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RADIOLYSIS OF PROPANE

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Gas-Phase Radiolysis of Propane

Effect of Pressure and Added Inert Gases

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The direct and inert-gas radiolysis, as well as the vacuum ultra-violet photolysis of $\text{CD}_3\text{CH}_2\text{CD}_3$, $\text{CH}_3\text{CD}_2\text{CH}_3$ and $\text{C}_3\text{H}_8 + \text{C}_3\text{D}_8$ mixtures have been investigated in the presence of radical scavengers. The major conclusions are: (a) at atmospheric pressures, neutral propane decomposition contributes to the observed products although to a lesser extent than parent ion decompositions; (b) a variation in pressure has a pronounced effect on the fragmentation of the parent ion; (c) the hydrogen atoms in the ethyl ion are randomized in the direct as well as in the inert-gas sensitized radiolysis; (d) rearrangement in the parent ion is of minor importance in the radiolysis; (e) although the formation of propylene is related to the propyl ion, it is not necessarily produced by the neutralization of this ion.

In studies on the direct² and inert gas sensitized⁸ radiolysis of propane, the importance of ion-molecule reactions has been established. Also, investigations on the radiolysis of C_3D_8 in the presence of non-deuterated compounds^{10, 13} have demonstrated that it is feasible to obtain reliable relative rate constants of ionic reactions occurring at atmospheric pressures. The role of neutral excited molecule decompositions, however, has not been settled. Also, relatively little is known about the effect of pressure on the fragmentation of the parent ion.

The present study, which includes mainly experiments on $\text{CD}_3\text{CH}_2\text{CD}_3$ and $\text{C}_3\text{H}_8 + \text{C}_3\text{D}_8$ mixtures was initiated in the hope that some of these questions could be answered in a more precise way.

EXPERIMENTAL

MATERIALS

$\text{CH}_3\text{CD}_2\text{CH}_3$, $\text{CD}_3\text{CH}_2\text{CD}_3$ and C_3D_8 were obtained from Merck, Sharp and Dohme of Canada, Limited. The mass spectrum of propane- d_8 showed 3 % $\text{C}_3\text{D}_7\text{H}$. The purity of propane- d_2 has been described earlier.² The C^{13} corrected mass spectrum of propane- d_6 obtained at 70 Ve, given in part in table 1, agrees well with that of Condon⁶ except that the sample obtained from Merck contains only 1.5 % propane- d_7 .

From the isotopic analysis of the methane fraction produced in the pyrolysis of the propane- d_6 sample, it could be deduced that it consisted of 94 % $\text{CD}_3\text{CH}_2\text{CD}_3$ and 6 % $\text{CD}_2\text{HCH}_2\text{CD}_3$.

IRRADIATION PROCEDURE

The experimental technique was essentially the same as that described previously. Experiments above 2 atm pressure were carried out in a stainless steel cylindrical cell with a volume of 10 cm³ (1.1 cm int. diam.). The temperature of the stainless steel reaction cell was maintained at 95°C during irradiation. All other experiments were carried out in cylindrical Pyrex vessels with a volume of 500 cm³ (15 cm in height). The National Bureau of

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TABLE 1.—MASS SPECTRAL PATTERN OF $\text{CD}_3\text{CH}_2\text{CD}_3$

<i>m/e</i>	70 eV	13.0 eV
27	31.1	0.6
28	61.1	1.6
29	117.3	3.7
30	218.4	72.8
31	76.3	17.0
32	438.3	66.9
33	26.2	3.4
34	20.3	5.8
46	23.8	1.5
47	17.9	13.9
48	20.9	14.5
49	125.4	118.8
50	100.0	100.0
51	1.4	1.5

consolidated 21-101, 50 μ amp

Standards 50,000 Curie Co^{60} γ -ray source was used. The dosimetry was carried out by measuring the hydrogen produced in the radiolysis of ethylene at one atmosphere ($G_{\text{H}_2} = 1.28$), and independently, by measuring the saturation ion current in a cell similar to that of Back et al.³ Taking $W = 24$ eV, the energy absorbed by propane was 10^{19} eV $\text{M}^{-1} \text{sec}^{-1}$. No correction factor (cp. Toi *et al.*¹⁴) has been used for the experiments performed at high pressures. Consequently, the G values obtained at densities above 0.02 g/cm³ may be as much as 30 % too low. In most radiolysis experiments, conversions based on the production of hydrogen were somewhat less than 0.1 %.

The photolysis experiments were carried out using an air-cooled electrodeless discharge lamp to excite the resonance lines of xenon and krypton. The lamp contained a cold finger which was cooled to -80 or -195°C in order to eliminate the emission bands of water. A spherical reaction vessel with a volume of 1 l. was used in all experiments. Conversions in the photolysis experiments varies between 0.05 and 0.1 %.

RESULTS AND DISCUSSION

Only a fraction of the results are presented in this paper. Tables containing most of the data can be obtained from the authors upon request. All experiments reported in this study have been carried out in the presence of free radical scavengers, usually NO.

CONTRIBUTION OF NEUTRAL PROPANE DECOMPOSITION

In earlier studies on the gas-phase radiolysis of hydrocarbons, good quantitative agreement has often been reported between the observed products and those calculated from the 70 eV mass spectrometric cracking pattern. From this, it was often concluded that the neutral excited molecule decompositions play a negligible role. However, any quantitative agreement is necessarily fortuitous, not only because the 10^{-6} sec cracking pattern does not exactly represent the fragmentation of the parent ion at elevated pressures, but also because not all ionic reactions occurring at atmospheric pressures are well understood at present.

In order to evaluate the importance of neutral excited propane in the radiolytic system, certain aspects of the neutral propane and propane ion decompositions are discussed in some detail.

NEUTRAL PROPANE DECOMPOSITION

$\text{CD}_3\text{CH}_2\text{CD}_3$ and $\text{CH}_3\text{CD}_2\text{CH}_3$ were photolyzed at 1470 and 1237 Å in the presence of 2 % NO. A few typical results are given in table 2. In addition to the

TABLE 2.—PHOTOLYSIS OF $\text{CD}_3\text{CH}_2\text{CD}_3$, $\text{CH}_3\text{CD}_2\text{CH}_3$ AND $\text{C}_3\text{H}_8 + \text{C}_3\text{D}_8$

	exciting lines	distributions						
		D_2	HD	H_2	CD_4	CD_3H	CH_3D	CH_4
I. $\text{C}_3\text{H}_8 + \text{C}_3\text{D}_8 + \text{NO}$ (1 : 1 : 0.04)	Xe	31.9	7.6	60.5	40.0	2.7	1.2	56.1
	Kr	30.9	21.8	47.3	52.4	0.8	0.8	45.9
II. $\text{CH}_3\text{CD}_2\text{CH}_3 + \text{NO}$ (1 : 0.02)	Xe	45.9	23.9	30.2	—	—	74.8	25.2
	Kr	26.0	29.9	44.1	—	—	84.6	15.4
III. $\text{CD}_3\text{CH}_2\text{CD}_3 + \text{NO}$ (1 : 0.02)	Xe	8.9	23.6	67.4	9.8	90.2	$\frac{\text{C}_2\text{D}_3\text{H}}{\text{C}_2\text{D}_2\text{H}_2}$ 1.83	$\frac{\text{C}_3\text{D}_6}{\text{C}_3\text{D}_5\text{H}}$ 1.76
	Kr	19.2	52.2	28.6	7.7	92.3	0.81	0.46

hydrogen/methane = 19.0 (Xe lines), 3.2 (Kr lines)

observations reported before,¹¹ the following points are of interest to the present study.

(i) H_2 and CD_3H are, within experimental error, equal to C_3D_6 and $\text{C}_2\text{D}_3\text{H}$, respectively, thus indicating that the diradicals produced in the primary processes

rearrange into propylene and ethylene respectively.

(ii) Elimination of methylene from propane occurs at both wavelengths :

since in the photolysis of $\text{C}_3\text{D}_8 + \text{C}_3\text{H}_8 + \text{NO}$ mixtures, ethane consisted entirely of C_2D_6 and C_2H_6 , while, in the photolysis of $\text{CD}_3\text{CH}_2\text{CD}_3 + \text{NO}$ mixtures, $\text{CD}_3\text{CH}_2\text{D}$ was the only ethane produced.

(iii) In the photolysis of $\text{CD}_3\text{CH}_2\text{CD}_3 + \text{NO}$, the ratio $\text{CD}_4/\text{CD}_3\text{H}$ decreases slightly with decrease in wavelength from 0.11 at 1470 Å to 0.08 at 1237 Å. Similarly, in the photolysis of $\text{CH}_3\text{CD}_2\text{CH}_3 + \text{NO}$ mixtures, the ratio of process (4) to process (5) is 0.34 at 1470 Å and 0.18 at 1237 Å :

Hence reaction (4), which requires less energy than (5), becomes relatively more important at the longer wavelength as noted before.¹¹

(iv) There is a drastic change in the relative product distribution between the two wavelength regions. At 1470 Å, the elimination of "molecular" hydrogen prevails, while at 1237 Å, dissociations of the type

predominate, the first process being the most important.

DECOMPOSITION OF THE PARENT ION

The mass spectral cracking pattern of propane- d_6 is unique in that the ratio of process (9) to (8) :

can readily be deduced. Mass 31 can unambiguously be ascribed to (8) except for the correction due to $C_3D_5H_3$ impurity. Then, assuming that the ethylene ions formed by both mechanisms make the same total contribution to the cracking patterns of $CD_3CH_2CD_3$ and C_3H_6 , the ratio of process (9) to (8) can be calculated to be approximately 2.3. At 13.5 eV, a value of approximately 4.5 can be deduced for this ratio. Comparison of these two values with the less accurate estimate of 4.4 ± 0.7 and > 7.5 which has been deduced² from the cracking patterns of $CH_3CD_2CH_3$ at 70 and 13 eV respectively, shows that there is an intramolecular isotope effect favouring the H-atom transfer.

Furthermore, (a) an isotope effect of a comparable magnitude exists in the photolysis, and (b) the elimination of CH_4 and CD_4 from $CH_3CD_2CH_3$ and $CD_3CH_2CD_3$, respectively, is favoured at low energies in both the neutral propane molecule and the parent ion.

The values for the ratio CH_4/CH_3D and CD_4/CD_3H , obtained in the photolysis, are more than an order of magnitude smaller than those obtained for the propane ion, perhaps because the excess energy available in the neutral excited propane molecule is considerably higher than in the propane ion.

EVALUATION OF RADIOLYSIS DATA

Because most of the evidence for neutral excited molecule decomposition in the radiolysis of propane will be based on the formation of molecular methane in $CD_3CH_2CD_3$, it should be first noted that, in the direct as well as in the inert-gas sensitized radiolysis of $C_3D_8 + C_3H_8 + NO$ mixtures, the methane fraction consists mainly of CD_4 and CH_4 . Below 1 atm, CD_3H and CH_3D constitute about 5 and 3 %, respectively, of the total methane fraction. Above 1 atm, there is a gradual increase in the partially labelled methanes, but even at 25 atm, they amount to only 9 and 7 %, respectively, of the methane fraction.

Up to 25 atm, HD is not more than 20 % of the total hydrogen fraction and is smaller than both D_2 and H_2 . At pressures below 1 atm, the average distribution is: H_2 , 56.6 %; HD, 15.4 %; D_2 , 28.0 %. Thus, in the presence of radical scavengers and up to 25 atm, methane is nearly exclusively formed by an elimination from propane while hydrogen is largely produced by a detachment process.

(i) The ratio CD_4/CD_3H , obtained in the radiolysis of $CD_3CH_2CD_3$ (table 3), is considerably lower than that deduced from the mass spectrometric cracking pattern. This ratio, which decreases with increase in pressure, cannot be reconciled with the mass spectrometric observation that the ratio of process (9) to process

TABLE 3.—FORMATION OF METHANE AND HYDROGEN IN THE RADIOLYSIS OF $CD_3CH_2CD_3$

	total pressure	hydrogen distribution (%)				G values		
		CD_4/CD_3H	D_2	HD	H_2	hydrogens	CD_4	CD_3H
I. $CD_3CH_2CD_3-NO$ (1 : 0.03)	0.3 cm	1.05	—	—	—	—	0.533	0.508
	2 cm	0.90	30.9	42.5	26.6	2.01	0.412	0.457
	1.9 atm	0.70	31.0	40.4	28.5	2.06	0.294	0.419
	21.8 atm	0.56	24.0	40.0	36.0	1.61	0.131	0.234
	37.7 atm	0.52	20.4	39.3	40.3	1.87	0.117	0.225
II. $CD_3CH_2CD_3-Xe-NO$ (1 : 8 : 0.03)	19.18 cm	1.32	24.5	37.7	37.9	—	—	—
	50.0 atm	0.69	18.1	38.9	43.2	—	—	—

(8) becomes larger at lower electron energies. In order to bring the methane distributions, determined in the low pressure experiments (table 3), into agreement with those deduced from the 70 eV cracking pattern, one has to assume that not

more than 50 % of the observed CD_3H originates from the parent ion. Because the degree of excitation of the parent ion no doubt diminishes with increase in pressure, one may expect the relative probability of process (9) to process (8) to decrease as well so that, at elevated pressures, practically none of the CD_3H will be produced by elimination from the parent ion. At the same time, one may expect an increasing contribution of neutral excited molecule decomposition to the formation of CD_4 . Thus, it may be estimated from the results in table 3 that the G value of methane elimination from neutral propane is 0.25 ± 0.05 , independent of pressure. A similar value can be obtained from the earlier study of $\text{CH}_3\text{CD}_2\text{CH}_3$ using the revised value of 0.18 for the ratio $\text{CH}_4/\text{CH}_3\text{D}$ obtained in the photolysis at 1237 Å.

(ii) An increase in the pressure of $\text{CD}_3\text{CH}_2\text{CD}_3$ increases the ratios $\text{C}_2\text{D}_3\text{H}/\text{C}_2\text{D}_2\text{H}_2$ (0.73 at 2 cm, and 1.3 at 37.7 atm) and $\text{C}_3\text{D}_6/\text{C}_3\text{D}_5\text{H}$ (0.11 at 0.3 cm and 0.60 at 37 atm). These trends which approach the photochemically observed distributions at 1470 Å are, in view of a gradual decrease of the total yields, most likely due to diminishing contributions of ionic reactions with the resulting effect that neutral excited molecule decomposition shows up more clearly. Consistent with these observations are the increases with pressure of the relative yield of D_2 and of the ratio $\text{C}_2\text{H}_3\text{D}/\text{C}_2\text{H}_2\text{D}_2$ seen before² in the radiolysis of $\text{CH}_3\text{CD}_2\text{CH}_3$.

(iii) As shown before,^{2, 10} a small fraction of the ethane is produced by a detachment process ($G = 0.05 \pm 0.02$). A process such as

is apparently of negligible importance. In the mass spectrum of $\text{CD}_3\text{CH}_2\text{CD}_3$, the fragment corresponding to mass 16 which may also be produced from secondary fragmentation process is a minor one (4 % of the ethyl ion at 70 eV and 0.05 % at 20 eV). On the other hand, the photolysis experiments discussed above clearly show that the elimination of ethane from neutral propane is of importance. It is of interest to note that the ethane produced in the radiolysis of benzene + $\text{CD}_3\text{CH}_2\text{CD}_3$ mixtures contains approximately 75 % CD_3CDH_2 .

These observations, as well as previous ones,² lead to the conclusion that, below 1 atm, roughly 10-20 % of the overall products can be ascribed to neutral propane decompositions. Similar estimates have been obtained in the radiolysis of methane¹ and *n*-butane.⁵ It is difficult to evaluate the degree of excitation of the neutral propane molecules in the direct radiolysis. However, since the G value of D_2 ($G = 0.2$) obtained in the radiolysis of $\text{CH}_3\text{CD}_2\text{CH}_3$ represents the maximum value for the elimination of a hydrogen molecule from the middle carbon atom of propane, comparison of this value with the estimated G value of 0.25 for the elimination of methane from the neutral propane molecule shows that the ratio of the two processes is similar to or lower than that obtained in the photolysis at 1237 Å. Thus, below 1 atm, the degree of excitation is at least as high as that of the excited molecules produced in the photolysis at 1237 Å while, at pressures above 1 atm, propane molecules, excited to lower levels, apparently contribute to the products as well.

It is more difficult to estimate the contribution of neutral excited propane decomposition in the inert-gas sensitized radiolysis. However, a number of observations indicate that neutral excited propane molecules are produced. For instance, in the xenon-induced decomposition the ratio $\text{CD}_4/\text{CD}_3\text{H}$, although higher than in the direct radiolysis at comparable pressures, is still considerably lower than the value of 3 deduced by Futrell⁹ from the charge-exchange mass spectrum of $\text{CD}_3\text{CH}_2\text{CD}_3$. A decrease of this ratio with an increase in pressure is also noted. The pronounced enhancement of the relative yield of H_2 , as compared to the direct

radiolysis, is not unexpected if one considers that, in view of the photolysis experiments carried out with the xenon resonance line, the excited propane formed in process (11) should mainly eliminate hydrogen from the middle carbon atom.

Similarly, in the radiolysis of $\text{CH}_3\text{CD}_2\text{CH}_3 + \text{Xe}$ (1:10) mixtures, the hydrogen fraction consists of 16 % D_2 as compared to 9.7 % in the direct radiolysis carried out at comparable pressures. On the basis of these observations, it can be estimated that, in the xenon-induced radiolysis, more than 10 % of the hydrogen is formed by process (11).

Finally, in the radiolysis of $\text{Kr} + \text{CD}_3\text{CH}_2\text{CD}_3$ (10:1) mixtures, a value of 0.52 at a pressure of 20 cm is obtained for the ratio $\text{CD}_4/\text{CD}_3\text{H}$ which is again lower than the value of approximately one obtained by Futrell⁹ in the mass spectrometer.

EFFECT OF PRESSURE ON THE FRAGMENTATION OF THE PARENT ION

In order to obtain a meaningful comparison between the yields of the fragment ions produced in the radiolysis with those deduced from the mass spectral cracking pattern, it is essential to obtain some information about the effect of pressure on the products produced in the radiolytic system.

The major objective of the experiments on $\text{C}_3\text{H}_8 + \text{C}_3\text{D}_8$ mixtures is to follow the variation in yield of the ethyl and vinyl ions with pressure. For these two ions, the hydride transfer reaction

is exothermic and it will be tentatively assumed that under our conditions this constitutes the only mode of reaction. In the radiolysis of $\text{C}_3\text{H}_8 + \text{C}_3\text{D}_8$ mixtures in the presence of radical scavengers, it may be assumed that, after making an approximate correction for the amount of $\text{C}_3\text{D}_7\text{H}$ present in the starting material, $\text{C}_2\text{D}_5\text{H}$ and $\text{C}_2\text{D}_3\text{H}$ are only produced by reaction of the C_2D_5^+ and C_2D_3^+ ions, respectively. Because, in all experiments, $\text{C}_2\text{D}_5\text{H}$ is, within experimental error, equal to $\text{C}_2\text{H}_5\text{D}$ and $\text{C}_2\text{D}_3\text{H}$ is equal to $\text{C}_2\text{H}_3\text{D}$, reaction (12) does not show an isotope effect and consequently the amount of fully deuterated and nondeuterated ethane and ethylene formed in (12) should be equal to the yield of the compounds containing one H or one D atom. Any residue may be ascribed to molecular elimination processes.

TABLE 4.—FRAGMENTATION OF THE PARENT ION; EFFECT OF PRESSURE
G values

	total pressure	density g/cm ³	vinyl ion	ethyl ion	vinyl ion/ethyl ion
I. $\text{C}_3\text{H}_8 + \text{C}_3\text{D}_8 + \text{Ar} + \text{NO}$ (1:1:60:0.05)	2.17 cm	—	0.502	0.815	0.616
	13.43 cm	—	0.310	1.04	0.298
	1.62 atm	—	0.165	1.68	0.098
	56.6 atm	—	0.041	1.71	0.024
II. $\text{C}_3\text{H}_8 + \text{C}_3\text{D}_8 + \text{NO}$ (1:1:0.05)	3 cm	—	0.201	1.32	0.152
	23 cm	—	0.179	1.64	0.109
	* ~1 atm	—	0.30	1.79	0.167
	1.7 atm	0.0035	—	1.77	—
	4.4 atm	0.0089	—	1.41	—
	16.0 atm	0.032	0.069	1.16	0.064
	43 atm	0.21	0.013	0.49	0.026

* values calculated¹⁵ for fragmentation of propane ion at 10^{-10} sec collision interval.

The effect of pressure on the fragmentation of the parent ion is demonstrated in table 4 which shows the variation of $G_{\text{ethyl ion}}$ and $G_{\text{vinyl ion}}$ over a 2000-fold pressure range for $\text{C}_3\text{H}_8 + \text{C}_3\text{D}_8 + \text{Ar}$ (1:1:20) mixtures. The decrease of vinyl ion yields and the increase of the ethyl ion yields with increase in pressure can be qualitatively accounted for by considering the secondary reaction

It can be seen that, at low pressures, values for the yield ratio $\text{C}_2\text{D}_3^+/\text{C}_2\text{D}_5^+$ approach but do not coincide with the value of 2.8 deduced from the argon exchange mass spectrum (2 V) reported by Patterson and Lindholm.¹² On the other hand, in contrast to the experimental results, the calculated breakdown curves for propane predict that, for a collision interval of 10^{-10} sec (corresponding to a pressure of 1 atm), no vinyl ions are produced in the argon-sensitized radiolysis.¹⁵ Nevertheless, the results given in table 4 confirm at least qualitatively the conclusion of Futrell and Tiernan⁸ that a change in time-scale between the mass spectrometric investigation and the radiolysis has a pronounced effect on secondary ion decompositions. A similar trend with pressure is observed in the direct radiolysis of equimolar $\text{C}_3\text{H}_8 + \text{C}_3\text{D}_8$ mixtures. In this case, there is good correspondence between the G values deduced from the calculated 10^{-10} sec breakdown pattern of propane and the G values observed around 20 cm total pressure. Also, at high densities, there is a pronounced decrease of $G_{\text{C}_2\text{D}_5^+}$ although, at the critical pressure (density, 0.2 g/cm³), ethyl ions are still produced.

REARRANGEMENTS IN THE ETHYL ION

It has been proposed² that, in the radiolysis of propane + I_2 mixtures, ethane is mainly formed by the exothermic hydride transfer reaction

Proof was mainly based on the observation that ethane- d_3 , formed in the radiolysis of propane- d_2 , consisted mainly of $\text{CD}_2\text{HCH}_2\text{D}$. It was thus suggested that the hydrogen atoms in the ethyl ion undergo a rapid randomization prior to or during reaction. Because this conclusion was based on the interpretation of a complex mixture of isotopically labelled ethanes, a confirmation seemed necessary. This was achieved by studying the radiolysis of $\text{CD}_3\text{CH}_2\text{CD}_3$ in the presence of an excess of cyclohexane (1:4). Under these conditions, the ethyl ions react mainly with cyclohexane¹⁶ to produce

to give $\text{C}_2\text{D}_3\text{H}_3$ as the major isotopically labelled ethane. A mass spectrometric analysis of the ethane- d_3 thus produced indicated that it consisted of both $\text{CH}_2\text{DCD}_2\text{H}$ and CD_3CH_3 in a 2 to 1 ratio. This observation corroborates the conclusion reached earlier² that the hydrogen atoms in the ethyl ions reshuffle statistically.

From the isotopic analysis of the ethanes produced in the He, Ne, Ar, and Kr sensitized radiolysis of both $\text{CH}_3\text{CD}_2\text{CH}_3$ and $\text{CD}_3\text{CH}_2\text{CD}_3$, it could be concluded that the hydrogen atoms are completely randomized in all cases. This may be contrasted with the observation⁴ that the degree of reshuffling in the sec-propyl ion produced in the gas-phase radiolysis of isobutane increases with the recombination energy of the inert gas. This difference may be mainly due⁴ to the relatively higher energy requirement for randomization in the sec-propyl ion.

In the xenon-sensitized radiolysis of propane, the interpretation of the ethane fraction is more complex. For instance, in the direct radiolysis and in the He, Ne, Kr and Ar sensitized radiolysis of $\text{CH}_3\text{CD}_2\text{CH}_3$, a constant value of 2.3 ± 0.1 is observed for the ratio $\text{C}_2\text{D}_2\text{H}_4/\text{C}_2\text{D}_3\text{H}_3$, but values as low as 1.24 are obtained in the radiolysis of Xe + $\text{CH}_3\text{CD}_2\text{CH}_3$ mixtures. Similarly, a value of 1.75 ± 0.05 is obtained for the ratio $\text{C}_2\text{D}_4\text{H}_2/\text{C}_2\text{D}_3\text{H}_3$ in the direct radiolysis of $\text{CD}_3\text{CH}_2\text{CD}_3$ (from 2 cm to 37.7 atm) as well as in the He, Ne, Kr and Ar sensitized radiolysis while values as low as 1.15 are observed in the xenon-induced decomposition of $\text{CD}_3\text{CH}_2\text{CD}_3$. The reason for the anomalous behaviour of the xenon mixtures is not known. The isotopic distribution of ethanes formed in the radiolysis of xenon + C_3H_8 + C_3D_8 mixtures indicates that ethane, as in the other systems, is mainly formed by a hydride transfer reaction. A plausible interpretation would be that an intermediate such as XeC_2H_3^+ is involved in the hydride transfer reaction:

and similar species such as XeCH_3^+ have been observed in the mass spectrum of Xe + CH_4 mixtures.⁷ It is conceivable that XeC_2H_3^+ would show a stronger preference for abstracting a hydride ion from the secondary carbon atom in propane than the smaller ethyl ion. At any rate, an analysis of the isotopic ethanes formed in the $\text{CH}_3\text{CD}_2\text{CH}_3$ + Xe mixtures indicates that the hydrogen atoms are completely randomized in whatever ion leads to the formation of ethane.

REARRANGEMENT IN THE PROPANE ION

Randomization in the parent ion may also lead to the formation of $\text{CH}_2\text{DCD}_2\text{H}$. However, on the basis of the mass spectral cracking pattern of $\text{CD}_3\text{CH}_2\text{CD}_3$, it can be demonstrated that exchange of the H atoms plays a relatively minor role. Rearrangement in the parent ion would necessarily lead to the formation of the ions $\text{C}_2\text{D}_4\text{H}^+$ and C_2D_5^+ . However, the mass spectrum given in table 1 shows that masses 33 and 34 are of relatively minor importance. Consistent with this is the observation that, in the radiolysis of $\text{CD}_3\text{CH}_2\text{CD}_3$ at pressures around 2 cm, the products C_2D_6 and $\text{C}_2\text{D}_5\text{H}$ are respectively 3.1 and 6.5 % of the total ethane fraction while, at pressures of 21 atm and above, C_2D_6 and $\text{C}_2\text{D}_5\text{H}$ constitute only 1.5 and 3.6 % of the ethane fraction or less.

In this connection, however, in addition to the formation of ethane by a hydride transfer reaction and by molecular elimination, there is an additional, although relatively minor, process which may contribute to the yield of ethane. Experiments carried out with C_3H_8 + C_3D_8 + NO mixtures indicate that the ethane- d_4 produced in the radiolysis of C_3H_8 + C_3D_8 mixtures is larger than one can expect from the amount of $\text{C}_3\text{D}_7\text{H}$ present in the starting material and the yield of $\text{C}_2\text{D}_4\text{H}_2$ relative to that of $\text{C}_2\text{D}_5\text{H}$ gradually decreases with increase in pressure. At a pressure of 3 mm, the corrected yield of $\text{C}_2\text{D}_4\text{H}_2$ is approximately 14 % of the yield of $\text{C}_2\text{D}_5\text{H}$ while, at pressures above 20 atm, it is less than 1 %. A reaction such as

would account for these observations. This is one of the reactions which has been proposed by Field to occur in the mass spectrometer (private communication).

The observation that the yield of $\text{C}_2\text{D}_4\text{H}_2$ relative to that of $\text{C}_2\text{D}_5\text{H}$ diminishes with increase in pressure is consistent with the fact that the yield of methane, formed by elimination from the parent ion and, consequently, also that of the corresponding ethylene ion decreases faster than the ethyl ion from 2 cm to 20 atm. From our

results, it cannot be decided to what extent a reaction such as (17) would contribute to the formation of C_2D_6 and C_2D_5H in the radiolysis of $CD_3CH_2CD_3$.

NEUTRALIZATION PROCESSES

No clear answer can be given as to which ions undergo neutralization or as to what the neutralization products are. The propyl ion formed in reaction (14) may be considered as the major relatively unreactive ion in the radiolysis of propane. On the other hand, propylene which is a major product may⁸ have the propyl ion as a precursor. This is substantiated by the observations that (a) about 90 % of the propylene produced in the radiolysis of $C_3D_8 + C_3H_8 + NO$ mixtures at pressures above 1 atm consists of C_3D_6 and C_3H_6 ; (a) the addition to propane of a compound such as benzene which reacts¹⁰ with carbonium ions drastically reduces the yield of propylene although it does not quench the formation of other products such as ethylene, methane, and hydrogen,¹¹ and (c) the addition of 10 % cyclohexane to C_3D_8 quenches the formation of propylene while C_3D_7H appears as an important product which is consistent with the fact that sec-propyl ions react readily with cyclohexane.⁵ The above observations, however, do not constitute conclusive proof for the formation of propylene by the neutralization of the propyl ion. Recent experiments¹ on the radiolysis of methane have shown that, ethyl and propyl ions readily react with radical scavengers, higher hydrocarbons, or reaction products, even though these compounds may constitute less than 0.02 % of the total reaction mixture. In view of these findings, it is conceivable that under our experimental conditions, the propyl ion will interact with reaction products or with NO, rather than undergo neutralization. For instance, a proton transfer reaction of the type

which has been shown⁵ to occur for a number of compounds (M) could account for the formation of propylene.

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