

PRIMARY PROCESSES IN THE PHOTOCHEMICAL DECOMPOSITION OF 1,1,1-TRICHLOROETHANE AT 147 nm

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Summary

The major product observed in the 147 nm photolysis of 1,1,1-trichloroethane (CH_3CCl_3) is 1,1-dichloroethylene (CH_2CCl_2). Vinyl chloride and acetylene, however, are also formed in significant quantities. The CH_2CCl_2 is undoubtedly produced by the molecular elimination of HCl. Symmetry considerations suggest that the electronically excited state of CH_3CCl_3 initially formed yields CH_2CCl_2 via an intermediate electronically excited state of CH_3CCl_3 of lower symmetry. The olefin itself may well be electronically excited at the time of its formation. Other parallel primary processes include the elimination of molecular chlorine and carbon-carbon bond fission.

The extinction coefficient of CH_3CCl_3 at 147 nm and 296 K was determined to be $\epsilon = (1/PL) \ln(I_0/I) = 475 \pm 75 \text{ cm}^{-1} \text{ atm}^{-1}$.

Introduction

There have been a number of recent investigations into the ultraviolet and vacuum ultraviolet photolyses of haloethanes [1 - 8]. At 147 nm molecular eliminations, particularly of HX, are the dominant primary processes. For haloethanes containing at least one carbon-chlorine bond and no more than two carbon-fluorine bonds the higher excited states formed at 147 nm (8.4 eV) have been characterized as "molecular Rydberg" states [9, 10] and there is no reason not to suppose that there is a direct correlation between these observations. The chlorine substituted haloethanes, however, all begin to absorb at around 6 eV, corresponding to a valence transition represented by $\bar{\text{Cl}} \rightarrow (\text{C}-\text{Cl})^*$ and implying excitation of an electron from a chlorine lone pair orbital to a valence shell orbital that is antibonding with respect to carbon-chlorine [9]. As a result carbon-chlorine bond cleavage is the major mode of photodecomposition at longer wavelengths [11]. In terms of the localization and delocalization of electrons the electronic states formed at approximately 6 eV can be thought of as heavily localized with respect to

the carbon-chlorine bond, while those at 147 nm are somewhat delocalized such that the carbon-carbon interaction is strongly bonding and the carbon-hydrogen and carbon-halogen interactions are somewhat antibonding with respect to the corresponding ground states.

The photolysis of 1,1-C₂H₄Cl₂ at 147 nm [5] not only gave rise to significant and presumably α,β -HCl elimination but also to the α,α elimination of molecular chlorine. The photolysis of 1,1,1-C₂H₃Cl₃ at 147 nm was undertaken to examine further the competition between what must now certainly be α,β hydrogen chloride elimination and α,α dehalogenation.

Experimental

The apparatus, reaction vessel and xenon resonance lamp used in these experiments have been described previously [5]. The trimethylamine photoionization actinometer used to measure light intensities and hence quantum yields has also been described elsewhere [12]. Measurement of the saturation photoionization currents of mixtures of (CH₃)₃N and CH₃CCl₃ at 296 K yielded a value of $475 \pm 75 \text{ cm}^{-1} \text{ atm}^{-1}$ for the extinction coefficient of CH₃CCl₃ at 147 nm. In runs using HI the net amount of light absorbed by the CH₃CCl₃ was calculated using the literature value of $50 \pm 20 \text{ cm}^{-1} \text{ atm}^{-1}$ for the extinction coefficient of HI [13].

In early experiments a significant decrease in the transmission of the lithium fluoride window was observed after each experiment. By subsequently working at low intensities ($(1.0 \pm 0.1) \times 10^{13} \text{ photon s}^{-1}$) and low conversions (0.02 - 0.1%) this decrease in intensity during each run never exceeded a few per cent. However, the window was still cleaned after each run using an abrasive slurry of CCl₄ and Al₂O₃. The contamination of the window was thought to be due to subsequent reactions of the product CH₂CCl₂. Therefore analyses were performed immediately upon completion of each experiment.

Product analysis was by isothermal gas chromatography (Hewlett-Packard Model 5830A, with twin flame ionization detectors) using 3 m Porapak N and Porapak T columns (3 mm i.d.) at 125 °C and at helium flow rates of 25 cm³ min⁻¹. The use of flame detectors only prevented specific analysis for HCl and Cl₂. The reaction products 1,1-C₂H₂Cl₂, C₂H₃Cl, CH₃Cl, C₂H₆, C₂H₄, C₂H₂ and CH₄ were identified by comparison of their retention times with those of authentic samples from which calibration factors were also obtained. The peak identified as CHCl had the same retention time as the major product arising from the photolyses of CH₂CCl₂, *cis*-CHClCHCl and *trans*-CHClCHCl [14]. It was assigned the same detector sensitivity as that of acetylene. The absence of significant yields of higher molecular weight products was established by analyses using a Porasil S/Carbowax 4000 column capable of eluting hexachlorinated hydrocarbons within 45 min at 125 °C at a helium flow rate of 30 cm³ min⁻¹.

The trichloroethane (CH₃CCl₃) was obtained from the J. T. Baker Chemical Company. A final estimated purity of 99.994% was obtained by

fractional distillation using a 125 theoretical plate spinning band column. The NO, HI and CF₄ were obtained from Matheson. The NO and HI were further purified by low temperature trap-to-trap distillations. The CF₄ (99.7%) was used without further purification. Precise measurements of low pressures were obtained using a fused quartz Bourdon gauge (Texas Instruments Model 145).

Results

The results are summarized in Table 1. Each entry in the table is the average of at least two nearly identical experiments. Quantum yields were independent of the overall percentage conversion in the range 0.02 - 0.1%. The accuracy of the quantum yields is estimated to be $\pm 10\%$ for yields in excess of 0.1 and $\pm 15\%$ for quantum yields significantly less than 0.1.

The major product is CH₂CCl₂. Its yield increases somewhat as a function of increasing pressure and also very slightly with the addition of HI and NO. The yield of CH₂CHCl increases quite markedly with increasing pressure and at low pressures would appear to be marginally enhanced by the addition of HI. However, the main purpose of adding HI to the system is simply to "trap" radicals, particularly methyl radicals as methane. It is doubtful whether very small modifications to the quantum yields of other products can be considered significant with respect to the primary processes. The yield of acetylene decreases with increasing pressure such that the sum of the quantum yields of CH₂CHCl and CHCH is a constant (runs 1 - 7). The production of small quantities of CHCl is readily suppressed by an increase in pressure. As expected the yield of CH₄ increases in the presence of HI and is zero in the presence of NO. Analysis for CH₄ in the presence of large quantities of CF₄ (runs 6 and 7) was not possible. The small yield of ethylene is obviously of free radical origin. No C₂H₄ is formed in the presence of NO and little, if any, in the presence of HI. Similarly ethane is undoubtedly of radical origin. The little that is produced in the absence of HI and NO is seen at the higher pressures. Small yields of methyl chloride are also observed in runs in which NO is absent. Exploratory experiments in which CH₄ was added in a 100-fold excess in an attempt to trap chlorine atoms did not result in any increase in CH₃Cl or C₂H₆. Chloroform (CHCl₃) may well have been a product in some runs. However, it could not be detected in the presence of a large excess of CH₃CCl₃. The absence of any significant yield of higher molecular weight products has previously been mentioned.

Discussion

Elimination of HCl

The large and fairly constant yield of CH₂CCl₂ and the absence of radical products that would arise from the expulsion of one or more chlorine

TABLE 1
Quantum yields of products obtained in the 147 nm photolysis of CH_2CCl_3

Run	$P(\text{CH}_2\text{CCl}_3)$ (Torr)	$P(\text{additive})$ (Torr)	Quantum yields Φ									
			CH_4	C_2H_4	C_2H_6	CH_3Cl	C_2H_2	CHClCl	$\text{C}_2\text{H}_3\text{Cl}$	CH_2CCl_2		
1	1.37		0.045	0.044	0.0	0.022	0.22	0.021	0.066	0.52		
2	2.42		0.045	0.044	0.0	0.022	0.21	0.019	0.071	0.52		
3	3.13		0.045	0.044	0.0	0.021	0.21	0.017	0.069	0.53		
4	4.56		0.045	0.043	0.006	0.018	0.19	n.d.	0.085	0.54		
5	11.96		0.043	0.042	0.006	0.018	0.15	0.009	0.095	0.57		
6	7.36	CF_4 89	n.d.	0.010	0.012	0.017	0.14	0.0	0.14	0.57		
7	10.37	CF_4 357	n.d.	0.0	0.027	0.015	0.089	0.0	0.19	0.58		
8	1.28	HI 0.094	0.11	0.0	0.0	0.014	0.19	0.017	0.085	0.55		
9	4.92	HI 0.51	0.12	0.0	0.0	0.013	0.16	0.010	0.090	0.57		
10	5.01	HI 0.45	0.11	0.0	0.0	0.017	0.17	0.014	0.095	0.56		
11	9.96	HI 0.80	0.11	0.008	0.0	0.016	0.14	0.010	0.10	0.59		
12	6.14	HI 0.50 CF_4 50	0.12	0.0	0.0	0.009	0.11	0.0	0.13	0.60		
13	5.07	NO 0.55	0.0	0.006	0.0	0.008	0.14	0.013	0.090	0.56		
14	12.59	NO 1.14	0.0	0.0	0.0	0.0	0.15	0.008	0.11	0.58		
15	25.08	NO 2.87	0.0	0.0	0.0	0.0	0.12	0.0	0.13	0.58		
16	54.16	NO 5.51	0.0	0.0	0.0	0.0	0.10	0.0	0.14	0.57		
17	10.86	CF_4 238 NO 1.1	0.0	0.0	0.0	0.0	0.075	0.0	0.18	0.58		
18	7.36	CF_4 522 NO 0.84	0.0	0.0	0.0	0.0	0.065	0.0	0.19	0.60		

n.d. indicates not determined.

or hydrogen atoms from CH_3CCl_3 leads us to conclude that the major primary mode of photodecomposition in the 147 nm photolysis of CH_3CCl_3 is the molecular elimination of HCl from a short lived electronically excited state of trichloroethane ($\text{CH}_3\text{CCl}_3^\dagger$):



It is to this, by far the most important primary process, that the following discussion is mainly, though not exclusively, devoted.

With reference to the ground electronic states of CH_3CCl_3 , CH_2CCl_2 and HCl, reaction (2) is about 13 kcal mol^{-1} endothermic*. At 147 nm the photon energy is $194 \text{ kcal mol}^{-1}$. If CH_2CCl_2 and HCl were to be formed in their ground states there would be an excess energy of about 181 kcal to be distributed between them as energy of vibrational excitation. The vibrational energy content of HCl must be less than its bond strength ($103 \text{ kcal mol}^{-1}$) if it is not to dissociate into atoms. This in turn requires that the vibrational energy content of ground state CH_2CCl_2 be at least 78 kcal mol^{-1} , with the distinct probability that it is much more and substantially in excess of the activation energy for HCl elimination** to give CHCCl . The absence here of significant yields of the appropriate acetylene, CHCCl , leads us to believe that one or both of the products of reaction (2) are more likely to be electronically excited at the time of their formation. However, the first excited singlet state of HCl is not accessible [18]. Therefore it is only electronic excitation of the CH_2CCl_2 which need be considered. There is evidence for a number of electronic states of CH_2CCl_2 corresponding to energies of less than $180 \text{ kcal mol}^{-1}$. The optical spectrum of dichloroethylene shows a number of transitions in the region 155 - 260 nm [19]. Wampler and Böttenheim [14] and Moore [20] refer to a triplet state at about 90 kcal above the ground state. Ausubel and Wijnen [21] have photolyzed CH_2CCl_2 using a medium pressure mercury arc, *i.e.* at wavelengths longer than 200 nm, and have proposed that two electronically excited states of CH_2CCl_2 are formed. One state is believed to decompose by carbon-chlorine bond fission while the other is believed to undergo mainly HCl elimination. The ratio of CH_2CCl radicals to CHCCl was found to be pressure dependent, an indication that at least one of these excited states was fairly long lived. It is therefore quite possible that some, if not all, of the CH_2CCl_2 formed here is similarly excited. However, since the CH_2CCl_2 in this case is the product of a photodecomposition and the extent of its further decomposition is obviously small, it is likely that its degree of vibrational excitation would be less than those species created by direct photolysis using

*Values of ΔH_f^0 were obtained from Franklin *et al.* [15] and Chao *et al.* [16].

**The activation energy for the elimination of HCl from $\text{C}_2\text{H}_3\text{Cl}$ has previously been estimated [5] to be approximately 61 kcal mol^{-1} using the method described by Benson and Haugen [17]. The activation energy for the elimination of HCl from 1,1- $\text{C}_2\text{H}_4\text{Cl}_2$ should not be significantly greater and certainly much less than 78 kcal mol^{-1} .

a mercury arc and hence the CH_2CCl_2 should be even more easily quenched. Thus only at low pressures would one expect $\text{CH}_2\text{CCl}_2^\dagger$ from reaction (2) to decompose to any extent by the following reactions proposed by Ausubel and Wijnen [21]:



The increase here in the yield of vinyl chloride at low pressures in the presence of HI ($\Delta\Phi \approx 0.02$) can be interpreted as evidence for reaction (3) and the yield of CHCCl ($\Phi \approx 0.02$) at low pressures as evidence for reaction (4). Together these two processes would account for most of the small decrease in the quantum yield of CH_2CCl_2 ($\Delta\Phi \approx 0.06$) with decreasing pressure (see runs 1 - 7). There is no reason to suppose that the two states proposed by Ausubel and Wijnen would be formed here in the same ratio as in their work. There is also no reason why one state could not be the product of the other, in this instance through some process such as an internal conversion. This would then only require the initial formation of one excited state of CH_2CCl_2 in reaction (2).

On the basis of the above discussion, though it is qualitative in nature, we believe that the CH_2CCl_2 produced in reaction (2) is formed in at least one electronically excited state. This leads us to propose further that the most likely (singlet) state is that corresponding to the very broad $\pi \rightarrow \pi^*$ ($^1A_1 \rightarrow ^1A_1$) transition observed in the ultraviolet spectrum of CH_2CCl_2 [19]. An examination of processes (1) and (2) with respect to the overall changes in symmetry that must occur will indicate that the initially formed excited state of CH_3CCl_3 must itself transform to an intermediate state of a symmetry which correlates with the products (CH_2CCl_2 (1A_1) and ground state HCl).

This is best illustrated by assuming initially that the $\pi \rightarrow \pi^*$ state of CH_2CCl_2 is planar and of C_{2v} symmetry, *i.e.* an A_1 state with the same symmetry as the electronic ground state. Since HCl itself is produced in its ground state and its resolution in C_{2v} symmetry is therefore also A_1 [22], the direct product of the symmetry states of CH_2CCl_2 and HCl then yields an A_1 state for the symmetry of the immediate precursor, that is the CH_3CCl_3 intermediate. If the initial excitation of the trichloroethane (C_{3v} symmetry) at 147 nm is analogous to other chloroethanes, then the excited MO is a molecular Rydberg type. In C_{3v} symmetry the np Rydberg orbitals transform as the $a_1 + e$ irreducible representations[†] and one may then derive from the orbital transitions $a_1 \rightarrow e$, $a_2 \rightarrow e$, $e \rightarrow e$ and $e \rightarrow e$ respectively the following possible excited states 1E , 1E , $^1E + ^1A_1 + ^1A_2$ and $^1E + ^1A_1 + ^1A_2$ for CH_3CCl_3 . Resolution of these symmetry species into C_{2v} gives the states 1A_1 , 1A_2 , $^1B_1 + ^1B_2$ and there is thus a correlation of an intermediate of C_{2v} symmetry with the 1A ground and excited states of CH_2CCl_2 . Reaction (1) may then be rewritten

[†]Note that the ns Rydberg orbitals transform as an a_1 irreducible representation.

presence of HI may be fortuitous. It is certainly difficult to propose any reactions of methyl radicals that would yield both ethane and ethylene. In previous papers [4 - 8] we have noted the unusual reactivity of the hot substituted ethyl radicals produced at these short wavelengths. The formation of very hot and possibly electronically excited CH_3 and CCl_3 radicals at fairly large concentrations fairly close to the window may also result in reactions not observed in thermal systems. One could of course postulate a number of other exotic primary processes and subsequent radical reactions to explain the formation of small yields of C_2H_4 , C_2H_6 and CH_3Cl ; however, they would be purely speculative and unrelated to the major primary processes.

In summary the 147 nm photolysis of 1,1,1-trichloroethane is similar to the 147 nm photolysis of 1,1-dichloroethane [5]. Molecular HCl elimination is the dominant primary process in both cases and the yields are very similar (about 60%).

The olefin products accompanying HCl elimination undergo very little subsequent decomposition, which we have in both cases attributed to the formation of electronically excited states which are more efficiently deactivated than the corresponding vibrationally excited ground states. The smaller and less pressure dependent yield of C_2H_2 observed in the 147 nm photolysis of 1,1- $\text{C}_2\text{H}_4\text{Cl}_2$ was thought to arise from the electronically excited $\text{C}_2\text{H}_3\text{Cl}$ formed by the α, β -HCl elimination. In the present study we are inclined to assign the somewhat larger and more pressure dependent yield of C_2H_2 to the decomposition of the vibrationally excited ground state of $\text{C}_2\text{H}_3\text{Cl}$ arising from the α, α elimination of Cl_2 .

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