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Primary Products and Secondary Reactions in the Photodecomposition of Methyl Halides^{1,2a}

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CH₃I, CH₃Br, and CH₃Cl have been photolyzed at 184.9 nm and CH₃I at 253.7 nm, using CO, C_2H_4 , C_2H_6 , C_3H_8 , C_3D_8 , and CD₄ as scavengers to assist in the identification of the primary decomposition products. The quantum yield of methylene formation (CH₃X + $h\nu \rightarrow$ CH₂ + HX) is less than $\sim 10^{-3}$ in all cases. Carbon-hydrogen bond rupture occurs with a quantum yield of $\sim 10^{-2}$ in the photolysis of CH₃I at 184.9 nm. Evidence is given on the relative effectiveness of CH₃I and hydrocarbons in thermalizing hot CH₃ radicals and on preferential abstraction from C-H bonds relative to C-D bonds by hot CH₃ radicals. Rupture of the carbon-halogen bond in CH₃Cl is the predominant path of photodecomposition, as earlier investigations (and the present work) show it to be in CH₃Br and CH₃I. The quantum yield of photosensitized CH₂ production by reaction of C₃H₈ with I₂ excited at 184.9 nm is shown to be $<10^{-3}$.

Introduction

When CH_3I absorbs at 253.7 or 184.9 nm, and when CH_3Br or CH_3Cl absorb at 184.9 nm, the transition is to an antibonding orbital localized on the C-X bond.³ In each case, the absorbed energy is more than sufficient to cause decomposition of the methyl halide by any one of four paths:^{2a}

$$CH_3 X \rightarrow CH_3 + X$$
 (1)

 $CH_3 X \rightarrow CH_2 X + H$ (2)

$$CH_3 X \rightarrow CH_2 + HX$$
 (3)

$$CH_3X \rightarrow CHX + H_2$$
 (4)

In CH_3I^4 and CH_3Br^5 the quantum yield of path 1 is close to unity. However, evidence for H_2 production in the photolysis of $CH_3I_1^{6a}$ HT formation in the photolysis of CH_3I^7 indicates some contribution by the other pathways, although this may be very small since the experiments were designed only to give qualitative evidence on products by sensitive tracer methods^{6b,7} and no yields have been reported. Because of the inherent interest in the modes of rupture and because of the possibility that the methylenic fragments may be the precursors of chain lengthened products which have been observed in such systems, we have done experiments which set upper limits on the yields of CH_2 produced by activation of CH_3I at 253.7 nm and of CH_3I , CH_3Br , and CH_3Cl at 184.9 nm. Reactions with additives used in setting the limits include the following:

$${}^{1}\mathrm{CH}_{2} + \mathrm{CO} \to \mathrm{CH}_{2}\mathrm{CO}$$

$$\tag{5}$$

$${}^{3}CH_{2} + CO \rightarrow CH_{2}CO$$
(6)

$$CH_2 + C_2H_4 \rightarrow c-C_3H_6 \tag{7}$$

$$\rightarrow C_3 H_6 \tag{8}$$

$${}^{*}CH_{2} + C_{3}H_{8} \rightarrow CH_{3} + C_{3}H_{7}$$

$$(9)$$

$${}^{1}CH_{2} + C_{3}H_{6} \rightarrow C_{4}H_{10} \tag{10}$$

$$\operatorname{GH}_2 + \operatorname{GH}_4 \to \operatorname{GH}_2 \operatorname{DCD}_3 \tag{11}$$

In addition to setting limits on the CH₂ yields, the investigation has provided information on H₂ and D₂ yields in CH₃I-C₃D₈ and CD₃I-C₃H₈ mixtures, including the relative importance of C-H (C-D) bond rupture and concerted H₂ (D₂) elimination. Knowledge of the prop-

erties of hot CH_3 radicals formed by the photolysis of CH_3I has been extended.

Some results in the literature which are of interest relative to the work reported here include the following: (1) Multiple fragmentation occurs in the vacuum UV photolysis of CH₃Cl in Ar and N₂ matrices at 14 K.⁸ (2) Molecular rather than atomic elimination occurs in many other systems following various methods of excitation, e.g., H₂ from CH₄ at 123.6 nm,⁹ HF from CH₃F at 147.0 nm,¹⁰ other photon activated eliminations,¹¹ and decompositions activated by radical combination¹² and by nuclear recoil atoms.¹³ Evidence had been obtained on the relative yields of the ²P_{1/2} and ²P_{3/2} states of iodine from the photolysis of CH₃I and other alkyl iodides.^{14a-c} The lifetime of the excited states of CH₃I formed by 240–320-nm radiation is 7×10^{-14} s.^{14d} About 12% of the energy in excess of the bond energy in the photodecomposition of CH₃I at 266.2 nm is present as vibrational energy.^{14b}

Experimental² Section

Gaseous samples were photolyzed in a 10 cm long 22 mm i.d. cylindrical quartz cell with flat Suprasil end windows or in 9 mm i.d. Suprasil tubing. Each cell was connected through a graded seal and greaseless stopcock to a ground joint used for attachment to the vacuum line. After photolysis, the cells were cleaned with aqueous HF to remove brownish deposits which frequently formed on the windows.

Two Hanovia SC2537 low-pressure mercury arcs with Suprasil end windows irradiated the 22 mm i.d. cells simultaneously from both ends. About 1×10^{15} photons s⁻¹ of 184.9-nm and 7.5×10^{15} photons s⁻¹ of 253.7-nm radiation entered the cell when the lamps were 1 cm from the windows. The 9-mm i.d. vessels, irradiated in the center of a helical low pressure mercury arc, received ~1 $\times 10^{17}$ photons s⁻¹ of 184.9 nm over an 11 cm length of the tubing.

For photolyses at 253.7 nm the radiation below 230.0 nm was cut out by a 2-mm thick Vycor filter, or by using a Vycor tube as the reaction cell with the spiral lamp. The Vycor transmitted ~75% of the 253.7-nm radiation. To remove 253.7 nm while transmitting 184.9 nm, an ozone filter^{15a} with a transmittance of 50% at 184.9 nm and 0.1% at 253.7 nm was used with the spiral lamp. With the end-on lamps the 253.7-nm radiation was removed by γ -irradiated LiF filters^{15b} which transmitted ~30% at 184.9 nm and <0.04% at 253.7 nm or by interference filters^{15c} which transmitted ~24% at 184.9 and 0.09% at 253.7 nm. Since the lamp intensity at 253.7 nm is 7.5 times that at 184.9 nm, about 3% of the radiation transmitted by the interference filter is at 253.7 nm.

The radiation intensities incident on samples were determined by HBr actinometry at 184.9 nm¹⁶ and HI actinometry at 253.7 nm.^{15b} The optical densities were ≥ 2 for both the actinometers and samples. The decomposition of the actinometer gas was kept below 0.004 to preclude¹⁶ error from the H + X₂ \rightarrow HX + X reaction. The X₂ produced was determined spectrophotometrically using an extinction coefficient of 169 M⁻¹ cm⁻¹ for Br₂ at 420.0 nm¹⁷ and of 578 M⁻¹ cm⁻¹ for I₂ at 500.0 nm.^{18a}

Analyses for CH₂CO, H₂, HD, D₂, and deuterated alkanes were made with an AEI MS-10 mass spectrometer.^{2a} Gas chromatography with a Poropak Q column was used for CH₄, C₂H₄, C₂H₆, C₃H₆, C₃H₈, c-C₃H₆, *i*-C₄H₁₀, and *n*-C₄H₁₀. A column of 20% SF 96 silicone oil on Chromosorb P was used for hydrocarbons with higher boiling points and for alkyl iodides.^{2a} Product identification was assisted by plots of product emergence time vs. boiling point for known compounds. For each product studied

TABLE I	: Upp	er Limi	its of	CH ₂ f	from	CH ₃	[at	253.7	nm
and from	CH,I,	CH ₃ Br,	and (CH (C	l at 1	84.Š	nm	L	

System	CH ₂ species	Φ (upper limit)	
CH ₃ I-C ₃ H ₈ ^a CH ₂ I-C ₂ H ₂ ^a	¹ CH ₂ CH ₂	$4 imes10^{-6}$ 5 × 10^{-5}	
$CH_{3}Br-C_{2}H_{4}$	CH_2^2	1×10^{-3}	
CH ₃ Cl-CO	¹ CH ₂	1×10^{-2}	
CH ₃ CI-CO CH ₂ CI-C ₂ H	¹ CH ²	6×10^{-3} 1 × 10^{-3}	
$CH_{3}I-C_{2}H_{4}$	CH_2	2×10^{-2}	
CH ₃ I-C ₂ H ₄ -O ₂	¹ CH ₂	2×10^{-3}	
CH ₃ I-CO	°CH ₂	2×10^{-3}	
CH ₃ I-CD	$^{1}CH_{2}^{2}$	2×10^{-2} 2×10^{-2}	
CH ₃ I-C ₃ H ₈	$^{1}CH_{2}^{2}$	8×10^{-2}	
CH ₃ I-C ₃ H ₈ -O ₂	¹ CH ₂	2×10^{-2}	
CH ₃ I-C ₂ H ₆ CH ₃ I-C ₂ H ₆ -O ₂	¹ CH ₂	$\frac{8 \times 10^{-3}}{2 \times 10^{-3}}$	

^a 253.7-nm photolysis, all others 184.9 nm.

quantitatively, a calibration curve of peak area vs. amount injected was determined.

Reaction mixtures were prepared by standard vacuum line techniques. A liquid nitrogen trap separated the line from the mercury diffusion pump and a column of silver powder separated it from the mercury manometer. Stopcocks and ground joints were greased with Kel-F 90 or Halocarbon grease, or greaseless stopcocks with Teflon plugs and Viton O-rings were used. Known pressures of condensible reagents were obtained from reservoirs cooled by slush baths at temperatures chosen to give the desired vapor pressures. Following filling of the reaction cell at such a pressure, the vapor was condensed in a corner of the cell with liquid nitrogen. Additional condensible reagents were then condensed from calibrated volumes. Noncondensible additives (CH_4, CO, O_2) were allowed to fill the cell to pressures measured on the manometer while the cell was at room temperature except for the tip in which the condensibles were held at 77 K.

Methyl chloride (Matheson 99.5% purity) was degassed at 77 K. Methyl bromide (Matheson 99.5% purity) was degassed at dry ice temperatures which raised the purity to 99.9%. Eastman methyl iodide was purified from the 0.05% C₂H₄ which it contained by degassing at dry ice temperature or by preparative gas chromatography. The CO, CH₄, and C₂H₄ used were all of \geq 99.5% purity as listed by the manufacturer (Matheson) or determined by us. Cyclopropane (Baker) was listed as 99.0%. Analytical checks for contaminants were made on unirradiated reaction mixtures in parallel with all irradiated samples.

Results

Upper Limits on CH_2 Yields. Upper limits set on the quantum yields for CH_2 production by photolysis of CH_3I , CH_3Br , and CH_3Cl are given in Table I. These estimates are based on the amount of light absorbed by the methyl halides, ^{18b} the observed product yields, and the fraction of the CH_2 expected to react with the scavenger relative to the halide, assuming the rate constant ratios of Table II. The data from which the limits were derived, and their interpretation, are discussed below.

 $C\dot{H}_3Br-C_2\dot{H}_4$ Experiments. Six mixtures of ~35 Torr of CH₃Br and 100 Torr of C₂H₄ were photolyzed for times up to 1000 min at an absorbed intensity of 184.9-nm radiation of 3×10^{14} photons s⁻¹. The principal hydrocarbon products were CH₄ and C₃H₈, with quantum yields of ~1 $\times 10^{-2}$ and 1×10^{-3} , respectively. Trace amounts of propylene and the absence of detectable cyclopropane set an upper limit of ~1 $\times 10^{-4}$ on their quantum yields and

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TABLE II:	Relative Rate	Constants for
Reaction of	Methylene ^a	

Rate constant data, 300 K	Ref
$k(CH_3Br)/k(C_2H_4) = 1.3$ ${}^{3}k(CO)/{}^{3}k(CH_3CI) = 3-5$ ${}^{1}k(CO)/{}^{1}k(CH_3CI) = 0.1$ ${}^{1}k_3(CH_3CI)/{}^{1}k(CH_3CI) \sim$	25 12b 12b
$\frac{\frac{^{1}k_{3}(CO)^{1}k(CH_{2}CO)}{^{1}k(CH_{2}CO)^{1}k(CH_{3}Cl)} = 0.072}{\frac{^{1}k_{3}(CO)}{^{1}k_{3}(CO)} = \frac{^{1}k_{3}(CO)^{1}k(CH_{2}CO)}{^{1}k(CH_{2}CO)} = 0.072$	12b
${}^{1}k(CO) {}^{1}k(CH_{2}CO){}^{1}k(CO)$ $(0.1)(1/0.12) = 0.83$ ${}^{1}k_{3}(C_{3}H_{3}) = {}^{1}k(C_{3}H_{5})$ ${}^{1}k(CH_{3}CI) = {}^{1}k(C_{3}H_{5})$ ${}^{1}k(CH_{3}I) = {}^{1}k(CH_{3}CI)$ ${}^{3}k(CH_{3}I) = {}^{3}k(CH_{3}CI)$ ${}^{6}k(CH_{3}I) = {}^{3}k(CH_{3}CI)$	12b,26 27 b c b
$k(CH_3I)/k(C_2H_4) = 1.3$ $k(CH_3Br)/k(C_2H_4) = 1.3$ $^1k(C_2H_6) = ^1k(C_3H_6)$ $k(I_2)/k(O_2) = \sim 25$ $^1k(O_2)/^1k(C_3H_6) < 0.46$ $^1k(I_2)/(k(C_3H_6)) \sim$	c,25 b 28 27
$\frac{k(l_2)^{-k}(O_2)}{k(O_2)^{1}k(C_3H_8)} = 11.5$ ¹ k(CD ₄)/ ¹ k ₃ (CD ₄) = 1.19 S/D = 1 for CH ₂ DCD ₃ * at 78 Torr of CD ₄	27,28 d d

^a ${}^{1}k(X)$ and ${}^{3}k(X)$ are the rate constants for the reactions of ${}^{1}CH_{2}$ and ${}^{3}CH_{2}$ with X, respectively. k(X)makes no distinction between singlet and triplet CH_{2} reacting with X. ${}^{1}k_{3}(X)$ is the rate constant for deactivation of ${}^{1}CH_{2}$ to ${}^{3}CH_{2}$ by collision with X. ^b Assumed. ^c Assumed. These assumptions give a rate constant for the reaction of singlet methylene with $CH_{3}I$ lower than it really is because the reaction of singlet methylene with a halide is electrophilic in nature (ref 12b) and therefore should be faster with the iodide than the bromide or chloride atoms. ^d Estimated from data in ref 34a. Uncertainties are introduced by the secondary isotope effect and the dependence of the stabilization/ decomposition ratio of $CH_{2}DCD_{3}^{*}$ on the CH_{2} energy.^{34b}

TABLE III: Quantum Yields of Products of Photolysis of CH_3Cl at 184.9 nm^a

CH.Cl.	Cl.		Quantum yi	elds
Torr	Torr	CH₄	C_2H_4	C_2H_6
54 64	0 1	0.79 0.83	$2.4 imes10^{-3}\ b$	$1.5 imes 10^{-3}$
96	8	0.81	2.1×10^{-3}	6.9×10^{-4}

^a Full intensity of the two end-window lamps on endwindow cell, absorbed 184.9-nm intensity = 1.3×10^{15} photons s⁻¹. ^b Not determined.

an upper limit of 1×10^{-3} for the yield of CH₂ from CH₃Br. The propylene and C₃H₈ found may arise from sources other than CH₂, in which case the quantum yield of the latter is less than the upper limit noted. Photolysis of 100 Torr of C₂H₄ for 1110 min with an absorbed 184.9-nm intensity of 1.8×10^{14} photons s⁻¹ gave C₃H₆ and C₃H₈ quantum yields of 3.5×10^{-4} and 2.1×10^{-3} , respectively, but no cyclopropane or methane (quantum yields <10⁻⁴). Hot *n*-propyl radicals, formed from addition of hot methyl radicals to ethylene, can produce propylene by unimolecularly decomposing, by abstracting a Br atom from CH_3Br to form C_3H_7Br which unimolecularly decomposes, and by disproportionation with methyl radicals after collisional stabilization. Propylene may also be produced by reaction of methyl radicals with C_2H_3 formed by abstraction of H from C_2H_4 by hot methyl radicals.²

 CH_3Cl-CO Experiments. Two samples of 60 Torr of CH_3Cl and 300 Torr of CO were photolyzed for 8 and 18 min at 184.9 nm with an absorbed intensity of 1.0×10^{17} photons s⁻¹. No CH_2CO was found in the products. An amount equal to 0.6% of the CH_4 formed would have been detectable. This sets an upper limit of 6×10^{-3} on the quantum yield of ${}^{3}CH_{2}$ and 1×10^{-2} on the quantum yield of ${}^{1}CH_{2}$, by reasoning from reactions 12, 5, 6, and 13–16 for their formation and consumption.

 $CH_{2}Cl \xrightarrow{hv} {}^{1}CH_{2}({}^{3}CH_{2}) + HCl$ (12)

 ${}^{1}\mathrm{CH}_{2}({}^{3}\mathrm{CH}_{2}) + \mathrm{CH}_{3}\mathrm{Cl} \rightarrow \mathrm{CH}_{2}\mathrm{Cl} + \mathrm{CH}_{3}$ (13)

 ${}^{1}CH_{2} + M \rightarrow {}^{3}CH_{2} + M$ (14)

 $CH_2CO^* + M \rightarrow CH_2CO + M$ (15)

 $CH_2CO^* \rightarrow CH_2 + CO$ (16)

The experiments were done at pressures in excess of the minimum required for collisional stabilization (reaction 15) of ketene produced from methylene formed by photolysis of ketene, ^{12b,29} or $Hg(^{3}P_{1})$ photosensitized decomposition of ketene.³⁰ The energy available to be partitioned between the CH_{2} and HCl of reaction 12 is 64 kcal mol⁻¹, whereas that from the $Hg^{3}(P_{1})$ reaction gives 33 kcal mol⁻¹ to the products of ketene decomposition. If the higher energy leads to significantly higher ketene decomposition, the CH_{2} formed would react, at lower energy, with CO to re-form ketene.

Quantum yields from the photolyses of CH_3Cl without additive and in the presence of Cl_2 are given in Table III.

 $CH_3Cl-C_3H_8$ Experiments. Photolysis of CH₃Cl at 184.9 nm in the presence of C_3H_8 produces CH₄ as the predominant hydrocarbon product, with much smaller amounts of C_2H_4 , C_2H_6 , and the isomeric butanes (Table IV).

The butanes may be formed by one or more of the following processes: (a) insertion of ${}^{1}CH_{2}$ into a C-H bond; (b) stabilization of the combination of CH₃ and C₃H₇ radicals; or (c) conceivably substitution of hot CH₃ for H in C₃H₈. The C₄H₁₀ yields in the presence of Cl₂, which scavenges thermal radicals, place a limit of $\sim 4 \times 10^{-4}$ on the C₄H₁₀ yield due to ${}^{1}CH_{2}$ insertion. The pressures used were within the region giving complete stabilization of hot butane molecules formed from ${}^{1}CH_{2}$ insertion into C₃H₈.³¹ From these data, 10^{-3} is set as an upper limit for the primary quantum yield for the production of singlet methylene from photolysis of CH₃Cl at 184.9 nm.

 CH_3I-CO Experiments. No ketene was found from the photolyses of CH_3I-CO mixtures with CO pressures from 51 to 346 Torr, CH_3I pressures from 9 to 19 Torr, absorbed 184.9-nm intensities from 1×10^{14} to 1×10^{17} photons s⁻¹, and total absorption of 2×10^{18} to 3×10^{20} photons.

TABLE IV: Quantum Yields from the Photolysis of CH₃Cl-C₃H₈ Mixtures at 184.9 nm

CH.Cl.	C.H.	Scavenger	Photolysis ^a		Quan	tum yields	× 10 ³	
Torr	Torr	Torr	time, min	$\overline{CH_4}$	C_2H_4	C_2H_6	<i>i</i> -C ₄ H ₁₀	<i>n</i> -C ₄ H ₁₀
41	113	0	180	600	4	3	2	0.3
39	124	8 Cl ₂	180	b	b	b	$\bar{0.1}$	0.3
40	123	0	240	b	ь	ь	1.5	0.2
40	125	2.7 NO	240	200	1.8	2	1	0.2

^a Full intensity of two end-window lamps on end-window cell, absorbed 184.9-nm intensity = 1.3×10^{15} photons s⁻¹. ^b Not determined.

TABLE V: Quantum Yields from the Photolysis of $CH_3I-C_2H_4$ Mixtures at 184.9 nm^a

CH.I.	CH4I. C.H.		H.I. C.H., O.,		Quantum yield $\times 10^3$			
Torr	Torr	Torr	C ₃ H ₆	C ₃ H ₆	c-C₃H ₆			
0	100	0	0.35	2.1	0			
8.6	100	0	1.6	7	2.5			
8.6	101	0	1.3	7.6	2.3			
8.8	100	2.5	0.33	2	0.3			

 a Photolysis with two end-window lamps for 1110 min with absorbed intensities from 1.3×10^{14} to 1.8×10^{14} photons s^-1.

Ketene would have been observed if present at $\geq 2\%$ of the CH₄ produced. The competing reactions for any CH₂ formed would be (5) and (6), competing with the CH₃I analogue of (13). From consideration of the rate constants and reactant ratios, it may be concluded that the quantum yields of singlet and triplet methylene are both less than 2×10^{-3} . The estimate assumes that the quantum yield of CH₄ was ~0.08, as it was for eight samples of 8.6 Torr of CH₃I photolyzed with similar intensities and doses.

 $CH_3I-C_2H_4$ Experiments. Gas chromatographic analysis of $CH_3I-C_2H_4$ mixtures following photolysis at 184.9 nm showed five products, using the Porapak Q column: propylene, propane, cyclopropane, methane, and a peak in the region of the butanes. Table V gives typical quantum yields for the C_3 hydrocarbons, based on the total light absorbed by the mixtures.

The quantum yield of propylene from the photolysis of pure C_2H_4 is 3.5×10^{-4} . Assuming this yield is the same in the $CH_3I-C_2H_4$ mixtures which give a total propylene yield of $\sim 1.5 \times 10^{-3}$ and taking account of the different extinction coefficients and pressures of the CH_3I and C_2H_4 , the propylene quantum yield due to absorption by CH_3I is determined to be 6.4×10^{-3} . The total propylene plus cyclopropane quantum yield due to CH₃I absorption is similarly determined to be $\sim 1.9 \times 10^{-2}$. If this yield were all due to CH₂ produced from CH₃I, the CH₂ quantum yield would be 2×10^{-2} (after correcting for loss of CH₂ by reaction with CH₃I and assuming the ratio of the rate constants for the reaction of CH₂ with CH₃I and C₂H₄ is the same as the ratio for reaction with CH₃Br and C₂H₄ (Table II)).

The total propylene yield sets a high limit on the CH_2 yield since the unimolecular decomposition of hot n- C_3H_7 radicals, formed by the addition of hot CH_3 to C_2H_4 , is an important source of propylene in the pressure range studied.²

The presence of 2.5 mol % O_2 in $CH_3I-C_2H_4$ mixtures caused a large decrease in the C_3H_6 and $c-C_3H_6$ quantum yields (Table V). Singlet methylene reactions are relatively unaffected by the addition of O_2 , while reactions involving ${}^{3}CH_2$ are greatly diminished.³² The quantum yields of $c-C_3H_6$ (3 × 10⁻⁴) and C_3H_6 (3 × 10⁻⁴) formed in the presence of O_2 allow an estimate of 2 × 10⁻³ as the upper limit for the quantum yield of ${}^{1}CH_2$ produced from CH_3I .

Rowland and co-workers⁷ have reported the formation of cyclopropane and propylene from the photolysis of $CH_3I-C_2H_4$ mixtures, but with no estimate of quantum yields.

 CH_3I -Alkane Experiments at 184.9 nm. The quantum yields at 184.9 nm of propane from CH_3I - C_2H_6 mixtures (Table VI) and of butane from CH_3I - C_3H_8 mixtures (Table VII) in the absence of radical scavengers are ~0.04. These yields are greatly reduced by a few per cent of O₂ or NO which are used to distinguish between products formed by ¹CH₂ and those originating from ³CH₂ or other radical precursors.³³ The CH₃I-C₂H₆ experiments in the absence of O₂ and with 5.8 Torr of O₂ set upper limits of 0.08 and 2×10^{-3} respectively for the quantum yield of ¹CH₂. For the CH₃I-C₃H₈ experiments, the upper limit is 0.08, in the

TABLE VI: Quantum Yields from the Photolysis of CH₃I-C₂H₆ Mixtures at 184.9 nm^a

 CHI	СН	0	Final I		Quantum yields	
Torr	Torr	Torr	Torr	CH ₄	$C_3H_8 \times 10^3$	I ₂
 8.5	129	0	0	0.9	43	0
8.6	131	1.4	0.10	0.1	9.4	0.068
8.5	130	2.8	0.16	0.091	3.9	0.098
8.8	129	5.8	0.20	0.086	0.73	0.13
8.5	133	30.8	0.36 ^b	с	C	0.26 ^b

^a Absorbed 184.9-nm intensities: 1.5×10^{14} to 1.9×10^{14} photons s⁻¹. LiF filters used with end-window lamps and cell. Photolysis time 240 min. ^b The I₂ yield is a lower limit because some I₂ may have been left in the solid phase. If an average I₂ pressure during this experiment is taken as 0.2 Torr, then the quantum yield of I₂ due to radiation absorbed by CH₃I is calculated to be 0.51. ^c Not determined.

TABLE VII: Butane Quantum Yields from the Photolysis of CH₃I-C₃H₈ Mixtures at 184.9 nm^a

С н С н	Scavenger	Final I				
Torr	Torr	Torr	Butane $\times 10^3$	$I_2 \times 10^2$	i-Bu/n-Bu	
131	0	0.006	39.2	0.52	0.30	
133	0	0.013	40.4	0.61	0.35	
170	0	0.015	31.3	0.68	0.34	
85	0	0.011	37.9	0.64	0.33	
65	Ō	0.016	38.1	0.88	0.37	
50	0	0.019	35.0	1.0	0.38	
202	Ō	0.024	32.4	1.1	0.33	
85	02.5	0.20	0	8.0	0	
124	00.7	0.068	7.8	2.4	0.23	
133	0.0.35	0.045	17.1	1.5	0.32	
134	O.,0.55	0.074	11.1	2.8	0.28	
152	0	0.06	Ь	0.70	0.35	
149	Ò	0.10	ь	0.67	0.42	
151	NO.2.7	b	Trace	b	0.46	

^a Using 8.7 Torr of CH_3I , 184.9-nm light intensities from end-window lamps with LiF filters of $(1.5 \pm 0.5) \times 10^{14}$ photons s⁻¹ for first 11 experiments and $(3.2 \pm 0.4) \times 10^{14}$ for remainder. Photolysis times for the last three experiments were 625, 1000, and 1000 min, respectively, the rest were 300-400 min. ^b Not determined.

TABLE VIII: Quantum Yields from the Photolysis of $CH_3I-C_3H_8$ Mixtures at 253.7 nm^a

Photolysis	Quantum yields ^b						
time, min	CH ₄	$C_2H_6 imes 10^4$	$I_2 \times 10^4$	Butanes			
80	0.031	2.1	С	С			
200	0.027	1.1	7.1	С			
420	0.032	0.6	8.2	<4 × 10 ⁻⁶			

^{*a*} End-window lamps with Vycor filters. 8.4 Torr of CH_3I , 130 Torr of C_3H_8 . ^{*b*} Trace amounts of ethylene also observed. ^{*c*} Below detectability limit.

absence of O_2 , and 0.02 in the presence of 0.7 Torr of O_2 . These values have been corrected for absorption of radiation by I_2 .

The ratios CH_4/CH_3D and CD_3H/CD_4 for the $CH_3I-C_3D_8$ and $CD_3I-C_3H_8$ experiments (corrected to equal pressures of reactants) are 9 and 6, respectively, indicating significant isotope effects in the abstraction of an H (or D) atom by the hot methyl radicals produced from CH_3I by 184.9-nm radiation. Similarly, such hot methyl radicals produced in an equimolar mixture of CH_3I and CD_4 abstract preferentially from the C-H bonds relative to the C-D bonds, giving a CH_4/CH_3D ratio of 4.

The quantum yield of CH_2DCD_3 found for the 184.9-nm photolysis of CH_3I in CD_4 was $\sim 4 \times 10^{-3}$. Assuming this to all result from 1CH_2 insertion into CD_4 , and correcting for the fraction of 1CH_2 converted to 3CH_2 by collision with CD_4 and the fraction of the CH_2DCD_3 which decomposes before collisional stabilization (see footnote *d*, Table II), an upper limit of 2×10^{-2} may be estimated for the quantum yield of 1CH_2 .

 CH_3I -Alkane Experiments at 253.7 nm. No cyclopropane ($\Phi < 5 \times 10^{-5}$) was found from the 253.7-nm photolysis of gaseous CH_3I - C_2H_4 mixtures and no butanes ($\Phi < 4 \times 10^{-6}$) from CH_3I - C_3H_8 mixtures (Table VIII), indicating that the yield of methylene from the photolysis of methyl iodide at this wavelength is very low.²

Hydrogen Production from $CH_3I-C_3H_8$ Systems. Photolyses at 184.9 nm of 8.6 Torr of CH_3I with 10 Torr of C_3D_8 , 8.6 Torr of CD_3I with 11 Torr of C_3H_8 , and 8.6 Torr of CH_3I with 11 Torr of C_3H_8 all yielded hydrogen, the ratios of the total hydrogen to total methane yield being 0.06, 0.09, and 0.10, respectively. The quantum yield for hydrogen formation is estimated to be ~0.01. The hydrogen distributions (H₂:HD:D₂) from the CH₃I-C₃D₈ and CD₃I-C₃H₈ mixtures were 2.7:6.2:1 and 3.3:7.8:1, respectively.

 $I_2-C_3H_8$ Photolysis. I₂ molecules excited by 184.9-nm light in CH₄ initiate steps which produce C₂, C₃, and C₄ products in low quantum yields and such I₂* molecules photosensitize HF elimination from CH₃F and CF₃H.^{4,20,23} The possibility therefore had to be considered that I₂ formed in CH₃I-C₃H₈ mixtures might cause CH₂ formation. We have found no evidence for C₄H₁₀ formation (Φ < 10⁻³) during 184.9-nm photolysis of I₂-C₃H₈ mixtures, indicating the absence of significant ¹CH₂ formation.

Discussion

Methylene Yields. The results given in Table I indicate that the quantum yields of CH_2 from the 184.9-nm photolysis of CH_3I , CH_3Br , and CH_3Cl are less than ~ 1 $\times 10^{-3}$, and set an upper limit on the CH_2 yield from the 253.7-nm photolysis of CH_3I of 5×10^{-5} . Reactions of CH_2 cannot be a source of products in excess of these limits in photolyses of the methyl halides.

Products from CH_3Cl . The predominant process following absorption of 184.9-nm photons by CH_3Cl is rupture of the C-Cl bond, as indicated by the high CH_4 quantum yields with and without added hydrocarbons (Tables III and IV). Related work has shown that excited CH_2TCl^{*13a} and $CH_3^{38}Cl^{*13b}$ molecules formed by substitution into CH_3Cl of ³H and ³⁸Cl recoiling from nuclear reactions also decompose primarily by C-Cl bond rupture. The tritium recoil reaction in $CH_3Cl-C_2H_4$ mixtures gave little cyclopropane and propylene-*t* indicating little decomposition of CH_2TCl^* to give CH_2 .^{13a} The production of ClO from the flash photolysis of CH_3Cl-O_2 mixtures has also been cited as evidence for the $CH_3Cl \rightarrow CH_3 + Cl$ process.³⁵

Methane formation from CH₃Cl must be due to abstraction of H from CH₃Cl by hot methyl radicals formed by the primary dissociation and to the reaction of thermal methyl radicals with HCl formed by abstraction of H atoms by Cl atoms. Reported activation energies for abstraction of H from CH₃Cl and HCl by methyl radicals are 9.4 and 2.3 kcal mol⁻¹, respectively;³⁶ for abstraction of H from CH₃Cl and C₃H₈ by Cl, they are 3.1,³⁷ 0.98 ± 0.13³⁸ (primary H), and 0.66 ± 0.13³⁸ (secondary H), respectively.

The rupture of CH₃-Cl bonds by 184.9-nm radiation results in 70.9 and 68.4 kcal mol⁻¹ partitioned between the methyl radical and the chlorine atom in the ${}^{2}P_{3/2}$ and ${}^{2}P_{1/2}$ states, respectively.² Both states have been observed in photolyses of HCl, Cl₂, CCl₄, and CF₃Cl.³⁹ If 70.9 kcal mol⁻¹ goes into translational energy of the CH₃ + Cl, the energy of the Cl atom is 20.5 kcal mol⁻¹. It is unlikely that the Cl + CH₃Cl \rightarrow CH₃ + Cl₂ reaction, for which an activation energy of 25 kcal mol⁻¹ has been reported,³⁷ plays a significant role in the CH₃Cl system.

The ethane and ethylene formed in the 184.9-nm photolysis of CH₃Cl and CH₃Cl-C₃H₈ mixtures must result from the combination of $CH_3 + CH_3$ and $CH_3 + CH_2Cl$ to form excited ethane and ethyl chloride molecules. The hot C_2H_5Cl formed has ~91 kcal mol⁻¹ excess vibrational energy, well above the critical energy of 55 kcal mol^{-1} for HCl elimination.^{12b,40} The rate constant for HCl elimination is equivalent to the collisional frequency at 300 Torr of $\rm CH_3 Cl.^{41}$ In the experiments of Tables II and III, the majority of the hot C_2H_5Cl must have dissociated to give ethylene, with 1,2 elimination favored.^{13a} The rates of dissociation of the hot ethane to $2CH_3$ and stabilization are equal at 240 Torr.³³ Hot 1,2-dichloroethane, formed by combination of two chloromethyl radicals, undergoes unimolecular HCl elimination with a rate constant equal to the collisional frequency at 16 $Torr^{12b,42}$ and therefore would be nearly completely stabilized at the pressures used. No attempt was made to detect this product.

 $CH_3Br-C_2H_4$ Experiments. The low yields of hydrocarbons in the 184.9-nm photolyses of $CH_3Br-C_2H_4$ mixtures ($\Phi_{CH_4} = 1 \times 10^{-2}$, $\Phi_{C_3H_8} = 1 \times 10^{-3}$) indicate that most of the CH3 radicals formed react with brominecontaining radicals or initiate polymer chains by addition to C_2H_4 (solid deposits were formed). Φ_{CH_3} is ~1.⁵ C-Br rupture also predominates in excited CH_2TBr formed by tritium recoil atoms.⁴³ The CH₄ observed in the photolysis must result from abstraction of H from CH_3Br and C_2H_4 by hot CH_3 . The reported activation energies for these reactions are 10.1 and 10 kcal mol⁻¹, respectively.³⁶ The CH₃ radicals from 184.9-nm photolysis of CH₃Br are formed with 72 or 63 kcal mol⁻¹ of translational energy accompanying formation of $^2P_{3/2}$ and $^2P_{1/2}$ bromine atoms, respectively, if none of the energy of the photon enters vibrational modes. Hot CH_3 radicals also add to C_2H_4 to form excited $n-C_3H_7$,² the rate constant ratio⁴⁴ for abstraction relative to addition being 0.1.

The hot bromine atoms from the photolysis of CH_3Br in C_2H_4 may abstract H from CH_3Br and C_2H_4 and may

initiate chain reactions 45 by addition to C_2H_4 before or after thermalization. Only ground state $(^2P_{3/2})$ Br atoms have been observed from CH_3Br by kinetic spectroscopy, but CH_3Br has been shown to quench ${}^2P_{1/2}Br$ atoms from the photolysis of CF₃Br.⁴⁶

CH4 Yields from CH3I and CH3I Mixtures at 253.7 nm. The quantum yield for CH₄ production from the photolysis of 8.6 Torr of CH_3I at 253.7 nm is tenfold higher in the presence of 130 Torr of C_3H_8 (Table VIII) than in pure⁴ CH₃I. This difference must be due to a higher probability per collision for abstraction of an H atom from C_3H_8 by hot CH₃ than from CH₃I. Similar results have been reported by Doepker and Ausloos⁴⁷ with CD₃I with and without CH₃CD₂CH₃ or CD₃CH₂CD₃ as additives. They report a 3.6-fold higher probability for abstraction of secondary hydrogen atoms than primary hydrogen atoms. Thermalization of hot CH₃ radicals by CH₃I may occur both by deactivation on collision without reaction CH₃* + $CH_3I \rightarrow CH_3 + CH_3I$ and, quite possibly, by the iodine exchange reaction $CH_3^* + CH_3I \rightarrow CH_3I + CH_3$. Whittle⁴⁸ and Fox⁴⁹ have shown that thermalized CF₃ radicals abstract an I atom from methyl iodide about 10² times faster than an H atom from methyl iodide, and Henderson⁵⁰ found that the relative reactivities of hot methyl radicals from the 253.7-nm photolysis of CH₃I for abstraction of H and Cl from chlorinated hydrocarbons decrease with increasing thermal activation energy. If hot methyl radical abstract with the same ratio as thermalized CF3 radicals, the yield for thermalization by the exchange reaction would be about 0.3, compared to the methane quantum yield of 3×10^{-3} found in pure CH₃I.

In contrast to our results in the gas phase, which show no evidence of cyclopropane, and hence of CH₂ production in the 253.7-nm photolysis of $CH_3I-C_2H_4$ mixtures, cyclopropane is produced in similar photolyses in the solid state.⁵¹ Speculatively, this may be ascribed to reaction of C_2H_4 with CH_2 formed by disproportionation in the parent cage $(CH_3 + I \rightarrow CH_3I^* \rightarrow CH_2 + HI)$ or to a concerted reaction of CH₃I* with C₂H₄.

CH₄ Yields, Isotope Effects, and Hydrogen Yields from CH₃I and CH₃I Mixtures at 184.9 nm. As at 253.7 nm, the CH_4 yields from the photolysis of CH_3I at 184.9 nm are much higher in the presence of hydrocarbon additives. For example, we have found $\Phi_{CH_4} = 0.9$ with C_3H_8 , after correction for absorption by the I2 generated during photolysis, compared to 0.08 in pure CH₃I. This may be attributed to the same factors discussed for the 253.7-nm activation. The yield of CH_4 from pure CH_3I is about an order of magnitude higher at 184.9 nm than at 253.7 nm, as found both in the earlier work⁴ and the present work. Since the energy available in excess of that necessary for bond rupture is much in excess of the activation energy for H abstraction both with 184.9- and 253.7-nm activation (76.6 and 34.7 kcal mol⁻¹, respectively, for $I(^{2}P_{1/2})$ production), it appears that the difference in yields must result from a difference in distribution of the energy between translational and internal. Photofragment spectroscopy studies^{14b} of CH₃I dissociation at 266.2 nm have shown that the energy given the CH_3 radicals is primarily translational and moderation studies^{4,52} on the radicals produced at 253.7 nm likewise indicate that their energy is primarily translational. Further evidence for a difference in vibrational-translational energy distribution of the CH₃ produced at 184.9 and 253.7 nm is our evidence for an isotope effect on the methane yields from photolysis of $CH_3I-C_3D_8$ and $CD_3I-C_3H_8$ mixtures at 184.9 nm as contrasted to the absence⁴⁸ of such an effect at 253.7 nm. Similarly, translationally hot CF_3 radicals produced by

photolysis of CF₃I at 253.7 nm show only minor isotope effects on H abstraction⁵³ while vibrationally hot CF₃ from photolysis of CF₃Br at 184.9 nm abstract H atoms from CH_3CD_3 and CH_2D_2 5.3 times more readily than D atoms.⁵⁴

The H_2 :HD:D₂ distributions of 2.7:6.2:1 and 3.3:7.8:1 from the 184.9-nm photolysis of CH₃I-C₃D₈ and CD₃I- C_3H_8 mixtures requires that a major portion of the hydrogen results from C-H or C-D bond rupture in the photolytic act, followed by H or D abstraction by the ejected H or D atom. Hydrogen has been observed as a product of the photolysis of CH₃I at 184.9 nm by Martin,^{6a} and subsequently Beverly and Martin^{6c} found a value of 0.06 for the H_2/CH_4 ratio from the photolysis. Molecular elimination of H_2 has been reported.^{6b} The ratios of total hydrogen to total methane yields found in our studies were 0.10, 0.06, and 0.09 for CH₃I-C₃H₈, CH₃I-C₃D₈, and $CD_3I-C_3H_8$ mixtures, respectively. The isotope effects preclude estimation of a quantum yield for molecular hydrogen elimination from our data, other than that it is less than the yield of C-H bond rupture by 184.9-nm radiation.

Production of D_2 in the $CH_3I-C_3D_8$ and H_2 in the $CD_3I-C_3H_8$ mixtures was unexpected. The most probable mechanism appears to be replacement of a hydrogen atom of propane by a hot methyl radical followed by hydrogen abstraction by the displaced atom. Evidence for such replacement reactions has been reported,54 and questioned.7

Rationale for Differences in Methane Yields from Photolyses of CH_3Cl , CH_3Br , and CH_3I . The exothermicities for the 184.9-nm photolyses of CH₃I, CH₃Br, and CH_3Cl producing ${}^2P_{1/2}$ halogen atoms are not far different (76.6, 74.9, and 68.4 kcal mol⁻¹, respectively), yet the methane quantum yields are 0.08 ± 0.02 , 0.020 ± 0.003 ,⁵ and 0.81, respectively. The activation energies for the abstraction of an H from the methyl halides by a thermal methyl radical are all about 10 kcal mol^{-1.36} The activation energy for the abstraction of a Cl atom from CH₃Cl by CF₃ is ≥ 6 kcal mol⁻¹ more than the activation energy for abstraction of an H atom from CH₃Cl.⁴⁹ For CH₃I and CH_3Br , the activation energy for the abstraction of the halogen atom is lower than the activation energy for hydrogen abstraction.⁴⁹ The same trend in reaction probabilities for abstraction of halogen and hydrogen from CH_3X by hot CH_3 is expected. Therefore, the lower methane quantum yield for the photolyses of CH₃I and CH₃Br than for the photolysis of CH₃Cl at 184.9 nm may result partially from a greater percentage of hot methyl radicals abstracting a halogen atom, and replacing a hot methyl radical with a thermal methyl radical. In the absence of additives, thermal methyl radicals must react primarily with each other at the onset of photolysis in all three media. As illumination proceeds, they must react with the I_2 , HBr, and HCl products.

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Photolysis Mechanism of Aqueous Tryptophan¹

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Flash photolysis experiments indicate that monophotonic photoionization is the principal initial photolysis act in aqueous tryptophan under high intensity, 265-nm laser excitation, leading to the Trp⁺ radical cation $(\lambda_{max} 580 \text{ nm})$ with quantum yield 0.12 ± 0.01 and e_{aq} with quantum yield 0.10 ± 0.01 from pH 4 to 8. The neutral Trp radical (λ_{max} 510 nm) is formed by deprotonation with rate constant 1.5×10^6 s⁻¹. The disappearance of e_{aq} follows a complex decay inconsistent with homogeneous kinetics. The results are in agreement with a recombination model in which the electron diffuses through the medium as a quasi-free entity, during which period back reactions with the original radical, or electrons and radicals generated in nearby pairs, compete with scavenging by tryptophan or added solutes. The well-established result that Trp yield observed after electron decay is not enhanced by oxygen or other eaq scavengers is attributed to the formation of an unstable intermediate product of the electron-radical back reaction which subsequently oxidizes additional tryptophan to Trp.

Introduction

Tryptophan (Trp) is a major chromophore in most proteins and has been the subject of numerous investigations of its electronic and photochemical properties.² Previous flash photolysis studies have shown that the initial products when aqueous Trp is irradiated in the

280-nm band are the triplet state 3Trp (λ_{max} 460 nm), the neutral radical oxidation product Trp (λ_{max} 510 nm), and the radical cation Trp⁺ (λ_{max} 580 nm).³ The same radicals are formed by ionizing radiation when anion radicals such as Br_2^- or $(CNS)_2^-$ react with aqueous Trp.^{4,5} The previous work has shown also that formation of the Trp radical in