Radiolysis of Methane. Formation of Acetylene*

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The 60Co-gamma radiolysis (at 200 to 2000 torr) and the pulse radiolysis (100 to 760 torr) of methane has been investigated with the specific purpose of elucidating the mode of formation of acetylene. The following two reactions account for the formation of acetylene in the pulse radiolysis:

\[ \text{C}_3\text{H}_5^+ + e \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 + \text{H} \]  

I

\[ \text{C}(1\text{S} \text{ or } 1\text{D}) + \text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + \text{H}_2 \]  

II

Addition of SF₆ as an electron scavenger eliminates reaction I as a source of acetylene, but increases the yield of ethylene through the occurrence of a reaction such as:

\[ \text{C}_3\text{H}_5^+ + \text{SF}_6^- \rightarrow \text{C}_2\text{H}_4 + \text{HF} + \text{SF}_5. \]

In the low dose rate 60Co-gamma radiolysis of CH₄—NO mixtures, reaction II is the only mode for formation of acetylene. The C(1S or 1D) atoms which undergo reaction II are formed in the gamma radiolysis and pulse radiolysis, as well as in the 10 and 11.6–11.8 eV photolyses, through the dissociation process:

\[ \text{CH}_4 \rightarrow \text{C} + 2\text{H}_2. \]

In the gamma radiolysis, the C₃H₅⁺ ion apparently is intercepted by accumulated products before undergoing homogenous neutralization process I. In the 16.7–16.8 and 21.2 eV photolyses, evidence is presented that the ions do not undergo homogenous neutralization.

Key words: Acetylene formation; electron scavenger; ion pair yields; methane; pulse radiolysis; vacuum ultraviolet photolysis.

1. Introduction

The yield and mode of formation of acetylene in the radiolysis of CH₄ at atmospheric pressures have been a matter of speculation for many years [1–7]. Ion pair yields of acetylene varying between 0.0 and 0.25 have been reported in various studies in which the dose rates were in the range 10¹⁸ to 10²² eV/g·s. There are indications that \( M(\text{C}_3\text{H}_2)/N_+ \) increases with an increase in dose rate [5] or decreases in absorbed dose [1]. Actually, consistently high values for \( M(\text{C}_3\text{H}_2)/N_+ \) have recently been reported in studies where a field emission source was employed [6–8] which delivered 3 to 60 ns electron pulses with average dose rates which were about five orders of magnitude higher than those in the linear accelerator studies [5]. In contrast with the lower dose rate studies the agreement between the three Febetron² studies [6–8] was excellent; \( M(\text{C}_3\text{H}_2)/N_+ \) ranged from 0.15 to 0.23. Only a limited amount of information is available concerning the mechanisms of formation of acetylene. It has been shown [9–10] that acetylene appears as a major product at electron energies which correspond to the onset of ionization of CH₄. Application of an electric field technique [10] further indicated that only 27 percent of the acetylene is produced in an ionic reaction. We wish to report new observations which, in our opinion, clarify the mode of formation of acetylene in low as well as in high dose rate radiolysis experiments.

2. Experimental Procedure

The 60Co-gamma experiments were performed in the NBS source (dose rate: 10¹⁸eV/g·s). Cylindrical Pyrex reaction vessels provided with a break seal were used. These were heated to the melting point of Pyrex prior to filling. After condensing the CH₄ or CD₄ in the reaction vessels they were sealed off. For a more detailed description of the experimental procedure we refer the reader to an earlier publication from this

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²Figures in brackets indicate the literature references at the end of this paper.

²Certain commercial materials are identified in this paper in order to adequately specify the experimental procedure. Such identification does not imply recommendation or endorsement by the National Bureau of Standards.
laboratory [11]. Field emission sources delivering ~60 and ~3 ns pulses (Febetron 705 and 706) were used in the pulse radiolysis experiments. The dose per pulse was determined using N2O as a dosimeter [12], taking G(N2) = 12.4. The reaction vessels used in the pulse radiolysis experiments were cylindrical vessels (5 cm long and 3.7 cm internal diameter). Aluminum windows which were 4 mil thick were attached to each end of the cell with vacuum epoxy cement. The cells were evacuated and filled through a Teflon valve. They were positioned in such a manner that the electron beam covered the entire front window.

The type of reaction vessel and the rare gas resonance lamps used in this study have been described before [13]. Neon and helium resonance lamps emitting 74.3–73.6 nm (16.66–16.84 eV), and 58.4 nm (21.2 eV) radiation respectively were used. Both the neon and helium resonance lamps were provided with aluminum windows 1500 Å thick which were entirely leak-free, and could withstand a pressure differential between the reaction vessel and the interior of the resonance lamp of 100 torr or more. The photon flux of the helium and neon resonance lamps was 5 × 10^{13} and 2 × 10^{13} quanta/s, respectively.

Because in the pulse radiolysis experiments, saturation ion currents during the course of an experiment using the neon or the helium resonance lamp, the decay in the light flux was no more than five percent from beginning to end. The output of the resonance lamps was monitored by periodically measuring the saturation ion currents during the course of an irradiation.

In all experiments, the yields of acetylene and ethylene were determined by gas chromatography (squalane column). Isotopic analyses were performed by trapping acetylene from the exit of a gas chromatograph (silica gel column) followed by introduction of the total sample on a high resolution mass spectrometer operated at 13 and 70 eV. Methane was purified by repeated low temperature distillation and mass spectrometric analysis showed that methane d_4 contained 5 percent CD_3H.

3. Results

In tables 1 and 2, the yield of a product, X, measured in the radiolysis and photoionization experiments is reported as M(X)/N_+, or molecules, M, of product X formed per positive ion, N_+, in the system. This allows a meaningful comparison between the product yields in the radiolysis and photoionization experiments. Because in the pulse radiolysis experiments, saturation ion current cannot be measured, the G-values based on the N_2O dosimetry are converted to M(X)/N_+ values by taking a W-value of 26.7 eV for methane [15].

### Table 1. Radiolysis of methane, acetylene and ethylene yields

<table>
<thead>
<tr>
<th>Duration of pulse ns</th>
<th>Dose/pulse eV/g × 10^{-19}</th>
<th>Number of pulses</th>
<th>CH_4 pressure (Torr)</th>
<th>Additive (Torr)</th>
<th>C_2H_2</th>
<th>C_2H_4</th>
<th>C_2H_6</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>0.68</td>
<td>1</td>
<td>300</td>
<td>SF_6·3.0</td>
<td>0.205</td>
<td>0.407</td>
<td>0.008</td>
<td>This work.</td>
</tr>
<tr>
<td>60</td>
<td>0.68</td>
<td>1</td>
<td>300</td>
<td>SF_6·3.0</td>
<td>0.208</td>
<td>0.575</td>
<td>0.025</td>
<td>Do.</td>
</tr>
<tr>
<td>60</td>
<td>3.3</td>
<td>1</td>
<td>300</td>
<td>SF_6·3.0</td>
<td>0.194</td>
<td>0.304</td>
<td>0.018</td>
<td>Do.</td>
</tr>
<tr>
<td>60</td>
<td>3.83</td>
<td>1</td>
<td>300</td>
<td>SF_6·3.0</td>
<td>0.218</td>
<td>0.432</td>
<td>0.008</td>
<td>Do.</td>
</tr>
<tr>
<td>60</td>
<td>0.83</td>
<td>2</td>
<td>300</td>
<td>SF_6·3.0</td>
<td>0.204</td>
<td>0.370</td>
<td>0.012</td>
<td>Do.</td>
</tr>
<tr>
<td>60</td>
<td>0.83</td>
<td>4</td>
<td>300</td>
<td>SF_6·3.0</td>
<td>0.210</td>
<td>0.343</td>
<td>0.019</td>
<td>Do.</td>
</tr>
<tr>
<td>60</td>
<td>3.3</td>
<td>1</td>
<td>100</td>
<td>SF_6·3.0</td>
<td>0.240</td>
<td>0.386</td>
<td>0.016</td>
<td>Do.</td>
</tr>
<tr>
<td>60</td>
<td>3.3</td>
<td>1</td>
<td>100</td>
<td>SF_6·3.0</td>
<td>0.304</td>
<td>0.623</td>
<td>0.017</td>
<td>Do.</td>
</tr>
<tr>
<td>~70</td>
<td>3.3</td>
<td>1</td>
<td>400–700</td>
<td>SF_6·3.0</td>
<td>0.185</td>
<td>0.258</td>
<td>n.d.</td>
<td>[6].</td>
</tr>
<tr>
<td>~70</td>
<td>3.3</td>
<td>1</td>
<td>100</td>
<td>SF_6·3.0</td>
<td>0.148</td>
<td>0.185</td>
<td>n.d.</td>
<td>[6].</td>
</tr>
<tr>
<td>3</td>
<td>0.49</td>
<td>1 to 16</td>
<td>760</td>
<td>SF_6·3.0</td>
<td>0.23</td>
<td>0.28</td>
<td>0.019</td>
<td>[7].</td>
</tr>
<tr>
<td>3</td>
<td>0.58</td>
<td>10</td>
<td>100</td>
<td>SF_6·3.0</td>
<td>0.162</td>
<td>0.324</td>
<td>0.019</td>
<td>[8].</td>
</tr>
</tbody>
</table>

Low dose rate 60CO^-γ radiolysis (10^{-19} eV/g, s)

<table>
<thead>
<tr>
<th></th>
<th>C_2H_2</th>
<th>C_2H_4</th>
<th>C_2H_6</th>
<th></th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO-2</td>
<td>0.016</td>
<td>0.177</td>
<td></td>
<td></td>
<td>This work.</td>
</tr>
<tr>
<td>NO-5</td>
<td>0.015</td>
<td>0.170</td>
<td></td>
<td></td>
<td>Do.</td>
</tr>
<tr>
<td>NO-10</td>
<td>0.015</td>
<td>0.165</td>
<td></td>
<td></td>
<td>Do.</td>
</tr>
<tr>
<td>NO-20</td>
<td>0.014</td>
<td>0.150</td>
<td></td>
<td></td>
<td>Do.</td>
</tr>
<tr>
<td>Acetone-5</td>
<td>0.020</td>
<td>0.350</td>
<td></td>
<td></td>
<td>Do.</td>
</tr>
</tbody>
</table>

The pulse radiolysis values of M(C_2H_2)/N_+ and M(C_2H_4)/N_+ obtained in the course of the present study under a variety of conditions are presented in table 1 together with those reported by other investigators [6–8]. M(C_2H_2)/N_+ is essentially independent of the dose rate (dose per pulse), total absorbed dose and pulse duration. This probably accounts for the good agreement between the different studies. On the other hand, M(C_2H_4)/N_+ decreases with the number of pulses delivered. This was found to be the case for 3 ns experiments (table 1) and 60 ns experiments. The
Photolysis

Pulse in the presence of a free radical scavenger the occurrence of the reaction:

RadioLysis and photolysis of $0.013\ CH_4$ -NO (l00 $4.1$. Formation of Acetylene in the Gamma Radiolysis as an additive.

An increase in pressure in the $\gamma$-radiolysis of a mixture from a slight decrease of $M(C_2H_4)/N_+$ is independent of dose over the range $0.45 - 0.03$ and is therefore of no particular relevance in the following discussion, but this and other aspects of the pulse radiolysis are presently being explored.

An increase in pressure in the $^{60}$Co radiolysis of a $CH_4$ -NO (100 : 1) mixture from 200 to 2000 torr caused a slight decrease of $M(C_2H_2)/N_+$ (table 1). Similarly, in the gamma radiolysis of a $CD_4$ -NO (100 : 1) mixture from 500 to 2000 torr, $M(C_2D_2)/N_+$ decreased from 0.013 to 0.010. In the $^{60}$Co radiolysis, $M(acetylene)/N_+$ is independent of dose over the range 0.5 to 4 eV/g $\times 10^{13}$. Also, the ion pair yield of $C_2H_2$ is within experimental error unchanged when NO is replaced by $O_2$ as an additive.

4. Discussion

4.1. Formation of Acetylene in the Gamma Radiolysis and Vacuum Ultraviolet Photolysis of Methane

In the gamma radiolysis of a $CH_4$ -CD$_4$ (1:1) mixture in the presence of a free radical scavenger (NO), more than 90 percent of the acetylene consists of $C_2H_2$ and $C_2D_2$ (table 3). This striking result can be explained by the occurrence of the reaction:

Table 3

Radiolysis and photolysis of $CH_4$ -CD$_4$ (1:1) mixtures, isotopic composition of the acetylene fraction

<table>
<thead>
<tr>
<th>Additive</th>
<th>C$_2$D$_2$</th>
<th>C$_2$HD</th>
<th>C$_2$H$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mole %</td>
<td>Distribution %</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Pulse radiolysis*.............</td>
<td>33.8</td>
<td>27.6</td>
<td>38.6</td>
</tr>
<tr>
<td>SF+0.3</td>
<td>43.3</td>
<td>13.3</td>
<td>43.4</td>
</tr>
<tr>
<td>NO-1.0</td>
<td>33.4</td>
<td>26.6</td>
<td>40.0</td>
</tr>
<tr>
<td>$^{60}$Co $\gamma$-Radiolysis.............</td>
<td>NO-1</td>
<td>42.1</td>
<td>6.1</td>
</tr>
<tr>
<td>Photolysis 11.6-11.8 eV.............</td>
<td>NO-1</td>
<td>36.5</td>
<td>4.0</td>
</tr>
</tbody>
</table>

*Dose/pulse $3.3 \times 10^{19}$ eV/g, pulse duration 60 ns, total pressure: 300 torr.

C + CH$_4$ $\rightarrow$ C$_2$H$_4$ $\rightarrow$ C$_2$H$_2$ + H$_2$ \hspace{1cm} (1)

where the carbon atom is C($^1D$) and/or C($^1S$). The presence of reactive C atoms in the radiolysis of methane is not unexpected in view of the fact that an absorption spectrum attributed to C($^1S$) has previously been reported in the pulse radiolysis of methane [16]. C($^3P$) atoms are reactive towards methane ($k < 5 \times 10^{-15}$ cm$^3$/molecule-s) [17-18] and are removed by reaction with NO [18]:

C($^3P$) + NO $\rightarrow$ CN + O \hspace{1cm} (2)

$k = 1.1 \times 10^{-16}$ cm$^3$/molecule-s.

It has been shown that carbon atoms are also produced in the photolysis of methane at 10 eV and at 11.6-11.8 eV [19], where the acetylene formed in a $CH_4$ -CD$_4$ (1:1) mixture again consists nearly entirely of $C_2H_2$ and $C_2D_2$ (table 3). At 11.6-11.8 eV, the carbon atoms can only be produced in the dissociative processes:

\[ CH_4 \rightarrow C(^1D) + 2H_2 \left( \sum_g \right) \] \hspace{1cm} (3)

\[ \rightarrow C(^1S) + 2H_2 \left( \sum_g \right) \times 0 \] \hspace{1cm} (4)

The energy requirements for processes 3 and 4, which must occur via an excited CH$_2$ intermediate, are 9.6 and 11.0 eV, respectively. Because an overall fragmentation process such as:

\[ CH_4 \rightarrow C(^1D) + H_2 \left( \sum_g \right) + 2H \] \hspace{1cm} (5)

would require at least 14 eV, decomposition of intermediates such as CH or CH$_3$ can be excluded as sources of C($^1D$) or C($^1S$) in the photolysis.

The source of the carbon atoms in the radiolysis is not so obvious; in addition to the decomposition of neutral excited methane molecules (reactions 3 and 4), the production of C atoms through the neutralization of ions must be considered. However, neutralization processes can not contribute to C atom formation.
to any significant extent, since the major unreactive ions in the methane system [11, 20], C\(_2\)H\(_4^+\), C\(_2\)H\(_4^+\), and CH\(_2^+\), would have to be in an excited state at the time of neutralization in order to make the formation of C\(_1^+(D)\) or C\(_1^+(S)\) energetically feasible. Because these unreactive ions will undergo many collisions with CH\(_4\) prior to neutralization, the neutralization of an excited ion is extremely unlikely. Corroborative evidence that the C atoms (e.g., the acetylene) do not have an ionic precursor comes from the results of a photolysis experiment carried out with 16.7–16.8 eV photons. At this energy, the quantum yield of ionization in methane is unity [21], and the relative abundances of the major primary ions are about the same as in the gamma radiolysis [22–23]; thus, the fact (table 2) that in this experiment the yield of acetylene is negligible, indicates that C atoms are indeed not formed in ionic neutralization reactions in methane. In the photolysis of methane with 21.2 eV photons (table 2), the yield of acetylene is at least a factor of ten higher than at 16.6–16.7 eV, (although still much lower than the yield observed in the gamma radiolysis). This can be explained by the fact that at 21.2 eV, the quantum yield of ionization is slightly lower than unity (~0.96) [21]. That is, about 4 percent of the photons absorbed would lead to the formation of “superexcited” methane molecules, which, because of their high energy content might be expected to yield C atoms with a relatively high probability.

Further evidence that the acetylene in the gamma radiolysis does not have an ionic precursor is provided by the results of an experiment in which acetone was added to methane. In such an experiment, it is to be expected that the unreactive C\(_2\)H\(_4^+\) and CH\(_2^+\) ions formed in methane would quantitatively transfer a proton to the acetone; in this experiment (table 1) the yield of acetylene is close to the yield observed in the absence of acetone.

The absence of any appreciable decrease of M(C\(_2\)H\(_4\))/N\(_0\), with pressure in the \(^{60}\)Co-gamma experiments (table 1) as well as in the 11.6–11.8 eV photolysis [19] indicates that the dissociative lifetime of the insertion product, C\(_2\)H\(_4^*\), must be quite short (\(<10^{-9}\) s). The energy content of C\(_2\)H\(_4^*\) formed in reaction 1 is 7.4 or 8.8 eV, depending on whether C\(_1^+(D)\) or C\(_1^+(S)\) is the reactant. RRKM calculations show that if the C\(_2\)H\(_4^*\) formed in reaction 1 is a vibrationally excited ground state molecule its lifetime will be well below 10\(^{-10}\) s [24–25].

4.2. Formation of Acetylene in the Pulse Radiolysis of Methane

In the pulse radiolysis of a CH\(_4\)-CD\(_4\) (1:1) mixture, nearly one third of the acetylene consists of C\(_2\)HD (table 3), in contrast to the low dose rate and photolysis experiments, where this isomeric analogue was formed only in very low yields. Thus, some mode of formation of acetylene other than reaction 1 must be occurring under these high dose rate conditions.

Accepting a rate constant of 10\(^{-9}\) cm\(^3\)/molecule-s for the reaction [26]

\[ \text{CH}_3^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_4^+ + \text{H}_2. \]  

(6)

It can be calculated on the basis of a modified WR16 computer program [27–28] that at the average dose rates reported in table 1, more than 99.9 percent of the CH\(_3^+\) ions react to produce C\(_2\)H\(_4^+\). Assuming a rate constant of less than 10\(^{-15}\) cm\(^3\)/molecule-s for reaction of C\(_2\)H\(_4^+\) with CH\(_4\) [20] and a value of 1.9 \times 10\(^{-6}\) cm\(^3\)/molecule-s for the charge recombination rate constant [28], computation shows that at the high dose rates prevailing in the pulse radiolysis experiments all C\(_2\)H\(_4^+\) ions will undergo homogeneous neutralization. When neutralization occurs by combination of C\(_2\)H\(_4^+\) with an electron, one can expect the expulsion of an H-atom to occur

\[ \text{C}_2\text{H}_4^+ + e \rightarrow \text{C}_2\text{H}_4^* \rightarrow \text{C}_2\text{H}_4^* + \text{H}. \]  

(7)

After rupturing the C-H bond, 6.7 eV is to be distributed among the two fragments. If one makes the reasonable assumption that most of the excess energy is taken up by C\(_2\)H\(_4^*\) as internal energy, a pressure dependent fraction of these C\(_2\)H\(_4^*\) species may be expected to dissociate:

\[ \text{C}_2\text{H}_4^* \rightarrow \text{C}_2\text{H}_2 + \text{H}_2. \]  

(8)

Experimental observations indicate that the neutralization process 7 followed by dissociation 8 accounts for a major fraction of the acetylene produced in the pulse radiolysis of CH\(_4\). For instance, addition of SF\(_6\) to CH\(_4\) drastically lowers M(C\(_2\)H\(_2\))/N\(_0\) and increases M(C\(_2\)H\(_4\))/N\(_0\), by roughly a corresponding amount (table 1). It is to be expected that the C\(_2\)H\(_4^*\) formed by neutralization with SF\(_6^-\) would have less energy, and therefore would be less likely to undergo dissociation than those C\(_2\)H\(_4^*\) species formed in reaction 7. Computer calculations which take into account the pulse shape, show that if one accepts a thermal electron capture rate constant for SF\(_6^-\) of 2 \times 10\(^{-7}\) cm\(^3\)/molecule-s [29], more than 99 percent of the C\(_2\)H\(_4^+\) ions will be neutralized by SF\(_6^-\) rather than by recombination with an electron. (This is corroborated by the fact that a three-fold variation in the mole percent of SF\(_6\) added to methane does not affect the yields of C\(_2\)H\(_2\) and C\(_2\)H\(_4\) as shown by the results given in table 1.) If the electron in reaction 7 is replaced with a SF\(_6^-\) ion:

\[ \text{C}_2\text{H}_5^+ + \text{SF}_6^- \rightarrow \text{C}_2\text{H}_5^* + \text{SF}_6 \rightarrow \text{C}_2\text{H}_4^* + \text{H} + \text{SF}_6. \]  

(9)

it follows from the electron affinity [30] of SF\(_6\) that the energy content of the neutral C\(_2\)H\(_4^*\) entity formed in process 9 will be approximately 1.5 eV lower than that produced in the electron combination process 7. The excess energy will be even lower if neutralization involves a chemical reaction [31] such as

\[ \text{C}_2\text{H}_5^+ + \text{SF}_6 \rightarrow \text{C}_2\text{H}_4^* + \text{HF} + \text{SF}_5. \]  

(10)

112
The residual acetylene formed in the presence of SF₆ consists largely of C₂H₂ and C₃D₃, and thus must be formed mainly by the C atom insertion reaction 1. However, the relative yield of C₂D HD in the CH₄·CD₄·SF₆ pulse radiolysis experiment (table 3) is somewhat higher than the corresponding yield in the gamma radiolysis of a CH₄·CD₄·NO mixture, indicating the probable occurrence of the radical-radical reaction [32]:

\[ ^3\text{CH}_2 + ^3\text{CD}_2 \rightarrow \text{C}_2\text{HD} + \text{HD}. \]  

(11)

Triplet methylene (\(^6\text{CH}_2\)) is known to be unreactive towards methane [32-33] and is removed by NO in the low dose rate radiolysis experiments.

In the pulse radiolysis of pure methane, the ion pair yield of acetylene is seen to decrease from 0.24 to 0.15 when the pressure is raised from 100 to 775 torr. The fact that in the pulse radiolysis, the effect of pressure on the yield of acetylene is considerably more pronounced than in the \(^6\text{Co}\)-gamma radiolysis can be rationalized in terms of the energy content of the precursor \(\text{C}_2\text{H}_4^+\) species. In the low dose rate gamma radiolysis, the \(\text{C}_2\text{H}_4^+\) precursor of acetylene originates in reaction 1 with a maximum energy content of at least 7.4 eV, while the \(\text{C}_2\text{H}_4^+\) formed in the pulse radiolysis in reaction 7 originates with 6.7 eV excess energy.

### 4.3 General Considerations and Conclusions

In the preceding two sections we have concluded that in the gamma radiolysis and vacuum ultraviolet photolysis of methane, acetylene originates from the dissociation of excited ethylene formed by the insertion of C atoms into methane (reaction 1). In the pulse radiolysis of pure methane, where the ion pair yield of acetylene is much higher, it was concluded that most of the acetylene comes from the dissociation of excited ethylene formed when the ethyl ion is neutralized (reactions 7 and 8). Then the question is why the neutralization of the unreactive ethyl ion does not contribute to acetylene formation in the gamma radiolysis or vacuum ultraviolet photolysis of methane. In order to answer this we must consider that under conditions such that an unreactive ion undergoes homogenous neutralization, the lifetime of the ion, \(\tau\), will be

\[ \tau = (Ik)^{-1/2}. \]

where \(I\) is the number of ions formed per unit volume per second and \(k\) is the neutralization rate constant. Taking a value of \(1.9 \times 10^{-6} \text{ cm}^3/\text{molecule-s}\) for \(k\) [28], we calculate that at a pressure of 200 torr at the dose rate of the gamma radiolysis experiments reported here, an ethyl ion would undergo about \(2 \times 10^6\) collisions before being neutralized by an electron. (Under the conditions of the pulse radiolysis experiments, an ethyl ion would undergo only about \(10^3\) collisions before being neutralized by an electron.) Thus in the gamma radiolysis experiments any reactive compound present in amounts as small as \(10^{-3}-10^{-4}\) percent might be expected to intercept the ethyl ions before they are neutralized. It has in fact been experimentally demonstrated [20] that under low dose rate conditions, ethyl ions are effectively intercepted by \(10^{-4}\) percent propane. Thus, it is not at all surprising that we see no evidence for the neutralization of ethyl ions in the low dose rate gamma radiolysis experiments, since at the conversions of these experiments (0.01-0.1%) it is very likely that the ethyl ions will be intercepted by accumulated products long before undergoing neutralization.

In the 16.7-16.8 eV and 21.2 eV photolyses, on the other hand, there is evidence that ethyl ions do undergo neutralization, but their neutralization does not lead to the formation of acetylene. That is, the ion pair yield of ethylene in the 16.7-16.8 and 21.2 eV photolyses (where, as mentioned before, essentially all products have ionic precursors) is about 0.3-0.35. (This may be contrasted with ethylene yield of 0.15-0.18 observed in the gamma radiolysis, where the ethylene has been shown [11] to be formed largely in a nonionic process.) The high yield of ethylene observed in the 16.7-16.8 and 21.2 eV photolysis experiments suggests that ethyl ions are undergoing neutralization to give \(\text{C}_2\text{H}_4\) molecules that do not have sufficient energy to dissociate further. That the ethylene does have a \(\text{C}_2\text{H}_4\) precursor is shown by the results of two experiments in which foreign compounds were added to intercept the ethyl ion. In the presence of added acetone, the ethyl ions will react quantitatively to form ethylene:

\[ \text{C}_2\text{H}_5^+ + \text{CH}_3\text{COCH}_3 \rightarrow \text{C}_2\text{H}_4 + (\text{CH}_3\text{COCH}_3)\text{H}^+. \]

It is significant, then, that the yield of ethylene is about the same in the presence and absence of added acetone (table 2). When isobutane is added to methane, the ethyl ions will also be quantitatively intercepted, by the reaction:

\[ \text{C}_2\text{H}_5^+ + \text{i-C}_4\text{H}_{10} \rightarrow \text{C}_2\text{H}_6 + \text{i-C}_4\text{H}_5. \]

(13)

In the presence of isobutane, the ethylene yield is only about one-tenth of its value in the photolysis of pure methane or methane-O₂ mixtures. Thus, it can be concluded that in the 16.7-16.8 eV and 21.2 eV photolyses, the ethyl ion undergoes some process (which is not observed in the gamma radiolysis) to form ethylene which does not dissociate further to form acetylene. Thus, homogenous neutralization by an electron (reactions 7 and 8) or by SF₆ (table 2) is excluded. Because of the high extinction coefficient of methane at these energies, these photolysis experiments may not result in the formation of a high concentration of ions in a region of space quite close to the window, but a tenable explanation of the results given in table 2 might be that the ions undergo heterogeneous neutralization on the window.

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5. References


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