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PHOTOLYSIS OF METHANE: QUANTUM YIELD OF C(^{1}D) AND CH

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SUMMARY

It is demonstrated that C(^{1}D) and CH($^2\pi$) species are formed in the photodissociation of CH_4 at $\lambda = 123.6$ nm [Φ(C) $= 0.4 \pm 0.1 \times 10^{-3}$, Φ(CH) $= 5.9 \pm 0.5 \times 10^{-2}$] and at $\lambda = 104.8$–106.7 nm [Φ(C) $= 6.5 \pm 0.5 \times 10^{-3}$, Φ(CH) $= 0.23 \pm 0.03$]. There is no evidence for C or CH production at wavelengths where the photoionization quantum yield is equal to unity.

INTRODUCTION

The formation of CH radicals in the photolysis of methane has been reported by a number of investigators[1–3]. Evidence has also been obtained[3] for the formation of C atoms upon photolysis of CH_4 in an argon matrix at 14 K. It is, however, recognized[3] that secondary photolysis of free radicals such as CH_2 or CH_3 may account for the formation of C and CH in the matrix study and possibly also for the formation of CH in the flash photolysis[1]. In the conventional gas phase low intensity photolysis of methane, secondary photolysis is of negligible importance. In such experiments C(^{1}D) and CH($^2\pi$) can be detected through the products of their fast reaction with CH_4[4–6].

$$C(^1D) + CH_4 \rightarrow C_2H_4^* \rightarrow C_2H_2 + H_2 \; (k_1 = 3.2 \times 10^{-11} \text{ cm}^3\text{/molecule-sec}) \tag{1}$$

$$CH(^2\pi) + CH_4 \rightarrow C_2H_5^* \rightarrow C_2H_4 + H \; (k_2 = 0.25-3 \times 10^{-11} \text{ cm}^3\text{/molecule-sec}) \tag{2}$$

Furthermore, quantum yields of these stable end-products, C_2H_2 and C_2H_4, can easily be determined and can be related to those of the primary dissociative processes.

EXPERIMENTAL PROCEDURE AND RESULTS

CH_4 was photolyzed at wavelengths of 123.6 nm (10 eV), 106.7–104.8 nm (11.6–11.8 eV), 74.37–73.59 nm (16.66–16.84 eV), and 58.44 nm (21.21 eV). Enclosed rare gas resonance light sources were used[7] which were provided with CaF_2, LiF or Al windows depending on the wavelength region of the particular lamp. Actinometry was based on saturation ion current measurements in the case of the helium and neon resonance experiments, and at the longer wavelength on the production of CO in the photolysis of CO_2 ($\Phi_{CO} = 1$)[8]. Each value given in Table 1 is the average of 10 to 15 experiments.

TABLE 1

QUANTUM YIELDS OF ACETYLENE AND ETHYLENE IN THE FAR ULTRA-VIOLET PHOTOLYSIS OF METHANE

Photon energy (eV)	Methane (torr)	Quantum yields	
		Acetylene	Ethylene
10	CH_4 (10 to 700)	$0.4 \pm 0.1 \times 10^{-3}$	0.059 ± 0.005
	CD_4 (5 to 600)	n.d.	0.037 ± 0.005
11.6–11.8	CH_4 (10 to 650)	$6.5 \pm 0.5 \times 10^{-3}$	0.23 ± 0.03
	CD_4 (5 to 500)	$5.2 \pm 0.2 \times 10^{-3}$	0.184 ± 0.03
16.66–16.84*	CH_4 (10.5)	$\leq 0.1 \times 10^{-3}$	0.03 ± 0.01
21.2*	CH_4 (10.5)	2×10^{-3}	0.04 ± 0.01

* 1 mole % iso-C_4H_{10} added to remove $C_2H_5^+$ ions.
1 mole % NO added in all experiments.

The quantum yields given in Table 1 were found to be independent of the type and concentration (0.1 to 5 mole %) of free radical scavenger used (O_2 or NO). Also, $\Phi(C_2H_2)$ and $\Phi(C_2H_4)$ were independent of pressure up to approximately 500 torr within the indicated experimental error (Table 1). At both 123.6 and 104.8–106.7 nm, $\Phi(C_2H_2)$ and $\Phi(C_2H_4)$ are seen to diminish by 20 to 30% when the pressure of methane is raised from 500 to 1500 torr. The same remarks apply to the CD_4 experiments except that the quantum yields are consistently lower.

Nitric oxide was added to methane in most experiments, primarily to remove CH_3, $^3CH_2(^3\Sigma_g^-)$, and $C(^3P)$. These radicals are known[5,9–11] to react very slowly with CH_4 and will therefore in an unscavenged system contribute to the formation of C_2H_2 and C_2H_4 by radical–radical reactions such as:

$$C(^3P) + CH_3 \rightarrow C_2H_2 + H \qquad (3)$$

$$^3CH_2 + {}^3CH_2 \rightarrow C_2H_2 + H_2 \qquad (4)$$

$$^3CH_2 + CH_3 \rightarrow C_2H_4 + H \qquad (5)$$

In the neon and helium resonance photolysis, isobutane was added, in order to remove $C_2H_5^+$ ions by the reaction:

$$C_2H_5^+ + \text{iso-}C_4H_{10} \rightarrow C_2H_6 + C_4H_9^+ \qquad (6)$$

Neutralization of $C_2H_5^+$ is known[12] to lead to the formation of C_2H_4 as well as C_2H_2.

DISCUSSION

The virtual absence of C_2HD and $C_2H_2D_2$ in the 10 and 11.6–11.8 eV photolysis of an equimolar CH_4—CD_4 mixture in the presence of NO (Table II), demonstrates that under these conditions the insertion reactions (1) and (2) account for the formation of acetylene and ethylene. As is illustrated by the λ = 123.6 nm data given in Fig. 1, $\Phi(C_2H_2)$ and $\Phi(C_2H_4)$ are, in agreement with earlier observations[13], much higher in the photolysis of unscavenged methane than in the photolysis of CH_4—NO mixtures. The higher quantum yields in pure methane can be accounted for by the occurrence of reactions (4) and (5). As seen from the data given in Fig. 1, addition of an inert gas raises $\Phi(C_2H_2)$ and $\Phi(C_2H_4)$.

TABLE 2

PHOTOLYSIS OF CH_4–CD_4 (1:1) MIXTURES–ISOTOPIC ANALYSIS

Photon energy (eV)	NO (mole %)	C_2H_4	C_2DH_3	$C_2D_2H_2$	C_2D_3H	C_2D_4
10	1	39.5	24.0	2.7	17.6	16.1
	none	31.2	22.2	12.2	15.2	19.2
11.6–11.8	1	36.8	25.8	2.2	17.5	17.5
16.66–16.84	1	33.5	15.7	22.3	15.6	12.9
		C_2H_2	C_2HD	C_2D_2		
11.6–11.8	1	59.5	4.0	36.5		
	none	44.0	25.0	31.0		

Total pressure: 10 torr

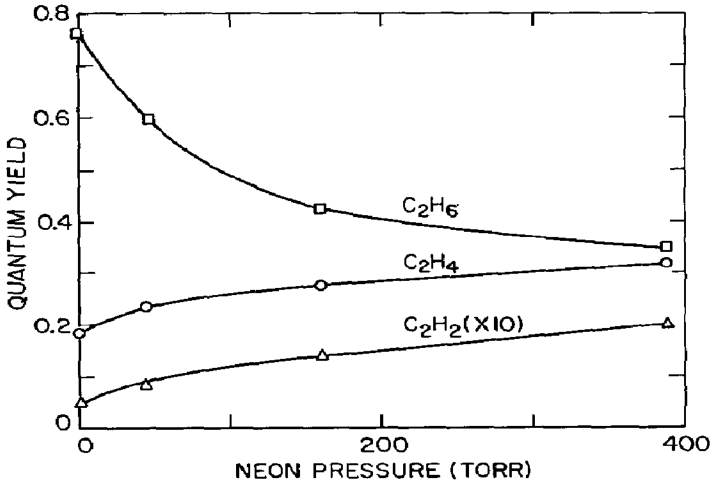

Fig. 1. Effect of neon added to 5.0 torr CH_4. Wavelength: 123.6 nm.

The effect of an inert gas on the products, which has also been reported previously by Hellner *et al.*[13], is to be ascribed to the collision induced conversion of $^1CH_2$ to $^3CH_2$, which results in an increased participation of reactions (4) and (5). The fact that the acetylene and ethylene observed in the unscavenged photolysis of a CH_4-CD_4 mixture (Table 2) contain C_2HD and $C_2H_2D_2$ is consistent with the occurrence of reactions (4) and (5).

At $\lambda = 123.6$ nm (10 eV) the yields of C_2H_2 and C_2H_4 observed in the photolysis of CH_4-NO mixtures (Table I) can be unambiguously ascribed to $C(^1D)$ and $CH(^2\pi)$ respectively. Furthermore, energetic considerations limit the formation of these species to the following overall dissociative processes:

$$CH_4^* \rightarrow CH(^2\pi) + H_2\ (^1\Sigma_g{}^+) + H\ (^2S) \qquad (7)$$

$$CH_4^* \rightarrow C(^1D) + 2H_2\ (^1\Sigma_g{}^+) \qquad (8)$$

Processes (7) and (8), which probably occur in two steps, require a minimum energy of 8.45 and 8.7 eV respectively. At $\lambda = 123.6$ nm, the $C(^1D)$ must be produced by elimination of molecular H_2 from the internally excited CH_2 formed in the well established[2,13-15] primary process:

$$CH_4 + h\nu \rightarrow CH_2 + H_2 \qquad (9)$$

while $CH(^2\pi)$ may result from the dissociation of CH_2 and/or CH_3 formed in the less important primary process:

$$CH_4 + h\nu \rightarrow CH_3 + H \qquad (10)$$

An increase of the photon energy from 10 to 11.6–11.8 eV results in a 15-fold and 4-fold increase of the quantum yields of the C and CH species reacting with CH_4 (Table I) respectively. This sharp increase of Φ(C) and Φ(CH) over this energy range is to be expected, in view of the fact that the lower photon energy (10 eV) is less than 2 eV above the minimum energy requirement for overall processes (7) and (8). At 11.6–11.8 eV there is sufficient energy to excite C atoms to the ^1S state. $C(^1S)$ atoms are known[16,17] to react more slowly than $C(^1D)$ atoms but may still be expected to insert into the CH bond of CH_4 to form C_2H_2 as a product. It is to be noted, however, that the quantum yields of C atoms given in this paper do not include the yield of $C(^3P)$ atoms which may be formed by a collision induced intersystem crossing of $C(^1D)$ or $C(^1S)$.

At 16.66–16.84 eV, $\Phi(C_2H_2)$ and therefore Φ(C), is essentially zero (Table I). This observation is not unexpected since the photoionization quantum yield is equal to one in this energy range[18]. Apparently, CH radicals are also formed in very low yield at 16.66–16.84 eV. The ethylene which in the absence of iso-C_4H_{10} is produced with a 10-fold higher quantum yield ($\Phi \sim 0.3$) is, in consistency with its isotopic distribution (Table II) most likely produced by reaction of the ethyl ion. In a CH_4-CD_4 experiment carried out in the presence of an ethyl ion scavenger (iso-C_4H_{10}) and a free radical scavenger (NO) the ethylene ($\Phi = 0.03$) which is reduced by a factor of 10 still contained ~15% $C_2H_2D_2$, indicating that undefined ionic reactions rather than reaction of CH may be responsible for its formation. It is of interest that Cook and Metzger[19] who irradiated CH_4 with photons ranging from 12.5 to 22 eV observed fluorescence ($\lambda > 300$ nm) beginning at photon energies of ~ 13 eV and dropping to zero at about 17 eV. A plausible source for this emission would be the $^2\Delta$ state of CH whose formation *via* process (11):

$$CH_4^* \rightarrow CH(^2\Delta) + H_2 + H \tag{11}$$

is energetically feasible at energies greater than 12.15 eV. The fact that the fluorescence drops to zero around 17 eV would be in agreement with the lack of evidence for CH in the neon resonance photolysis experiments. The lack of evidence for C and CH in the photoionization of CH_4 at 16.66–16.84 eV indicates that the $C(^1S)$ and $CH(^2\pi)$ species observed[6,16] in the pulse radiolysis of CH_4 may have to be ascribed to fragmentation of neutral excited CH_4 molecules formed by electron impact rather than an ionic mechanism. It may finally be noted that there is a slight increase in $\Phi(C_2H_2)$ in going from 16.66–16.84 eV to 21.2 eV (Table I). The reappearance of C_2H_2 as a measurable product in the helium resonance experiments can be tentatively related to the fact[18] that the ionization quantum yield diminishes slightly to some value below unity (~0.96) at 58.4 nm. It is to be expected that dissociation of superexcited methane molecules formed at 21.2 eV will yield C atoms with a high probability.

The present study does provide only a limited amount of information concerning the excited state of CH_2 which dissociates to $C(^1D)$ and possibly $CH(^2\pi)$. At the lowest photon energy (10 eV) it is energetically feasible to produce vibrationally excited CH_2 radicals in the $^1B_1$ state or the second $^1A_1$ state[20]. The absence of a noticeable pressure effect up to 500 torr (Table I) would indicate that the dissociative lifetime of the precursor(s) of C and CH is less than 10^{-9} sec. The drop seen at higher pressures can be ascribed to deactivation of the $C_2H_4^*$ and $C_2H_5^*$ intermediates formed in reactions (1) and (2) respectively or to deactivation of the precursor of the C and CH reactants. The energy content of the $C_2H_4^*$ intermediate is 7.4 or 8.8 eV depending on whether $C(^1D)$ or (^1S) is the reactant. RRKM calculations show[21,22] that if $C_2H_4^*$ is a vibrationally excited ground state molecule its dissociative lifetime will be less than 10^{-10} sec at these energies.

The relatively low values of $\Phi(CH)$ reported in this study raises some questions concerning the origin of CH produced in a flash photolysis study of CH_4 carried out by Braun *et al.*[4]. Considering that in the apparatus used by these authors[23], most of the light below 110 nm is absorbed by LiF, the average primary quantum yield of CH over the effective wavelength range (110–140 nm) must be in the vicinity of 0.1 ± 0.05. Besides the possibility[4] of secondary photolysis of intermediates, recent data relating to the kinetics of CH_2 radicals[10] show that some of the stable end-products (C_2H_2 and C_2H_4) originally ascribed to reactions of CH may have CH_2 as precursor. On the other hand, the abundance of CH observed in two independently determined neutral electron impact mass spectra of CH_4[24,25], seem to be on the low side (~6.5% of neutral decomposition). The mean energy of the neutral excited and superexcited CH_4 molecules formed by electron impact is not exactly known, but can be estimated to be in the vicinity of 12–13 eV[26]. Judging from the rapid rise of CH production with increase in energy (Table I) of the neutral excited CH_4, as well as the abundant production of CH($^2\Delta$) species at electron energies up to 100 eV[27] a greater abundance of CH would be expected than was reported[24,25]. Also, the present study shows that C atoms must be produced in the electron impact excitation of CH_4.

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