

Photochemistry of Methane in the Photoionization Region*

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Methane was irradiated with microwave operated helium (21.2 eV) and neon (16.7–16.8 eV) resonance lamps which were separated from the reaction vessel by an aluminum window. The quantum yields of the stable end products have been determined at methane pressures ranging from 1 to 20 torr. Over this pressure range the abundances of the primary ions, determined through various diagnostic experiments, are within experimental error the same at 21.2 eV as at 16.7–16.8 eV ($\text{CH}_4^+ \approx \text{CH}_3^+ \approx 0.5$, $\text{CH}_2^+ \leq 0.02$), and are in good agreement with the primary mass spectra obtained in a photoionization mass spectrometer under collision free conditions ($P < 10^{-5}$ torr). The C_2H_5^+ which is formed by the reaction: $\text{CH}_3^+ + \text{CH}_4 \rightarrow \text{C}_2\text{H}_5^+ + \text{H}_2$ loses a proton by an undetermined mechanism to give C_2H_4 as a product.

There is no evidence for the formation of neutral fragments such as H_2 , C, CH or CH_2 at 16.7–16.8 eV. The fact that the ionization quantum is equal to unity in this energy range accounts for the absence of these intermediates. At 21.2 eV where ($\Phi_{\text{ionization}} = 0.95$) there is concrete evidence for the formation of carbon atoms ($\Phi(\text{C}) \geq 0.002$).

In an attempt to demonstrate the usefulness of enclosed neon and helium resonance light sources in the ion-molecule kinetic studies, the relative probabilities of transfer of H^- over D^- from various partially deuterium labeled hydrocarbons to C_2H_5^+ (or C_2D_5^+) has been determined.

The results presented in this article resolve the existing disagreements between previous helium resonance photolysis studies on CH_4 .

Key words: Ion-molecule reaction; ion pair yield; methane; photochemistry; photoionization; quantum yields.

1. Introduction

In a pioneering study, Back and Walker [1]¹ carried out the first photochemistry study on lower hydrocarbons in the photoionization region using the self-reversed 58.4 nm (21.2 eV) helium resonance line. The apparatus used was windowless and the photolysis vessel was separated from the light source (microwave discharge through helium) by a fast flow separation system. Significant experimental results were obtained even though such an open device limited the reactant pressure range in the reaction vessel (< 0.3 torr) and resulted in a certain degree of uncertainty concerning the monochromaticity of the incident radiation. More recently, thin (1500 to 4000 Å thick) aluminum films supported on a metal screen have been used to separate the light source from the reaction vessel and to filter out light at wavelengths > 90 nm [2–6]. Such devices were first used in 1968 to reexamine certain aspects of the photolysis of methane at 58.4 nm at reactant pressures up to 15 torr.

The present paper describes a more detailed study of the photochemistry of CH_4 in the photoionization region using an enclosed helium as well as a neon

resonance ($\lambda = 74.37$ – 73.59 nm) light source. An attempt is made to resolve the existing disagreements in the yields of the chemical products formed in the windowless apparatus used by Back and Walker [1] as compared to the enclosed light source apparatus employed by Jensen and Libby [2]. Finally, reactions of the major ions, CH_5^+ and C_2H_5^+ , formed in the photoionization of methane with various hydrocarbons are explored in order to assess the feasibility of using enclosed helium and neon resonance light sources in the study of ionic reactions.

2. Experimental Procedure

2.1. Apparatus

The design of the titanium-gettered light sources and of the reaction vessel has been described in a recent report from this laboratory [7]. The aluminum windows (0.61 in in diameter) were supplied by the Sigmatron Co., Goleta, California [8]. They consisted of a 1500 ± 100 Å film supported on a nickel screen. The windows were examined for pin-holes under a microscope and were tested for their pressure resistance. The approximately 50 photolysis experiments carried out in the course of this investigation at differential pressure readings up to 60 torr, were carried out by using one and the same enclosed light source. Transformation

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¹ Figures in brackets indicate the literature references at the end of this paper.

of the helium lamp to a neon resonance light source, and vice versa, was accomplished by interchanging the rare gases in the body of the enclosed lamp. The pressure in the helium lamp was 1.6 torr and that in the neon lamp was 1.2 torr. In a recent detailed examination [9] of the output of a helium resonance lamp it was shown that at a helium pressure of 1.2 to 2 torr the 53.7 nm line transmitted through a 1500 Å window is approximately 2 percent of the intensity of the 58.4 nm line. The total output of the helium lamp used in this study was approximately 2×10^{13} photons/s. The same lamp filled with neon had a light flux of 0.8×10^{13} photons/s. The output of the lamp, which was monitored by measuring the saturation ion current in CH₄ showed only very minor fluctuations (2 to 5%) from one experiment to the next. The volume of the reaction vessel equipped with nickel electrodes was 220 cm³.

2.2. Materials

All chemicals used in this study were purified by gas chromatography. The methane-*d*₄ contained 5 percent CD₃H. The cyclohexane,1,1,2,2,3,3-*d*₆ sample used in some experiments contained 10.3 percent cyclohexane-*d*₅, 2.4 percent cyclohexane-*d*₇ and 0.3 percent cyclohexane-*d*₈. Propane-1,1,1,3,3,3-*d*₆ contained 6 percent CD₂HCH₂CD₃ and 1.7 percent CD₃CHDCD₃. More than 93 percent of the isobutane-*d*₁ consisted of (CH₃)₃CD. The calculated isotopic compositions of the products reported in this paper have been corrected statistically to bring the data up to 100 percent deuterium purity.

3. Results

All product yields are expressed in terms of quantum yields (Φ). Because the ionization quantum yield of methane is close to unity in the wavelength region covered in this study [10–11], quantum yields are essentially equivalent to ion pair yields (number of product molecules per positively charged ion produced in the system). The absolute accuracy of the quantum yield values given in tables 1 and 2 are estimated to be ± 15 percent. Besides the products listed in tables 1 and 2, hydrogen and several higher molecular weight hydrocarbon products such as *i*-C₄H₁₀ and *i*-C₅H₁₂ were observed. The quantum yields of *i*-C₄H₁₀ and *i*-C₅H₁₂ were seen to increase with the number of photons absorbed in the system and were therefore ascribed to secondary reactions involving accumulated products. The values of $\Phi(i\text{-C}_4\text{H}_{10})$ and $\Phi(i\text{-C}_5\text{H}_{12})$ for the lowest conversion experiment listed in table 1 were 0.003 and 0.002 respectively.

Hydrocarbon products with more than five carbon atoms were not observed at low conversions ($\Phi < 0.005$). The quantum yield of hydrogen in the 58.4 nm photolysis of a CH₄-CD₄-NO (1:1:0.01) mixture at a pressure of 10 torr was 0.4 ± 0.1 . Its isotopic composition was as follows: H₂-44.6 percent, HD-26.5 percent, D₂-28.9 percent. In the 58.4 nm photolysis of a CH₄-*i*-C₄D₁₀ (1:0.01) mixture at a pressure of 20 torr $\Phi(\text{hydrogen})$ was 0.55 ± 0.1 and consisted of H₂-67.8 percent, HD-16.7 percent and D₂-15.5 percent. Both hydrogen

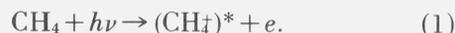
analysis experiments were carried out at relatively high conversion (1.5×10^{17} photons absorbed by 10 torr of methane in the 220 cm³ reaction vessel). The isotopic composition of the ethylene produced in the 58.4 nm photolysis of the CH₄-CD₄-NO (1:1:0.01) mixture is as follows: C₂D₄-14 percent, C₂D₃H-16 percent, C₂D₂H₂-22 percent, C₂DH₃-16 percent, C₂H₄-32 percent. Photolysis of an equimolar CH₄-CD₄ in the presence of 1 mole percent *i*-C₄H₁₀ yielded: C₂D₄-16 percent, C₂D₃H-17 percent, C₂D₂H₂-21.5 percent, C₂DH₃-13.5 percent, and C₂H₄-32 percent.

The isotopic analysis of the ethane formed in the neon resonance photolysis of a CD₄-C₃H₈-O₂ (1:0.01:0.1) mixture at a total pressure of 20 torr, was as follows: C₂D₅H-47.2 percent, C₂D₄H₂-0.5 percent, and C₂H₆-52.3 percent. The ethane formed in the helium and neon resonance photolysis of CD₄-*i*-C₄H₁₀-O₂ (1:0.01:0.01) mixtures consisted nearly entirely (> 97 percent) of C₂D₅H.

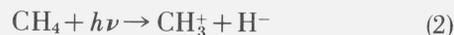
4. Discussion

4.1. General Comments

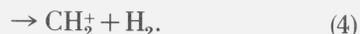
Recent determinations of the photoionization quantum yield (Φ_+) of CH₄ at 58.4 nm and at 74.37–73.59 nm indicate that approximately one ion pair is produced for each photon absorbed by methane [10–11]. It follows that in this wavelength region there is one predominant primary process



The ion pair formation process



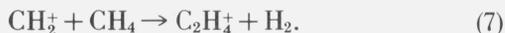
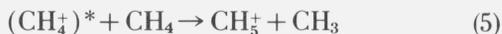
is apparently of minor importance [12–13]. The helium and neon resonance photoelectron spectrum shows one broad band over the range 12.7 to 16–17 eV, exhibiting three maxima associated with the ionization of the *t*₂ orbital [14–15]. Besides the ionization potential at 12.7 eV, there is a second I.P. near 23 eV, ascribed to ionization from the *a*₁ orbital, which is however of no concern in this study. A fraction of the vibrationally excited (CH₄⁺)^{*} formed in process 1 can dissociate to produce CH₃⁺ (appearance potential 14.2 eV) and CH₂⁺ (appearance potential 15.2 eV) [12–13]



The abundances of CH₄⁺, CH₃⁺, and CH₂⁺ observed in a photoionization mass spectrometer [12] using an enclosed helium resonance lamp such as the one used in the present study are: CH₄⁺-48 percent, CH₃⁺-50 percent, and CH₂⁺-2 percent. The abundances observed with a neon resonance lamp are CH₄⁺-47 percent, CH₃⁺-51 percent and CH₂⁺-2 percent. It is to be noted that both distributions are at variance with the abundances obtained in previous photoionization mass spectrometric studies [13] in which a

differentially pumped continuous light source was used.

The major initial bimolecular reactions occurring in the photoionization of CH₄ are [16]



The product ions CH₅⁺, C₂H₅⁺ and C₂H₄⁺ are unreactive towards CH₄ [16] and will therefore be converted to neutral products by heterogeneous or homogeneous neutralization or by proton transfer to traces of H₂O. At higher conversions these ions will react with accumulated products [17–19].

From the foregoing, one would expect H₂, C₂H₆, and C₂H₄ to be major products in the far ultraviolet photolysis of “pure” methane. This is borne out by the data given in tables 1 and 2 as well as in the Results Section. Although there is essentially little to be learned from product yields such as the ones given in tables 1 and 2 for the “pure” CH₄ system it is nevertheless of some interest to compare the product yields obtained in this study at 58.4 nm with those reported previously by other investigators [1–2] (table 1) and to interpret some of the observations in the light of the remarks made above.

a. Effect of Conversion

The fact that upon addition of O₂ to CH₄, Φ(C₂H₆) is reduced from approximately 0.3 to 0.01 at 58.4 and 74.3–73.6 nm indicates that C₂H₆ is produced mainly by a free radical reaction such as:



The increase of Φ(C₃H₈) and Φ(*n*-C₄H₁₀) with an increase in the number of photons absorbed (tables 1 and 2) can be ascribed to H-atom scavenging by the C₂H₄ product molecules



This mechanism, which has previously [20] also been shown to occur in the 10 eV photolysis of CH₄, is corroborated by the fact that Φ(C₂H₄) diminishes at higher conversion and that Φ(C₃H₈) is sharply reduced upon addition of O₂. The increase of Φ(C₂H₆) with the number of photons absorbed in the system can at least in part be ascribed to combination of the C₂H₅ radicals formed in reaction 9 with H-atoms. It is clear however that at very high conversion the decrease in Φ(C₂H₄) is not entirely compensated by the increase of the quantum yields of C₂H₆, C₃H₈ and *n*-C₄H₁₀. Complex ion-molecule reaction chains initiated by the addi-

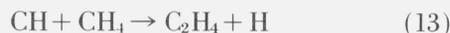
tion of C₂H₅⁺ to C₂H₄ [19] may cause a further reduction in the quantum yield of C₂H₄. Although the conversion effects noted in this study could account for the low quantum for C₂H₄ reported by Jensen and Libby [2], they do not account for the extremely low quantum yield of C₂H₆ (table 1) reported by these authors. In view of the fact that the Φ(C₂H₆) is seen to be essentially reduced to zero by O₂, it may be surmised that air contamination in the CH₄ accounts for the observations of Jensen and Libby [2].

b. Formation of Ethylene

The ethylene originates apparently from the C₂H₅⁺ ion formed in reaction 6. Addition of small amounts of isobutane to CH₄ drastically reduces Φ(C₂H₄) both in the neon and helium resonance experiments (tables 1 and 2). This reduction which is accompanied by a corresponding increase of Φ(C₂H₆) in the presence or in the absence of O₂ is to be accounted for [17] by the removal of the C₂H₅⁺ ion via the hydride ion transfer reaction

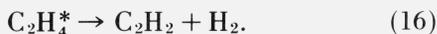


Formation of C₂H₆ in reaction 12 is substantiated by the fact that more than 90 percent of the ethane formed in the photoionization of CD₄-*i*-C₄H₁₀-O₂ mixtures (see Results) consists of C₂D₅H. Also, Φ(C₂H₆) is seen to be independent of the concentration of *i*-C₄H₁₀ (see table 1). Furthermore, it is to be noted that Φ(C₂H₆) is close to the value predicted from the abundance of CH₃⁺ in the primary photoionization mass spectrum [12–13]. At these low concentration of *i*-C₄H₁₀, the reduction of the yield of C₂H₄ cannot be attributed to inhibition of the insertion reaction



which was previously suggested [2] to be the main mode of formation of C₂H₄ in the 58.4 nm photolysis of “pure” CH₄. It has indeed been shown recently [21] that CH reacts about equally fast with all lower alkanes. As noted before [22], the apparently low yield of CH species is consistent with the fact that dissociation of superexcited CH₄ molecules is of minor occurrence at 58.4 and 74.3–73.6 nm. Furthermore, the isotopic composition of the ethylene formed in the photoionization of CH₄-CD₄ and CH₄-CD₄-*i*-C₄H₁₀ mixtures (see Results) is not consistent with an insertion mechanism. In the CH₄-alkane mixture given in tables 1 and 2, Φ(C₂H₆) is approximately equal to the reduction in Φ(C₂H₄), indicating that in “pure” methane most of the C₂H₅⁺ ions yield C₂H₄ as a neutral product. Pulse radiolysis experiments [23] have shown that if the neutralization occurs by electron recombination, acetylene is produced through the following reaction sequence:





Because at a methane pressure of 100 torr approximately 50 percent of the excited C_2H_4 formed in process 15 were shown to dissociate [23], the low yield of C_2H_2 in the photoionization experiments (tables 1 and 2) rules out reaction 14 as an important mode of neutralization of the C_2H_5^+ ion. Proton transfer on the aluminum window surface and/or to H_2O desorbed from the wall is a likely explanation for the nearly quantitative conversion of C_2H_5^+ ions to C_2H_4 . The fact that addition of a proton acceptor such as acetone to CH_4 (table 2)



does not significantly alter $\Phi(\text{C}_2\text{H}_4)$ observed in pure methane supports the above interpretation. It is of interest at this point to compare our data with those obtained by Walker and Back [1] in a windowless apparatus. It is seen (table 1) that with the exception of $\Phi(\text{C}_2\text{H}_2)$, the agreement between the two studies is excellent. Considering that Walker and Back [1] used a continuous CH_4 -He flow through a windowless reaction vessel, their high C_2H_2 yields are most likely to be attributed to gas phase neutralization (reaction sequence 14–16). The isotopic analysis of the ethylene obtained in the photolysis of a CH_4 - CD_4 - $i\text{-C}_4\text{H}_{10}$ mixture (see Results), indicates that the residual ethylene ($\Phi \sim 0.03$) observed in the CH_4 - $i\text{-C}_4\text{H}_{10}$ experiments (tables 1 and 2) may be accounted for by ineffective scavenging of the C_2H_5^+ ions by $i\text{-C}_4\text{H}_{10}$.

Unreactive ethylene ions formed in reaction 7 may conceivably also contribute to the formation of C_2H_4 . However, the very low yield of $\text{C}_2\text{D}_4\text{H}_2$ (~ 0.005) observed in a CD_4 - C_3H_8 (1:0.01) experiment (see Results) carried out in the presence of O_2 indicates that the well established ion-molecule reaction [24]:



does not occur to any significant extent in such an experiment. Since approximately 50 percent of the C_2D_4^+ ions would react through the competing reaction channel [25]:



the quantum yield of C_2D_4 is estimated to be about 0.01. This low value is in excellent agreement with the value of 0.0093 for $\Phi(\text{CD}_4^+)$ recently derived from the neon resonance photoionization mass spectrum of CD_4 [12]. The value estimated here is, however, lower than that indicated by the primary mass spectrum of CD_4 obtained in an earlier mass spectrometric photoionization study [13].

c. Formation of Hydrogen

The fact that at 58.4 nm, the quantum yield of hydrogen observed in a CH_4 - CD_4 -NO mixture (see Results)

is, within experimental error, equal to the quantum yield of ethane obtained in the CH_4 - $i\text{-C}_4\text{H}_{10}$ experiments (table 1) indicates that it is nearly exclusively formed as the neutral product of reaction 6 and, to a much lesser extent, reaction 7. The isotopic composition of the hydrogen in the CH_4 - CD_4 experiment is actually reasonably consistent with that predicted on the basis of $\text{CH}_3^+(\text{CD}_4^+)$ reacting with $\text{CH}_4(\text{CD}_4)$. At least, the observed value of 1.1 for the product ratio D_2/HD is close to the predicted value of 1.13–1.25 [26]. Apparently, H-atoms which are formed via the unimolecular dissociation of the CH_4^+ ion (reaction 3) and possibly also by neutralization mechanisms are scavenged by NO. However, the low value of $\Phi(\text{H}_2)$ and $\Phi(\text{HD})$ (see Results) obtained in the photolysis of a CH_4 - $i\text{-C}_4\text{D}_{10}$ mixture in the absence of NO indicates that a considerable fraction of the H-atoms disappear from the system by reaction on the wall and by addition to olefinic products. It is therefore not surprising that there is good agreement between the quantum yields of hydrogen obtained here and the value reported previously by Jensen and Libby [2]. On the other hand, the much higher value (~ 5) obtained in the windowless apparatus of Walker and Back [1] may be explainable by a number of factors, including the differences in neutralization mechanism mentioned in the previous section, or perhaps to experimental difficulties in analyzing the H_2 product in the presence of excess helium.

d. Superexcited Methane

A comparison of the quantum yields of the products obtained in the photolysis of pure CH_4 with the neon and helium resonance lamps (tables 1 and 2) shows that there are actually no significant differences. This is not surprising in view of the fact that the helium and neon resonance photoelectron spectra and mass spectral cracking patterns are very similar. This is also indicated by the fact that the primary ion abundances (CH_4^+ , CH_3^+ , CH_2^+) are about the same in the He^* and Ne^* Penning ionization of CH_4 [27]. More importantly, because the ionization quantum yield is close to unity both at the neon and helium resonance line [10–11] the contribution of superexcited CH_4 fragmentation, which would introduce new intermediates (C, CH, CH_2) to the system [22], is minor over the entire wavelength region [28]. A striking confirmation of this view follows from a recent far ultraviolet study of CH_4 by Welch and Judge [29] in which no emission due to excited CH or CH_2 species could be observed over the range 62 to 77 nm. Emission was however seen at shorter and higher wavelengths. It is however of interest that the consistent values of $\Phi(\text{C}_2\text{H}_2)$ obtained in the 58.4 nm photolysis of CH_4 - $i\text{-C}_4\text{H}_{10}$ mixtures can be attributed to $\text{C}(^1\text{S})$ or $\text{C}(^1\text{D})$ atoms formed by the fragmentation of superexcited methane molecules



followed by the insertion mechanism [30]



TABLE 1. *Photolysis of CH₄ at 58.4 nm*

| CH ₄ | O ₂ | Additive | Photons absorbed × 10 ⁻¹⁵ | C ₂ H ₂ | C ₂ H ₄ | C ₂ H ₆ | C ₃ H ₆ | C ₃ H ₈ | <i>n</i> -C ₄ H ₁₀ |
|-----------------|----------------|--|---|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|--|
| Pressure (Torr) | | | Quantum yields | | | | | | |
| 4.8 | | | 5 | 0.005 | 0.43 | 0.25 | 0.007 | 0.036 | |
| 4.8 | | | 10 | .006 | .40 | .31 | .017 | .075 | 0.007 |
| 4.8 | | | 20 | .006 | .39 | .34 | .011 | .10 | |
| 4.8 | | | 29 | .006 | .35 | .38 | .013 | .13 | .026 |
| 4.8 | | | 145 | .004 | .15 | .44 | .010 | .18 | .036 |
| 4.8 | 0.05 | | 10 | .002 | .35 | .01 | .006 | .01 | |
| 1.95* | | | 60 | | .08 | .0016 | | | |
| 2.0* | | | 120 | | .063 | .017 | | | |
| 0.23** | | | | .12 | .32 | .36 | | | |
| 10.5 | | <i>i</i> -C ₄ H ₁₀ -0.45 | | .002 | .058 | .75 | .062 | .66 | |
| 5.4 | .05 | <i>i</i> -C ₄ H ₁₀ -0.05 | | .002 | .049 | .46 | .043 | .43 | .242 |
| 10.5 | .10 | <i>i</i> -C ₄ H ₁₀ -0.10 | | .002 | .046 | .46 | .034 | .42 | .23 |
| 20.5 | .20 | <i>i</i> -C ₄ H ₁₀ -0.20 | | .002 | .029 | .46 | .027 | .43 | .23 |
| 10.5 | .10 | <i>n</i> -C ₄ H ₁₀ -0.10 | | .002 | .061 | .518 | .042 | .26 | |
| 10.5 | .10 | <i>i</i> -C ₅ H ₁₂ -0.10 | | .002 | .070 | .42 | .017 | .04 | .25 |

Reaction cell volume: 220 cm³.

* Ref. [2]

** Ref. [1]

TABLE 2. *Photolysis of CH₄ at 74.3–73.6 nm*

| CH ₄ | O ₂ | Additive | Photons absorbed × 10 ⁻¹⁵ | C ₂ H ₂ | C ₂ H ₄ | C ₂ H ₆ | C ₃ H ₆ | C ₃ H ₈ | <i>n</i> -C ₄ H ₁₀ |
|-----------------|----------------|---|---|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|--|
| Pressure (Torr) | | | Quantum Yields | | | | | | |
| 4.9 | | | 5 | 0.001 | 0.43 | 0.24 | 0.0021 | 0.024 | |
| 4.9 | | | 20 | .001 | .41 | .27 | .008 | .060 | |
| 4.9 | | | 40 | .002 | .29 | .27 | .008 | .072 | 0.015 |
| 4.9 | | | 120 | .001 | .22 | .30 | .009 | .090 | .015 |
| 10 | | | 15 | ~.0006 | .39 | .28 | .006 | .057 | |
| 10 | 0.2 | | 15 | ~.0006 | .33 | .010 | .007 | .018 | |
| 10 | 0.2 | Acetone-0.1 | 15 | ≤.0001 | .44 | .003 | .003 | .001 | |
| 10 | 0.2 | <i>i</i> -C ₄ H ₁₀ -0.1 | | ≤.0001 | .03 | .46 | .03 | .443 | .213 |
| 10 | 0.2 | C ₃ H ₈ -0.2 | | ≤.0001 | .03 | .75 | .20 | | |

The near absence of C₂H₂ as a product in the corresponding neon resonance experiments is tentatively ascribed to the fact that in this wavelength region neutral excited CH₄ molecules are produced with a quantum yield very close to zero as compared to ~0.05 at 58.4 nm [11].

4.2. Ion-Molecule Reactions

The photolysis of methane with helium or neon resonance radiation is an ideal method for the study of reactions of CH₃⁺ and C₂H₅⁺ ions. This is so because of the relative simplicity of the primary ion spectrum (CH₄⁺ and CH₃⁺ account for 95 percent of the primary ions), and because of the negligible contribution of reactive free radical species (C, CH, CH₂) which would be present if the dissociative processes of super-

excited methane molecules had to be considered. Although of some intrinsic interest, the results which will be discussed here serve more as an illustration of the type of information about ion-molecule reaction kinetics which can be gained from this type of experiment.

a. Reactions of the Ethyl Cation

As already indicated earlier in the Discussion, the ethane product observed in the photolysis of CH₄-*i*-C₄H₁₀-O₂ mixtures is nearly all (except for a minor contribution from a reaction of the C₂H₄⁺ ion) formed by the transfer of a hydride ion to C₂H₅⁺ from the isobutane. Taking advantage of this fact, a number of deuterium labeling experiments have been carried out in order to assess the mechanistic details of the

hydride transfer reactions between the ethyl ion and a number of hydrocarbon molecules. Table 3 summarizes the experimental observations relating to these questions. The relative rate constants given in the last column of table 3 are based on the determination of the C_2D_5H (C_2H_6) and C_2D_6 (C_2H_5D) products formed in the irradiation of CD_4 (CH_4) in the presence of about 5 percent partially deuterated hydrocarbon, and with O_2 present as a radical scavenger (see Results).

TABLE 3. H^- and D^- transfer to the ethyl cation

| λ nm | Reactants* | | $k(H^-)/k(D^-)$ |
|-----------------|------------|-----------------------------|-----------------|
| | Ion | Molecule | |
| 74.4–73.6 | $C_2D_5^+$ | <i>c</i> - $C_6H_6D_6^{**}$ | 1.05±0.05 |
| 58.4 | $C_2D_5^+$ | <i>c</i> - $C_6H_6D_6$ | 1.06±0.05 |
| 58.4 | $C_2H_5^+$ | <i>c</i> - $C_6H_6D_6$ | 1.09±0.05 |
| 74.4–73.6 | $C_2D_5^+$ | $CD_3CH_2CD_3$ | 0.63±0.02 |
| 74.4–73.6 | $C_2D_5^+$ | $(CH_3)_3CD$ | 6.1±0.3 |
| 58.4 | $C_2D_5^+$ | $(CH_3)_3CD$ | 6.4±0.3 |
| 58.4 | $C_2H_5^+$ | $(CH_3)_3CD$ | 6.1±0.3 |

*Total pressure: 20 torr.

**Cyclohexane-1,1,2,2,3,3,3-*d*₆.

The relative rate data given in the last column of the table indicate that reaction of the $C_2D_5^+$ ion with the symmetric molecule, cyclohexane-1,1,2,2,3,3,3-*d*₆, shows that there is a slight (5 percent) preference for reaction of an ethyl ion at the CH_2 position



rather than the CD_2 position

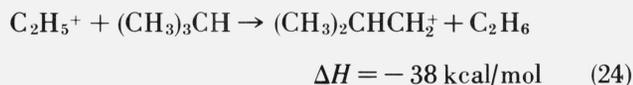


Both reactions are exothermic by 35 kcal/mol [31]. It is not surprising that the relative importance of reactions 22 and 23 does not change as a function of the energy of the photons used to produce the $C_2D_5^+$ ions in CD_4 . Though the $C_2D_5^+$ ions may be formed with different energy contents in experiments performed at different energies, in these dilute mixtures any excess energy will be dissipated by unreactive collisions with methane before reaction with the additive can occur. The increase in k_{22}/k_{23} which is seen when $C_2D_5^+$ is replaced by $C_2H_5^+$ (table 3) is too small to be considered as a genuine isotope effect.

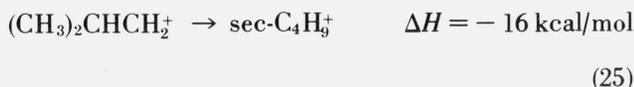
In the reaction of ethyl ions with propane and isobutane, preferential reaction sites are indicated by the ratio $k(H^-)/k(D^-)$ given in table 3. In the case of $CD_3CH_2CD_3$, for instance, a value of 0.63 ± 0.02 is obtained for transfer of H^- ($\Delta H_{rn} = -22.5$ kcal/mol) over transfer of D^- ($\Delta H_{rn} = -6.5$ kcal/mol); this is nearly a factor of two higher than the ratio of H to D atoms in the reactant molecule. The value for this ratio obtained here is in reasonable agreement with the

somewhat less reliable value of 0.57 derived in an earlier $CD_3CH_2CD_3$ radiolysis study [24] and the value of 0.33 ± 0.01 obtained in a tandem mass spectrometer experiment [32].

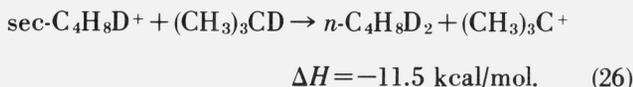
In the case of $(CH_3)_3CD$, the ratio $k(H^-)/k(D^-)$ is 6.1, independent of wavelength and isotopic labeling of the reactant ion. The statistical value of this ratio is 9.0; the fact that the observed value is closer to the statistical value in the case of isobutane than in the case of propane may be explained by the fact that reaction at the primary and tertiary sites in isobutane are both more exothermic ($\Delta H = -8$ and -38 kcal/mol, respectively) than reaction at the primary and secondary positions in propane ($\Delta H = -6.5$ and -22.5 kcal/mol, respectively). In addition, steric effects may play a role in these reactions, and there is a possibility that the weaker tertiary bond in isobutane is strengthened by the deuterium labeling. It is interesting to note that *n*-butane is an important product in all CH_4 -*i*- C_4H_{10} experiments (tables 1 and 2). One of the most obvious routes by which this product may be formed is through the isomerization of the $(CH_3)_2CHCH_2^+$ ion formed in the hydride transfer reaction:



to the thermodynamically more stable *sec*-butyl ion:



Such a mechanism is strikingly demonstrated by the observation that 95 percent of the *n*-butane observed in the photoionization of CH_4 - $(CH_3)_3CD$ - O_2 mixtures consists of *n*- $C_4H_8D_2$. Stable *sec*- $C_4H_8D^+$ ions formed in the isomerization are indeed expected to react with $(CH_3)_3CD$ exclusively by the exothermic reaction channel:

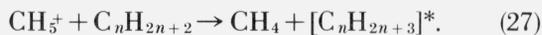


Apparently a fraction of the isobutyl ions formed in reaction 24 isomerize to the *t*- $C_4H_9^+$ structure rather than to the *sec*- $C_4H_9^+$ structure, since the yield of *n*-butane is lower than that which would be predicted from the fact that about 85 percent of the ethyl ions are expected to undergo reaction 24.

b. Reactions of CH_3^+

In the 58.4 or 73.5–74.6 nm irradiation of pure CH_4 no neutral product can be unambiguously ascribed to the presence of CH_4^+ , and therefore of CH_3^+ , even though the latter ion must account for approximately 50 percent of the primary ion spectrum. The latter estimate is based on the fact that the only other major ion, CH_3^+ , has been shown to yield C_2H_4 with a quantum yield of 0.43 ± 0.06 . Addition of higher alkanes to

CH₄ does however reveal the presence of CH₅⁺, and does also provide some information concerning the proton transfer reaction



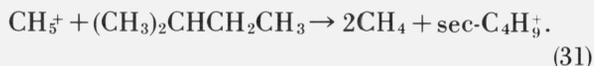
In CH₄-*i*-C₄H₁₀ mixtures (tables 1 and 2), Φ(C₃H₈) represents a minimum value of Φ(CH₅⁺). Isotopic labeling experiments in this and previous radiolysis and mass spectrometric studies have shown that the now well established reaction sequence



adequately accounts for the formation of C₃H₈. In addition, however, the following competing reaction channel must be considered:



where C₄H₉⁺ may be *i*-C₄H₉⁺ or *t*-C₄H₉⁺. The fact that Φ(C₂H₆ + C₃H₈) in the CH₄-*i*-C₄H₁₀-O₂ experiments does not add up to unity attests to the occurrence of reaction 30. On the same grounds the lower value for Φ(C₃H₈) observed in the CH₄-*n*-C₄H₁₀ experiment given in table 1 points to a relatively larger contribution of a dissociative proton transfer reaction analogous to 30 in agreement with mass spectrometric observations. The relatively high yield of *n*-C₄H₁₀ in the CH₄-*i*-C₅H₁₂ experiment (table 1) must be accounted for by preferential transfer of a proton to a CH₃ group to give sec-C₄H₉⁺



The smaller yield propane observed in the same experiment can be ascribed to proton transfer to CH₂ group.

5. References and Note

- [1a] Back, R. A., and Walker, D. C., J. Chem. Phys. **37**, 2348 (1962).
 [1b] Walker, D. C., and Back, R. A., Ibid. **38**, 1526 (1963).
 [2] Jensen, C. A., and Libby, W. F., Ibid. **49**, 2831 (1968).
 [3] Rebbert, R. E., and Ausloos, P., J. Am. Chem. Soc. **90**, 7370 (1968).
 [4a] Lias, S. G., Rebbert, R. E., and Ausloos, P., J. Chem. Phys. **52**, 773 (1970).
 [4b] Rebbert, R. E., Lias, S. G., and Ausloos, P., J. Res. Nat. Bur. Stand. (U.S.), **75A**, (Phys. and Chem.) No. 6, 607-612 (1972).
 [5a] Tellinghuisen, J. B., Winkler, C. A., Bennett, S. W., and Phillips, L. F., J. Phys. Chem. **75**, 3499 (1971).
 [5b] Tellinghuisen, J. B., Winkler, C. A., and Phillips, L. F., Ibid. **76**, 298 (1972).
 [6] Wauchop, T. S., and Broida, H. P., J. Geophys. Res. **76**, 21 (1971).
 [7] Gordon, R., Jr., Rebbert, R. E., and Ausloos, P., Nat. Bur. Stand. (U.S.), Tech. Note 496, 34 pages (1969).
 [8] Certain commercial equipment, instruments, or materials are identified in this paper in order to adequately specify the experimental procedure. In no case does such identification imply recommendation or endorsement by the National Bureau of Standards, nor does it imply that the material or equipment identified is necessarily the best available for the purpose.
 [9] Kinsinger, J. A., Stebbings, W. L., Valenzi, R. A., and Taylor, J. W., Anal. Chem. **44**, 773 (1972).
 [10] Bennett, S. W., Tellinghuisen, J. B., and Phillips, L. F., J. Chem. Phys. **75**, 719 (1971).
 [11] Rebbert, R. E., and Ausloos, P., J. Res. Nat. Bur. Stand. (U.S.), **75A** (Phys. and Chem.), No. 5, 481-485 (1971).
 [12] Sieck, L. W., and Gordon, R. Jr., Chem. Phys. Lett., in press.
 [13a] Dibeler, V. H., Krauss, M., Reese, R. M., and Harlee, F. N., J. Chem. Phys. **42**, 3791 (1965).
 [13b] Chupka, W. A., J. Chem. Phys. **48**, 2337 (1968).
 [14] Turner, D. W., "Molecular Photoelectron Spectroscopy" (Wiley-Interscience, 1970).
 [15] Potts, A. W., and Price, W. C., Proc. Roy. Soc. London **A326**, 165 (1972).
 [16] Futrell, J. H. and Tiernan, T. O., Chapter 4 in Fundamental Processes in Radiation Chemistry (Interscience Publ. New York, 1968).
 [17] Ausloos, P., Lias, S. G., and Gordon, R., Jr., J. Chem. Phys. **39**, 3341 (1963).
 [18] Haynes, R. M., and Kebarle, P., J. Chem. Phys. **45**, 3899 (1966).
 [19a] Munson, M. S. B., and Field, F. H., J. Am. Chem. Soc. **87**, 3294 (1965).
 [19b] Ibid. **87**, 4242 (1965).
 [20] Ausloos, P., Gordon, R., Jr. and Lias, S. G., J. Chem. Phys. **40**, 1854 (1964).
 [21] Bosnali, M. W., and Perner, D., Z. Naturforsch **26a**, 1768 (1971).
 [22] Rebbert, R., and Ausloos, P., J. of Photochemistry **1**, 171 (1972/73).
 [23] Rebbert R. E., and Ausloos, P., J. Res. Nat. Bur. Stand. (U.S.), **77A**, (Phys. and Chem.) No. 1, 109-114 (Jan.-Feb. 1973).
 [24] Ausloos, P., Lias, S. G., and Sandoval, I. B., Disc. Faraday Soc. **36**, 66 (1963).
 [25] Sieck, L. W., and Searles, S. K., J. Am. Chem. Soc. **92**, 2937 (1970).
 [26] Ausloos, P. J., and Lias, S. G., J. Chem. Phys. **38**, 2207 (1963).
 [27] Cermak, V., and Herman, Z., Coll. Czek. Chem. Commun. **30**, 169 (1965).
 [28] Ausloos, P., Molec. Photochem. **4**, 39 (1972).
 [29] Welch, A. R., and Judge, D. L., J. Chem. Phys. **57**, 286 (1972).
 [30a] Braun, W., Bass, A. M., Davis, D. D., and Simons, J. P., Proc. Roy. Soc. **312A**, 417 (1969).
 [30b] Husain, D., and Kirsch, L. J., Trans Faraday Soc. **67**, 2025 (1971).
 [31] Thermochemical values are mainly derived from: Franklin, J. L., Dillard, J. G., Rosenstock, H. M., Herron, J. T., Draxl, K., and Field, F. H., Nat. Bur. Stand. (U.S.), Nat. Stand. Ref. Data Ser. **26**, (1969).
 [32] Bone, L. I., and Futrell, J. H., J. Chem. Phys. **46**, 4084 (1967).

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