by vacuum distillation into an all-glass vessel 1.5×10 cm. This vessel was closed by a glass seal and opened after irradiation by a break-off. Radiolysis of alkyl iodide and alkane vapors was performed in a 500-cc. spherical flask having a thin "window" to reduce absorption of soft radiations. Again, the components were introduced by vacuum distillation, the vessel closed by a glass seal and re-entered through a break-off.

The radiations employed were of four classes: γ -radiations from a two curie Co⁸⁰ source ($t_{1/2} = 5.3$ yr., $\gamma = 1.1$, 1.3 mer.); X-rays generated at 45–50 Pkv. and 17 ma. in a Machlett AEG-50 X-ray tube; X-rays generated at 2 mv. and 100 μ a. in a Van der Graaf generator; and electrons at 2 mv. and 2 μ a. from the same machine. In all cases the irradiation time was varied to produce about 50% reaction with iodine. The times of exposure varied from about 20 hours to 2 minutes for the various kinds and energies of raditions. No effects of such changes in rate of decomposition upon the fragmentation patterns were observed.

After irradiation, alkyl iodide carriers were introduced into the reaction vessel on top of the frozen products. The carrier mixture usually consisted of 5 cc. of methyl iodide, 3 cc. each of the normal alkyl iodides up to carbon chain length one unit greater than the target substance, and 3 cc. of methylene iodide. Isopropyl iodide was also used in some cases.

Excess iodine was extracted with aqueous sulfite solution, after which the carrier mixture was washed with water and dried over phosphorus pentoxide. In some cases a water extract was made before iodine removal, in order to estimate the amount of hydrogen iodide produced. Such activity is reported as per cent. of total organic activity.

The organic iodide mixture was distilled in a Podblelniak Miniature Hyper-Cal Fractionating Column 1×30 cm., packed with a heligrid fabricated from Hastelloy B, a halogen resistant alloy. The reflux rate was maintained at approximately 100 cc. per hour and the reflux ratio at approximately 40:1. The distillate flowed through a capillary grid in front of a mica window Geiger counter arranged so that approximately 0.1 ml. of distillate was retained in front of the counter (see Fig. 1). The count rate was observed with a linear count rate meter. A Brown two-point recording potentiometer continuously recorded the activity

(18) I¹⁸¹ obtained in millicurie amounts as carrier-free iodide solution from the Isotopes Division, Carbon and Carbide Chemicals Company, Oak Ridge, Tennessee. of the distillate and the head temperature of the column. A pump and manostat were attached to the fractionation apparatus to permit distillation at reduced pressure in the case of higher iodides.



Fig. 1.—a, Geiger counter; b, mica window; c, capillary coil; d support.

For each fraction the head temperature and activity were expected to remain constant over a distillate volume of at least 0.5 cc. (approximately 30 min.) to be taken as a measure of the activity of that fraction. This activity was multiplied by the original carrier volume for comparison with other fractions on a percentage basis. Each fraction was collected separately for redetermination of activity or redistillation if desired.

Figure 2 depicts the values of pressure, temperature and activity encountered in the course of a typical distillation after irradiation of *n*-pentane. In this case, vinyl iodide carrier was also used. Clear values of activity associated with methyl iodide, ethyl iodide, *n*-propyl iodide, *n*-butyl iodide, *n*-amyl iodide and methylene iodide are observable. Little or no activity is associated with vinyl iodide, the *i*propyl iodide fraction is obscured by carry-over of ethyl



Fig. 2.—Radiolysis of pentane.

iodide, and the peak between *n*-butyl and *n*-amyl can probably be attributed to uncarried active secondary amyl iodides.

Figure 3 shows the activity record from two irradiations of propane (with 45 kv. X-rays and with 2 mv. X-rays) normalized to the same scale. The correspondence of the yields in the various fractions illustrates the reproducibility of the method and demonstrates the lack of dependence on the maximum energy of the quanta used.



Distillation time (min.). Proportional to distillate volume. Fig. 3.—Radiolysis of propane: duplicate experiments, normalized.

Relative yield data for the various substances studied are given in Tables I, II and III. The hydrogen iodide activity yield is given in terms of per cent. of total organic activity.

Special Tests.—Radiolysis of methane and ethane at an elevated temperature was performed by heating the reaction vessel with infrared lamps to a steady temperature of 80–100°, as indicated by a mercury thermometer in contact with the vessel. In this condition radiolysis with energetic electrons resulted in products experimentally indistinguishable from those obtained in experiments at room temperature (25°) (experiments 45 and 54).

• Several experiments were performed to test the validity of the fractional distillation as an analytical technique. A sample of ethyl iodide containing dissolved iodine (with I^{131}) was irradiated with electrons and fractionated in the usual manner, using methyl iodide and *n*-propyl iodide carriers in addition to the ethyl iodide already present. From this distillation a constant boiling, constant activity sample, 9.5 ml. in volume, was collected. This fraction was hydrolyzed with 50 ml. of 10% potassium hydroxide at 80°. After 2.5 hours, 5.5 ml. of organic iodide remained. This sample was washed, dried and its specific activity was compared with that of the unhydrolyzed iodide. The two values were experimentally indistinguishable.

A second sample of active ethyl iodide prepared as above was distilled in mixture with 3 ml. each of inactive methyl, *n*-propyl, *n*-butyl and methylene iodides in the usual fashion. Only the ethyl iodide fraction was radioactive.

Discussion

The Analytical Method.—It is especially important to allow complete condensation of the reaction products before carriers are added. Failure to do this may result in disproportionate loss of the more volatile active iodides during the addition of carriers. However, after complete mixing of carrier and active iodides, minor losses are not objectionable, since it is the specific activity of each fraction which is determined. In the case of methane, its volatility at liquid air temperatures made the collection problem especially severe, and many early experiments were discarded on this basis.

Comparison of the results of experiments performed under substantially the same conditions (such as No. 28, 29 and 30 on butyl iodide or No. 19, 20, 42, 43 and 44 on methane) indicates that the relative yields is approximately $\pm 5\%$. The reality of fractions amounting to less than 5% of the total

			LIQUID ALKYL	IODIDES					
Sample, iodides	Vol. of sample, ml.	Weight of I ₂ , mg.		Pro	Products (% of total activity)				
			Radiation	Me	$\mathbf{E}\mathbf{t}$	i-Pr	n-Pr	n-Bu	ene
Methyl	3.0	1.0	γ	66	15	••	a	••	19
Ethyl	3.0	2.0	γ	9	88	1	1	0	1
\mathbf{Ethyl}	3.0	1.0	γ	11	80	••	5	2	2
Ethyl	3.0	1.0	2 mv. X-ray	25	63		7	4	· 1
n-Propyl	3.0	1.0	γ	7	6		80	5	2
n-Butyl	3.0	1.0	γ	14	9		7	70	••
	Sample, iodides Methyl Ethyl Ethyl n-Propyl n-Butyl	Sample, iodidesVol. of sample, ml.Methyl3.0Ethyl3.0Ethyl3.0Ethyl3.0n-Propyl3.0n-Butyl3.0	Sample, iodides Vol. of sample, ml. Weight of I ₁ , mg. Methyl 3.0 1.0 Ethyl 3.0 2.0 Ethyl 3.0 1.0 Ethyl 3.0 1.0 Propyl 3.0 1.0 n-Propyl 3.0 1.0 n-Butyl 3.0 1.0	$\begin{array}{c c} & & & & & & \\ & & & & & \\ \hline Sample, & & & & \\ iodides & & & \\ ml, & & & \\ ml, & & \\ mg, & & \\ mg, & \\ mg, & \\ mg, & \\ mg, & \\ Radiation & \\ r \\$	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$\begin{array}{c c c c c c c c c c c c c c c c c c c $	$ \begin{array}{c c c c c c c c c c c c c c c c c c c $

TABLE I

^a Wherever leaders occur the carrier was not present.

TABLE II GASEOUS ALKYL IODIDES

Expt.	Sample,	Press. of sample,			Products (% of total activity)								
No.	iodidea	mm.	Radiation	\mathbf{Me}	Et	i-Pr	n-Pr	n-Bu	Methylene				
52	$Methyl^a$	93	e-	82	5	Ъ	••		13°				
10	Ethyl	140	2 mv. X-rays	27	· 55		6	3	9				
12	\mathbf{Ethyl}	140	50 kv. X-rays	34	66		0	0	· 0				
13	n-Propyl	40	50 kv. X-rays	15	6	11	56	6	6				
14	n-Propyl	40	50 kv. X-rays	17	5	5	61	5	7				
28	n-Butyl	14	50 kv. X-rays	11	6	3	3	73	4				
29	n-Butyl	10	50 kv. X-rays	9	7	2	2	74	6				
30	n-Butyl	10	50 kv. X-rays	9	8	••	••	68	15				

^a Pressure of iodine was 0.14 mm. in all cases. ^b Wherever leaders occur the carriers were not present. ^c Active HI 1% of total organic. TABLE III

-				ALKANE	5							
D		Press. of Press.				Pro	Mathat					
No.	Sample	mm.	mm.	Radiation	Me	Et	i-Pr	n-Pr	n-Bu	n-Am	ene	HI۵
19	Methane	120	0.14	2 mv. X-rays	74	5	a				21	
20	Methane	120	.14	2 mv. X-rays	74	5	••	••			21	
42	Methane	120	.07	e-	71	5		••			24	9.5
43	Methane	120	.14	·e-	77	5	••	••			18	15
44	Methane	120	.175	e-	76	5			••		19	15
45 ⁶	Methane	120	.14	e-	74	4					22	13.5
46	Methane	$22(CH_4)$.14	e-	77	6			•		17	5.4
		$18(H_2)$										
47	Methane	20	.14	e	80	4					16	7.8
48	Methane	20	.14	e-	77	4			••		19	4
50	Methane	334	.14	e-	80	7					13	3.5
51	Methane	576	.14	e-	77	5					18	7.8
21	Ethane	120	.14	2 mv. X-rays	30	40		10	10		10	
22	Ethane	120	.14	2 mv. X-rays	41	43	•••				16	
38	Ethane	745	.14	e-	28	55		5	3		9	21
54°	Ethane	120	.14	e-	30	46		4	4		16	9
23	Propane	120	.14	2 mv. X-rays	47	12	16	10	5		10	
25	Propane	120	.14	50 kv. X-rays	45	11	14	10	5	••	15	
32	Propane	140	.14	e-	40	10	11	11	10		18	
33	Propane	420	.14	e-	27	9	9	13	13		29	
34	Propane	745	.14	e-	17	8.1	9	8	8	••	49	••
35	Propane	21	.14	e-	52	11	9	9	5	••	14	
57	Propane	470	.14	e-	17	5	••	6	7	••	64	••
26	Butane	120	.14	50 kv. X-rays	20	14	29	13	10		14	
27	Butane	120	.14	50 kv. X-rays	9	12	28	18	13		20	••
55	Pentane	120	.14	e-	24	30	••	6	5	22	13	3
56	Neopentane	120	.14	e-	80	4		2	6	2	6	4

^a Wherever leaders occur the carrier was not present. ^b Runs 45 and 54 irradiated between 80 to 100°. ^c HI reported as per cent. of total organic activity.

is questionable. Large changes in activity from one carrier fraction to the next tax the separation powers of the fractionating and counting systems, since the volumes of carriers used were small and some intermingling of fractions in the column head and counting chamber is unavoidable. This probably increases the uncertainty especially in cases of weakly active fractions which follow highly active fractions. Such considerations place considerable doubt on the reality of such activities as that in the ethyl iodide fraction of the experiments on methane, in spite of careful attention to constant activity and constant boiling point in a given fraction.

May, 1952

The identification of a particular active fraction with the known carrier distilling at the same temperature seems quite clear, especially in the lowerboiling fractions. In addition to the constancy of boiling point and activity through an appreciable volume of distillate, the redistillation and hydrolysis experiments served to support this identification. With the higher-boiling iodides, the possibility of isomeric forms introduces some confusion, since not all possible carriers were introduced. Butyl iodide activity might well be a mixture of the isomers, all appearing with the carrier butyl iodide and, in the case of amyl iodide, clear indication of active secondary amyl iodides is present in Fig. 2.

For greater ease in correlation, the average values of the relative radical yields are shown in Figs. 4, 5 and 6 in the form of bar graphs.



Radiolysis of Alkyl Iodides.—In the radiolysis of the alkyl iodides, both liquids and vapors, the dominant characteristic of the radical yield values is the high yield of the parent substance. This may be taken as an indication that C–I bonds are broken more readily than C–C bonds. Since the only



diiodide carrier used was methylene, only in the case of methyl iodide is direct support presented for the similar conclusion that C–I bonds are broken more readily than C–H bonds. However, this is certainly very likely with all of the alkyl iodides. These effects are to be expected on two grounds: First, the C–I bond is by far the weakest in these molecules and second, the iodine atom has far more electrons than any other atom of the molecule, and therefore, ionization or excitation at this point is most likely.

In comparison with the liquid halides, the halide vapors generally show a higher ratio of C–C to C–I bond rupture. Butyl iodide appears to be an exception to this rule, which may be explained as a greater tendency toward collisional deactivation of excited states in the vapor state.

In both liquid and vapor states it may also be noted that the relative yield of methyl iodide decreases as the carbon chain length increases. Liquid butyl iodide does not follow this trend again and one is inclined to suspect that the experimental data in this case are faulty, especially since the values are based in only one experiment in this case. Such a decrease in relative methyl yield might be explained as an increasing opportunity to rupture other C-C bonds, processes which ought not to have greatly different energy requirements. The production of methylene radicals from ethyl and higher iodides must represent the rupture of two bonds in the primary process or, perhaps more likely, the subsequent reaction of an energetic radical formed in the primary process. The yield of this product is very small except from methyl iodide.

To consider in more detail the radiolysis of methyl iodide vapor, note that the per cent. of methylene iodide formed is about 13. On the other hand, very little active hydrogen iodide (ca. 1%) was formed, which appears to rule out a mechanism. involving C-H bond rupture

$$CH_{3}I \longrightarrow CH_{2}I + H$$
 (1)

$$CH_{21} + I_{2}^{*} - \rightarrow CH_{2}I_{2}^{*} + I$$
 (2)

$$H + I_2^* \longrightarrow HI^* + I$$
 (3)

since an equivalent amount of active hydrogen iodide would be formed. The mechanism proposed by Hamill and Schuler¹⁵ and by Schultz and Taylor¹⁹ for the photolysis and radiolysis of such compounds

$$CH_{3}I \xrightarrow{} CH_{3} + I \qquad (4)$$

$$CH_3 + CH_3I \longrightarrow CH_4 + CH_2I$$
(5)

$$CH_{2}I + I_{2}^{*} \longrightarrow CH_{2}I_{2}^{*} + I \qquad (6)$$

$$CH_3 + M \longrightarrow CH_3 + M$$
 (7)
 $CH_3 + I_2^* \longrightarrow CH_3 I^* + I$ (8)

 $CH_3 + I_2^* - \rightarrow CH_3I^* + I$ (8) where CH_3 indicates a hot methyl radical, appears

to satisfy those data also, and the ratio of methyl to methylene iodide may be taken as the ratio of the rates of the hot radical reaction 5 to the thermalization reaction 7.

Radiolysis of Alkanes.—The fragmentation patterns characteristic of the alkanes, as shown in Fig. 6, differ sharply from those found for the alkyl iodides. The radical corresponding to the parent substance is no longer dominant, except in the case of methane. Methyl radicals are frequently an important product although other small radicals, principally ethyl and propyl, are also formed in good yield. Methylene iodide is also a product of some importance. The contrast between normal pentane and neopentane is also noteworthy.

In some respects a complementary relation appears between these radical yield data and the mass spectral data as reported by Langer.⁸ The most important peak in the mass spectrum of neopentane is $C_4H_9^+$, while the present method indicates a large yield of methyl radicals, suggesting that an important primary process is

$$C(CH_3)_4 - \cdots \rightarrow C(CH_3)_3^+ + CH_3 + e \qquad (9)$$

In contrast, the mass spectrum of normal pentane shows the $C_3H_7^+$ ion to be most important, and the present work indicates a large yield of ethyl radicals

$$C_{3}H_{12} \longrightarrow C_{3}H_{7}^{+} + C_{2}H_{5}^{+} + e$$
 (10)

Butane does not obviously show such a complementary relationship, but with propane it again appears. $C_2H_5^+$ is the most important ion, while CH_3 is the most important radical.

In the radiolysis of methane variation of the pressures of the reagents, the temperature of the system and the intensity of the radiation appeared to have no effect upon the relative amounts of products. Therefore, their ratio must be determined by the primary processes, or in subsequent hot radical reactions. The yield of active hydrogen iodide, although somewhat variable, is clearly much less than that of methyl iodide and nearly equal to the yield of methylene iodide (remembering that the chance of having I^{131} in CH_2I_2 is twice that in monohalides). These facts suggest that a primary process

$$CH_4 \longrightarrow CH_8 + H$$
 (11)

produces a hot hydrogen atom, which then reacts efficiently with methane

$$H + CH_4 \longrightarrow CH_3 + H_2 \tag{12}$$

to produce hydrogen and another methyl radical. Thus only a fraction of the primary hydrogen atoms reach thermal energies, where they would efficiently react with iodine to yield active hydrogen iodide. Methylene radicals might be formed in a primary process such as

$$CH_4 \xrightarrow{} CH_2 + H_2$$
(13)

or in a subsequent reaction of hot methyl radicals formed by a reaction such as 11.

$$CH_3 + M \longrightarrow CH_2 + H + M$$
 (14)

Since the ionization potential of methane is about 14 volts, neutralization of the ion would be a highly exothermic process. If all of this energy appeared as relative translational energy of the methyl radical and hydrogen atom, their energies would be about 0.6 volt (14 kcal.) and 9.5 volts (215 kcal.), respectively, indicating the feasibility of reaction 12 but not reaction 14.

Radiolysis of ethane again showed no dependence on pressure of reactants of temperature. The relative yield of active hydrogen iodide was larger than in the case of methane, but still much less than that of ethyl iodide. Therefore the postulate of hot hydrogen atoms is again made

$$C_2H_6 \xrightarrow{} C_2H_5 + H \tag{15}$$

$$H + C_2 H_6 \longrightarrow C_2 H_\delta + H_2 \tag{16}$$

For the formation of methyl radicals in a concentration and temperature independent fashion one may write

$$C_2H_6 \longrightarrow 2CH_3 \tag{17}$$

but the mechanism of formation of methylene radicals is not immediately evident.

Radiolysis of propane shows a distinct effect of the propane pressure, (Table III). With increasing pressure the relative yield of methyl decreases and the yield of methylene increases in such a fashion that the sum of these two yields is approximately constant. Since the yields of other radicals remain approximately constant, it is tempting to assume that some reaction of thermal methyl radicals with propane produces methylene radicals. Any such reaction written, for instance

$$CH_3 + C_3H_8 \longrightarrow CH_2 + H_2 + C_3H_7 (?) \quad (18)$$

must also produce another radical. Since none appears in the distillation analysis and indeed, such reactions must be highly endothermic, this is not a satisfactory proposal. Another proposal which appears more reasonable is to assume that methyl and methylene radicals are both primary products of the same excited or ionized molecular state, by reactions such as

$$C_{3}H_{6} \xrightarrow{} C_{3}H_{8} \xrightarrow{} CH_{3} + C_{2}H_{4} + H \quad (19)$$

$$\xrightarrow{} CH_{2} + C_{2}H_{4} \quad (20)$$

and to assume a pressure effect on the relative efficiencies of these two processes. The rearrangement implied in reaction 20 may require collision with another molecule, the rate of such collisions in-, creasing with increasing pressure. Unfortunately these proposals are far from satisfactory and must be further tested before serious adoption.

⁽¹⁹⁾ R. D. Schultz and H. A. Taylor, J. Chem. Phys., 18, 194 (1950).