THE PHOTOCHEMISTRY OF ETHYL CHLORIDE

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Summary

Ethyl chloride and deuterium-labelled ethyl chlorides have been photo-lyzed at 184.9, 163.3, 147.0 and 123.6 nm in the gas phase and at 163.3 and 147.0 nm in the liquid phase. The use of NO, O_2 and HI as radical scavengers has permitted a determination of the quantum yields of primary photodecomposition processes as a function of wavelength. At low energies, excitation of an electron into an antibonding σ^* orbital leads primarily to C—Cl bond cleavage, while at higher energies this process is largely replaced by loss of HCl and hydrogen. Both 1,1- and 1,2-HCl eliminations are observed. The absence of significant amounts of hydrogen atom production at 163.3 nm and at low pressures suggests that one excited state may be responsible for HCl elimination and a second for chlorine atom loss, in agreement with the mechanism of Ichimura *et al.*

1. Introduction

Recent concern about the effects of chlorine atoms on stratospheric ozone has prompted research in this laboratory to determine the modes of decomposition of several halogenated methanes [1 - 3]. Our recent investigation into the photochemistry of methyl chloride [3] revealed that several primary processes are operative, depending on the exciting wavelength. Irradiation in the $\sigma^* \leftarrow n$ band results in C—Cl bond cleavage with a quantum yield approaching 1.0, while several other processes become important at shorter wavelengths. Until now there have been few studies on the photochemistry of ethyl chloride. Tiernan and Hughes [4] irradiated chloroethane at 123.6 nm and found ethylene to be the predominant product. Cremieux and Herman [5] found similar results both at 123.6 and 104.8 - 106.7 nm. Ichimura *et al.* [6] irradiated chloroethane at 147.0 nm, again with similar results. Several other halocarbons also show predominantly 1,2-XCl elimination at these wavelengths [7]. It has been suspected that at

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longer wavelengths C—Cl bond cleavage may be the dominant process, by analogy with the results from the photolysis of alkyl bromides [8] and iodides [9], 1,1-dichloroethane [10] and chloromethane [3], yet there has been no experimental verification of this important point.

The purpose of this research is to determine the primary photochemical processes which ethyl chloride undergoes at several wavelengths from 123.6 to 184.9 nm. To achieve this end experiments were carried out at various pressures and in the liquid phase in the presence and absence of NO, O_2 and HI as radical traps. Additionally, deuterated and partially deuterated ethyl chloride were used to clarify the reaction mechanisms.

2. Experimental procedure

2.1. Materials

Ethyl chloride was purified by trapping with liquid nitrogen the effluent from a gas chromatograph equipped with a squalane column. This treatment reduced the major impurity, ethylene, to a level of less than 1×10^{-4} %. Similar treatment of C_2D_5Cl reduced the C_2D_4 to less than 4×10^{-5} % while two unidentified impurities remained in quantities of 7×10^{-4} and 2×10^{-3} % but did not interfere with product analysis. The C_2D_5Cl had an isotopic purity of 99.22% per deuterium atom. CD_3CH_2Cl and CH_3CD_2Cl had isotopic purities of 99.4 and 98.8% per deuterium atom respectively, and were used without further purification except for the usual low temperature degassing procedures.

2.2. Product analysis

A gas chromatograph equipped with a 12 m squalane column was used. Identification of products was made by comparison of retention times with those of authentic samples. Mass spectral analysis of products and isotopic distribution patterns were determined on a high resolution mass spectrometer. In each case the results are corrected for isotopic purity.

2.3. Light sources and actinometry

Irradiation of wavelength 123.6, 147.0, 163.3 and 184.9 nm was obtained from microwave-operated krypton, xenon, bromine and mercury resonance lamps. The construction and operation of these lamps has been described previously [2, 11], as has the actinometry at 123.6, 147.0 and 163.3 nm [3]. The output of the lamps was reproducible except for that of the mercury lamp, which tended to decrease during a run in a non-reproducible manner. Therefore only relative quantum yields are available for this wavelength. Similarly only relative quantum yields are reported for the liquid phase experiments.

Total conversions were generally not more than 0.1% in order to minimize secondary reactions. Although errors in the quantum yields are difficult to assess, examination of the scatter from run to run suggests that the

TABLE 1

Quantum yields of products in photolysis of C_2H_5Cl at 296 K

Wavelength (nm)	Pressure (Torr)	CH_4	C_2H_2	C_2H_4	C_2H_6	C_3H_6	C_3H_8	CH_3Cl	C_2H_5Cl	C_4H_{10}	Total
123.6	18.1	0.062	0.18	0.67	0.11	0.025	0.009	0.015	0.23	n.d.	1.30
147.0	25	0.048	0.069	0.37	0.13	0.025	0.025	0.011	0.14	0.03	0.85
	Liquid, 0 °C[a]	0.046	0.013	0.22	0.37	n.d.[b]	n.d.	n.d.	0.17	0.19	(1.0)
163.3	25	0.025	0.023	0.16	0.41	n.d.	n.d.	n.d.	0.098	0.059	0.78
184.9	25[a]	0.014	0.031	0.22	0.40	0.005	0.009	n.d.	0.13	0.20	(1.0)

[a]Relative quantum yields.
[b]n.d., not determined.

TABLE 2

Photolysis of partially labelled ethyl chloride at 296 K

	Percentage distribution								
	CH$_3$CD$_2$Cl (25 Torr)				CD$_3$CH$_2$Cl (100 Torr)				
	123.6	147.0	163.3	184.9	123.6	163.3			184.9
CD$_2$CDH					23.8	17.0	18.8[a]	12.4[b]	28.0[a]
CD$_2$CH$_2$	85.3	81.5[a]	85.7	85.0	76.2	83.0	81.2[a]	87.6[b]	72.0[a]
CDHCH$_2$	14.7	18.5[a]	14.3	18.5					
CD$_3$H		5.6							
CD$_2$H$_2$		13.0							
CDH$_3$	18.4	11.6	6.6	4.0					
CH$_4$	81.6	69.7	93.4	96.0					
D$_2$	6.3	13.7	13	34					
HD	26.1	41.0	25	44					
H$_2$	67.6	45.3	62	22					

Total quantum yields

ϕ(H$_2$)	0.55	0.14	0.006	0.002					

[a]Measured in the presence of O$_2$.
[b]Liquid phase (0 °C).

results are reproducible to within 20%. Relative quantum yields for a given run are normally more accurate. The accuracy of the mass spectral data is estimated to be ±10%.

3. Results

The results from the gas phase photolysis experiments are presented in Table 1. The major products observed at longer wavelengths are primarily ethane, ethylene, vinyl chloride and n-butane. At shorter wavelengths ethylene and hydrogen become the dominant products; acetylene also becomes important, while the quantum yields of ethane and (particularly) n-butane decrease. The quantum yield of vinyl chloride shows a modest but irregular increase with increasing energy. Propane and propylene were also occasionally observed with quantum yields of less than 0.02. To the extent that literature data are available for comparison, these results agree reasonably well. The relative quantum yields at 123.6 nm (18.1 Torr) agree with those from Cremieux and Herman (5 Torr) [5] except for a factor of about 2.3 which may arise from errors in actinometry. Similarly the 147.0 nm measurements agree very well with those of Ichimura et al. [6]. Their quantum yield for ethylene is somewhat larger and their relative amounts of ethane and n-butane differ, but this discrepancy probably reflects any differences in light flux resulting in differing relative amounts of abstraction and recombination for ethyl radicals.

TABLE 3

Quantum yields for photolysis of C_2H_5Cl (25 Torr) + NO (1 Torr)

Wavelength (nm)	CH_4	C_2H_2	C_2H_4	C_2H_6	CH_3Cl	C_2H_3Cl
123.6	0.02	0.16	0.59	0.009	0.013	0.086
147.0	0.02	0.082	0.39	0.005	0.011	0.055
163.3	0.02	0.070	0.18	0.007	0.006	0.017
123.6[a]	0.01	0.082	0.57	0.003	0.011	0.060

[a] Using C_2D_5Cl, normalized to $\phi(C_2D_4) = 0.57$.

One liquid phase experiment using 147.0 nm irradiation was run for comparison and is also presented in Table 1. The results resemble the low energy experiments in that the quantum yields of acetylene and ethylene are small, while the quantum yields of ethane and n-butane are large.

For further analysis of the chemistry in the absence of quencher, the isotopic labelling of products arising from the photolysis of partially labelled ethyl chloride was examined. The results are presented in Table 2. When CH_3CD_2Cl is photolyzed most of the methane contains no deuterium atoms, but a small amount of CH_3D is formed, increasing from 4% at 213.9 nm to 18% at 123.6 nm. The composition of the hydrogen collected in these same experiments changes from a predominance of hydrogen at 123.9 nm to a more equal distribution at 189.4 nm. The composition of the ethylene indicates a predominance of $C_2D_2H_2$, but the other isomer, C_2DH_3, is present to the extent of about $(17.5 \pm 2)\%$ at all· wavelengths. Somewhat surprisingly, when the labelling is reversed in CD_3CH_2Cl most of the product ethylene is again $C_2D_2H_2$, while about $(20 \pm 6)\%$ of the opposite isomer is present. Addition of oxygen as a radical scavenger has no effect except at 184.9 nm where a substantial portion of the ethylene is formed from radicals.

Nitric oxide is an effective radical scavenger, so the photolysis of ethyl chloride in the presence of NO (Table 3) produces only those products which arise from non-radical processes, including any derived from "hot" radicals. In agreement with the literature results [5, 6] the only significant products formed are ethylene, acetylene and vinyl chloride. The quantum yields of each of these non-radical products decrease by a factor of about four as the wavelength is increased from 123.6 to 163.3 nm.

These results are supplemented by experiments with HI as a radical trap (Table 4). In these experiments the alkyl radicals abstract H from the HI to produce a hydrocarbon, which may be characterized by a specific labelling pattern when deuterated ethyl chloride is used. The most obvious change brought about by the addition of HI is the increase in the ethane quantum yield, particularly at the lower energies. At 184.9 nm the relative quantum yield of ethane is more than twice as large as in the absence of HI and accounts for more than 90% of the total quantum yield. Accompanying this change is the reduction in quantum yield of the other products,

TABLE 4

Quantum yields for photolysis of C_2D_5Cl + HI (25:1)

Wavelength	Pressure (Torr C_2D_5Cl)	D_2	HD	CD_4	CD_3H	CD_2H_2	C_2D_2	C_2D_4	C_2D_3H	C_2D_5H	$C(H,D)_3Cl$	$C_2(H,D)_3Cl$
123.6	25	0.09	0.41	0.006	0.039	0.016	0.078	0.54	0.03	0.12	0.033	0.058
147.0	25	0.12	0.27	0.003	0.050	0.013	0.079	0.41	0.02	0.34	0.058	0.072
163.3	25			0.065	0.065	0.065	0.004	0.073	0.013	0.80	0.007	0.008
	5[a]	0.016	0.050				0.020	0.15	0.15	0.74	0.008	0.079
184.9	25[a]			0.02	0.02	0.02	0.012	0.041	0.007	0.91	0.0	0.015

[a] Results normalized to total ϕ = 1.0 (excluding hydrogen).

TABLE 5

Effect of pressure on quantum yields[a] of C_2H_5Cl + HI (4%) at 163.3 nm

Pressure (Torr)	CH_4	C_2H_2	C_2H_4	C_2H_6	CH_3Cl	C_2H_3Cl
4	0.058	0.016	0.31	0.63	0.008	0.012
6	0.055	0.014	0.21	0.70	0.003	0.013
10	0.035	0.013	0.25	0.64	0.005	0.016
25	0.038	0.012	0.17	0.76	0.004	0.005
50	0.037	0.007	0.069	0.80	0.001	0.008
60	0.033	0.007	0.067	0.87	0.001	0.008
Liquid (0 °C)	0.011	0.003	0.17	0.72	0.061	0.032

[a]Results normalized to total ϕ = 1.0 (excluding hydrogen).

TABLE 6

Effect of pressure on quantum yields[a] of C_2H_5Cl + HI (4%) at 147.0 nm

Pressure (Torr)	CH_4	C_2H_2	C_2H_4	C_2H_6	CH_3Cl	C_2H_3Cl
4	0.053	0.090	0.35	0.38	0.034	0.088
13	0.054	0.051	0.37	0.45	0.036	0.092
25	0.039	0.074	0.34	0.44	0.023	0.095
60	0.037	0.067	0.34	0.48	0.037	0.081
100	0.045	0.066	0.32	0.49	0.017	0.078
140	0.043	0.065	0.31	0.48	0.039	0.088
Liquid (0 °C)	0.011	0.005	0.27	0.62	0.007	0.094

[a]Results normalized to total ϕ = 1.0 (excluding hydrogen).

ethylene, vinyl chloride and n-butane (80 - 90% reduction at 184.9 nm). The changes are less apparent at higher energies.

The isotope effects observed by comparing the results from the h-5 and d-5 compounds in Tables 3 - 6 are generally minor. However, there is a positive isotope effect of 2 - 3 for formation of ethylene and acetylene at 163.3 nm at 25 Torr, and a positive isotope effect of 2 for formation of acetylene at 123.6 nm.

Isotopic analysis of the photolysis of C_2D_5Cl in the presence of HI reveals that almost all of the ethylene in these experiments (85 - 95%) consists of C_2D_4 arising from molecular loss of DCl. The remainder is C_2D_3H, indicating some formation of C_2D_3 radicals. The majority of the methane formed at 123.6 and 147.0 nm is CD_3H, although some CD_2H_2 is formed. Similarly, most of the hydrogen formed is HD, although some D_2 appears. Small amounts of H_2 were also formed at 123.6 and 147.0 nm, but since this presumably arises from photolysis of HI these amounts were ignored.

Photolysis of ethyl chloride in the presence of HI was investigated as a function of pressure (Tables 5 and 6). The results show some interesting trends, which continue approximately into the liquid phase. At both 147.0

TABLE 7

Quantum yields of primary processes in photodecomposition of C_2D_5Cl (25 Torr)

Products		123.6 nm	147.0 nm	163.3 nm	184.9 nm[a]
(1)	$C_2D_5 + Cl$	0.12	0.36	0.80	0.91
(2)	$C_2D_4 + DCl$	0.27	0.16	0.04	0.049
(3)	$C_2D_4 + D + Cl$	0.30	0.27	0.05	0.049
(4)	$C_2D_4Cl + D$	0.11[b]			
(5)	$C_2D_3Cl + D_2$	0.058	0.072	0.008	0.015
(6)	$C_2D_2 + DCl + D_2$	0.078	0.079	0.004	0.012
(7)	$CD_3Cl + CD_2$	0.016	0.012	0.066	0.02
(8)	$CD_4 + CDCl$	0.006	0.003	0.066	0.02
(9)	$CD_3 + CD_2Cl$	0.039	0.046	0.006	0.02

[a]Total quantum yields of primary processes set equal to 1.0.
[b]Estimate (see text).

and 163.3 nm, the quantum yield of ethylene decreases with increasing pressure. This is a small decrease (14%) at 147.0 nm, but a major decrease (78%) at 163.3 nm. Similarly ethane shows a modest increase with pressure at 147.0 nm and a larger increase at 163.3 nm. Changes in the other products are small.

The sum of the quantum yields of the molecular products (represented by acetylene, ethylene and vinyl chloride in the presence of NO) and the radical products (methane and ethane in the presence of HI) should equal 1.0. Neglecting any isotope effects that may arise from the use of perdeuterated chloroethane in Table 4, the total quantum yield calculated in this way is 1.07 at 123.6 nm, 0.94 at 147.0 nm and 0.96 at 163.3 nm.
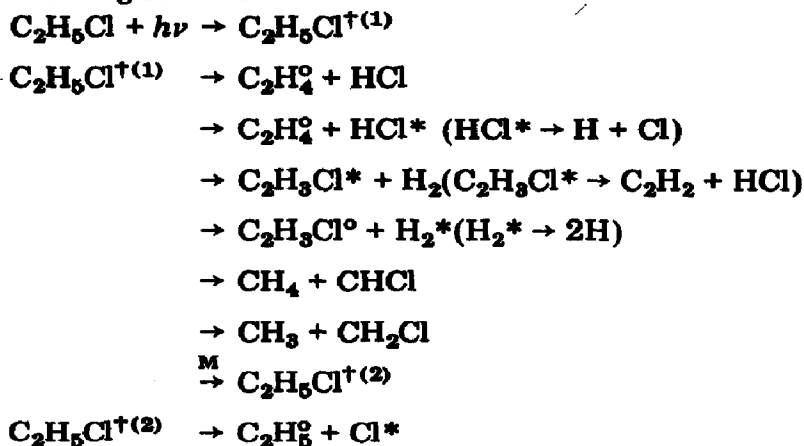
4. Discussion

There are a wide variety of decay processes available to photoexcited chloroethane. At low energies in particular there appears to be a preponderance of chlorine atom loss, while at higher energies molecular processes dominate. The primary processes at the four wavelengths can be largely determined by examining the results of the C_2D_5Cl–HI experiments. The conclusions are presented in Table 7, where the total quantum yield of primary processes is presented at each excitation wavelength.

Although the quantum yields for most of the primary processes are apparent from examination of the results of these experiments, $\phi(4)$ cannot be determined in this manner. Any C_2D_4Cl radicals present in an unexcited state will react to form C_2D_4HCl, which is experimentally indistinguishable from the bulk compound at the low concentrations in which it is present. Most probably this process is unimportant at all but 123.9 nm, since the

other primary processes account satisfactorily for a quantum yield of 1.0 at 147.0 and 163.3 nm. At 123.9 nm the total yield excluding step 4 is 0.89; by difference $\phi(4)$ can be estimated to be about 0.11.

In calculating $\phi(2)$ and $\phi(3)$, the quantum yield of ethylene formation was used as a base. $\phi(HD)$ was set equal to $\phi(3) + \phi(4)$, and $\phi(2) = \phi(C_2D_4 + C_2D_3H) - \phi(3)$. Process 3 may include several possible pathways: decomposition of excited DCl from step 2, loss of D from excited C_2D_5 and loss of Cl from vibrationally excited C_2H_4Cl. These three possibilities cannot be distinguished. Loss of D from excited C_2D_5 is thought to be unimportant (see later), at least at longer wavelengths. $\phi(5)$ was taken as the vinyl chloride yield and $\phi(6)$ is the quantum yield of acetylene. The quantum yield of D_2 formation in Table 4 should equal $\phi(5) + \phi(6)$ in Table 7, and this is approximately correct. The acetylene could come from decomposition of vibrationally excited molecules of either vinyl chloride or ethylene. The three modes of C—C bond cleavage (steps 7 - 9) are distinguished, where possible, by the isotopic distributions observed in methane. The total yield in these three steps has been set equal to the observed yield of methane (total) in the presence of HI.

A novel and interesting suggestion has been made by Ichimura et al. [6] regarding the formation of ethyl radicals at 147.0 nm. They suggest that two distinct excited states are responsible for chlorine atom loss and for molecular HCl elimination and other processes respectively as shown in the following scheme:

$$C_2H_5Cl + h\nu \rightarrow C_2H_5Cl^{\dagger(1)}$$

$$C_2H_5Cl^{\dagger(1)} \rightarrow C_2H_4^\circ + HCl$$

$$\rightarrow C_2H_4^\circ + HCl^* \ (HCl^* \rightarrow H + Cl)$$

$$\rightarrow C_2H_3Cl^* + H_2(C_2H_3Cl^* \rightarrow C_2H_2 + HCl)$$

$$\rightarrow C_2H_3Cl^\circ + H_2^*(H_2^* \rightarrow 2H)$$

$$\rightarrow CH_4 + CHCl$$

$$\rightarrow CH_3 + CH_2Cl$$

$$\overset{M}{\rightarrow} C_2H_5Cl^{\dagger(2)}$$

$$C_2H_5Cl^{\dagger(2)} \rightarrow C_2H_5^\circ + Cl^*$$

The assumption of the two excited states was based on the effect of pressure and NO on the quantum yields of the molecular and radical products, and on the absence of significant amounts of products which would have resulted from production of large quantities of chlorine or hydrogen atoms. We have found two lines of evidence which suggest that the two-state mechanism is substantially correct.

The appearance of residual ethylene in the presence of HI as a radical trap indicates that a fraction of the ethylene (varying with energy) must be
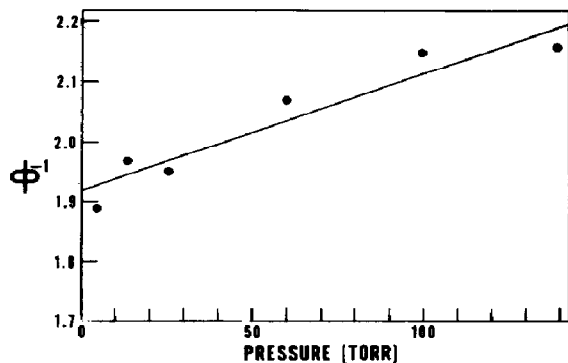
Fig. 1. Variation of reciprocal quantum yields with pressure at 147.0 nm in the presence of HI.
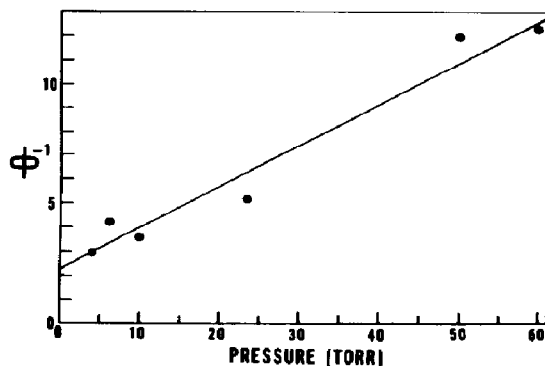
Fig. 2. Variation of reciprocal quantum yields with pressure at 163.3 nm in the presence of HI.

formed by either (a) molecular loss of HCl from excited C_2D_5Cl or (b) loss of a chlorine atom leaving an excited ethyl radical which then can decay either by loss of a hydrogen atom to form ethylene, or by collisional stabilization (followed by trapping by HI). The fact that the $[C_2H_4]:[C_2H_6]$ ratio changes with pressure, particularly at 163.3 nm, is consistent with both possibilities. The one characteristic which distinguishes between (a) and (b) is the fact that in (a) no hydrogen atoms need appear in connection with formation of ethylene, while in (b) one hydrogen and one chlorine atom form for each ethylene molecule. The quantum yield for HD of 0.05 at 5 Torr and 163.3 nm (Table 4) is significantly less than that of ethylene, indicating that the formation of ethylene is not accompanied by release of a hydrogen (deuterium) atom. Thus an excited state which may be stabilized by collisions is responsible for quenchable formation of ethylene, at least at 163.3 nm.

A second piece of evidence which supports the two-state hypothesis is the constancy of the 1,1-:1,2- elimination ratio observed by isotopic composition of the ethylene in the partially labelled experiments. If the first step in ethylene formation were loss of a chlorine atom, the remaining radical (excited) should lose a hydrogen atom from the 2 position to give CH_2CD_2. Therefore at least the 20% of ethylene which is formed by 1,1-elimination must be from a molecular process. If only this 20% were molecular and the remainder came from excited radical decomposition, we would expect the 1,1-:1,2- ratio to change with such variables as photon energy, pressure or isotopic labelling. The fact that there are no major changes, even in the liquid state, suggests that the two isotopic distributions both arise from the same or similar excited states. Furthermore, this observation, rules out the possibility that ethylene formation in this system comes from internal conversion to a vibrationally excited ground state of ethylene. Decomposition of such molecules would similarly occur exclusively by 1,2-elimination.

One may calculate the lifetime of the upper excited state for excitation at 147.0 and 163.3 nm in the manner used earlier [6]. If we plot ϕ^{-1} (C_2H_2 + C_2H_4 + C_2H_3Cl) *versus* pressure, in the presence of HI, the resulting slope will be k(stabilization)/k(reaction). The slope at 147.0 nm is 0.00198 ± 0.00031 (Fig. 1). Assuming that stabilization occurs upon each collision, k(stabilization) = 10^7 Torr^{-1} s^{-1}, then k(reaction) = 5.0 ± 0.8 × 10^9 s^{-1} or τ_0 = 0.20 ± 0.03 ns. This value is in good agreement with the rate of 2.8 × 10^9 s^{-1} reported by Ichimura *et al.* [6]. A similar plot made from the data at 163.3 nm shows a much greater pressure dependence (Fig. 2). The slope here is 0.176 ± 0.022, two orders of magnitude larger than at 147.0 nm. The corresponding reaction rate is 5.7 ± 0.7 × 10^7 s^{-1} and τ_0 is 18 ± 2 ns. This much slower reaction rate observed at lower energy is consistent with the idea of fragmentation from an upper vibrational level or levels of the excited state. In both plots the intercept of approximately 2 indicates that even from the upper state about half of the decay may be by radical processes, and therefore ethyl radicals may not be produced exclusively from the lower excited state.

The positive isotope effect observed for ethyl radical formation at 25 Torr and 163.3 nm can be explained by assuming that the lifetime of the higher excited state is longer for the fully deuterated molecule. The increased lifetime results in a greater sensitivity to collisional deactivations and therefore less formation of ethylene and acetylene compared with the non-deuterated molecule.

It is not easy to see why ethyl radicals formed from either state should be stable to further decomposition by hydrogen atom loss. If we tentatively identify the lower collisionally relaxed excited state with the $\sigma^* \leftarrow n$ state, which is responsible for the lowest absorption band, the energy of this state may be set approximately equal to 154.6 kcal mol^{-1}. This energy, which is that of 184.9 nm radiation, may be chosen because this wavelength appears to fall near the absorption onset. Since C—Cl bond cleavage requires 80.9 kcal mol^{-1} [12], there remains 73.7 kcal mol^{-1} to be apportioned among the translational and internal energy of the components. While the exact distribution of this energy is not known, we may calculate an upper limit for the amount of vibrational energy which can be accomodated in the ground state ethyl radical. At 184.9 nm and 25 Torr there is no apparent decomposition of the ethyl radicals, so the lifetime of the vibrationally excited radical must be at least 4 ns (the time between collisions). According to the calculations of Rabinovitch and Setser [13] an ethyl radical which survives for this time can possess no more than 45 kcal mol^{-1} total vibrational energy, since hydrogen atom loss is endothermic by only 39.6 kcal mol^{-1} [12]. Thus a minimum of 29 kcal mol^{-1} must appear as kinetic energy or electronic energy in one or both of the fragments. At shorter wavelengths the additional excitation energy must be similarly distributed into translational or electronic energy, since ethyl radicals do not appreciably decompose to ethylene at either 163.3 nm (see above) or 147.0 nm [6].

The secondary reactions available to this system have already been discussed in part and will not be extensively considered here. Most of the reac-

tions in the absence of radical quenchers can be determined approximately from the data in Table 1, although the actual book-keeping of the various radical fragments is rather involved. Some of the important secondary reactions in the absence of radical scavengers will be as follows:

$$Cl + C_2H_5Cl \longrightarrow HCl + C_2H_4Cl \tag{10}$$

$$H + C_2H_5Cl \xrightarrow{0.40} H_2 + C_2H_4Cl \tag{11}$$

$$\xrightarrow{0.60} HCl + C_2H_5 \tag{12}$$

$$C_2H_5 + C_2H_5Cl \longrightarrow C_2H_6 + C_2H_4Cl \tag{13}$$

$$C_2H_5 + HCl \longrightarrow C_2H_5 + Cl \tag{14}$$

$$2C_2H_4Cl \xrightarrow{0.25} C_2H_3Cl + C_2H_5Cl \tag{15}$$

$$\xrightarrow{0.75} C_4H_8Cl_2 \tag{16}$$

The relative rates indicated for reactions (11) and (12) are those derived for hydrogen or chlorine atom abstraction by thermal hydrogen atoms [14]. Reaction (13) is expected to be slow, with an activation energy estimated to be 11 kcal mol^{-1} [5]. "Hot" ethyl radicals, however, may react readily by this path [5]. When significant amounts of HCl have accumulated, reaction (14) may be favored [4]. Reactions with other radicals are the only likely reactions of the chloroethyl radical, and processes (15) and (16) represent probable pathways for reaction. The relative rates of these two processes represent the known disproportionation/recombination ratio for the chloroethyl radical [15]. Methyl and chloromethyl radicals arising from primary processes (7) - (9) are relatively unimportant but are responsible for formation of the C_1 and C_3 products.

If we compare the actual quantum yields of ethylene and vinyl chloride in the absence of scavenger with the theoretical yields which can be calculated from the above equations and Table 7, it is seen that the calculated yields are on the average about twice the observed yields. A similar deficiency in ethane quantum yield has been noted by Ichimura *et al.* [6]. The discrepancy may be explained by the fact that neither the ethyl nor chloroethyl radicals are very reactive. They may thus undergo collisions and reactions with the wall, which removes them from the system and makes the yields of ethane and vinyl chloride abnormally small.

Acknowledgments

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