

GAS-PHASE PHOTODECOMPOSITION OF CARBON TETRACHLORIDE*

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Summary

The gas-phase photolysis of CCl_4 was investigated at 213.9, 163.3 and 147.0 nm in the presence of HCl, HBr, and C_2H_6 . Quantum yields of the products measured in these mixtures at a temperature of 300 K led to the conclusion that at 213.9 nm over 90% of the photodecomposition can be attributed to the photodissociative process:



independent of pressure (5 - 60 Torr). At 163.3 nm, CCl_2 is formed via the photodecomposition process:



Contrary to earlier suggestions, CCl_2 is unreactive towards CCl_4 . Combination with other radicals and insertion into HCl are the major modes of reaction of CCl_2 .

Experiments carried out at 313.0 nm show evidence for the occurrence of photodissociation of CCl_4 . On the assumption that absorption of a photon by CCl_4 invariably leads to the detachment of a chlorine atom, the absorption cross-section at 313.0 nm is $\leq 3.7 \pm 0.4 \times 10^{-26} \text{ cm}^2 \text{ molecule}^{-1}$ (300 K). This result indicates that photodecomposition of CCl_4 in the troposphere is of minor importance as compared to other processes including diffusion up to the earth's stratosphere.

Introduction

There is substantial evidence in the literature that at wavelengths in the vicinity of 250 nm, detachment of a Cl atom represents the major primary photodissociative process [1 - 3]:



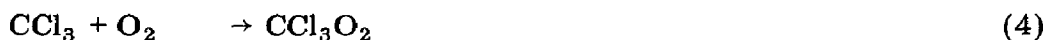
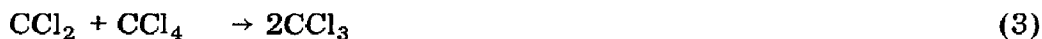
Nevertheless, observation of small amounts of C_2Cl_4 and *c*- $\text{C}_6\text{H}_{11}\text{CHCl}_2$ in

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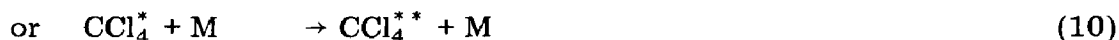
the 250 nm photolysis of CCl_4 -*c*- C_6H_{12} mixtures [2] led to the suggestion that CCl_2 radicals are produced via the photodissociative process:



More recently, Jayanty *et al.* [4] reached the conclusion that the occurrence of process (2) predominated in the shorter wavelength photolysis (213.9 nm) of CCl_4 at pressures below 10 Torr. Their conclusion is based on the observation that the quantum yield of COCl_2 is equal to 2 in the low pressure photolysis of CCl_4 - O_2 mixtures. It was assumed that process (2) followed by the following reaction mechanism could account for this result:



Because the quantum yield of COCl_2 was found to decline to a value of unity with an increase in pressure, the following more detailed photodissociative mechanism was suggested:



where CCl_4^* and CCl_4^{**} represent two distinct vibrational and/or electronic excited states of CCl_4 .

The formation of CCl_2 radicals was also evidenced by Davis *et al.* [3] in the photolysis of CCl_4 - Br_2 mixtures, where CCl_2Br_2 was observed as a product at 184.9 nm but not at 253.7 nm. On the basis of their data, the latter investigators could not decide if CCl_2 is formed via process 2 or via the alternate route:



They did, however, favor process (2), and further concluded that the CCl_2 insertion (followed by decomposition) reaction (3) is relatively fast in view of the fact that a substantial amount of bromine was needed to intercept the CCl_2 species.

The present study was undertaken in an attempt to find out (a) if process (2) and/or (12) is responsible for the formation of CCl_2 and (b) if the quantum yield of CCl_2 is indeed pressure dependent at 213.9 nm as indicated by the results of Jananty *et al.* [4].

As demonstrated in a recent study [5], Cl atom yields can be determined with reasonable accuracy in the photolysis of halocarbons in the presence of

alkanes because the Cl atoms undergo a fast hydrogen atom abstraction reaction with the alkanes. As will be shown later, the CCl_2 radicals do not react efficiently with CCl_4 or alkanes, but can nevertheless be monitored by using HCl as an interceptor molecule.

In addition to the short wavelength (213.9 - 147 nm) photolysis, experiments have been performed at the longer wavelengths which penetrate the ozone layer to reach the troposphere. The main purpose of these laboratory experiments was to verify if photolysis in the troposphere can be ruled out. This is generally assumed to be the case [6]. However, there are no reliable absorption cross-section measurements or photodecomposition experiments at $\lambda > 290$ nm in the literature to support this assumption. In one study [7], wavelengths as high as 285 nm have been used to photodissociate CCl_4 . Because the primary purpose of that investigation was to elucidate the kinetics of CCl_3 radicals, no absorption cross-section or photodecomposition quantum yields were measured.

Experimental

Materials

Analytical reagent grade CCl_4 from Mallinckrodt and reagent ACS spectrograde CCl_4 from Eastman were used in several of the photolysis experiments. The only impurity observed upon passing these chemicals through a squalane or a silicone rubber column was CHCl_3 (~0.05%). By treating the CCl_4 with NaOH, the CHCl_3 content was reduced to approximately 0.005%. As will be shown later, treatment with NaOH also removed traces of HCl which must have been present in these materials.

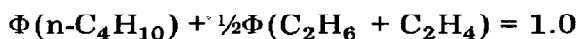
Gas chromatographs equipped with flame ionization detectors and squalane or silicone rubber columns were used for quantitative analysis of all products. Identification and calibration of the products was carried out by injecting known samples of hydrocarbons, CHCl_3 , C_2Cl_4 , CH_2CCl_2 and C_2Cl_6 .

Light sources and actinometry

The light source used in the 147, 163.3, and 213.9 nm photolysis experiments, as well as the actinometry at these wavelengths have been described in a previous publication [5]. The design of the reaction vessels used in these experiments was also the same as that used in the CF_2Cl_2 and CFCl_3 investigations. For the long wavelength experiments, a medium pressure mercury arc was employed with the following spectral energy distribution at the lines of interest: 313 nm, 100; 302.5 nm, 44; 296.7 nm, 23; 289.4 nm, 15; 280.4 nm, 15; 275.3 nm, 13; 265.2 nm, 51; 253.7 nm, 28. A cylindrical Pyrex reaction vessel (10 cm long) was used whose flat 0.3 cm thick Pyrex window showed the following transmission characteristics: 313.0 nm, 75%; 302.5 nm, 53%; 296.7 nm, 40%; 289.4 nm, 21.2%; 280.4 nm, 5.0%; 275.3 nm, 1.5%; 265.2 nm, 0.12%; 253.7 nm, < 0.01%. The distribution of the mercury

resonance radiation passing through the Pyrex window was therefore as follows: 313.0 nm, 100.0; 302.5 nm, 31.0; 296.7 nm, 12.3; 289.4 nm, 4.2; 280.4 nm, 0.97; 275.3 nm, 0.26; 265.2 nm, 0.082; 253.7 nm, < 0.004. In several of the experiments, a Corning 0-54 filter was affixed to the Pyrex window. The transmission of this filter was as follows: 313.0 nm, 37%; 302.5 nm, 1.8%; 296.7 nm, < 0.02%; 289.4 nm, < 0.04%; 280.4 nm, < 0.04%; 275.3 nm, < 0.04%; 265.2 nm, < 0.02%; 253.7 nm, < 0.01%. Therefore, the composition of the radiation passing through a Corning 0-54 filter into the Pyrex reaction vessel is as follows: 313.0 nm, 100.0; 302.5 nm, 1.51; 296.7 nm, < 7×10^{-3} ; 289.4 nm, < 4×10^{-3} ; 280.4 nm, < 6×10^{-4} ; 275.3 nm, < 3×10^{-4} ; 265.2 nm, < 4×10^{-5} ; 253.7 nm, < 10^{-6} . In order to obtain a relatively high light flux, the light from the mercury arc was focused by means of a short focal length quartz lens.

Diethylketone is used as an actinometer for these long wavelength experiments. This molecule offers the advantage that it does not absorb mercury radiation above 313.0 nm [8], thus avoiding the necessity of having to use an interference filter which would cause a reduction of the incident light. Furthermore, diethylketone photodissociates with a quantum yield of unity at 300 K to give CO, n-C₄H₁₀, C₂H₆, and C₂H₄ as products [8]. Because two C₂H₅ radicals are formed per quantum absorbed by diethylketone:



At the intensities used in these experiments, the quantum yield of ethane is equal to that of ethylene because disproportionation between C₂H₅ radicals is the only mode of formation of these products. An average value of $k_{\text{disproportionation}}/k_{\text{recombination}}$ obtained from 10 actinometry experiments is 0.132 ± 0.002 . The diethylketone experiments indicate that with the 0-54 filter in place, 8×10^{15} quanta/s of 313 nm radiation enter the Pyrex reaction vessel.

In order to verify if decomposition of CCl₄ occurs at 313 nm, CCl₄-C₂H₆ (50:1) mixtures were irradiated for periods ranging from 40 to 70 hours, at CCl₄ pressures ranging from 10 to 60 Torr. Such experiments led to the decomposition of 0.002 to 0.004% of the CCl₄. The C₂H₅Cl product could be measured with an accuracy of about 10%, while the other major product, C₂Cl₆, could be determined with an estimated accuracy of 30%. Apparently, at these low conversions and long radiation times, C₂Cl₆ is partly lost to the wall of the reaction vessel. Heating of the wall to approximately 370 K prior to injecting the irradiated sample on a chromatograph was necessary in order to obtain meaningful determinations of the C₂Cl₆ yield. Removal of the 0-54 filter increased the decomposition rate of CCl₄ by nearly a factor of 10, making it possible to measure other products such as n-C₄H₁₀ and C₂H₅CCl₃ with reasonable accuracy ($\pm 10\%$).

Because the absorption cross-section at wavelengths above 270 nm are not known at the present time, the yields of the products are expressed in terms of a cross-section for product formation. This type of information, at least for the 0-54 filter experiments, can be translated into terms of quantum

yields, once the absorption cross-section at 313 nm is known. For the case of the Pyrex cell, the absorption cross-sections would have to be weighted at the various wavelengths according to the relative intensity (as given above) of the light entering the cell in order to calculate a quantum yield averaged over the region 270 to 313 nm.

Results and Discussion

Photolysis of CCl₄ in the presence of HCl and HBr (Table 1)

At 213.9 nm, addition of as much as 1 Torr of HCl to 30 Torr of CCl₄ does not affect the quantum yield of C₂Cl₆ observed in pure CCl₄. Also, CHCl₃ appears as a minor product. Apparently under the experimental conditions used (295 K, 10¹⁴ quanta/s) the abstraction reaction:



does not occur to any significant extent.

In contrast, the addition of HBr quenches the formation of C₂Cl₆ and leads to the production of CHCl₃ with a quantum yield of approximately unity. It is apparent that this finding can best be explained through the occurrence of the fast abstraction reaction [7]:



At 163.3 and 147 nm, C₂Cl₆ is only a minor product in the photolysis of pure CCl₄. This can be attributed to a low quantum yield of CCl₃ radicals. The photolysis of CCl₄-HBr mixtures at 163.3 and 147 nm leads to values of 0.25 and 0.03, respectively, for the quantum yield of CHCl₃, which confirms the relatively minor role played by CCl₃ radicals in the short wavelength photolysis of CCl₄. In contrast with the 213.9 nm experiment described above, the addition of HCl to CCl₄ in amounts as small as 0.1% results in the appearance of CHCl₃ as a major product. The quantum yield of this product is 0.65 at 163.3 nm and 0.46 at 147 nm, independent of the concentration of HCl. The most likely explanation for this unexpected result is the occurrence of the insertion reaction:



It has been shown before [9] that CF₂ and CHF radicals undergo insertion reactions with hydrogen halides. An alternate interpretation involving an abstraction of a hydrogen atom from HCl by an excited CCl₃ radical can be ruled out. First, the quantum yield of CCl₃H is independent of the ratio of HCl/CCl₄ and second, the quantum yield of CCl₃H is much lower in the photolysis of CCl₄-HBr experiments than in the corresponding CCl₄-HCl mixtures. Oxygen reduces the quantum yield of CCl₃H by approximately a factor of two. The quantum yield of the residual CCl₃H is not greatly

TABLE 1

Photolysis of CCl_4 in the presence of HCl and HBr

Wavelength λ (nm)	Pressure (Torr)		Quantum yields	
	CCl_4	additive	CHCl_3	C_2Cl_6
213.9	5.0	—	<0.05	0.13
	5.0	HCl: 0.1	0.06 ± 0.03	0.12
	30.0	HCl: 1.0	0.06 ± 0.03	0.11
	30.0	HBr: 0.1	0.95 ± 0.1	<0.005
163.3	31.7*	—	0.20 ± 0.05	0.04
	31.7	—	0.08 ± 0.05	0.04
	31.7	HCl: 0.1	0.63 ± 0.1	0.01
		HCl: 1.0	0.59 ± 0.1	0.01
		HCl: 1.0, O_2 : 0.6	0.26 ± 0.05	<0.005
		HCl: 1.0, O_2 : 1.4	0.26 ± 0.05	<0.005
		HCl: 1.0, O_2 : 3.0	0.27 ± 0.05	<0.005
		HBr: 0.2	0.25 ± 0.05	<0.005
147.0	34.6	HCl: 0.2	0.45 ± 0.05	<0.005
		HCl: 0.3	0.49 ± 0.05	~ 0.003
		HCl: 0.6	0.47 ± 0.05	<0.005
		HCl: 1.4	0.44 ± 0.05	~ 0.003
		HBr: 0.6	0.03 ± 0.05	<0.005

*Unpurified reagent grade CCl_4 . In all other experiments, CCl_4 was treated with NaOH.

Temperature: 300 K.

affected when the ratio O_2/HCl is varied by a factor of 5. The partial reduction of the quantum yield of CCl_3H by oxygen can be accounted for by assuming that CCl_2 is formed in two different electronic states, one of which reacts faster with O_2 than with HCl. Alternatively, it is conceivable that CCl_2 reacts both by insertion into HCl and by abstraction to yield a CCl_2H radical which by recombination with a Cl atom would produce CCl_3H . If the second interpretation is correct, the quantum yield of CCl_3H observed in the oxygen-free CCl_4 -HCl experiments represents only a lower limit for the quantum yield of CCl_2 . In this study, no attempt was made to verify if $\text{CCl}_2\text{HCCl}_2\text{H}$ is a product in HCl experiments.

It follows from the interpretation of the results given in Table 1 that in the 213.9 nm photolysis of CCl_4 , CCl_2 radicals play a minor role even below the pressure region where Jayanty *et al.* [4] proposed that the quantum yield of CCl_2 is unity. On the other hand, in agreement with Davis *et al.* [3], at shorter wavelengths, CCl_2 plays an important role.

The findings reported so far rule out the occurrence of the proposed insertion reaction (3). At 300 K, reaction (3) can be ignored, because even in reagent grade CCl_4 , which contains only traces of HCl, CCl_3H is found as a product at 163.3 nm (Table 1) while the quantum yield of C_2Cl_6 is less than 0.04 under all experimental conditions. Furthermore, the quantum

TABLE 2

Quantum yields of products formed in the photolysis of $\text{CCl}_4\text{-C}_2\text{H}_6$ (1:0.5) mixtures

	213.9 nm	163.3 nm	147.0 nm
CH_4	<0.001	0.066	0.07
CHCl_3	0.12	0.62	0.40
C_2H_4	0.12	0.15	n.d.
CH_2CCl_2	0.01	0.16	0.19
C_2Cl_4	<0.001	0.009	0.01
C_2Cl_6	0.18	0.015	<0.005
$\text{C}_2\text{H}_5\text{Cl}$	0.05	0.06	0.04
C_3H_8	<0.001	0.08	0.10
$\text{C}_2\text{H}_5\text{CCl}_3 + \text{CH}_3\text{CHCCl}_2$	0.42	0.18	0.02
n- C_4H_{10}	0.24	0.68	0.50
Derived quantum yields:			
C_2H_5	1.05 ± 0.1^a	1.9 ± 0.2^b	1.4 ± 0.2^b
CCl_3	0.9 ± 0.1^a	0.25 ± 0.05^b	0.04 ± 0.02^b
CCl_2	0.05 ± 0.03^a	0.76 ± 0.2^b	0.6 ± 0.2^b

Pressure of CCl_4 : 30 Torr. Conversion: 0.05 to 0.15%. I_a : 10^{13} - 10^{14} quanta/s.^a Averaged over 15 experiments (5 to 60 Torr of CCl_4).^b Averaged over 5 experiments (20 to 60 Torr of CCl_4).

yield of CCl_3H in the $\text{CCl}_4\text{-HBr}$ experiments carried out at 163.3 and 147 nm is much smaller than one would predict on the basis of reaction (3). The $\text{CCl}_4\text{-C}_2\text{H}_6$ experiments discussed below further confirm that if reaction (3) occurs at all, its rate constant at 300 K must be very low.

Photolysis of $\text{CCl}_4\text{-C}_2\text{H}_6$ mixtures

213.9 - 147 nm (Table 2)

Table 2 gives the quantum yields of the products formed in the photolysis of $\text{CCl}_4\text{-C}_2\text{H}_6$ (1:0.5) mixtures at a total pressure of 45 Torr. At 213.9 and 163.3 nm, the quantum yields of the products listed in Table 2 are within 10% invariant of the pressure of CCl_4 (5 to 60 Torr) and the ratio $\text{CCl}_4/\text{C}_2\text{H}_6$ (3 to 0.1). Also, the product distribution and absolute yields were the same as observed in a similar series of experiments carried out at 253.7 nm. The formation of these products can be accounted for by a reaction mechanism which is analogous to that proposed earlier for the photolysis of CFCl_3 or CF_2Cl_2 in the presence of ethane.

Hydrogen atom abstraction from C_2H_6 :



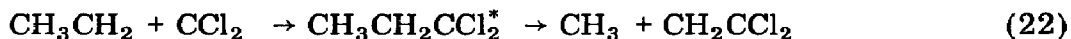
is followed by the following reaction mechanism:





According to Gregory and Wijnen [10], $k_{20}/k_{19} = 0.24 \pm 0.04$, while k_{18}/k_{17} is equal to 0.132 ± 0.002 . On the basis of these rate constant ratios, over 80% of the quantum yield of ethylene observed in the photolysis of CCl_4 - C_2H_6 mixtures at 213.9 and 163.3 nm can be accounted for by the occurrence of reactions (18) and (20). At 147 nm, C_2H_4 is also formed by direct photolysis of C_2H_6 and therefore, its quantum yield does not provide an insight into the validity of the proposed mechanism at this wavelength. Accepting the above mechanism, a value of 3.5 ± 0.3 was obtained for $k_{19}^2/k_{17} \cdot k_{21}$ averaged over 15 CCl_4 - C_2H_6 experiments carried out at 213.9 nm at varying pressures and compositions. This is in good agreement with the value of 3.2 ± 0.4 derived from the photolysis of CCl_4 - $(\text{C}_2\text{H}_5)_2\text{CO}$ mixtures [10]. In the lowest pressure experiments (5 Torr) about 15% of the vibrationally excited $\text{C}_2\text{H}_5\text{CCl}_3$ formed in reaction (19) decomposed to yield CH_3CHCl_2 . The yield of this product is added to that of the stabilized $\text{C}_2\text{H}_5\text{CCl}_3$ in all calculations (Table 2).

While the reactions of CCl_3 and C_2H_5 are well established, much less is known about the reactivity of CCl_2 . It is clear, however, that three products in the 163.3 and 147 nm photolysis, C_2Cl_4 , CCl_3H , and CH_2CCl_2 , are formed with much higher quantum yields than at 213.9 nm. By analogy with what is known about the CF_2 and CFCl radicals, the CH_2CCl_2 product can be tentatively ascribed to the recombination reaction:



Similarly, the small quantum yield of C_2Cl_4 observed at 163.3 and 147 nm can be attributed to the reaction:



As was seen in the short wavelength photolysis of CF_2Cl_2 - C_2H_6 mixtures [5], CH_4 and C_3H_8 appear as significant products (Table 2). These can be accounted for by reaction of the CH_3 radicals formed in process (22).

The formation of CHCl_3 as a major product at 163.3 and 147 nm can, in part, be accounted for by the insertion of CCl_2 into HCl (reaction 15). The high quantum yield of n-butane in these experiments indicates that the yield of HCl formed via reaction (16) must be relatively high. Reaction of CCl_2 with HCl is confirmed by the observation that addition of 0.3% HCl to a CCl_4 - C_2H_6 mixture completely inhibits the formation of CH_2CCl_2 and of C_2Cl_4 , without affecting the quantum yields of the other products. On the other hand, it is not clear why insertion of CF_2 or CFCl into the HCl product was not observed in a previous study of the photolysis of CF_2Cl_2 - C_2H_6 and CFCl_3 - C_2H_6 mixtures. This apparent inconsistency will be dealt with in more detail in a forthcoming report on the photolysis of CHFCl_2 and CHF_2Cl .

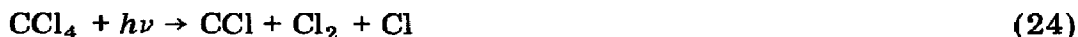
TABLE 3

Photolysis of CCl₄ at 270 - 313 nm

	$\sigma \times 10^{26} \text{ (cm}^2 \text{ molecule}^{-1}\text{)}^a$		
	Pyrex cell 300 K ^b	Pyrex cell + 0-54 filter	
		300 K ^b	376 K
C ₂ H ₄	0.6 ± 0.1	<0.02	<0.4
C ₂ H ₅ Cl	11.0 ± 1.0	3.7 ± 0.4	23.0 ± 2.0
n-C ₄ H ₁₀	0.21 ± 0.02	<0.2	<0.4
C ₂ H ₅ CCl ₃	2.9 ± 0.5	<0.2	<2.0
C ₂ Cl ₆	10.0 ± 3.0	n.d.	15.0 ± 10.0

Pressure CCl₄: 60 Torr; pressure C₂H₆: 1.0 Torr.^aProduct cross-section (see experimental section).^bAveraged over five experiments.

Reactions (15) to (23) account for all of the products except for C₂H₅Cl. The latter product is probably formed by abstraction of a Cl atom from CCl₄. Accepting the proposed reaction mechanism, quantum yields of C₂H₅, CCl₃, and CCl₂ can be derived in a straight-forward manner [5]. The values given in Table 2 show rather large error limits which reflect the inaccuracy of the quantum yield measurements of some of the minor products. In agreement with the CCl₄-HBr experiments, a rapid decrease in the quantum yield attributed to CCl₃ occurs when the wavelength is decreased. Furthermore, the variations in the quantum yield of CCl₂ with wavelength are in agreement with the interpretation of the CCl₄-HCl experiments (Table 1). It is now evident that the photolysis of CCl₄ at 213.9 nm can best be described by a detachment of one Cl atom from CCl₄ in the primary process, while at 163.3 nm, detachment of two Cl atoms from CCl₄ accounts for about 75% of the photodecomposition. The drop in the derived quantum yields of C₂H₅, CCl₃, and CCl₂ from 163.3 to 147 nm cannot be accounted for by the proposed mechanism. The occurrence of an additional fragmentation process:



requiring 7.6 eV, may be operational at 147 nm (8.4 eV). Evidence for the formation of CCl at 147 nm has been presented by Davis *et al.* [3] who observed CClBr₃ in the photolysis of CCl₄-Br₂ mixtures. Even though in our experiments no products which could be ascribed to reaction of CCl were observed, formation of CCl cannot be ruled out. In summary, these results in conjunction with those reported by other investigators show that from 213.9 nm to 285 nm the photolysis of CCl₄ occurs mainly via process (1).

313 nm

Photolysis of $\text{CCl}_4\text{-C}_2\text{H}_6$ mixtures carried out with the medium pressure mercury arc (see experimental) focused on a Pyrex cylindrical cell gave products (see Table 3) which can be accounted for by process (1). Because in these experiments, the steady state concentration of the C_2H_5 radicals is approximately 10^3 times smaller than for the experiments represented in Table 2, recombination reactions involving C_2H_5 are relatively less important as compared to abstraction of a Cl atom from CCl_4 to give $\text{C}_2\text{H}_5\text{Cl}$ as a product. Provided C_2H_5 is entirely formed by reaction (16), the quantum yield of the Cl atoms is given by the expression:

$$(\text{Cl}) = 2.26 (\text{C}_4\text{H}_{10}) + 1.24 (\text{C}_2\text{H}_5\text{CCl}_3) + (\text{C}_2\text{H}_5\text{Cl})$$

When a Corning 0-54 filter is inserted between the mercury lamp and the Pyrex reaction vessel, there is an additional drop of more than a factor of ten in the absorbed intensity with the resulting effect that products such as C_4H_{10} and $\text{C}_2\text{H}_5\text{CCl}_3$ were below the detection limit. One can, therefore, make the approximation that the yield of $\text{C}_2\text{H}_5\text{Cl}$ represents the yield of Cl atoms or the extent of decomposition of CCl_4 according to process (1). With the 0-54 filter in place, the cross-section of decomposition as given by the yield of $\text{C}_2\text{H}_5\text{Cl}$ is $3.7 \times 10^{-26} \text{ cm}^2 \text{ molecule}^{-1}$ at 300 K, and $2.3 \times 10^{-25} \text{ cm}^2 \text{ molecule}^{-1}$ at $376 \pm 5 \text{ K}$. The 300 K value is not unreasonable if one considers the absorption cross-section of CCl_4 reported in the literature (Fig. 1) over the range 180 - 253.7 nm. If one accepts that at 313 nm, photodecomposition occurs for each quantum absorbed by CCl_4 , the measured photodecomposition cross-section can be equated to the absorption cross-section. It is seen (Fig. 1) that at 300 K, a value of $3.7 \times 10^{-26} \text{ cm}^2 \text{ molecule}^{-1}$ is within reasonable agreement with what would be expected from a near straight-line extrapolation of the cross-section from 253.7 to 313 nm. The 6.2-fold increase of $\text{C}_2\text{H}_5\text{Cl}$ observed when the temperature is raised from 300 K to 376 K seems reasonable if one considers that a similar temperature increase at 250 nm causes a 2.5-fold increase in the absorption cross-section. As expected, the experiments carried out in the absence of the 0-54 filter show a higher decomposition cross-section. The observed increase (Table 3) corresponds within a factor of 2 with that calculated on the basis of the transmission curve of Pyrex (see experimental) and the absorption cross-sections at each mercury resonance line obtained by interpolation between 253.7 and 313.0 nm (Fig. 1). Because the photodecomposition cross-section in the Pyrex vessel experiments was found to be independent of the pressure of CCl_4 (10 to 60 Torr) it may be surmised that the excited CCl_4 molecules formed at all of the mercury resonance lines transmitted through Pyrex do not undergo collisional deactivation.

At the time of this writing, reliable absorption cross-sections of gaseous CCl_4 at wavelengths above 280 nm are not available. If it turns out that the absorption cross-section is higher than the photodecomposition cross-section reported here, one would have to conclude that a second electronically excited CCl_4 is formed which does not undergo photodecomposition but which could still be reactive towards oxygen.

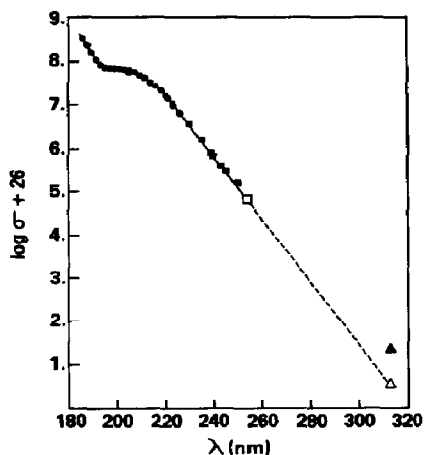


Fig. 1. Absorption cross-section ($\text{cm}^2 \text{ molecule}^{-1}$) of CCl_4 versus wavelength. ●, Ref. [11], room temperature; ■, ref. [12], 303 K; □, ref. [2], 300 K; △ (300 K) and ▲ (376 K) based on photolysis (see discussion).

In conclusion, it can be stated that accepting a photodecomposition cross-section of $3.7 \times 10^{-26} \text{ cm}^2 \text{ molecule}^{-1}$ at 313 nm rules out any extensive photodissociation of gaseous CCl_4 in the troposphere. Furthermore, the actual photodecomposition cross-section might still be lower than that derived from the observed yield of $\text{C}_2\text{H}_5\text{Cl}$. For instance, if residual impurities would still have been present in CCl_4 , their photolysis might have led to the production of free radicals which could result in the formation of $\text{C}_2\text{H}_5\text{Cl}$.

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