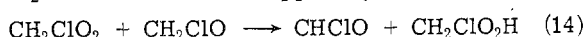
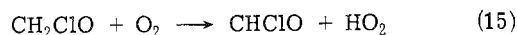


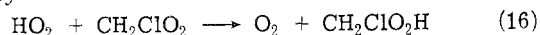
The CH₂ClO radicals must disappear by one of two routes



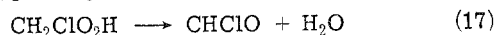
or



followed by



Presumably the CH₂ClO₂H has some stability since its expected mass spectral peaks were detected. However most of it decomposes, possibly on the walls, *via*



Thus $\Phi\{\text{CHClO}\} = 2.0$ and there is no chain process.

As the reaction proceeds the CHClO can decay *via* reactions 9 and 10. Since the times to reach the maximum in [CHClO] are greater in the CH₃Cl than in the CH₂Cl₂ system, reaction 11 may play a more important role. However if we ignore reaction 11, then

$$[\text{CH}_3\text{Cl}]_{\text{max}}/[\text{CHClO}]_{\text{max}} = k_{10}/k_{11}$$

The ratio $[\text{CH}_3\text{Cl}]_{\text{max}}/[\text{CHClO}]_{\text{max}}$ was found to be ~ 1.8 . Since $k_{11} = 3.6 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ at 32°,⁸ then $k_{10} \sim 6.5 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$, a value in reasonable agreement with the value of $7.4 \times 10^8 \text{ M}^{-1} \text{ sec}^{-1}$ found in the CH₂Cl₂ system.

Acknowledgment. This work was supported by the Environmental Protection Agency through Grant No. 800949 for which we are grateful.

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Effect of Wavelength in the Gas-Phase Photolysis of Carbon Tetrachloride at 253.7, 184.9, 147.0, and 106.7 nm

Douglas D. Davis, John F. Schmidt, Charles M. Neeley, and Robert J. Hanrahan*¹

Department of Chemistry, University of Florida, Gainesville, Florida 32611 (Received June 17, 1974)

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The photolysis of gaseous carbon tetrachloride at pressures from 30 to 100 Torr and 25° has been studied using light of 253.7, 184.9, 147.0, and 106.7 nm produced by electrodeless discharge lamps. Qualitatively, there is a clear trend toward increasing molecular fragmentation with increasing photon energy. At 253.7 nm, only Cl₂ and C₂Cl₆ are formed; $\phi(\text{Cl}_2) = \phi(\text{C}_2\text{Cl}_6) = 0.11$. Added Br₂ is consumed with a quantum yield of unity, and CCl₃Br is the only organic product. At 184.9 nm, $\phi(\text{Cl}_2) = \phi(\text{C}_2\text{Cl}_6) = 0.048$, but a small amount of C₂Cl₄ is also formed. With added Br₂, $\phi(-\text{Br}_2) = 1.6$, and both CCl₃Br and CCl₂Br₂ are produced. Formation of 1,1-dichlorocyclopropane in the presence of added ethylene gives strong evidence for the presence of dichlorocarbene at 184.9 nm (and presumably also at lower wavelengths). At 147.0 nm, $\phi(\text{Cl}_2) \approx \phi(\text{C}_2\text{Cl}_6) = 0.085$, but a yield of C₂Cl₄ equal to 40–90% of the C₂Cl₆ yield was also noted. Preliminary results at 106.7 nm indicate that C₂Cl₄ is the predominant organic product at that wavelength. It is suggested that CCl₃· radicals are formed at all wavelengths, that CCl₂ becomes important at 184.9 nm and below, and that CCl· fragments contribute at 147.0 and 106.7 nm.

Introduction

A search of the literature on photolysis of carbon tetrachloride reveals several papers on the liquid-phase system²⁻⁴ as well as papers on the radiolysis of the liquid compound.^{5,6} Several research groups have been concerned with the photolysis of carbon tetrachloride mixed with various hydrocarbons.⁷ Apparently, no work on the photolysis of the pure compound in the gas phase has been reported. The present study was initiated because of our interest in other aspects of the reaction dynamics of carbon tetrachlo-

ride, including radiolysis of CCl₄-NH₃ mixtures in the liquid phase,⁸ radiolysis of CF₄-CCl₄ mixtures in the gas phase,⁹ and fast-flow microwave discharge studies of gaseous CF₄-CCl₄ mixtures.¹⁰

The present work includes measurements of the production of Cl₂ and organic products (C₂Cl₆, C₂Cl₄) from the pure compound at 253.7, 184.9, 147.0 and 106.7 nm; quantum yields are reported for all wavelengths. Scavenging by Br₂ was also studied at the same wavelengths (except 106.7), including consumption of bromine and production

of organic bromides. A brief investigation of the role of added O_2 was made at 253.7 nm. Furthermore, several experiments were performed at 184.9 nm to assess the role of dichlorocarbene in the photolysis mechanism, including trapping of CCl_2 with ethylene and an investigation of the effect of the concentration of added Br_2 on the ratio of product yields CCl_2Br_2/CCl_3Br . The observation of a marked pressure effect on the Cl_2 yield at 184.9 nm is also interpreted on the basis of the role of CCl_2 in the mechanism.

Experimental Section

The carbon tetrachloride used in this work was Fischer reagent grade purified by preirradiation according to the method of Firestone.⁵ It was immediately placed under vacuum at liquid nitrogen temperature on a mercury-free high-vacuum line, which was used for all of the present experiments. The light sources were electrodeless glow discharge lamps fabricated from 34/45 male standard taper joints, which plugged directly into matching joints of 5-l. (for 253.7-nm work) or 1-l. (184.9 nm and lower) reaction vessels. For 253.7-nm work a 3-mm Vycor window was used and for 184.9 nm an extremely thin Vitrosil quartz window was used; LiF was used at the lower wavelengths. Since CCl_4 absorbs 184.9-nm light much more strongly than 253.7-nm light, presence of light of the higher wavelength was not significant. Photolysis lamps were activated by a Raytheon PGM 10 \times 1 microwave generator operating at 2450 MHz; a Type C antenna was used. Analyses for Cl_2 and Br_2 were done using a Beckman DU spectrometer; the entire sample was frozen into a removable cuvet for analysis, and was redegassed before continuing the experiment. For higher boiling products, the sample was condensed into the liquid state and an appropriate sample taken with a microsyringe. Analyses were done on a Microtek GC2000R gas chromatograph with a hydrogen flame detector. The entire glass system used for photolysis was grease free. All stopcocks were Fischer-Porter O ring sealed Teflon-glass valves. Connections were made using glass O-ring joints with Teflon O rings. The lamp was sealed in place using Kel-F wax. The lamp window was sealed to the glass body by epoxy cement. During the course of the photolysis at 184.9 nm and lower wavelengths, the cell contents were stirred with a solenoid-driven gas circulating pump. This was not necessary for 253.7-nm work since the light beam traversed the entire diameter of the photolysis cell with only 20% attenuation.

At 253.7 nm actinometry was done by measuring H_2 production from HBr ($\phi_{H_2} = 1.00$).¹¹ At 184.9 nm the N_2O actinometer was used; N_2 production was measured ($\phi_{N_2} = 1.44$).¹² The light sources were found to vary by $\pm 10\%$ during the experiments. Actinometry at 147.0 and 106.7 nm was based on production of CO from CO_2 ($\phi_{CO} = 1.00$).¹³ Properties of the light sources and actinometry data are summarized in Table I. This table also gives the extinction coefficient of gaseous CCl_4 at the several wavelengths employed. The absorption spectrum of CCl_4 was determined using a McPherson Model 218 vacuum ultraviolet monochromator with double-beam attachment and ratio-recording electronics. A typical spectral scan of CCl_4 at a pressure of 0.075 Torr (as measured by an MKS Baratron capacitive micromanometer) in an 8.0-cm cell is shown in Figure 1. (A partial description of the vacuum ultraviolet spectrum of CCl_4 , and some related discussion, can be found in the literature.^{14,15})

TABLE I: Summary of Light Sources

Wavelength, nm	253.7	184.9	147.0	106.7 ^c
Gas	Hg	Hg	Xe	Ar
Window	Vycor	Quartz	LiF	LiF
Actinometry gas	HBr	N_2O	CO_2	CO_2
Measured product	H_2	N_2	CO	CO
Assumed ϕ	1.00	1.44	1.00	1.00
Measured I_0 , quanta/sec	1×10^{16}	4×10^{15}	7×10^{14}	1×10^{15}
$\epsilon(CCl_4)$, atm^{-1}/cm^{-1}	0.08	46	240	<i>b</i>

^c The Ar resonance lamp emits light at both 104.8 and 106.7 nm; we refer to the more intense, higher wavelength line for convenience. ^b May be small.

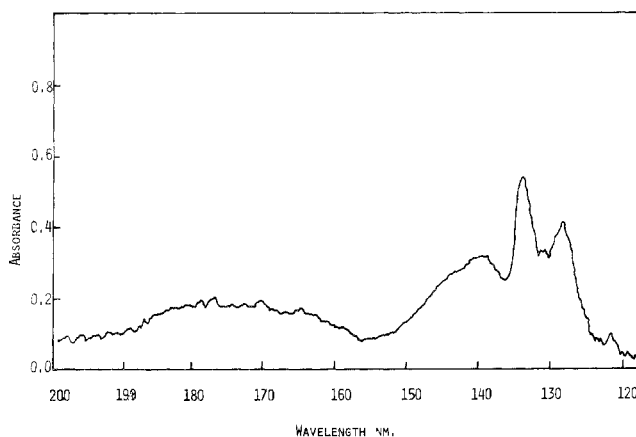


Figure 1. Absorption spectrum of CCl_4 in the gas phase at 0.075 Torr pressure and 25°, as determined using a McPherson Model 218 scanning vacuum ultraviolet spectrophotometer with a 8-cm cell.

Experimental Results

Photolysis at 253.7 nm. Chlorine Production. A series of experiments was performed to measure the production of Cl_2 from pure degassed CCl_4 at 253.7 nm. In these runs the CCl_4 pressure was chosen as 100 Torr (close to its saturation value) because of the very low extinction coefficient of the compound at this wavelength. In four duplicate runs, initial Cl_2 quantum yields were 0.108, 0.084, 0.112, and 0.129, giving an average value of 0.108 ± 0.016 . A typical plot of chlorine concentration *vs.* photolysis time (Figure 2) shows that the rate of chlorine production decreases with increasing photolysis time. (A summary of quantum yields for chlorine production at 253.7, 184.9, 147.0, and 106.7 nm is given in Table II.)

Bromine Scavenging. Several experiments with *ca.* 0.2 Torr added Br_2 gave initial quantum yields for Br_2 consumption of 0.78, 0.92, and 0.97. It appears reasonable to assume that the primary quantum yield for C-Cl bond rupture is unity, particularly since a correction for light absorption by product $BrCl$ was not made. (Absorption measurements were made at 500 nm, somewhat on the long wavelength side of the Br_2 maximum and even farther above the $BrCl$ maximum, in order to minimize interference by $BrCl$.) A typical graph of Br_2 concentration *vs.* photolysis time is shown in Figure 3; Br_2 is consumed linearly at short times, but the rate falls off somewhat as the

TABLE II: Product Yields in CCl₄ Photolysis

Wavelength, nm	253.7	184.9	147.0	106.7
$\phi(\text{Cl}_2)^a$	0.11 ± 0.02	0.048	0.083	0.013
$\phi(\text{C}_2\text{Cl}_6)$	($\approx \text{Cl}_2$)	0.05	0.087	(0.034) ^b
$\phi(\text{C}_2\text{Cl}_4)$	0	~0.0005	0.05	0.027

^a Chlorine quantum yields refer to 100 Torr for 253.7- and 184.9-nm photolyses, and to 30 Torr for 147.0- and 106.7-nm experiments. At 184.9 nm the chlorine quantum yield was found to be pressure dependent; see Figure 6. Pressure effects were not investigated at other wavelengths. The apparent low quantum yield at 106.7 nm may be due to inefficient light absorption by CCl₄, or to development of color centers in the LiF window. ^b Maximum C₂Cl₆ yield at 120-min photolysis time; see text.

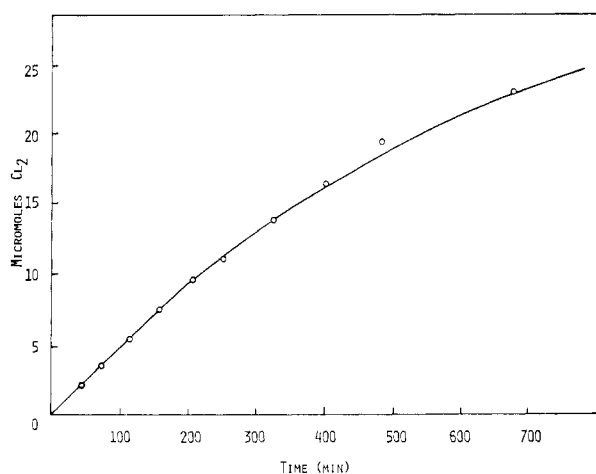


Figure 2. Production of Cl₂ in the gas-phase photolysis of CCl₄ at 253.7 nm. The experimental conditions were 100 Torr of CCl₄, 25°, 5-l. reaction vessel.

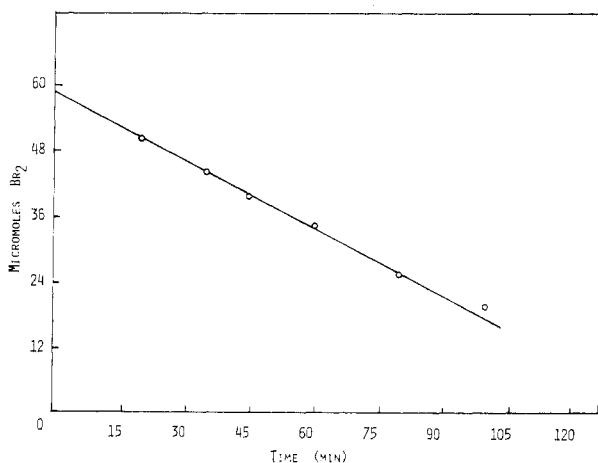


Figure 3. Consumption of added Br₂ scavenger in the gas-phase photolysis of CCl₄ at 253.7 nm. The experimental conditions were 100 Torr of CCl₄, 25°, 5-l. reaction vessel.

Br₂ concentration is depleted, possibly due to competition between Br₂ and BrCl for free radicals. (Table III summarizes bromine scavenging results at 253.7, 184.9, and 147.0 nm.)

Oxygen Scavenging. Primarily to assess the consequences of (possibly) imperfect degassing of CCl₄, a brief investigation was made of the effect of added O₂ on CCl₄ photolysis. It will be seen in Figure 4 that addition of sever-

TABLE III: Bromine Scavenging in CCl₄ Photolysis

Wavelength, nm	253.7	184.9	147.0
$\phi(-\text{Br}_2)$	0.9 ± 0.1	1.6 ± 0.1	
Organic products	CCl ₃ Br ^a ($\phi \approx 1$)	CCl ₃ Br ^b CCl ₂ Br ₂	CCl ₃ Br CCl ₂ Br ₂ CClBr ₃

^a 2% residual C₂Cl₆. ^b Ratio CCl₂Br₂/CCl₃Br varies from less than 0.1 to 0.6, depending on the Br₂ concentration (1–20%).

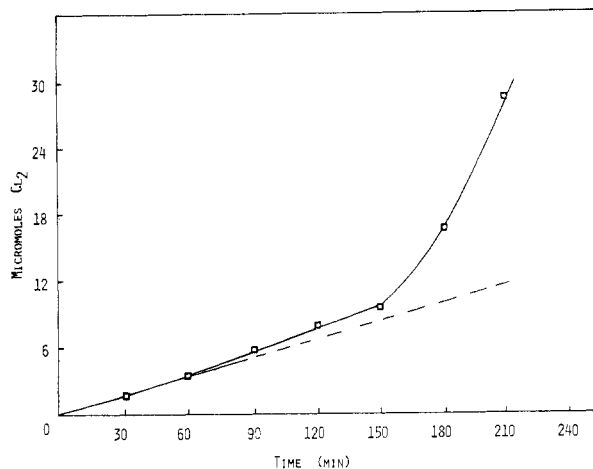


Figure 4. Effect of added O₂ on the production of Cl₂ in the gas-phase photolysis of CCl₄ at 253.7 nm. From 0 to 60 min photolysis time, no added O₂; from 60 to 150 min, several milliTorr added O₂; from 150 to 210 min, several Torr added O₂. The experimental conditions were 100 Torr of CCl₄, 25°, 5-l. reaction vessel.

al milliTorr of O₂ has only a slight effect, but addition of several Torr O₂ pressure causes $\phi(\text{Cl}_2)$ to increase to about 1.0. We conclude that the system displays no abnormal sensitivity to added O₂; the results are broadly consistent with our conclusion that ϕ of the primary process is unity. (A more definite conclusion would require further investigation, particularly identification of products. Formation of phosgene and Cl₂ is reasonable, and compatible with $\phi(\text{Cl}_2) \approx 1.0$, however.)

Organic Products. In the photolysis of pure CCl₄ at 253.7 nm, the only organic product detected was C₂Cl₆. Measurement of its yield at two different photolysis times showed that $\phi(\text{C}_2\text{Cl}_6) = \phi(\text{Cl}_2)$ within experimental error ($\pm 10\%$). (Quantum yields for the formation of organic products in the photolysis of CCl₄ at the four wavelengths studied are included in Table II.)

In the presence of added Br₂, $\phi(\text{CCl}_3\text{Br}) = 0.9$, and this was the only significant organic product. A small amount of C₂Cl₆, about 2% of the CCl₃Br yield, was also found.

Photolysis at 184.9 nm. Pure CCl₄. The photolysis of CCl₄ at 184.9 nm is superficially similar to the photolysis at 253.7 nm; in experiments with CCl₄ pressure of 100 Torr, $\phi(\text{Cl}_2) = 0.048$. A typical graph showing chlorine production as a function of photolysis time is shown in Figure 5. Again, C₂Cl₆ is the main organic product, with $\phi(\text{C}_2\text{Cl}_6) = \phi(\text{Cl}_2)$ at several different photolysis times; typically, a ratio of C₂Cl₆/Cl₂ of 51/49 was found. However, a small yield of C₂Cl₄, equal to about 1% of the C₂Cl₆ yield, was also found. There appeared to be a small yield of polymer on the photolysis vessel walls, but no attempt was made to measure it. This deposit was removed by intermittent photolysis of oxygen after approximately 90 min of CCl₄ photolysis.

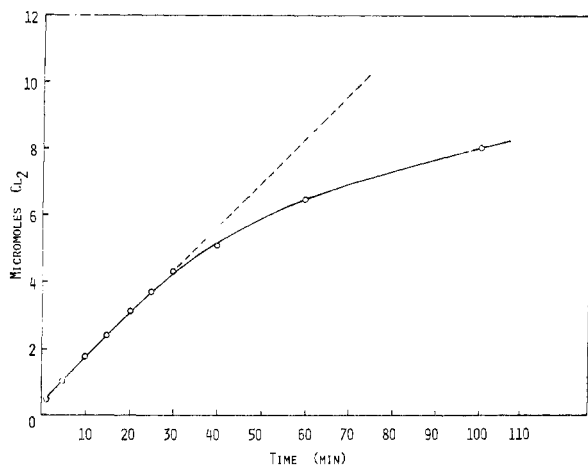


Figure 5. Production of Cl_2 in the gas-phase photolysis of CCl_4 at 184.9 nm. The experimental conditions were 100 Torr of CCl_4 , 25°, 1-l. reaction vessel.

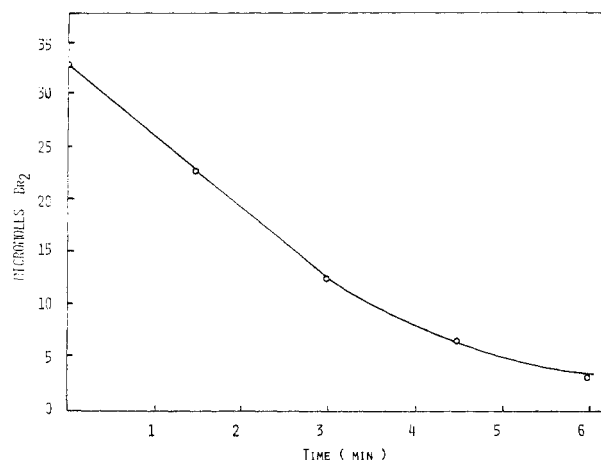


Figure 7. Consumption of added Br_2 scavenger in the gas-phase photolysis of CCl_4 at 184.9 nm. The experimental conditions were 100 Torr of CCl_4 , 25°, 1-l. reaction vessel.

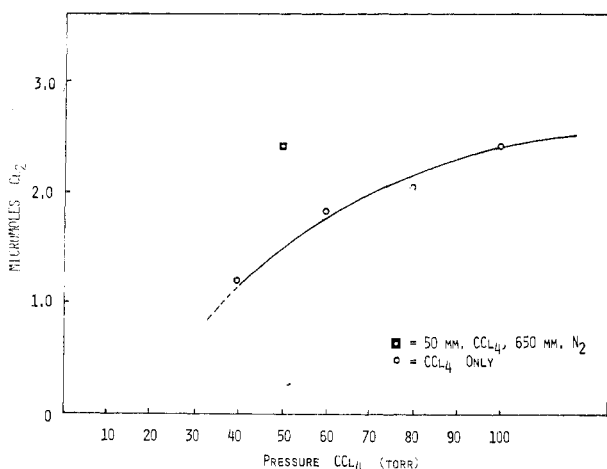


Figure 6. Production of Cl_2 at a fixed photolysis time vs. pressure in the photolysis of CCl_4 at 184.0 nm: (O) pure CCl_4 ; (□) 50 Torr of CCl_4 , 650 Torr of N_2 . Experiments done at 25° using a 1-l. reaction vessel.

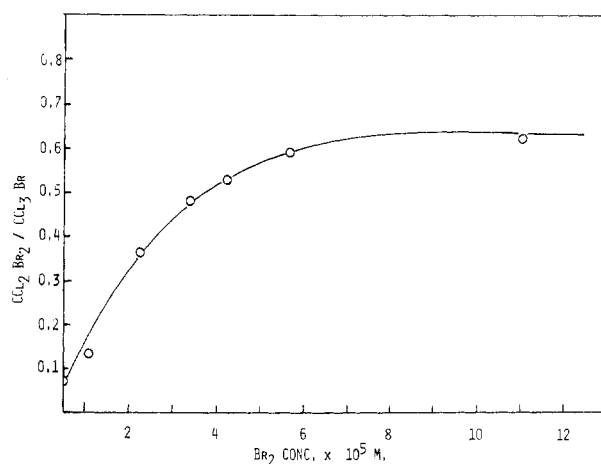


Figure 8. Effect of the Br_2 concentration on the ratio of CCl_2Br_2 to CCl_3Br produced in the gas-phase photolysis of CCl_4 at 184.9 nm. Pressure of CCl_4 100 Torr at 25° in a 1-l. reaction vessel. Concentration range corresponds to 0.05–1 mol % Br_2 .

Several lines of speculation suggested to us that the photolysis of CCl_4 at 184.9 nm might be pressure dependent. To provide evidence on this point, the effect of CCl_4 pressure on the Cl_2 production rate was measured in a series of experiments. The results are shown in Figure 6. It can be seen that the chlorine yield increases by a factor of about 2.5 between a CCl_4 pressure of 30 and 100 Torr. Addition of 650 Torr of N_2 to a sample of 50 Torr of CCl_4 increased the chlorine yield to the limiting value expected at large carbon tetrachloride pressures.

Scavenger Experiments. As in the photolysis at 253.7 nm, initially added bromine is removed by photolysis at 184.9 nm; a typical experiment is shown in Figure 7. In two experiments, we found $\phi(-\text{Br}_2) = 1.6 \pm 0.1$.

A separate set of bromine scavenger experiments was done to measure organic products. To make sure that Br_2 was the exclusive scavenging agent, photolysis time was limited to 1 min or less. In a typical experiment, the product mixture had the following composition: CCl_3Br , 73%; CCl_2Br_2 , 26%; C_2Cl_6 , 0.15%; $\text{C}_2\text{Cl}_4\text{Br}_2$, 0.07%; and $\text{C}_2\text{Cl}_5\text{Br}$, trace.

In a further experiment, an investigation was made of the effect of bromine concentration on the relative yields of organic bromide products. In Figure 8 the ratio of the yield

of CCl_2Br_2 to CCl_3Br is plotted. It can be seen that the relative yield of CCl_2Br_2 increases toward a limiting value of about 0.7, with added Br_2 .

As will be discussed further below, we interpret the production of CCl_2Br_2 in the photolysis at 184.9 nm as evidence for the participation of dichlorocarbene in the photolysis mechanism. In an effort to obtain further evidence on this point, experiments were conducted with ethylene added as a carbene scavenger. Figure 9 shows a graph of the quantum yield of the adduct, 1,1-dichlorocyclopropane, as a function of the composition of the photolysis mixture. This is not a simple experiment to interpret, since C_2H_4 absorbs light at 184.9 nm. The upper curve in Figure 9 is calculated assuming that only the fraction of the light absorbed by CCl_4 gives the adduct; the lower curve utilizes the entire absorbed light intensity in the calculation. Assuming that the activation must reach CCl_4 (either directly or by energy transfer) in order to form the adduct, $\phi(\text{CCl}_2)$ equals approximately 0.5–1.0 according to this experiment. (It should be noted that excited $\text{C}_3\text{H}_4\text{Cl}_2$ might be formed, isomerizing to give $\text{CH}_2=\text{CH}-\text{CCl}_2\text{H}$ or $\text{CCl}_2=\text{CH}-\text{CH}_3$. Due to experimental difficulties, neither of these would have been detected in our gas chromatography experiments. The latter superimposes on the tail of the CCl_4

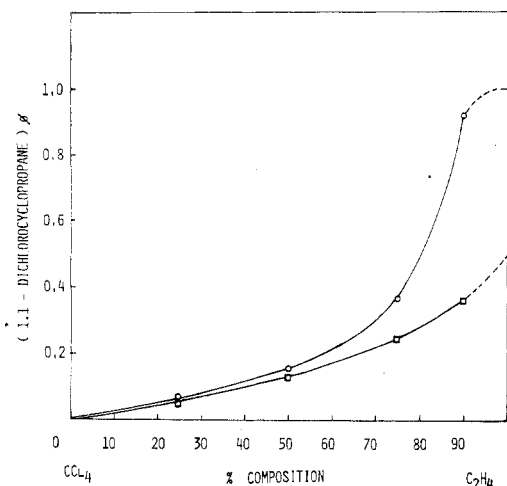


Figure 9. Quantum yield for production of 1,1-dichlorocyclopropane as a function of per cent added ethylene in the gas-phase photolysis of CCl_4 - C_2H_4 mixtures at 184.9 nm: (O) calculation of ϕ based on energy absorbed in CCl_4 only; (□) calculation of ϕ based on all energy absorbed in systems. Total pressure 100 Torr at 25°, 1-l. reaction vessel.

peak, and the former should appear at the same point on the chromatogram as $\text{C}_2\text{H}_4\text{Cl}_2$, which is also produced. Hence, a portion of the CCl_2 yield may be masked in the ethylene scavenging experiments.)

Photolysis 147.0 and 106.7 nm. Pure CCl_4 . Photolysis of pure degassed CCl_4 with a xenon resonance lamp at 147.0 nm produced Cl_2 , C_2Cl_6 , and C_2Cl_4 ; quantum yields were 0.083, 0.087, and 0.05, respectively. We suggest that the increase of the quantum yield of C_2Cl_4 , compared with the higher wavelengths, is particularly significant. Preliminary experiments were done at 106.7 nm, using an argon resonance lamp. Although the intensity of the photolysis lamp was measured as $1.3 (\pm 0.1) \times 10^{15}$ quanta per sec, we cannot confirm its spectral purity, since our McPherson monochromator has little if any light transmission below 110 nm. We could see nothing in the spectrum below the Lyman α line at 121.7 nm. Fairly rapid development of color centers in the LiF windows does suggest substantial light intensity below 110 nm, however.

The chemical behavior of the system under photolysis at 106.7 nm appears to be rather complex. The Cl_2 and C_2Cl_4 yields increase regularly with dose, but the total moles of C_2Cl_6 formed maximize at short photolysis times and actually decrease regularly between 120 and 360 min of photolysis. Average quantum yields for Cl_2 and C_2Cl_4 were 0.013 and 0.027, respectively; the apparent quantum yield of C_2Cl_6 was 0.034 at 120 min of photolysis, 0.012 at 240 min, and 0.002 at 360 min. (Due to the rapid production of color centers in the windows at this wavelength, our reported quantum yield measurements should be interpreted with caution.) The ratio of C_2Cl_4 to C_2Cl_6 varies from 0.8 at 120 min to 13 at 360 min, and in general is much larger than at higher wavelengths. It appears that C_2Cl_6 is labile under photolysis at 106.7 nm; it may absorb light of this wavelength much more efficiently than the parent CCl_4 .

Scavenger Experiments. Although bromine scavenging was not attempted at 106.7 nm, some preliminary work was done at 147.0 nm. Organic products included not only CCl_3Br and CCl_2Br_2 , formed at 184.9 nm, but also CClBr_3 . We suggest that formation of this compound, as well as the increasing proportion of C_2Cl_4 among the products at the lower wavelength, is evidence of increasing fragmenta-

TABLE IV: Lamp Aging in CCl_4 Photolysis at 147.0 nm

Lamp age, hr	Lamp intensity, quanta sec^{-1}	$\phi(\text{Cl}_2)$	$\phi(\text{C}_2\text{Cl}_6)$
35-42	7.6×10^{14}	0.083	0.087
52-54	7.1×10^{14}	0.031	0.039
65-67	6.5×10^{14}	0.020	0.020

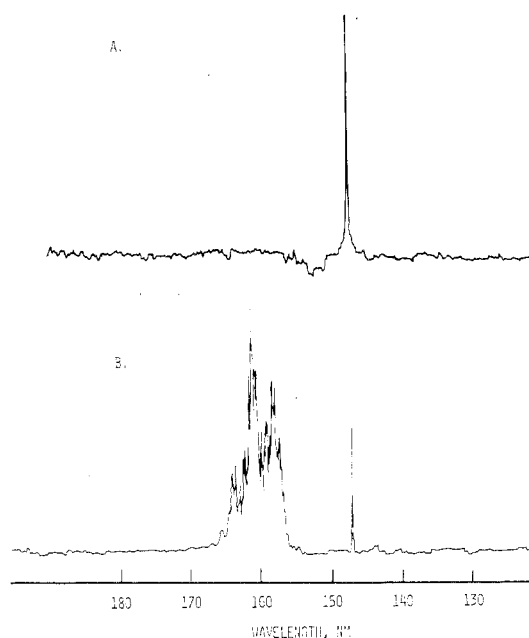


Figure 10. Output spectra of newly prepared (A) and aged (B) xenon resonance lamps. See text for details.

tion of CCl_4 with decreasing wavelengths of the photolysis light.

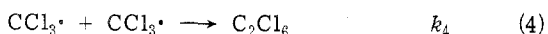
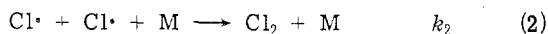
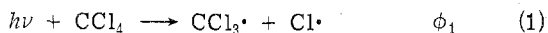
Actinometry Problems

We report here a problem with actinometry at 147.0 nm, since it could be of significance to other workers in vacuum ultraviolet photochemistry. During a series of measurements using the xenon resonance lamp, intermittent measurements of the intensity of the lamp were made, and the results appeared to indicate only moderate lamp aging; the results are summarized in Table IV. Measurements at approximately 35, 55, and 65 hr of lamp life indicated a slow decrease in lamp intensity from 7.6×10^{14} to 6.5×10^{14} quanta/sec. Nevertheless, there appeared to be a continuing decrease in product yield per unit photolysis time as the lamp aged. The apparent quantum yields for Cl_2 and C_2Cl_6 production fell from about 0.08 when the lamp was 35 hr old, to 0.02 when the lamp was 65 hr old. This apparently contradictory situation can be resolved by examining the output spectrum from the newly prepared and an aged lamp, as shown in Figure 10, and comparing this with the spectrum of CCl_4 shown in Figure 1. It will be seen that the newly prepared lamp has a strong output of nearly pure 147.0-nm light; this wavelength is well absorbed by CCl_4 , as can be seen in Figure 1. In the case of an aged lamp, however, the intensity at 147.0 nm has decreased markedly, and a complex and unidentified spectrum at 160 nm had developed. Figure 1 shows that, coincidentally, the absorption spectrum of CCl_4 has a minimum at about 155 nm, amounting at that wavelength to less than 10% of its maximum value. In contrast, the CO_2 actinometer gas absorbs

well through out this wavelength region. It appears that the "impurities spectrum" may efficiently decompose CO_2 , but may be nearly nonactinic for CCl_4 .

Discussion

The results at 253.7 nm appear to be readily explained by a mechanism involving only chlorine atoms and trichloromethyl radicals at intermediates



The fact that any appreciable product yield can be found in this system is due to the circumstances that reaction 5, perhaps surprisingly, has an activation energy of 8 kcal/mol¹⁶ and therefore a collisional probability very much less than unity. (From simple collision theory, the collision efficiency would be $e^{-8000/RT}$ or about 10^{-6} .) This reaction must become important in the photolysis of pure carbon tetrachloride at long photolysis times, which undoubtedly explains the tendency toward a plateau in Figure 2. It is reasonable, on the basis of the present results, to conclude that $\phi_1 = 1$. Although $\phi(-\text{Br}_2)$ was found to be 0.9, the difference between this value and 1.00 is probably within experimental error. During the early stages of photolysis with added Br_2 , the stoichiometry of the scavenging reaction is expected to be



so that the quantum yield of CCl bond rupture corresponds to $\phi(-\text{Br}_2) = 1.0$. Since the primary absorption act in CCl_4 , in the broad band extending from about 170 to 250 nm, is probably an $n-\sigma^*$ transition to a repulsive state,¹⁵ it is reasonable that this step should have unit efficiency. We propose here a simple kinetic scheme which allows a reasonable interpretation of the magnitude of the quantum yields for Cl_2 and C_2Cl_6 production, during the short time photolysis regime in which reaction 5 can be neglected. The key step in the mechanism is the competition represented by reactions 3 and 4, which controls whether a net production of C_2Cl_6 occurs, or whether back reaction to give the original CCl_4 takes place. This competition can be formulated as

$$\text{rate (4)/rate (3)} = k_4[\text{CCl}_3\cdot]^2/k_3[\text{CCl}_3\cdot][\text{Cl}\cdot] \quad (7)$$

From the steady-state calculation for Cl and CCl_3 concentrations

$$[\text{CCl}_3]/[\text{Cl}] = (k_2M/k_4)^{1/2} \quad (8)$$

and

$$\frac{\text{rate (4)}}{\text{rate (3)}} = \left(\frac{k_4}{k_3}\right)\left(\frac{k_2M}{k_4}\right)^{1/2} \quad (9)$$

It can be seen that

$$\phi_{\text{C}_2\text{Cl}_6} = \left(\frac{\text{rate (4)}}{\text{rate (3)} + 2 \text{rate (4)}}\right)\phi_1 \quad (10)$$

where $\phi_1 = 1$

$$\approx \text{rate (4)/rate (3)} \quad (11)$$

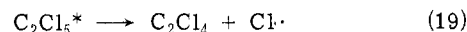
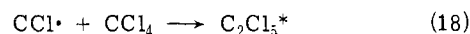
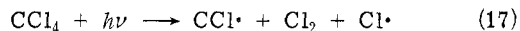
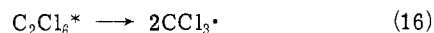
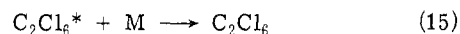
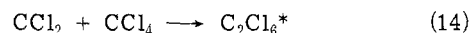
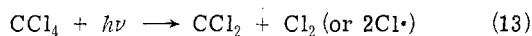
and if $k_3 \approx k_4$

$$\phi_{\text{C}_2\text{Cl}_6} = \left(\frac{k_2M}{k_4}\right)^{1/2} = \left(\frac{\text{rate 3 - body}}{\text{rate 2 - body}}\right)^{1/2} \quad (12)$$

Since the C_2Cl_6 quantum yield is predicted to be approximately equal to the square root of the ratio of the three-body to a two-body rate process, it would be reasonable to expect a C_2Cl_6 yield of a magnitude of 0.1 or even smaller. Unfortunately, it was not practical to investigate the pressure dependence suggested by eq 12, since CCl_4 absorbs light of 253.7 nm very poorly even at 100 Torr pressure.

It is clear that there must be an additional primary process at 184.9 nm. A mechanism involving only $\text{CCl}_3\cdot$ radicals could not account for the substantial yield of CCl_2Br_2 formed in the presence of added Br_2 . Production of 1,1-dichlorocyclopropane in the presence of added ethylene is additional evidence for the formation of CCl_2 as an intermediate. Participation of reactions 1-5 as in the photolysis at higher wavelengths probably persists, but the fragments involved may possess excess translational or internal energy.

In order to interpret the photolysis at 184.9 nm and lower wavelengths, we propose the following additional reactions



Production of dichlorocarbene (reaction 13) accounts for the formation of CCl_2Br_2 at 184.9 nm and all lower wavelengths, as well as formation of 1,1-dichlorocyclopropane in the presence of added ethylene. The marked pressure dependence of the Cl_2 yield (and presumably also the C_2Cl_6 yield) at 184.9 nm is probably due, at least in part, to the necessity of a subsequent collision (reaction 15) to dispose of the internal energy resulting from formation of a new C-C bond in reaction 14. A simple analysis of the pressure dependence data does not appear feasible, however, because the dynamic scheme represented by eq 7-12 must also participate at 184.9 nm. The necessity of adding a rather substantial amount of Br_2 to reach the limiting yield of CCl_2Br_2 relative to CCl_3Br , as shown in Figure 8, suggests that reaction 14 is rather efficient and difficult to compete with.

Production of CClBr_3 at 147.0 nm strongly suggests a new process producing $\text{CCl}\cdot$ fragments at this wavelength. It also appears reasonable to relate the emergence of a significant yield of C_2Cl_4 at the lower wavelengths to $\text{CCl}\cdot$ fragments, and the reaction sequence 17-18-19 seems to be a reasonable interpretation. If CCl_2 were the precursor, it would be hard to explain the lack of C_2Cl_4 at 184.9 nm.

It is possible to make an estimate of the primary quantum yields of CCl_3 and CCl_2 at 184.9 nm from the yield for bromine consumption, using the relation

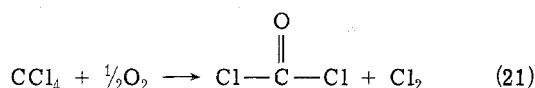
$$2\phi(\text{CCl}_2) + \phi(\text{CCl}_3) = 1.6 \quad (20)$$

We assume that the sum of the two quantum yields is unity, giving $\phi(\text{CCl}_2) = 0.6$ and $\phi(\text{CCl}_3) = 0.4$. The stoichi-

ometry implied by eq 20 is valid either if CCl₂ reacts directly with Br₂, or if it inserts into CCl₄ giving two CCl₃• radicals *via* reaction 16. In the latter case, one CCl₂ fragment gives two molecules of CCl₃Br in place of one CCl₂Br₂. Since the maximum ratio of CCl₂Br₂ to CCl₃Br achieved at high scavenger concentration is 0.7, it again appears that the insertion reaction is quite efficient. (Another possible assumption is that these are two types of CCl₂ fragments, presumably singlet and triplet states, and that one of them (the singlet) is almost immune to bromine scavenging.)

The data shown in Figure 9 for production of 1,1-dichlorocyclopropane at 184.9 nm are not incompatible with a yield of CCl₂ as high as 0.6, but the data are hard to interpret because C₂H₄ also absorbs light at this wavelength. Other complications include the possible production of an open-chain dichloropropene (which may have been masked in the analysis) and the low efficiency of C₂H₄ as a carbene scavenger. Qualitatively, however, formation of 1,1-dichlorocyclopropane is strong evidence for participation of CCl₂ in the reaction.

Interpretation of the O₂ scavenging experiment at 253.7 nm appears straightforward. It is evident from Figure 4 that the primary quantum yield for C-Cl bond rupture must be considerably greater than the net yield of Cl₂ and C₂Cl₆ in the unscavenged system. This conclusion is in qualitative agreement with the bromine scavenger data. Additionally, if the stoichiometry of the reaction in the presence of O₂ is assumed to be



then the oxygen scavenging results are in quantitative agreement with bromine scavenging. It has been known for many years that phosgene is formed when CCl₃• radicals are generated in the presence of oxygen; Steacie¹⁶ gives a discussion of the possible mechanisms involved.

An interesting and fundamental question concerns the nature of the primary photophysical act at the several wavelengths studied; in particular, is there more than one electronic state involved? Based on detailed studies of several halomethanes,^{14,15,17} it is likely that the entire broad band extending from about 160 nm to over 200 nm (with a slight tail out as far as 254 nm) is attributable to a single process, the nσ* transition. One or more other processes come in below 160 nm, generally interpreted as transitions of nonbonding halogen electrons to Rydberg states.^{14,17}

It is particularly significant that the same nσ* transition gives only reaction 1 at 254 nm, but gives both reactions 1 and 13 at 185 nm. It is strongly suggested that additional vibrational energy makes possible the split giving CCl₂ at 185 nm. This observation suggests that photolysis of CCl₄ at 254 nm, but at an elevated temperature, might also give dichlorocarbene. This process has, in fact, recently been

observed by Tedder and coworkers.⁷ For this reason we suggest that the conjugate product in reaction 7 is probably Cl₂ rather than 2Cl•, since the latter would not be energetically feasible at 254 nm, even at elevated temperature.

Extending to lower wavelengths the concept that higher vibrational levels in the n-σ* excited state lead to further fragmentation, we suggest that the same model applies to formation of CCl• fragments. We suggest that the initially formed Rydberg state undergoes internal conversion to a high vibrational level of the lower-lying n-σ* state,¹⁸ which can fragment to give CCl•, CCl₂, or CCl₃•, depending on how much energy may be lost in deactivating collisions before dissociation occurs. The implicit assumption that predissociating states are involved is not unreasonable, since fine structure has been observed in Rydberg bands of CF₂Cl₂ and CFCl₃.¹⁵

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- (18) As pointed out by one of the referees of this paper, the low wavelength spectrum of CCl₄ is not fully understood, and it is possible that more than one n-σ* transition may be involved. This possibility does not affect the gist of our conclusions, however.