Table I. Lifetimes of Intermediate Complexes

Ion	Neutral	Intermediate complex	$k_b/\Sigma k_u$, cc/molecule ($\sim$)	$\tau = 1/k_u$, sec ($\sim$)
CH_5^+	C_2H_4	$C_3H_9^{+*}$	$<5 \times 10^{-19}$	$<5 \times 10^{-9}$
	C_3H_6	$C_4H_{11}^{+*}$	$<5 \times 10^{-19}$	$<5 \times 10^{-9}$
	$i\text{-}C_4H_8$	$C_5H_{13}^{+*}$	$<5 \times 10^{-19}$	$<5 \times 10^{-9}$
	C_2H_2	$C_3H_7^{+*}$	1×10^{-17}	1×10^{-7}
$C_2H_5^+$	C_3H_6	$C_5H_{11}^{+*}$	1×10^{-18}	1×10^{-8}
	$i\text{-}C_4H_8$	$C_6H_{13}^{+*}$	1×10^{-18}	1×10^{-8}
	C_2H_2	$C_4H_7^{+*}$	4×10^{-16}	4×10^{-6}
$C_3H_5^+$	C_2H_2	$C_5H_7^{+*}$	5×10^{-16}	5×10^{-6}

sociations of intermediate complexes in ethylene and obtained values for $1/k$ of the order of 10^{-7} sec.

Treating the other data qualitatively, we know that the lifetimes of the $(C_4H_9^+)^*$ complex from $C_2H_5^+ + C_2H_4$ and the $(C_6H_{13}^+)^*$ complex from $C_3H_7^+ + C_3H_6$ must be roughly 10^{-6} sec because of the large concentrations of the stabilized ions. On the other hand, the lifetime of the $(C_8H_{17}^+)^*$ complex from $C_4H_9^+ + C_4H_8$ must be lower, perhaps 10^{-8} sec, and this small lifetime is probably due to the rapid reversible decomposition of any complex since no other products were detected.

It is of interest to note in Table I that the more unsaturated the complex intermediate, the longer its lifetime or the greater the extent of collisional stabilization. This difference in lifetimes does not appear to be solely the result of differences in energy of the excited intermediate complexes above the ground states of the ions. $(C_3H_9^+)^*$, which is not appreciably stabilized by collision, has about 241 kcal/mole energy if formed by addition of CH_5^+ to C_2H_4. $\Delta H_f(C_3H_9^+)$ is not known, but if the molecule is stable, we would estimate it at

215–220 kcal/mole.[1b,3] Consequently, the excitation energy is 20–25 kcal/mole. On the other hand, $(C_3H_7^+)^*$ formed from CH_5^+ and C_2H_2 has about 283 kcal/mole, roughly 90 kcal/mole above the $sec\text{-}C_3H_7^+$ ion, and it is stabilized to a much greater extent.

There appears to be a fundamental difference in the nature of the intermediate complexes. CH_5^+ probably reacts with olefins predominantly through a loose complex involving no new C–C bond formation, perhaps something like the stripping model.[19] This is the same type of complex which we suggested for reactions with the paraffins.[1b] We feel it likely that there would be no scrambling of hydrogens in this complex. The complex with acetylene obviously involves C–C bond formation and the resultant allyl ion would probably show appreciable H–D mixing if appropriate deuterated compounds were used.

Similarly, $C_2H_5^+$ reacts with the higher olefins predominantly by a loose complex, but perhaps there are small amounts of strongly bound species. The absence of appreciable H^--transfer reactions suggests that the attack is primarily at the olefinic bond. We are at a loss for good explanation for the long-lived complexes with $C_2H_5^+ + C_2H_4$ and $C_3H_7^+ + C_3H_6$ and the short-lived complex for $C_4H_9^+ + i\text{-}C_4H_8$. Obviously, much further work needs to be done to determine the patterns of reactivities of hydrocarbon ions.

(19) A. Henglein in ref 3b, p 63.

Photolysis of Condensed Allyl Chloride[1]

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Abstract: The photolysis at 254 nm of liquid allyl chloride at 27° and of solid allyl chloride at 77°K has been studied by microphotochemistry. By the use of aqueous acetone as an actinometer, quantum yields for 18 products containing six or fewer carbon atoms were determined. The primary process proposed is cleavage of the carbon–chlorine bond to give allyl radical. Mechanisms for the formation of the products are given.

Few studies of the photochemistry of halogenated olefins have been reported. The results on several haloethylenes are summarized in a review article,[2] and results on vinyl chloride have been recently reported.[3] The uv photolysis of allyl iodide[4] was found to yield iodine with a quantum yield of 0.07, and allyl chloride–

mercury mixtures[5] gave mercurous chloride and polymer under uv irradiation.

We have recently reported some results on the photolysis of condensed allyl chloride, solid and liquid.[6] The study was primarily directed at the possible formation of hydrochloric acid and various C_3 hydrocarbons in order to gain information on the primary process. In the present paper, we have extended the investigation to

(1) This investigation was supported by a grant from the National Science Foundation.

(2) J. R. Majer and J. P. Simons, *Advan. Photochem.*, 2, 137 (1964).

(3) T. Fujimoto, A. M. Rennert, and M. H. J. Wijnen, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, Paper PHYS-135.

(4) W. West and B. Paul, *Trans. Faraday Soc.*, 28, 688 (1932).

(5) O. A. Reutov and M. A. Besprozvannyi, *Dokl. Akad. Nauk SSSR*, 80, 765 (1951).

(6) D. H. Volman and R. W. Phillips, *Ber. Bunsenges. Phys. Chem.*, 72, 242 (1968).

include all identifiable compounds containing six or fewer carbon atoms.

Experimental Section

Sample Preparation. Allyl chloride, Eastman Kodak Co. reagent grade, was fractionally distilled using a Podbielniak type column. The fraction retained boiled in the range 44.5–44.7°. The absorption spectrum gave ϵ 0.20 M^{-1} cm^{-1} at 254 nm. The distilled allyl chloride was further purified by vpc using 2 m of 25% dinonyl phthalate on 60–80 mesh firebrick at 42°. The nmr spectrum of the purified compound agreed exactly with that found in the literature.[7]

Materials. Most comparison compounds used for the identification of products were commercial samples purified by distillation and vpc. However, several compounds not obtainable commercially were synthesized.

3-Chloro-1,5-hexadiene. The compound was prepared by the reaction of 1,5-hexadien-3-ol with phosphorus pentachloride according to the method of Levine and Haller.[8] The dried distilled product, bp 78–80° (203 mm) (lit.[9] 46–47.5° (90 mm)), n^{23}D 1.4482 (lit.[9] n^{20}D 1.4483), was subjected to vpc on a 304-cm 25% dinonyl phthalate column at 100°. Two compounds were isolated, 3-chloro-1,5-hexadiene and 1-chloro-2,5-hexadiene. The 3-chloro compound had the following characteristics: nmr (CCl$_4$), τ 3.83–5.00 (multiplet, 6 H, vinyl), 5.71 (quartet, 1 H, allylic C-3), 7.47 ppm (triplet, 2 H, methylene group); ir (CCl$_4$), 3090, 3020, 2990, 1850, 1640, 1420, 1260, 1215, 985, and 920 cm^{-1}; mass spectrum, parent peaks at m/e 116 and 118.

1-Chloro-2,4-hexadiene. This product was prepared and collected as described above. It had the following characteristics: nmr (CCl$_4$), τ 4.32 (multiplet 3 H, internal ethylenic), 5.00 (multiplet, 2 H, terminal vinyl), 6.03 (doublet, 2 H, methyl chloride group), 7.22 ppm (broad multiplet, 2 H, methylene group); ir (CCl$_4$), 3090, 2980, 1660, 1640, 1425, 1280, 990, 970, and 915 cm^{-1}; mass spectrum, parent peaks at m/e 116 and 118.

cis-1-Chloro-1,5-hexadiene. The compound was prepared from allylmagnesium bromide and 1,3-dichloropropene according to the procedure of Porter and Rust.[10] The synthesis yields a mixture of cis and trans isomers. The product obtained, bp 79–80° (213 mm) (lit.[10] 82° (200 mm)), was freed from residual 1,3-dichloropropane by preparatory vpc on a 20-ft 20% diethylene glycol adipate column at 150°. Separation on a 304-cm 24.5% dinonyl phthalate column at 100° yielded two compounds. The one with shortest retention time, lower boiling, was subsequently identified as cis from a comparison of ir spectra and by analogy to assignment of the cis and trans isomers of 1-chloropropene-1.[11] The cis compound had the following characteristics: nmr (CCl$_4$), τ 4.23 (multiplet, 3 H, internal ethylenic protons plus proton on C-1), 5.02 (multiplet, 2 H, terminal vinyl), 7.78 ppm (broad multiplet, 4 H, methylenic groups); ir (neat), 3090, 2985, 2920, 2855, 1630, 1440, 1350, 1320, 1300, 990, 910, and 720 cm^{-1}.

trans-1-Chloro-1,5-hexadiene. The higher boiling isomer, longer retention time, obtained above had the following characteristics: nmr (CCl$_4$), τ 4.12 (multiplet, 3 H, internal ethylenic protons plus proton on C-1), 5.02 (multiplet, 2 H, terminal vinyl), 7.88 ppm (broad multiplet, 4 H, methylenic groups); ir (neat), 3075, 2985, 2915, 2855, 1630, 1440, 1295, 1265, 1235, 995, 925, 815, 685, and 635 cm^{-1}.

5-Chloro-4-chloromethylpentene-1. Kharasch and Büchi[12] have prepared the bromo compound by allowing diethylallyl malonate to react with lithium aluminum hydride and treating the resulting 2-hydroxymethyl-4-penten-1-ol with phosphorus pentabromide. We have used their method to synthesize the chloro compound except that phosphorus pentachloride was substituted for the phosphorus pentabromide. The product, bp 62–64° (16 mm), was subsequently purified and collected by preparatory vpc on a 304-cm, 24.5% dinonyl phthalate column at 100°. The compound had the following characteristics: nmr (CCl$_4$), τ 4.0–5.1 (complex multiplet, 3 H, vinyl), 6.38 (doublet, 4 H, protons on carbon bearing chlorine), 7.80 ppm (broad multiplet, 3 H, remaining protons); mass spec-

trum, parent peaks at m/e 152, 154, and 156, peak height ratios 154/152 = 0.63, 156/152 = 0.10, in agreement with theory.

Photolysis Method. The photolytic procedures used were similar to those described for our microphotochemistry technique.[13] After five freeze–pump–thaw cycles, allyl chloride was distilled into quartz tubes, 1.0-mm i.d., 0.25-mm wall thickness, 4.0 cm long. With the sample at liquid nitrogen temperature, the quartz tube was sealed at a previously prepared constriction, thus minimizing the effect of ultraviolet light from glowing quartz. The amount of allyl chloride was determined by weighing the empty quartz tube and the two sections of tubing after filling and sealing. Except for a few large-scale experiments, about 2 × 10^{-4} mole of allyl chloride was used. The reaction tube was mounted inside a transparent quartz dewar vessel. For experiments with the solid at 77°K, the cell was immersed in liquid nitrogen. Irradiations were carried out using a mercury resonance arc housed in Vycor, thus limiting the emitted light to 254 nm since Vycor is opaque to 185-nm light.

Results

The results obtained, shown in Figures 1–5, at each time interval represent a separate irradiation with a fresh sample of allyl chloride and a new quartz micro-reaction cell.

Hydrocarbons. Methane, ethane, ethylene, propene, allene, and cyclopropane were identified and quantitatively analyzed by vpc using two sets of columns which rearranged the order of elution time for propene, allene, and cyclopropane. The first system[14] consisted of an activated alumina poisoned with 2% squalane column (1.5 mm × 162 cm) at 25°. The order of elution was methane, ethane, ethylene, propene, cyclopropane, and allene. The second system[15] consisted of 24.8% dinonyl phthalate on 60–80 mesh firebrick (2.0 mm × 304 cm) at 25° followed by 20.2% ethylene glycol, 7.3% silver nitrate on 60–80 mesh firebrick (5.0 mm × 304 cm) at 0°. The order of elution was methane, ethane, ethylene, cyclopropane, allene, and propene. A comparison of elution times with those of authentic samples could be considered as providing reasonable identification using one of the above systems. Comparison in the two systems which provided a rearranged order of elution yielded unequivocal identification of the above C$_3$ hydrocarbons. Quantitative analysis of these hydrocarbons was carried out in the second system. Determinations of methane, ethane, and ethylene were only roughly quantitative because they were present in such small amount.

Methylacetylene has an extremely long retention time in the first system and is irreversibly absorbed in the second system. The system successfully used for methylacetylene was 24.8% dinonyl phthalate on 60–80 mesh firebrick (2 mm × 304 cm) followed by activated silica gel (2 mm × 50 cm), both at 23°.

Analysis of 1,5-hexadiene was complicated by the fact that its boiling point, 59.6°, is about 15° higher than that of allyl chloride. On polar to moderately polar columns, the trailing edge of unreacted allyl chloride completely masked the hexadiene. However, on a very polar column, 25% Ucon Polar, 280X, on 60–80 mesh Chromosorb W (2.5 mm × 608 cm) at 60° followed by 25% 3,3'-oxydipropionitrile on 60–80 mesh firebrick (2.5 × 304 cm) at 23°, the diene was eluted prior to allyl chloride and separation was complete.

(7) "Selected NMR Spectral Data," Vol. 2, M.C.A. (M.C.R.P.) Serial No. 342, College Station, Texas, 1962.
(8) P. A. Levine and H. L. Haller, *J. Biol. Chem.*, 83, 185 (1929).
(9) M. S. Kharasch, W. Nudenburg, and E. Sternfeld, *J. Am. Chem. Soc.*, 62, 2034 (1940).
(10) L. M. Porter and F. F. Rust, *ibid.*, 78, 5571 (1956).
(11) L. F. Hatch and R. H. Perry, Jr., *ibid.*, 71, 3262 (1949).
(12) M. S. Kharasch and G. Büchi, *J. Org. Chem.*, 14, 84 (1949).

(13) K. Porter and D. H. Volman, *Bull. Soc. Chim. Belges*, 71, 831 (1962).
(14) J. H. Knox, "Gas Chromatography," John Wiley and Sons, Inc., New York, N. Y., 1968, p 42.
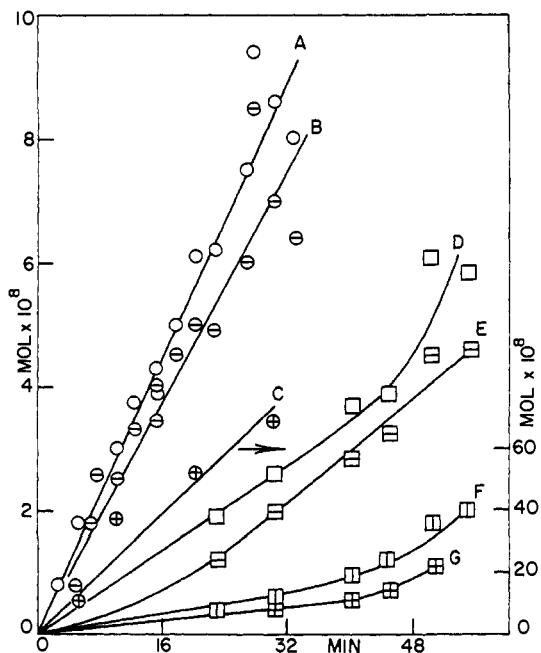(15) J. Shabtai, J. Herling, and E. Gil-Av, *J. Chromatog.*, 11, 32 (1963).

Figure 1. Formation of hydrocarbons: circles, 27°; squares, 77°K; A, D, propene, O, □; B, E, allene, ⊖, ⊟; C, hexadiene, ⊕; F, cyclopropane, ⊞; G, methylacetylene, ⊞.
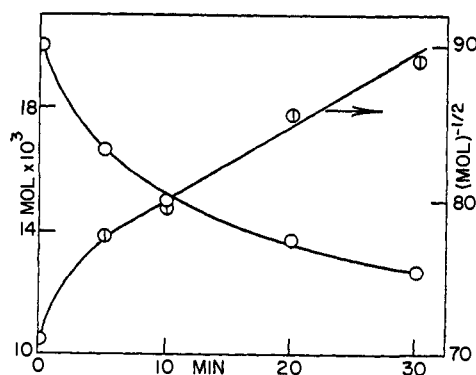

Figure 2. Removal of allyl chloride at 27°.

The hydrocarbon yields in the liquid at 27° and in the solid at 77°K are shown in Figure 1.

Allyl Chloride. The column used for 1,5-hexadiene could also be used to determine unreacted allyl chloride. The results obtained are shown in Figure 2.

Tricarbon Chlorine Compounds. For chromatographic analysis of the chlorinated hydrocarbons, a 24.8% dinonyl phthalate on 60–80 mesh firebrick (2 mm × 304 cm) at 94° was used. As allyl chloride was eluted from the column before the other chlorinated hydrocarbons, a bypass unit was incorporated to vent the allyl chloride to the atmosphere; otherwise, fouling of the detector system occurred. Peak identification was made by coincidence with authentic samples. However, because of peak overlap this was not completely satisfactory. Therefore, several large-scale photolyses were performed, following which the reaction products were separated from unreacted allyl chloride and polymer and subjected to chromatographic separation on the analytical column. Fractions were collected and products were identified by nmr and mass spectrometric analysis.
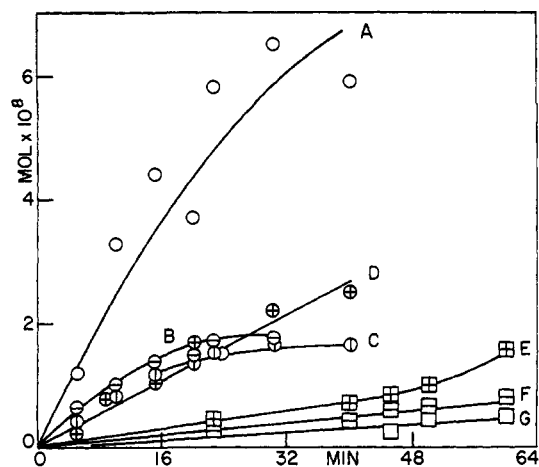

Figure 3. Formation of dichloropropanes and dichloropropenes: circles, 27°; squares, 77°K; A, G, 1,3-dichloropropane, O, □; B, F, cis-1,3-dichloropropene, ⊖, ⊟; C, trans-1,3-dichloropropene, ⊕; D, E, 1,2-dichloropropane, ⊕, ⊞.

1,3-Dichloropropane was identified by mass spectrometry and determined quantitatively by vpc. Because of the small quantity and the complexity of the mixtures, we were not successful in identifying 2,3-dichloropropane or 2,3-dichloropropene by nmr or mass spectrometry. Authentic samples of these two compounds gave identical retention times in vpc which coincided with a reaction product. This could be attributed to either of the two compounds or a mixture of the two, but for reasons developed in the discussion it seems most likely that the product is 2,3-dichloropropane.

Qualitative mass spectrometry indicated the presence of dichloropropene in two different fractions collected by chromatographic separation. From vpc coincidence times these were identified as cis-1,3-dichloropropene and trans-1,3-dichloropropene. However, vpc did not distinguish between the trans compound and 1-chloro-1,5-hexadiene, also a reaction product. The mole ratio of trans-1,3-dichloropropene to 1-chloro-1,5-hexadiene was determined by nmr performed on a fraction collected by vpc from the photolysis of the liquid in large-scale experiments. From this ratio, the vpc sensitivities for the individual compounds, and the chromatograms, the amount of trans-1,3-dichloropropene was determined.

The results obtained for the tricarbon chlorine compounds are shown in Figure 3. Results for the formation of trans-1,3-dichloropropene in the solid photolysis are not shown since we were not able to make a correction for 1-chloro-1,5-hexadiene.

Hexacarbon Chlorine Compounds. 3-Chloro-1,5-hexadiene and 1-chloro-1,5-hexadiene were identified and quantitatively determined by a combination of vpc, nmr, and mass spectrometry as already described for cis- and trans-1,3-dichloropropene. An additional C_6H_9Cl compound, determined by mass spectrometry and vpc, was also a reaction product. This compound was not identified. The results obtained for the chlorohexadienes are shown in Figure 4. The curve shown for trans-1-chloro-1,5-hexadiene obtained from photolysis at 77°K is uncorrected for trans-1,3-dichloropropene.
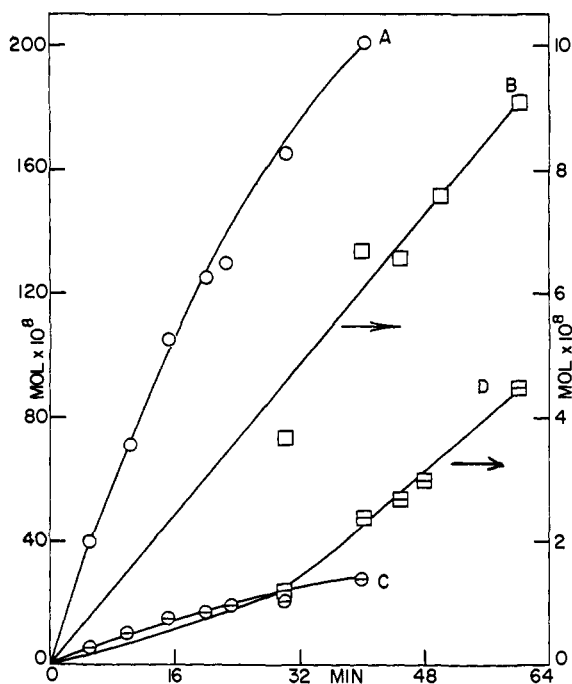
Figure 4. Formation of dichlorohexenes: circles, 27°; squares, 77°K; A, B, 5-chloro-4-chloromethylpentene-1, O, □; C, D, 5,6-dichlorohexene-1, ⊖, ⊟.

5-Chloro-4-chloromethylpentene-1 was identified and quantitatively determined by the combination of vpc, nmr, and mass spectrometry; there was no complication from peak overlap in vpc. An additional $C_6H_{10}Cl_2$ compound, determined by mass spectrometry and glpc, was also a reaction product. Although not identified this compound is probably 5,6-dichloropentene-1. The results obtained for the dichlorohexenes are shown in Figure 5.

Hydrogen Chloride. No hydrogen chloride was found by vpc using a katherometer detector. As katherometer detection is relatively insensitive compared to hydrogen-flame-ionization detection, we have devised a method to convert HCl to methane which can be determined by hydrogen-flame-ionization.[6] The reaction cell was crushed in an all-glass device and the vapors were passed over sodium bicarbonate which liberates carbon dioxide if HCl is present. After vpc separation the liberated carbon dioxide was reduced to methane by hydrogen in a hot nickel catalyst column. No HCl was found by this method and it is either absent or below the detection limit, 1×10^{-8} mole, of our method.

Hydrogen. No evidence for the formation of molecular hydrogen was obtained by mass spectrometry.

Polymer. For the liquid photolysis the rate of disappearance of allyl chloride was some ten times as great as the combined rate of appearance of all the found products containing up to six carbon atoms. In the large-scale experiments the solution became viscous on irradiation. Therefore, polymer is obviously formed in the liquid photolysis. No evidence for polymerization was obtained in the solid photolysis as we could detect no change in allyl chloride content in the solid photolysis. No observable change in allyl chloride was expected from the amounts of analyzed
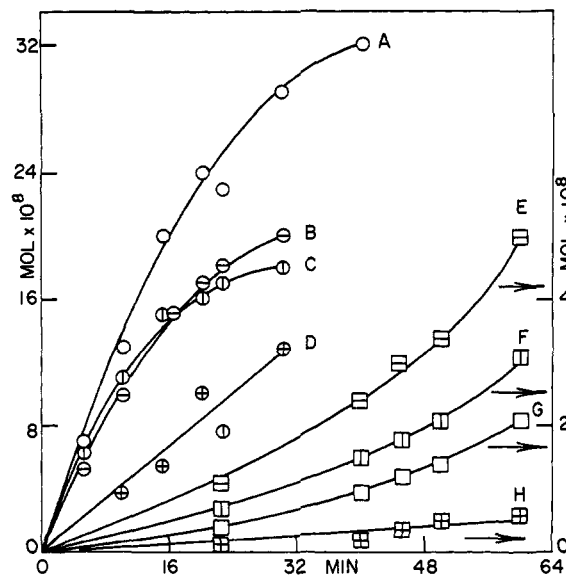

Figure 5. Formation of chlorohexadienes: circles, 27°; squares, 77°K; A, G, cis-1-chloro-1,5-hexadiene, O, □; B, E, trans-1-chloro-1,5-hexadiene, ⊖, ⊟; C, F, 3-chloro-1,5-hexadiene; ⊕, □; D, H, unidentified C_6H_7Cl, ⊕, ⊞.

products of photolysis, which accounted for less than 0.5% of the initial allyl chloride.

Reactivity Following Irradiation at 77°K. Irradiation at 77°K would be expected to produce free radicals whose reactions might continue over a considerable period of time. The analytical results would then be affected by the time elapsed between irradiation and analysis. We found, however, that the analytical results were not changed by holding the reaction cell at 77°K for 90 min following uv exposure.

Quantum Yield. A rough estimation of quantum yields was made by comparison with the quantum yield at 254 nm for the formation of methane from aqueous acetone at 27° we have determined previously.[16] An optical density equivalent to that of allyl chloride was obtained by using 0.17 M acetone. The results are given in Table I. In calculating the quantum yields, the initial rates as determined from Figures 1–5 were used except for methane, ethane, and ethylene, whose average rates of formation were used. In the absence of information, the absorption characteristics of the solid were taken as the same as for the liquid. Although this may give a large error in the calculation of quantum yields for the solid photolysis, comparative quantum yields for the products are valid.

Discussion

Our results at 77°K on the esr spectra of uv-irradiated allyl alcohol,[17] allyl bromide, and allyl cyanide,[18] and the results at 4°K on allyl iodide,[19] show the presence of allyl free radical, indicating that the primary process is cleavage of the bond between the allylic carbon and the substitution group. These results are confirmed by the experiments of Callear and Lee,[20,21] who have found the

(16) D. H. Volman and L. W. Swanson, J. Am. Chem. Soc., 82, 4141 (1960).
(17) K. A. Maas and D. H. Volman, Trans. Faraday Soc., 60, 1202 (1964).
(18) Unpublished results, this laboratory.
(19) E. L. Cochran, F. J. Adrian, and V. A. Bowers, J. Chem. Phys., 34, 1161 (1961).

	Liquid, 27°C	Solid, 77°K
Allyl chloride (removal)	12	...
5-Chloro-4-chloromethyl-pentene-1	0.13	0.3×10^{-2}
Unidentified $C_6H_{10}Cl_2{}^a$	1.9×10^{-2}	0.7×10^{-3}
cis-1-Chloro-1,5-hexadiene	2.3×10^{-2}	0.3×10^{-3}
trans-1-Chloro-1,5-hexadiene	1.6×10^{-2}	$0.8 \times 10^{-3\,b}$
3-Chloro-1,5-hexadiene	2.0×10^{-2}	0.5×10^{-3}
Unidentified C_6H_9Cl	0.7×10^{-2}	0.1×10^{-3}
cis-1,3-Dichloropropene	0.2×10^{-2}	0.2×10^{-3}
trans-1,3-Dichloropropene	0.2×10^{-2}	$...^c$
2,3-Dichloropropane	0.1×10^{-2}	0.2×10^{-3}
1,3-Dichloropropane	0.5×10^{-2}	0.1×10^{-3}
1,5-Hexadiene	4.1×10^{-2}	0
Propene	0.5×10^{-2}	0.1×10^{-2}
Allene	0.4×10^{-2}	0.9×10^{-3}
Cyclopropane	0	0.4×10^{-3}
Methylacetylene	0	0.2×10^{-3}
Methane	0.6×10^{-4}	0.7×10^{-4}
Ethane	0.4×10^{-4}	0.9×10^{-4}
Ethylene	0.3×10^{-4}	0.6×10^{-4}

^{a} Probably 5,6-dichlorohexene-1. ^{b} Uncorrected for trans-1,3-dichloropropene. ^{c} Included in trans-1-chloro-1,5-hexadiene.

absorption spectrum of allyl radical in the flash photolysis of a number of allyl compounds in the gas phase at ambient temperature. Inexplicably we did not observe allyl free radical in the esr spectrum of uv-irradiated pure allyl chloride at 77°K. However, allyl radical is definitely formed in the uv irradiation of dilute allyl chloride in methanol at 77°K as determined by esr.[22] This evidence together with the photochemical results makes it reasonable to propose that the principal primary process is

$$CH_2CHCH_2Cl + h\nu \longrightarrow Cl\cdot +$$
$$[CH_2=CH\dot{C}H_2 \quad \dot{C}H_2CH=CH_2] \quad (1)$$
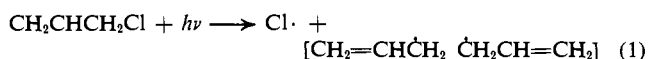
The absence of HCl in the products indicates that an intramolecular primary process either does not occur or is of minor importance. Further, the absence of molecular hydrogen is a strong indication that primary cleavage of a carbon–hydrogen bond does not occur as it would be expected that, if hydrogen atoms were formed, molecular hydrogen would be produced by abstraction reactions.

In the liquid photolysis, the major products are polymeric compounds. In fact the high quantum yield of polymer formation and the expectation that polymerization in allylic systems yields chains of only some three to six monomer units leads to the conclusion that the primary quantum yield may be unity and that geminate cage recombination does not occur in the liquid.

Free-radical chain polymerization initiated by light absorption to yield free radicals and terminated by radical–radical coupling yields the well-known general rate equation

$$-dM/dt = k_1[I_a]^{1/2}M \quad (2)$$

For weak absorption, series expansion of Lambert and Beers law for I_a and substitution in (2) yields

$$-dM/dt = k_3M^{3/2} \quad (3)$$

(20) A. B. Callear and H. K. Lee, Nature, 213, 693 (1967).
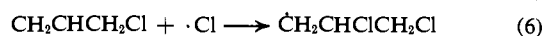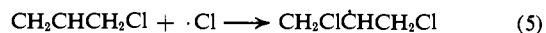(21) A. B. Callear and H. K. Lee, Trans. Faraday Soc., 64, 308 (1968).
(22) Experiments performed recently by Dr. P. Svejda in this laboratory.

and integration gives

$$M^{-1/2} = k_4t + M_0^{-1/2} \quad (4)$$

and a plot of $M^{-1/2}$ vs. t would yield a straight line. Such a plot has been made, Figure 2, and it may be observed that except for the initial portion, first 5 min, a straight line was obtained. Deviation from linearity is, perhaps, to be expected in the first portion because the initial formation of polymer would have a proportionally major effect on the viscosity of the solution.

Except for polymer the product formed in largest amount for both the liquid and the solid is 5-chloro-4-chloromethylpentene-1. The most probable reaction for chlorine atom is addition to the olefinic bond of allyl chloride

$$CH_2CHCH_2Cl + \cdot Cl \longrightarrow CH_2Cl\dot{C}HCH_2Cl \quad (5)$$
$$CH_2CHCH_2Cl + \cdot Cl \longrightarrow \dot{C}H_2CHClCH_2Cl \quad (6)$$

The dichloropropyl radicals would be formed in close proximity to allyl radicals in the same solvent cage and radical–radical coupling would be favored. For the 1,3-dichloropropyl radical the reaction

$$CH_2Cl\dot{C}HCH_2Cl + CH_2=CH\dot{C}H_2 \longrightarrow$$
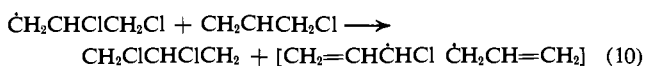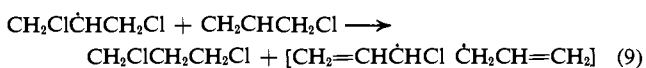$$CH_2ClCH(CH_2Cl)CH_2CH=CH_2 \quad (7)$$
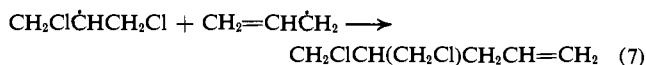
yields 5-chloro-4-chloromethylpentene-1. For the 1,2-dichloropropyl radical the reaction

$$\dot{C}H_2CHClCH_2Cl + CH_2=CH\dot{C}H_2 \longrightarrow$$
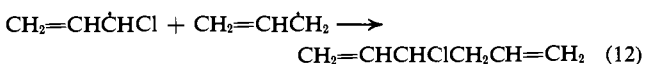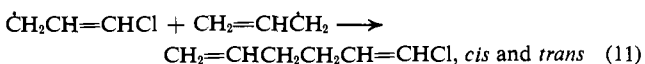$$CH_2ClCHCl(CH_2)_2CH=CH_2 \quad (8)$$
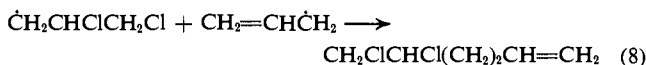
would yield 5,6-dichlorohexene-1. Evidence for hydroxyl radical addition to both β and γ positions of allyl alcohol has been reported.[23] Similar addition for chlorine atom to allyl chloride seems probable. Therefore it is logical that if reaction 5 followed by reaction 7 occurs, reaction 6 followed by reaction 8 should also occur, and hence that the unidentified $C_6H_{10}Cl_2$ compound is 5,6-dichlorohexene-1.

The dichloropropanes would be expected from the hydrogen-atom abstraction reactions

$$CH_2Cl\dot{C}HCH_2Cl + CH_2CHCH_2Cl \longrightarrow$$
$$CH_2ClCH_2CH_2Cl + [CH_2=CH\dot{C}HCl \quad \dot{C}H_2CH=CH_2] \quad (9)$$
$$\dot{C}H_2CHClCH_2Cl + CH_2CHCH_2Cl \longrightarrow$$
$$CH_2ClCHClCH_2 + [CH_2=CH\dot{C}HCl \quad \dot{C}H_2CH=CH_2] \quad (10)$$

Because of the low or zero activation energy for radical–radical coupling, the predominance of the dichlorohexenes over the dichloropropanes in both the liquid and solid is explicable.

Formation of chlorohexadienes is most readily explained by combination of chloroallyl and allyl radicals. Allylic hydrogen abstraction from allyl chloride as in (9) and (10) above or by any free radical would yield chloroallyl radical. Coupling with allyl radical would yield three different monochlorohexadienes, cis-1-chloro-1,5-hexadiene, trans-1-chloro-1,5-hexadiene, and 3-chloro-1,5-hexadiene.

$$\dot{C}H_2CH=CHCl + CH_2=CH\dot{C}H_2 \longrightarrow$$
$$CH_2=CHCH_2CH_2CH=CHCl, \text{ cis and trans} \quad (11)$$
$$CH_2=CH\dot{C}HCl + CH_2=CH\dot{C}H_2 \longrightarrow$$
$$CH_2=CHCHClCH_2CH=CH_2 \quad (12)$$

The three compounds are found in both the liquid and

(23) D. H. Volman and J. C. Chen, J. Am. Chem. Soc., 81, 4141 (1959).

solid photolysis. The additional compound of formula C_6H_9Cl which has not been identified could also be formed by radical–radical coupling but with molecular rearrangement.

Chloroallyl radical coupling with chlorine atom likewise would yield the observed cis-1,3-dichloropropene and trans-1,3-dichloropropene. The other possible compound from coupling, 3,3-dichloropropene-1, was not observed. This is, perhaps, not surprising as the enthalpy of this reaction is probably about 4–5 kcal/mole more endothermic than for the 1,3-dichloropropenes. The enthalpies of formation of the compounds are not known, but group approximation methods of calculating enthalpies of formation yield the above difference.

The simplest mechanism for the formation of 1,5-hexadiene is the combination of two allyl radicals

$$2CH_2\!\!=\!\!CH\dot{C}H_2 \longrightarrow CH_2CHCH_2CH_2CHCH_2 \qquad (13)$$

Disproportionation of allyl radicals would give propene and allene

$$2CH_2\!\!=\!\!CH\!-\!\dot{C}H_2 \longrightarrow CH_2CCH_2 + CH_3CHCH_2 \qquad (14)$$

The results in the liquid phase are consistent with that expected from these reactions. The initial quantum yield of 1,5-hexadiene is about 10 times that of either propane or allene as would be expected from the activation energies, both low but presumably a few kilocalories higher for reaction 14. Further the yields of propene and allene are almost equal.

In the solid, however, hexadiene is not formed which is consistent with the esr evidence that the spectrum of allyl radicals is not observed in irradiated pure solid allyl chloride. Therefore allyl radicals must be present at low concentration in the solid. Primary process 1 is about 52 kcal exothermic if a value of 60 kcal is used for the carbon–chlorine bond dissociation energy in allyl chloride.[24] As the chlorine atom and allyl radical have about the same mass, if the excess energy were distributed as kinetic energy only in the atom and radical, there would be almost equipartition of energy to conserve momentum. If, as is possible, chlorine atom was formed in the $^2P_{1/2}$ excited state rather than the $^2P_{3/2}$ ground state, chlorine atom would have only 2.3 kcal excitation energy. These considerations lead to the conclusion that allyl radical may have some 52 kcal excess energy and probably well over the equipartition value because of the vibrational modes

available in the allyl radical. Rebbert and Ausloos[25] have recently discussed the reactions of "hot" alkyl radicals in conjuction with halogen atoms in solid matrices. On the basis of their work and earlier studies, they conclude that most of the radicals will become thermalized and undergo geminate recombination, that diffusion of alkyl radicals from the solvent cage will play a minor role, and that the observed abstraction reactions can be attributed to "hot" radicals. Thus hydrogen-atom abstraction from allyl chloride to yield chloroallyl radical is favored. At the same time C_3H_6 would be formed. The excess energy in the radical is more than sufficient to form, by abstraction, either propene or cyclopropane, the formation of propene being about thermally neutral and the formation of cyclopropane being about 7 kcal endothermic. Likewise, abstraction of an hydrogen atom from allyl by any radical in the system would yield allene or methyl acetylene, both of which require rearrangement after hydrogen-atom abstraction. The presence of both products indicates that this also is a hot-radical process. By contrast, neither of the higher energy products, cyclopropene or methylacetylene, is found in the liquid photolysis.

Other hydrocarbons formed with very low quantum yields were methane, ethane, and ethylene. Callear and Lee[20,21] have detected methyl radical in the absorption spectrum of several allylic compounds undergoing flash photolysis. They speculate that this could come from an hydrogen atom shift followed by fission of the carbon–carbon bond. Hydrogen atom abstraction by methyl would yield methane, and methyl-methyl radical coupling would yield ethane. Many explanations for ethylene formation can be given; perhaps the simplest is abstraction of hydrogen atom by vinyl radical formed to a small extent in the primary process by fission of the carbon–carbon single bond in allyl chloride.

The mechanisms proposed above are the simplest possible ones which can explain the products. With the exception of the "hot" radical reaction proposed for the formation of cyclopropane in the solid, all of the reactions are either nearly thermally neutral or exothermic. Gas-phase studies, in which radical-molecule reactions can be minimized and in which kinetic parameters can be readily varied, should prove fruitful in further elucidation of the mechanism, and we are currently in the beginning stages of a study of the gaseous photolysis.

(24) T. L. Cottrell, "The Strengths of Chemical Bonds," 2nd ed, Butterworth & Co., Ltd., London, 1958, p 276.

(25) R. E. Rebbert and P. Ausloos, J. Chem. Phys., 48, 306 (1968).