PHOTOLYSIS OF ETHYL CHLORIDE (FREON 160) AT 147 nm

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Summary

Ethyl chloride (Freon 160) was photolyzed at 147 nm over a wide pressure range (1 to 500 Torr) in the presence and absence of NO. The effects of added He, Ar and CF_4 were also studied. The extinction coefficient of C_2H_5Cl at 147 nm was determined to be 107.2 ± 7.2 atm^{-1} cm^{-1} at 296 K. The results clearly indicate that the modes of photodecomposition are pressure dependent. At 1 Torr, the quantum yield for molecular HCl elimination is approximately 0.6 and for molecular H_2 elimination, approximately 0.1. At 500 Torr the corresponding quantum yields are approximately 0.2 and 0.05. The decreases in the quantum yields for molecular elimination are offset by an increasing contribution of the primary process yielding C_2H_5 and Cl. The results are interpreted in terms of the initial formation of one and possibly two electronically excited states which decompose mainly by molecular elimination of HCl and H_2. As the pressure is increased this state (or these states) are collisionally induced to cross over to an electronically excited state which decomposes exclusively by carbon–chlorine bond fission.

investigation of the photolysis of C_2H_5Cl by Cremieux and Herman [1] at 123.6 nm and ~106 nm. Cremieux and Herman proposed that the major primary mode of photochemical decomposition of C_2H_5Cl at 123.6 nm was the molecular elimination of HCl from an electronically excited state. Other primary processes proposed included the elimination of H_2 and the formation of C_2H_3 radicals. Tiernan and Hughes [2] also briefly studied the 123.6 nm photolysis of C_2H_5Cl as part of a more extensive investigation of the 50 keV radiolysis of C_2H_5Cl. Again the major primary process was thought to be HCl elimination from an unspecified excited state. Fewer products were identified in this latter investigation and the molecular elimination of H_2 to give C_2H_3Cl was not included as a primary process. Ethyl chloride has also been bombarded with 2.8 MeV electrons in the gas phase [3] where a substantial fraction of C_2H_5Cl molecules were induced to undergo molecular elimination and where C_2H_5, CH_3CHCl and CH_2ClCH_2 radicals were also produced by subsequent atom abstraction reactions of H and Cl formed in primary processes. Ethyl fluoride has been photolyzed at 147 nm [4] where the molecular eliminations of HF and H_2 were proposed as the major primary processes. In contrast the photolysis of ethyl iodide at 147 nm [5] results primarily in fission of the carbon–halogen bond. Carbon–halogen bond fission is also dominant in longer wavelength photolysis. Fujimoto and Wijnen [6] have investigated the photolysis of CD_3CHCl_2 using a medium pressure Hg arc, where extensive carbon–chlorine bond fission was evident. Ethyl bromide [7] and ethyl iodide [8] have been photolyzed at wavelengths greater than 200 nm, where again rupture of the carbon–halogen bond is the major primary process.

Thus it is generally accepted that modes of photochemical decomposition in the alkyl halides are wavelength dependent [9]. It is also clear from the literature that absorption of monochromatic radiation results in many competing modes of decomposition. The results obtained in this study

of ethyl chloride (107.2 ± 7.2 atm^{-1} cm^{-1} at 296 K) was measured by an adaptation of the technique described by Salomon and Scala [12]. Product analysis was by gas chromatography (Varian Aerograph 1740 with twin flame ionization detectors). The lower molecular weight products were separated and identified using a 3 m Porapak N column (3 mm i.d.) with a helium flow rate of 30 cm^3/min and the higher molecular weight products were separated using a 1.5 m SE30 column with a helium flow rate of 40 cm^3/min. Altogether twenty two reaction products were separated chromatographically of which nineteen were identified by comparison of their retention times with those of authentic samples and their sensitivities to the detectors subsequently determined. The quantum yields of the three unidentified products were always less than 0.01. Sampling was via an eight port gas sampling valve. H_2 and HCl while certainly major products could not be determined in this series of experiments.

Ethyl chloride was obtained from the Matheson Company. Prior to use, low boiling impurities were removed by trap-to-trap distillations at -98 °C. The major residual impurity was C_2H_3Cl ($\sim 0.01\%$). This remained unchanged despite numerous attempts by other purification procedures, such as preferential adsorption, to remove it. Quantum yields for C_2H_3Cl were obtained, therefore, after taking the presence of C_2H_3Cl into account. Nitric oxide of stated purity 99.5%, helium of stated purity 99.9% and argon of stated purity 99.999% were also obtained from the Matheson Company and used without further purification. Carbon tetrafluoride from Matheson was pumped on at the temperature of liquid nitrogen but residual traces of air could not be removed.

Results

Initial experiments were carried out at a fixed pressure of 12.7 Torr C_2H_5Cl and a constant intensity of $\sim 4 \times 10^{13}$ photons/s. The quantum yields of the principal products, C_2H_4, C_2H_2, C_2H_3Cl, C_2H_6, and n-C_4H_{10}, did not vary to any significant extent with photolysis time in the range 25 - 120 min. Because of the relatively large extinction coefficient of C_2H_5Cl, most experiments were carried out at this fairly low intensity in an attempt to minimize the formation of high concentrations of reaction products near the window. However, despite these precautions, we have reason to believe we were not quite successful.

TABLE 1

Quantum yields of products obtained in the 147 nm photolysis of C_2H_5Cl

Run	$P_{C_2H_5Cl}$ (Torr)	Additive (Torr)		Quantum Yields (ϕ)									
				CH_4	C_2H_4	C_2H_6	C_2H_2	C_3H_6	C_3H_8	CH_3Cl	C_2H_3Cl	$n-C_4H_{10}$	$trans-C_4H_8$
1	0.98	-		-	0.68	0.01	0.12	-	0.0	0.0	0.09	-	0.0
2	0.98	-		0.05	0.78	0.01	0.12	0.03	~0.0	0.0	0.11	0.03	0.0
3	1.1	-		0.03	0.74	0.02	0.13	0.03	~0.0	0.0	0.10	0.03	0.0
4	12.7	-		0.04	0.59	0.05	0.10	0.09	0.01	0.01	0.11	0.11	0.008
5	12.7	-		0.04	0.60	0.04	0.09	0.08	0.007	0.01	0.10	0.11	0.01
6	12.7	-		0.02	0.60	0.04	0.09	0.08	0.006	0.008	0.09	0.10	0.01
7	12.7	-		0.05	0.58	0.04	0.08	0.07	0.007	0.009	0.11	0.11	0.006
8	25.0	-		0.04	0.62	0.03	0.09	0.04	0.007	0.0	0.17	0.12	0.003
9	25.0	-		-	0.60	0.03	0.08	0.03	0.007	0.0	0.15	0.12	0.002
10	40.0	-		0.03	0.59	0.04	0.07	0.03	0.004	0.0	0.20	0.12	0.0
11	40.0	-		0.03	0.57	0.04	0.08	0.03	0.006	0.0	0.15	0.12	0.002
12	137	-		0.03	0.57	0.03	0.08	~0.0	~0.0	0.0	0.23	0.12	0.0
13	250	-		0.006	0.46	0.02	0.07	~0.0	~0.0	0.0	0.30	0.14	0.0
14	500	-		0.007	0.41	0.03	0.06	0.0	0.0	0.0	0.40	0.18	0.0
15	12.7	He	765	0.03	0.58	0.03	0.08	0.04	0.0	0.0	0.09	0.10	0.0
16	12.7	Ar	380	-	0.56	0.03	0.08	0.04	0.0	0.0	0.09	0.11	0.0
17	12.7	Ar	760	-	0.54	0.02	0.07	0.04	0.0	0.0	0.08	0.12	0.0
18	12.7	NO	1.0	0.02	0.42	0.0	0.08	0.0	0.0	0.0	0.08	0.008	0.006
19	12.7	NO	2.5	0.01	0.39	0.0	0.07	0.0	0.0	0.0	0.08	0.0	-
20	12.7	NO	5.0	0.02	0.41	0.0	0.09	0.0	0.0	0.0	0.06	0.0	0.006
21	12.7	NO	10.0	0.02	0.40	0.0	0.08	0.0	0.0	0.0	0.07	0.0	0.007
22	40	NO	5.0	-	0.41	0.0	0.08	0.0	0.0	0.0	0.07	0.0	0.01
23	130	NO	12.0	0.01	0.30	0.0	0.07	0.0	0.0	0.0	0.09	0.0	0.02
24	260	NO	30.0	~0.0	0.31	0.0	0.06	0.0	0.0	0.0	0.22	0.0	-
25	500	NO	76.0	~0.0	0.24	0.008	0.04	0.0	0.0	0.0	.0.25	0.0	-
26	12.7	NO 2.0 CF4 125		~0.0	0.32	0.0	0.07	0.0	0.0	0.0	0.08	0.0	-
27	12.7	NO 2.0 CF4 330		0.0	0.26	0.0	0.06	0.0	0.0	0.0	0.07	0.0	-
28	12.7	NO 2.0 CF4 580		0.0	0.22	0.0	0.04	0.0	0.0	0.0	0.07	0.0	-
29	12.7	NO 2.0 CF4 680		0.0	0.20	0.0	0.03	0.0	0.0	0.0	0.06	0.0	-

the products previously mentioned, at a pressure of 12.7 Torr, CH_3Cl, C_3H_8, $2-C_3H_7Cl$, $1,2-C_2H_6Cl_2$, cis- and trans-C_4H_8, $1-C_4H_9Cl$, $2-C_4H_9Cl$, $1,3-C_4H_8Cl_2$,

cis-C₄H₈	2-C₃H₇Cl	1-C₄H₉Cl	2-C₄H₉Cl	1,2-C₃H₆Cl₂	3-chloro-1-butene	1,3-C₄H₈Cl₂	2,3-C₄H₈Cl₂	1,4-C₄H₈Cl₂
0.0	-	-	-	-	-	-	-	-
0.0	-	-	-	-	-	-	-	-
0.0	-	-	-	-	-	-	-	-
0.005	-	-	-	0.04	-	0.02	0.04	0.007
0.006	0.006	0.05	0.02	0.02	0.01	0.03	0.03	0.008
0.007	-	-	-	0.02	-	0.02	0.03	0.006
0.004	-	-	-	-	-	-	-	-
0.001	-	-	-	-	-	-	-	-
0.0	-	-	-	-	-	-	-	-
0.0	-	-	-	-	-	-	-	-
0.001	-	-	-	-	-	0.02	0.10	0.01
0.0	-	0.01	0.007	-	-	-	-	-
0.0	-	0.04	0.01	-	-	-	-	-
0.0	-	0.04	0.02	-	-	-	-	-
0.0	0.01	0.06	0.03	0.02	0.01	0.05	0.05	0.008
0.0	0.01	0.05	0.03	0.02	0.01	0.04	0.04	0.008
0.0	0.01	0.06	0.04	0.01	0.02	0.06	0.06	0.01
0.0	0.0	0.0	0.0	0.01	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.01	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	0.01	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	-	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	-	0.0	0.0	0.0	0.0
0.0	0.0	0.0	0.0	-	0.0	0.0	0.0	0.0
-	-	0.0	0.0	-	0.0	-	-	-
-	-	0.0	0.0	-	0.0	-	-	-
-	0.0	0.0	0.0	∼0.0	0.0	0.0	0.0	0.0
-	0.0	0.0	0.0	∼0.0	0.0	0.0	0.0	0.0
-	0.0	0.0	0.0	∼0.0	0.0	0.0	0.0	0.0
-	0.0	0.0	0.0	∼0.0	0.0	0.0	0.0	0.0

A series of experiments in which 1 - 10 Torr of NO was added to 12.7 Torr of C_2H_5Cl showed that the precursors of CH_3Cl, C_2H_6, C_3H_6, C_3H_8, n-C_4H_{10} and the remaining C_3 and C_4 products, with perhaps the exception of the precursors of trans- C_4H_8 and 1,2-$C_3H_6Cl_2$, were readily scavenged by NO leaving only four principal products, C_2H_4, C_2H_2, C_2H_3Cl and CH_4. However, the quantum yield of C_2H_4 was at the same time markedly reduced. Slight decreases were also observed in the quantum yields of CH_4 and C_2H_3Cl.

Four runs in which 12.7 Torr of C_2H_5Cl and 2 Torr of NO were photo-lyzed in the presence of increasing pressures of CF_4 (125 - 680 Torr, runs 26 - 29) were compared with a series in which the pressure of C_2H_5Cl was varied from 12.7 to 500 Torr (runs 18 - 25) in the presence of NO. A similar
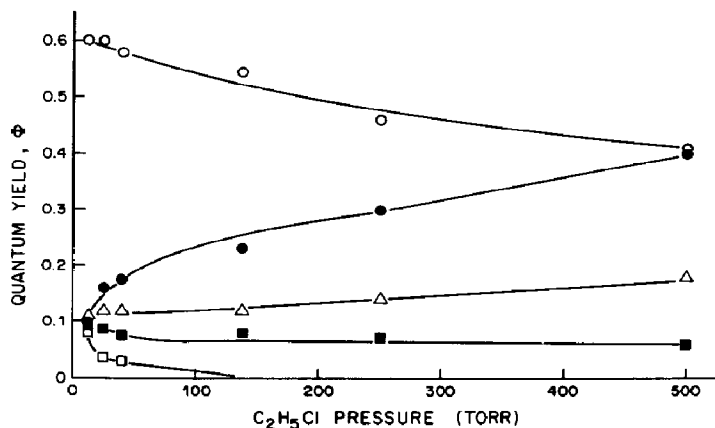
Fig. 1. Variation of quantum yields with pressure of C_2H_5Cl (12.7 to 500 Torr). o, C_2H_4; •, C_2H_3Cl; △, n-C_4H_{10}; ■, C_2H_2; □, C_3H_6.

comparison in the absence of NO was not possible since the CF_4 contained a sufficient quantity of oxygen (see experimental) to suppress the formation of the compounds which were also scavenged by NO. The comparison showed CF_4 to be similarly as effective as C_2H_5Cl with respect to decreasing the quantum yields of C_2H_4 and C_2H_2. In the case of vinyl chloride we are fairly confident in the quantum yields of C_2H_3Cl at C_2H_5Cl pressures (total or partial) equal to or less than 12.7 Torr. In the presence of NO and inert CF_4 (runs 26 - 29), $\Phi_{C_2H_3Cl}$ also decreases with increasing total pressure. The apparent increase in $\Phi_{C_2H_3Cl}$ with C_2H_5Cl pressure in the presence of NO (runs 22 - 25) is due to the aforementioned impurity. In the absence of NO there is undoubtedly some radical production of C_2H_3Cl. At ~500 Torr total pressure, the results would indicate that $\Phi_{C_2H_3Cl}$ from radical sources is ~0.15 (runs 14 and 25). However, since the overall quantum yield of C_2H_3Cl is overestimated at high C_2H_5Cl pressures, we believe this value to be also overestimated.

Runs in which 12.7 Torr C_2H_5Cl were photolyzed in the presence of high pressures of He and Ar showed that the monatomic gases were not very efficient at reducing the quantum yields of the major products.

Finally triplicate data were obtained for the photolysis of ~1 Torr of C_2H_5Cl, the transmittance being taken into account in calculating quantum yields. The conversions were unfortunately a little high at 0.25% whereas in all previous runs conversions were less than 0.1%. The increase in the quantum yield of C_2H_4 was much larger than expected and the yields of C_2H_6, C_3H_6 and C_4H_{10} were considerably reduced.

Discussion

It was evident from the work of Cremieux and Herman [1], that while C_2H_5Cl might appear to be the simplest member of the class because of its single halogen substitution, its photochemistry would be quite complex.
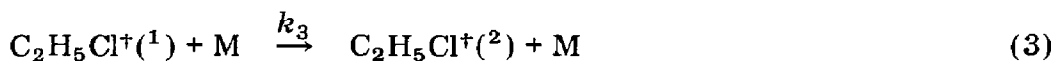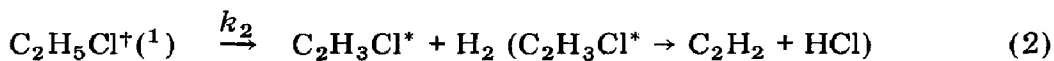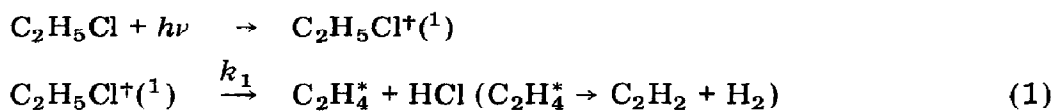
This is indeed the case. In many qualitative respects our results parallel those of the above authors, but there are some differences which are not unexpected in view of our introductory remarks. In the present case the method of stable product analysis is far from satisfactory in its ability to unambiguously identify primary processes. Of necessity many proposals are speculative and require lengthy discussion.

C_2H_4, C_2H_3Cl and C_2H_2

One of the most striking and mechanistically important aspects of the data as a whole is the observation that a large proportion of the C_2H_4 must be formed by a precursor which is *readily* scavenged by NO (see runs 5 and 18, for example). One interpretation of this is that the precursor(s) of C_2H_4 are *entirely* C_2H_5 radicals formed by fission of the carbon–chlorine bond such that the energy distribution of the vibrationally excited radicals is intersected by the activation energy for C–H bond rupture, ~40 kcal/mol [13]. Thus C_2H_5 radicals with energy above the threshold for decomposition are short lived and cannot be scavenged by NO and must yield C_2H_4 upon decomposition, while those radicals with near or below threshold energies can yield C_2H_4 via radical disproportionation. Analysis of this simple mechanism shows that this single explanation cannot be entirely correct since there are insufficient radical products (e.g. run 5) that would correspond to the large accompanying yields of Cl and H atoms. However, we are still led to the conclusion that the scavengeable fraction of C_2H_4 must arise mainly from disproportionation of radicals with energies less than those required to decompose. We return to this important point later in the discussion.

In the presence of NO the total quantum yield of C_2H_4, as well as that of C_2H_3Cl and C_2H_2 decreases slowly as the pressure of CF_4 increases (runs 26 - 29). This suggests that the precursor to these products is being gradually collisionally quenched. A collisionally induced conversion to the electronic ground state is not possible, since such a process would result in a very highly vibrationally excited species which at the pressure used would immediately decompose to C_2H_4 and very probably further to C_2H_2, and this is contrary to experimental observation. We are also unable to propose any photophysical process, such as collision-induced fluorescence, that would deactivate the excited state with a corresponding decrease in photochemical decomposition. It is therefore proposed that the non-scavengeable C_2H_4 is produced by molecular elimination of HCl from an initially formed excited state $C_2H_5Cl^{+}(^1)$ and that the precursor to the scavengeable C_2H_4 is the result of a collisionally induced cross over to another electronically excited state $C_2H_5Cl^{+}(^2)$ which decomposes by carbon–chlorine bond fission to yield scavengeable C_2H_5 radicals (with energies necessarily less than 40 kcal/mol) and very hot Cl atoms. This mechanism would result in a corresponding increase in radical products as the pressure is increased without producing "non-scavengeable" C_2H_4. This proposition is supported in particular by the increase in the quantum yield of C_4H_{10} with pressure in the absence of NO (see runs 4, 8, 10, 13, 14).

Pursuing this two state hypothesis further, one is tempted to make some further simplifying assumptions with a view to testing their validity. First, it is assumed that the initially formed electronically excited state is the only precursor to yield both C_2H_4 and C_2H_3Cl molecularly, and that the C_2H_2 results from decomposition of vibrationally excited C_2H_4 and/or C_2H_3Cl molecules. If it is further assumed that the cross over to the second electronically excited state is induced by a simple one-step collisional process, then for the primary processes the following general scheme can be written:

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

$$C_2H_5Cl^\dagger(^1) \quad \overset{k_1}{\rightarrow} \quad C_2H_4^* + HCl \ (C_2H_4^* \rightarrow C_2H_2 + H_2) \qquad (1)$$

$$C_2H_5Cl^\dagger(^1) \quad \overset{k_2}{\rightarrow} \quad C_2H_3Cl^* + H_2 \ (C_2H_3Cl^* \rightarrow C_2H_2 + HCl) \qquad (2)$$

$$C_2H_5Cl^\dagger(^1) + M \quad \overset{k_3}{\rightarrow} \quad C_2H_5Cl^\dagger(^2) + M \qquad (3)$$

$$C_2H_5Cl^\dagger(^1) \quad \overset{k_4}{\rightarrow} \quad products \qquad (4)$$

Reaction (4) is a general statement defining other primary processes, photophysical (if any) and photochemical such that the total quantum yield of the primary processes is unity. From this scheme it follows that a plot of $1/(\Phi_{C_2H_4} + \Phi_{C_2H_3Cl} + \Phi_{C_2H_2})$ vs. total pressure in the range 12.7 - 500 Torr and in the presence of NO should be a straight line of slope $= k_3/(k_1 + k_2)$. Figure 2, line III, shows that for the CF_4–NO data (runs 26 - 29) a very good linear relationship does in fact exist. In principle, it also follows that if the C_2H_2 arises solely from the decomposition of C_2H_3Cl, a plot of $1/\Phi_{C_2H_4}$ or $1/(\Phi_{C_2H_3Cl} + \Phi_{C_2H_2})$ vs. total pressure should be linear. Similarly, if the C_2H_2 arises solely from the C_2H_4, a plot of $1/\Phi_{C_2H_3Cl}$ or $1/(\Phi_{C_2H_4} + \Phi_{C_2H_2})$ should be linear. Figure 2, lines I and II, show that the data are insensitive to further analysis and therefore that C_2H_2 could originate from the C_2H_4 only, the C_2H_3Cl only, or both. Thermochemical considerations and the observation that it is the ratio of C_2H_2 to C_2H_3Cl that exhibits the greater pressure dependence, that would be indicative of competitive decomposition/stabilization, lead us, somewhat arbitrarily, to assume that the majority of the C_2H_2 arises from decomposition of vibrationally excited $C_2H_3Cl^*$. The slope of line I is equal to k_3/k_1. Assuming k_3 to have the usual value of $\sim 10^7$ Torr^{-1} s^{-1} we obtain a value for k_1 of $\sim 2.8 \times 10^9$ s^{-1} or a lifetime for the excited state of $\sim 3.6 \times 10^{-10}$ s, a not unreasonable value [6].

An analysis of the thermochemistry, however, shows that the molecular eliminations of HCl and H_2 from $C_2H_5Cl^\dagger(^1)$ are not as straightforward as may seem.

The energy of the photon is 194 kcal/mol and for the reaction, $C_2H_5Cl \rightarrow C_2H_4 + HCl$, $\Delta H = 17$ kcal/mol. There are thus 177 kcal of energy to be distributed between C_2H_4 and HCl such that the energy of C_2H_4 does not greatly exceed 80 kcal/mol, which is the energy required for C_2H_4 to elimi-
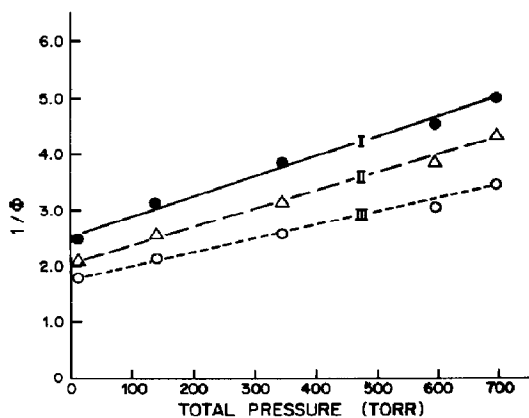
Fig. 2. Variation of reciprocal quantum yields with total pressure (12.7 - 500 Torr) in the presence of NO and CF_4. I, $1/\Phi_{C_2H_4}$; II, $1/(\Phi_{C_2H_4} + \Phi_{C_2H_2})$; III, $1/\Phi_{(C_2H_4} + \Phi_{C_2H_3Cl} + \Phi_{C_2H_2})}$.

nate H_2 [14]. If some or all of the C_2H_4 molecules possess energies significantly less than 80 kcal/mol, then some or all of the HCl molecules would have energies in excess of the H–Cl bond strength (103 kcal/mol) and would dissociate into atoms. Such a process is hardly distinguishable from the expulsion of a chlorine atom followed by that of a H atom from the very short lived ethyl radical that would result [15]. Final analysis of the data will indicate that molecular elimination of HCl to yield non-decomposable ethylene ($C_2H_4^0$) predominates. However, some $C_2H_4^0$ is accompanied by the formation of H and Cl atoms.

Similar thermochemical considerations apply to the elimination of the elements of H_2 to give vinyl chloride. For the reaction, $C_2H_5Cl \rightarrow C_2H_3Cl + H_2$, $\Delta H = 35$ kcal/mol. The observation that the ratio of $\Phi_{C_2H_2}/\Phi_{C_2H_3Cl}$ varies only from ~1.0 at low pressures (12.7 Torr) to 0.5 at ~700 Torr is indicative of the formation of C_2H_3Cl molecules with a wide energy distribution, probably intersected by the activation energy for HCl elimination [16]. For those C_2H_3Cl molecules formed with somewhat less than 60 kcal/mol excess energy ($C_2H_3Cl^0$), the energy available to the H_2 would exceed that required to break the H–H bond (104 kcal). Conversely, for all those decomposable molecules with energies greater than 60 kcal ($C_2H_3Cl^*$), there is insufficient energy to break the H_2 bond. Thus the yield of acetylene places a lower limit on the amount of molecular H_2 elimination and the yield of C_2H_3Cl an upper limit on the process $C_2H_5Cl^\dagger(^1) \rightarrow C_2H_3Cl^0 + H + H$.

Other products

The formation of C_3 products ($\Phi_{C_3H_6} = 0.08$ at 12.7 Torr) strongly suggests reactions between C_1 and C_2 radicals and hence a contribution to the primary processes by carbon–carbon bond cleavage. The residual CH_4 observed in the photolysis of 12.7 Torr C_2H_5Cl in the presence of NO (runs 18 - 21) indicates a very small contribution of the primary process $C_2H_5Cl^\dagger \rightarrow CH_4 + CHCl$. Since no CH_3Cl was seen, the similar production of CH_2 is excluded.

Since no CH_4 is observed at high pressures in the presence of NO, the excited state precursor to this product also appears to be collisionally quenched. The simplest interpretation is that the precursor is also $C_2H_5Cl^{\dagger}(^1)$. We have chosen to make the same assumption with respect to the carbon–carbon bond cleavage on the basis that some of the decrease in yield of C_3H_6 (runs 4 - 14) could be attributed to a collision-induced cross over from $C_2H_5Cl^{\dagger}(^1)$ to $C_2H_5Cl^{\dagger}(^2)$.

Mechanism

On the basis of the foregoing discussion reactions (5) to (11) summarize in more detail the primary decomposition processes where the indicated quantum yields refer to 12.7 and 500 Torr of C_2H_5Cl, and the quantum yield for reaction (11) is obtained by difference, in the light of lack of evidence for any photophysical processes.

		12.7 Torr	500 Torr	
$C_2H_5Cl^{\dagger}(^1)$	$\rightarrow C_2H_4^0 + HCl$	$\Phi_5 = 0.30$	$0.24 (= \Phi_5 + \Phi_6)$	(5)
	$\rightarrow C_2H_4^0 + HCl^*$ $(HCl^* \rightarrow H + Cl)$	$\Phi_6 = 0.10$		(6)
	$\rightarrow C_2H_3Cl^* + H_2$ $(C_2H_3Cl^* \rightarrow C_2H_2 + HCl)$	$\Phi_7 = 0.08$	0.04	(7)
	$\rightarrow C_2H_3Cl^0 + H_2^*$ $(H_2^* \rightarrow H + H)$	$\Phi_8 = 0.08$	0.07	(8)
	$\rightarrow CH_4 + CHCl$	$\Phi_9 = 0.02$	~ 0.0	(9)
	$\rightarrow CH_3 + CH_2Cl$	$\Phi_{10} = 0.06$	~ 0.0	(10)
$C_2H_5Cl^{\dagger}(^2)$	$\rightarrow C_2H_5^0 + Cl^*$	$\Phi_{11} = 0.36$	0.65	(11)
		$\Phi_T = 1.0$	1.0	

Since at low pressures very little of the $C_2H_5Cl^{\dagger}(^1)$ can have been induced to cross over to $C_2H_5Cl^{\dagger}(^2)$ because of the short lifetime of the former state, there must be an additional mechanism by which $C_2H_5Cl^{\dagger}(^2)$ is formed. We discuss this aspect of the mechanism later.

With reference to the quantum yields at 12.7 Torr of C_2H_5Cl, the sum of Φ_5 and Φ_6 must be equal to the observed value of 0.40 the quantum yield of non-scavengeable C_2H_4 observed in the presence of NO (runs 18 - 21), the individual contributions being estimated from a consideration of the overall mass balance. The quantum yield for reaction (7) corresponds to the yield of C_2H_2, and that of reaction (8) to the quantum yield of C_2H_3Cl observed in the presence of NO.

The quantum yield for reaction (10) of 0.06 was based upon an analysis of the yields of the C_3 compounds, a further contribution to the available CH_2Cl arising from hydrogen atom abstraction from C_2H_5Cl by the CHCl radicals produced in reaction (9). The main assumption here is that the CH_3 and CH_2Cl radicals combine with the more abundant ethyl and chloroethyl radicals (CH_3CHCl and CH_2ClCH_2) to form mainly monochloropropanes which at this pressure eliminate HCl to yield C_3H_6. Unfortunately analytical problems were such that expected increases in the yields of 1-C_3H_7Cl and

2-C_3H_7Cl at high pressures could not be verified. In fact, 1-C_3H_7Cl could not be analyzed under any conditions.

Turning to the question of the ultimate fate of Cl and H atoms produced in the system and their contributions to the observed products we conclude that these atoms are removed primarily by abstraction reactions with the parent C_2H_5Cl as evidenced by the independence of quantum yields of the major products with time. Most of the chlorine atoms produced are predicted to have kinetic energies larger than 70 kcal/mol, if the C_2H_5 radicals formed in reaction (11) are not to decompose to C_2H_4 and H. Thus it is not possible to predict the ratio of CH_3CHCl to CH_2ClCH_2 radicals formed by subsequent abstraction of H by Cl* atoms from the parent C_2H_5Cl. At these energies hot Cl atoms might even abstract chlorine from C_2H_5Cl to some extent to give C_2H_5 radicals, despite a value of 23 kcal/mol for the heat of the abstraction reaction. The H atoms can abstract H or Cl from C_2H_5Cl. For thermalized atoms the ratio of H abstraction to Cl abstraction is 0.68 [17]. The presence of CH_3CHCl radicals in this system, however, complicates any attempt to rationalize the possible disproportionation and combination reactions even if the radicals involved are thermalized. Cremieux and Herman [1] have quoted the value of 0.22 for the disproportionation/recombination ratio for C_2H_5 and C_2H_4Cl (structure unspecified) radicals based on data of Schindler [3] and Roquitte and Wijnen [18]. However, in as much as the last authors as well as Heicklen [19] produced only CH_2ClCH_2 of the two possible chloroethyl radicals in their systems, we are unable to link their data with the combination results of Schindler [3]. (There are fourteen possible disproportionation and combination reactions between C_2H_5, CH_2ClCH_2 and CH_3CHCl involving H atom transfer alone.) However, we have indicated earlier that the large amount of scavengeable C_2H_4 is due to disproportionation. A large proportion of radicals in this system are either formed initially with excess vibrational energy (albeit less than that required to decompose them) or perhaps acquire it upon being formed by reaction of the very hot Cl* atoms with C_2H_5Cl. If most of the light is absorbed in the region close to the window it is not inconceivable that the rate of disproportionation of vibrationally excited radicals is comparable to that for recombination because of lower probability of collisional deexcitation. Our data for C_2H_4 suggest that the most favoured disproportionation is that between C_2H_5 and C_2H_4Cl (of either kind) radicals where the saturated product is C_2H_5Cl. Although this provides a satisfactory explanation of our experimental observations, the somewhat embarrassing low yield of C_2H_6 has not escaped our attention.

Since processes (6), (8) and (10) give H and Cl atoms which in turn yield C_2H_4Cl radicals and further C_2H_5 radicals, it is necessary to attempt a detailed mass balance with respect to all the observed products resulting from radical precursors. However, all of these products, except the small yields of scavengeable CH_4 and CH_3Cl, can be linked to reactions involving C_2H_5 and C_2H_4Cl radicals and it is, therefore, only necessary to account for the total quantum yields of these radicals. An analysis of the products at

12.7 Torr (run 5) shows the total quantum yield of C_2H_5 to be ~ 0.6 and that of C_2H_4Cl to be ~ 0.5 and hence $\Phi_{C_2H_5} + \Phi_{C_2H_4Cl} \sim 1.1$. The individual values are quoted to one significant figure only since it is possible to assign the small amounts of C_2H_6 and C_2H_3Cl produced from radical sources to more than one disproportionation reaction. The quantum yields quoted for processes (5) to (11) at 12.7 Torr yield a calculated value of $\Phi_{C_2H_5}$ in the range 0.52 - 0.62 and for C_2H_4Cl a quantum yield in the range of 0.46 - 0.56, or a sum of $\Phi_{C_2H_5} + \Phi_{C_2H_4Cl} = 1.08$. The ranges of the calculated quantum yields assume that all Cl atoms abstract hydrogen from C_2H_5Cl, but that H atoms can either abstract solely chlorine atoms, or hydrogen and chlorine in the ratio 0.68 as previously indicated [17]. If H atoms abstract only Cl from C_2H_5Cl as they well might in this system, the individual quantum yields are: $\Phi_{C_2H_5} = 0.62$ and $\Phi_{C_2H_4Cl} = 0.46$. In view of all the uncertainties we feel that this is reasonably satisfactory, though circumstantial, agreement.

At higher pressures the quantum yields of the individual processes change as a result of the collision induced crossing of $C_2H_5Cl^{\dagger}(^1)$ to $C_2H_5Cl^{\dagger}(^2)$. Thus at 500 Torr of C_2H_5Cl the sum of Φ_5 and $\Phi_6 = 0.24$, the yield of C_2H_4 produced in the presence of NO (run 25). If we assume the same ratio for Φ_5/Φ_6 as obtained at 12.7 Torr, we obtain $\Phi_5 = 0.18$ and $\Phi_6 = 0.06$. Φ_7 and Φ_8 are extrapolated from the yields of C_2H_2 and C_2H_3Cl obtained in the presence of CF_4 and NO rather than the C_2H_5Cl–NO data for reasons which have been discussed. No methane at all was observed in the presence of NO and hence $\Phi_9 = 0.0$. Based upon the disappearance of C_3H_6 in the absence of NO, we conclude that Φ_{10} is also zero.

Examination of the processes (5) to (11) as before leads to calculated quantum yields in the range $\Phi_{C_2H_5} = 0.74 - 0.80$ and $\Phi_{C_2H_4Cl} = 0.71 - 0.77$, or $\Phi_{C_2H_5} + \Phi_{C_2H_4Cl} = 1.5$. It is again assumed that Cl atoms abstract only hydrogen from C_2H_5Cl and that H atoms either abstract only chlorine, or both H and Cl in the ratio 0.68. Lack of a complete analysis of the higher molecular weight products at 500 Torr and a gross uncertainty in the radical yield of C_2H_3Cl does not enable us to make a comparison with the experimental data as was done at 12.7 Torr. However, we are able to place lower limits upon $\Phi_{C_2H_5}$ and $\Phi_{C_2H_4Cl}$ of ~ 0.6 respectively, based only on those products measured. The sum of these numbers is 1.2, somewhat lower than the calculated value of 1.5, but the former figure does not take into account the dichlorobutanes which could not be determined because of experimental difficulties.

The three runs at ~ 1 Torr C_2H_5Cl (runs 1 - 3) show a significant decrease in radical products such as C_3H_6 and C_4H_{10}. The lack of any significant quantity of butane and therefore probably of any other radical combination products indicates that there can only be a small contribution from process (11), $C_2H_5Cl^{\dagger}(^2) \rightarrow C_2H_5^0 + Cl^*$, since it is this process which has been postulated to be mostly responsible for products with radical precursors. From the zero pressure intercepts in Fig. 2, the total quantum yield of non-scavengeable C_2H_4, i.e. $\Phi_5 + \Phi_6$, should be approximately 0.40, whereas the observed quantum yield at 1 Torr is 0.73. Thus a contribution of ~ 0.33 to

the quantum yield of C_2H_4 occurs at low pressures, very little of which can be attributed to radical disproportionation as was done at 12.7 Torr.

We tentatively interpret these last data in terms of the initial formation of another electronically excited state of C_2H_5Cl which has a fairly long lifetime ($\sim 10^{-7}$ s) with respect to molecular elimination of HCl. Thus at 12.7 Torr this state has been almost completely collisionally quenched to form $C_2H_5Cl^{\dagger}(^2)$. This in turn helps to account for the quantum yield of 0.36 assigned to process (11) at 12.7 Torr.

Despite the somewhat speculative nature of this discussion, it is apparent that the pathways by which C_2H_5Cl photodecomposes are not only probably wavelength dependent but also pressure dependent. Whatever errors there might be in detail with respect to the primary processes proposed, C_2H_5Cl decomposes mainly by molecular elimination of HCl and H_2 at very low pressures ($\sim 70\%$ at 1 Torr) and mainly by carbon–chlorine bond cleavage at high pressures ($\sim 70\%$ at 500 Torr). The facts that the quantum yields of C_2H_4 and C_2H_2 decrease with increasing pressure and the yields of radical products increase with increasing pressure we believe rule out the possibility of any collisional conversion to the ground electronic state. Further since there is no evidence that the overall quantum yield for the primary processes at any pressure is much less than unity (if not equal to one), the effect of the collisions must be to induce the cross over from at least one electronically excited state to another.

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