

PHOTOLYSIS OF ALLYL CHLORIDE

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Summary

The photolysis of gaseous allyl chloride at 229 nm and 300, 341 and 381 K yields 12 products containing six or fewer carbon atoms and not more than two chlorine atoms: 5-chloro-4-chloromethylpentene; 5,6-dichlorohexene; *cis*- and *trans*-1-chloro-1,5-hexadiene; 3-chloro-1,5-hexadiene; *cis*- and *trans*-1-chloro-2,5-hexadiene; 1,2-dichloropropane; 1,3-dichloropropane; 1,5-hexadiene; propene; allene. Quantum yields determined by using methyl formate as an actinometer are highest for 5-chloro-4-chloromethylpentene and hexadiene, being in the range 0.2 - 0.3. The primary process is cleavage of the C—Cl bond and the products result from a series of bimolecular reactions. From the yields of hexadiene and allene, the allyl radical disproportionation-combination rate constant calculated is $k_d/k_c = (0.07 \pm 0.01) \times \exp\{-(800 \pm 70)/T\}$. A comparison of the gas phase photolysis with our earlier condensed phase photolysis shows that neither geminate recombination, as for the solid, nor polymerization, as for the liquid, needs to occur.

1. Introduction

In a previous paper we reported studies on the photolysis at 254 nm of liquid allyl chloride at 300 K and of solid allyl chloride at 77 K [1]. The primary process proposed was cleavage of the C—Cl bond to give allyl radical. Quantum yields for 18 products containing six or fewer carbon atoms and two or fewer chlorine atoms, ranging in complexity from methane to isomeric dichlorohexenes, were determined. The principal differences between the liquid and solid results were the contributions from polymerization and from geminate recombination. For the liquid, the quantum yield of allyl chloride removal by polymer formation was over 40 times greater than that for the combined quantum yields of the other products; polymerization did not occur in the solid. Exclusive of polymer, the combined quantum yield of products for the liquid was about 0.3 whilst for the solid it was less than 0.01, indicating that geminate recombination was predominate in the solid phase. To complement the solid and liquid phase studies and hence to

encompass the common three states of matter, we carried out the investigation of the gas phase photolysis of allyl chloride which we now present.

2. Experimental details

Reactions were carried out in a conventional gas phase photolysis system employing a cylindrical quartz cell, 3.5 cm \times 10 cm outside diameter, 83.0 cm³ volume, contained in an air thermostat. The light source was an 18 W cadmium "omnirange spectral lamp" with an opening in the Pyrex outer jacket to permit UV emission. A parallel light beam impinging end-on to the reaction cell was obtained with a Supersil lens. The initial pressures of allyl chloride were 31.9, 35.9 and 40.2 Torr at 300, 341 and 381 K to give the same concentration, 1.70×10^{-6} mol cm⁻³, at each temperature.

After irradiation the entire contents of the reaction cell were swept into a thin-walled capillary tube, about 1.5 mm \times 4.5 cm, which was subsequently fuse sealed. The contents were submitted to vapor phase chromatography analysis by crushing the tube in carrier gas according to our microphotochemical methodology [1, 2].

3. Results

The experimental results obtained are shown in Figs. 1 - 5. Irradiations were carried out for the stated time interval, and the entire contents were then removed for analysis; complete analysis required four separate irradiations.

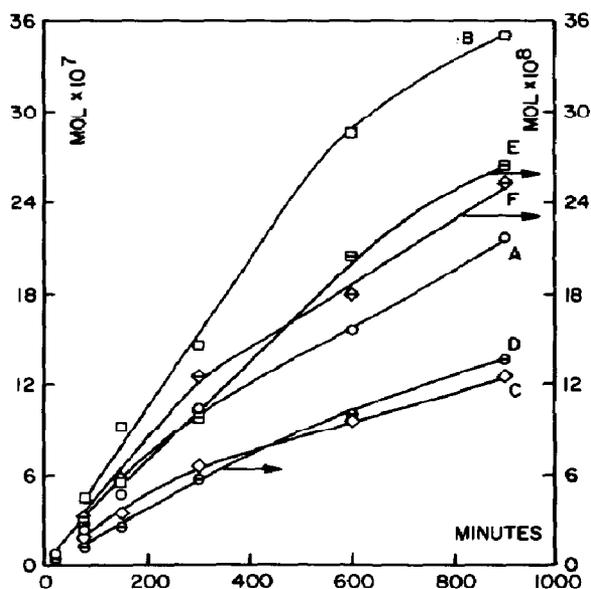


Fig. 1. Formation of dichlorohexenes: \circ , \ominus , 300 K; \square , \boxplus , 341 K; \diamond , \diamondsuit , 381 K; A (\circ), B (\square), C (\diamond), 5-chloro-4-chloromethylpentene-1; D (\ominus), E (\boxplus), F (\diamondsuit), 5,6-dichlorohexene-1.

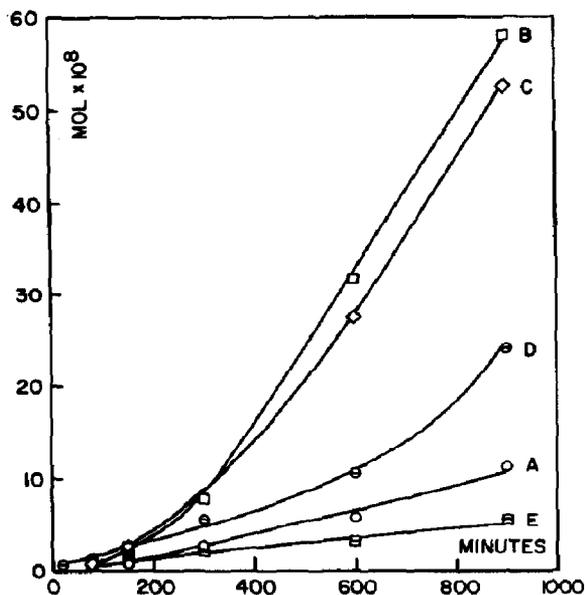


Fig. 2. Formation of dichloropropanes: \circ , \ominus , 300 K; \square , \boxminus , 341 K; \diamond , 381 K; A (\circ), B (\square), C (\diamond), 1,2-dichloropropane; D (\ominus), E (\boxminus), 1,3-dichloropropane.

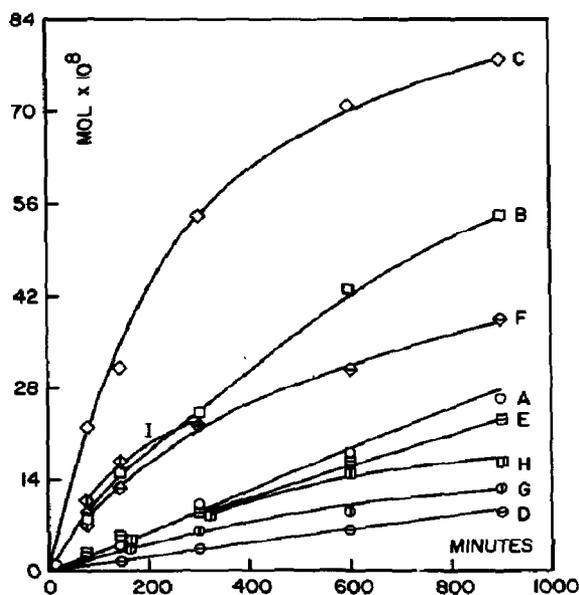


Fig. 3. Formation of chlorohexadienes: \circ , \ominus , \oplus , 300 K; \square , \boxminus , \boxplus , 341 K; \diamond , \diamondsuit , \heartsuit , 381 K; A (\circ), B (\square), C (\diamond), *cis*-1-chloro-1,5-hexadiene; D (\ominus), E (\boxminus), F (\diamondsuit), *trans*-1-chloro-1,5-hexadiene; G (\oplus), H (\boxplus), I (\heartsuit), 3-chloro-1,5-hexadiene.

tions at a stated time interval. The compounds from individual irradiations were analyzed according to groups: allyl chloride and 1,5-hexadiene; hydrocarbons except 1,5-hexadiene and methylacetylene; 5-chloro-4-chloromethylpentene, 5,6-dichlorohexene, unidentified dichlorohexenes, *cis*-1-chloro-1,5-hexadiene, *trans*-1-chloro-1,5-hexadiene, 3-chloro-1,5-hexadiene,

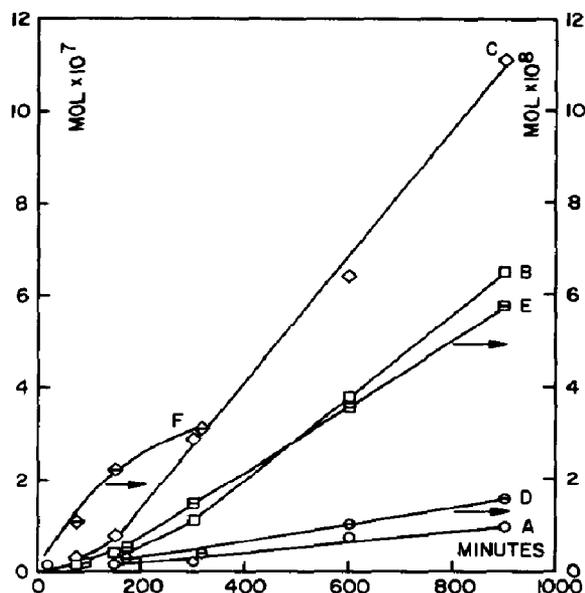


Fig. 4. Formation of chlorohexadienes: \circ , \ominus , 300 K; \square , \boxplus , 341 K; \diamond , \diamondsuit , 381 K; A (\circ), B (\square), C (\diamond), *cis*-6-chloro-1,4-hexadiene; D (\ominus), E (\boxplus), F (\diamondsuit), *trans*-6-chloro-1,4-hexadiene.

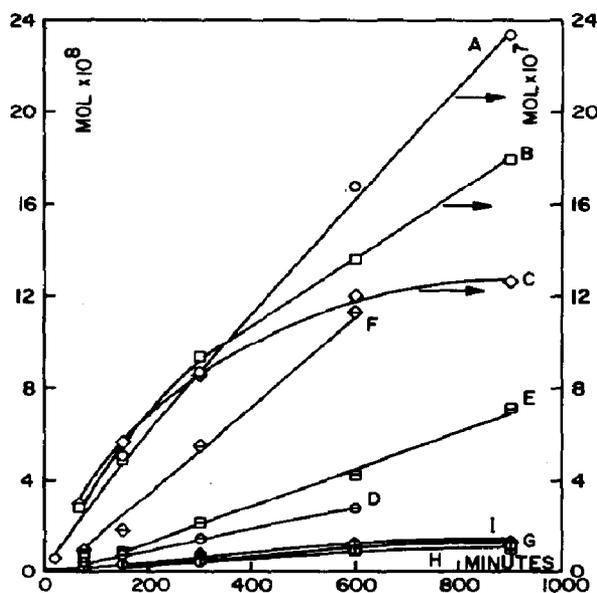


Fig. 5. Formation of hydrocarbons: \circ , \ominus , ϕ , 300 K; \square , \boxplus , \boxminus , 341 K; \diamond , \diamondsuit , ϕ , 381 K; A (\circ), B (\square), C (\diamond), 1,5-hexadiene; D (\ominus), E (\boxplus), F (\diamondsuit), propene; G (ϕ), H (\boxminus), I (ϕ), allene.

trans-1-chloro-2,5-hexadiene, *cis*-1-chloro-2,5-hexadiene, *cis*-1,3-dichloropropene, *trans*-1,3-dichloropropene, 1,2-dichloropropane and 1,3-dichloropropane; methylacetylene. Hence, the data represented in Figs. 1 - 5 derive from over 60 separate irradiations. An unidentified chlorohexadiene reported in the condensed phase studies is now identified as a mixture of *cis*-

and *trans*-3-chloro-2,5-hexadiene; also a previously unidentified dichlorohexene is now identified as 5,6-dichlorohexene.

The absorption spectrum of allyl chloride at pressures of 31.2 and 200.1 Torr was measured at 295 K using a Beckman spectrophotometer; Beer's law was followed. The relative intensities of spectral emissions from the cadmium lamp were determined with a Heath model EU-701 UV-visible single-beam spectrophotometer equipped with a Czerny-Turner 0.35 m grating monochromator, model EU-700-70. The relative intensities of the lamp emission lines and the corresponding extinction coefficients ϵ for allyl chloride are given in Table 1. It may be deduced that significant absorption occurs only at 228.8 and 226.7 nm.

TABLE 1

Absorption spectrum of allyl chloride and cadmium lamp emission

Wavelength (nm)	ϵ (allyl chloride) (l mol ⁻¹ cm ⁻¹)	Lamp emission ^a
224.1	5.24	0.3
226.7	3.17	9.7
226.8	3.13	0.2
228.8	2.07	100
231.0	1.33	0.3
233.0	0.92	0.3
248.5	0.05	0.05

^aRelative intensity.

With the above information quantum yields were determined by a modification of the method of equivalent optical densities [3] using methyl formate, $\Phi_d = 0.75$ at 25 °C [4], as the actinometer. From the absorption spectrum of methyl formate [5] the optical densities of methyl formate and allyl chloride were matched at 228.8 nm using 2.1 Torr and 31.2 Torr respectively at 300 K. Corrections for absorption by methyl formate and by allyl chloride at 226.7 nm were applied, and the quantum yields were calculated (Table 2).

4. Discussion

4.1. Principal reaction steps

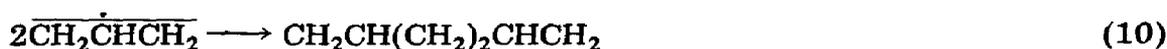
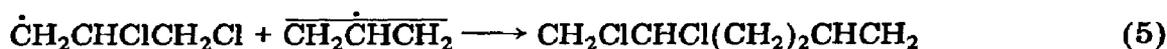
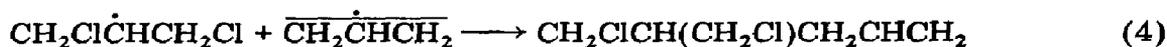
The primary process and reaction mechanisms which can account for the photolysis products except for *cis*- and *trans*-1-chloro-2,5-hexadiene are given in the following scheme:



TABLE 2

Initial quantum yields of product formation

	Solid 77 K	Liquid 300 K	Gas		
			300 K	341 K	381 K
Allyl chloride (removal)	—	12	2.0	2.4	2.5
5-chloro-4-chloromethylpentene	0.000	0.1	0.2	0.3	0.2
5,6-dichlorohexene	0.7×10^{-3}	0.02	0.01	0.03	0.03
<i>Cis</i> -1-chloro-1,5-hexadiene	0.3×10^{-3}	0.02	0.02	0.08	0.2
<i>Trans</i> -1-chloro-1,5-hexadiene	0.8×10^{-3}	0.02	0.009	0.03	0.09
3-chloro-1,5-hexadiene	0.5×10^{-3}	0.02	0.009	0.03	0.01
<i>Cis</i> -1-chloro-2,5-hexadiene	0.1×10^{-3}	0.007	0.002	0.01	0.03
<i>Trans</i> -1-chloro-2,5-hexadiene	0	0	0.001	0.002	0.001
<i>Cis</i> -1,3-dichloropropene	0.2×10^{-3}	0.002	0	0	0
<i>Trans</i> -1,3-dichloropropene	—	0.002	0	0	0
1,2-dichloropropane	0.2×10^{-3}	0.001	0.003	0.01	0.008
1,3-dichloropropane	0.1×10^{-3}	0.005	0.02	0.008	0
1,5-hexadiene	0	0.04	0.2	0.3	0.3
Propene	0.001	0.005	0.003	0.004	0.01
Allene	0.9×10^{-3}	0.004	0.001	0.002	0.003
Cyclopropane	0.4×10^{-3}	0	0	0	0
Methylacetylene	0.2×10^{-3}	0	0	0	0



4.2. Primary process

The electron spin resonance spectra of UV-irradiated allyl chloride frozen neat, or frozen in methanol solution, or as an inclusion compound in an adamantane matrix at ambient temperature indicate the formation of allyl radical [6]. Concurrent with bond cleavage to form free radicals, molecule elimination is a possibility in the photolysis of olefinic compounds. However, using a method in which HCl is converted to methane subsequently

determined by hydrogen flame ionization [1], we found no HCl. The method has a detection limit of 1×10^{-8} mol. Also, no evidence for the formation of molecular hydrogen was found by mass spectrometry. The primary process is therefore represented by eqn. (1).

4.3. The dichloro products

There are two most probable reactions for chlorine atoms: abstraction of a hydrogen atom from allyl chloride and addition to the olefinic bond of allyl chloride. As HCl was not found addition of a chlorine atom at either the γ or the β positions of allyl chloride (eqns. (2) and (3)) represents the only reactions of chlorine atoms required to explain the dichloro products.

Formation of the dichlorohexenes is most readily attributable to coupling of the dichloropropyl radicals formed in eqns. (2) and (3) with allyl radical (eqns. (4) and (5)). Except for 1,5-hexadiene, which is present in roughly comparable amounts, the most abundant product is 5-chloro-4-chloromethylpentene (eqn. (4)), approximately an order of magnitude greater than 5,6-dichlorohexene (eqn. (5)). As the secondary radical, 1,3-dichloroisopropyl (eqn. (2)), is more stable than the primary radical, 2,3-dichloropropyl (eqn. (3)), this is the predicted result from the expectation that thermodynamic stability leads to a higher probability of formation of the radical.

The expected abstraction of the α hydrogen atom of allyl chloride by the two dichloropropyl radicals yields 1,3-dichloropropane, 1,2-dichloropropane and the 1-chloroallyl radical (eqns. (6) and (7)). The yield of the 1,3 product is an order of magnitude less than that of the corresponding chlorochloromethylpentene while the yield of the 1,2 product is comparable with that of the corresponding dichlorohexene. Since the coupling reactions (eqns. (4) and (5)) have very low or even zero activation energies, and since hydrogen atom abstraction by the thermodynamically less stable radical, 1,2-dichloropropyl, should have an activation energy lower than that for abstraction by the more stable radical, 1,2-dichloroisopropyl, the observed yield comparisons are the logical ones. A more refined analysis is not warranted because we do not have information on compounds containing more than two chlorine atoms, e.g. tetrachlorohexanes, which would be produced by coupling of the dichloro radicals.

4.4. The monochloro products

Chlorohexadienes are expected from coupling of allyl with chloroallyl radicals. Coupling at the γ position of chloroallyl yields *cis*- and *trans*-1-chloro-1,5-hexadiene (eqn. (8)) while coupling at the α position yields 3-chloro-1,5-hexadiene (eqn. (9)). The other chlorohexadienes identified are *cis*- and *trans*-1-chloro-2,5-hexadiene; these could be formed by coupling but only with molecular rearrangement, conceivably an allylic shift of the chlorine atom.

4.5. Hydrocarbon products and the disproportionation-combination ratio for allyl

1,5-hexadiene is certainly formed by the combination of two allyl radicals (eqn. (10)). Disproportionation between allyl radicals leads to propene and allene (eqn. (11)). Although this is probably the preponderant mechanism for the formation of allene, propene is expected also from hydrogen atom abstraction from allyl chloride by allyl radical. Hence, propene is formed in greater amount than allene. The usual disproportionation-combination expression is given by the hexadiene-allene ratio

$$\frac{k_d}{k_c} = \frac{[\text{CH}_2\text{CH}(\text{CH}_2)_2\text{CHCH}_2]}{[\text{CH}_2\text{CCH}_2]} \quad (12)$$

and each time interval yields a separate experimental value for k_d/k_c . A plot according to the Arrhenius expression for k_d and k_c

$$\frac{k_d}{k_c} = \frac{A_d}{A_c} \exp\left\{-\frac{(E_d - E_c)}{RT}\right\} \quad (13)$$

shown in Fig. 6, yields $k_d/k_c = (0.068 \pm 0.011) \exp\{-(800 \pm 70)/T\}$ in the temperature range 300 - 381 K.

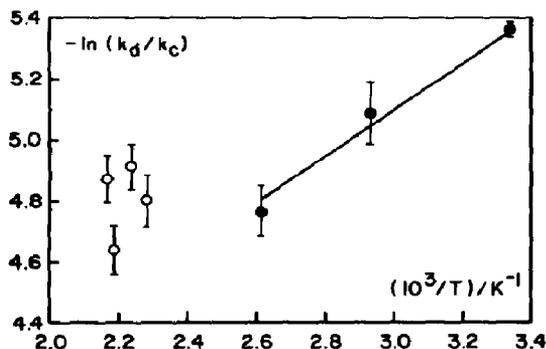


Fig. 6. Arrhenius plot for k_d/k_c : ●, this work (the points represent averages obtained from four experiments at 300 and 381 K and from five experiments at 341 K; the error bars are one standard deviation); ○, after James and Kambanis [7] (one experiment at each temperature with their given error limit).

The only other experiments leading to a calculation of the disproportionation-combination ratio for allyl radicals are those of James and Kambanis [7]: single experiments at each of four temperatures in the range 438 - 463 K. Their data are also represented in Fig. 6. James and Kambanis assumed temperature independence and averaged their four values to calculate $k_d/k_c = 0.008 \pm 0.001$. We have arbitrarily assigned this error limit to each experimental value and calculated error limits for the logarithmic values accordingly. The extrapolated value of our rate expression to the middle of their temperature range gives $k_d/k_c = 0.011 \pm 0.002$, in fair agreement with their result.

The combination rate constant k_c has been a subject of considerable interest and several experimental studies directed at its determination have been conducted. An evaluation of these studies and an experimental determination are reported by Tulloch *et al.* [8], who give $A_c = (1.69 \pm 0.03) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $E_c = -(1.1 \pm 0.1) \text{ kJ mol}^{-1}$ in the temperature range 293 - 571 K. From these values and our expression for k_d/k_c , $k_d = (0.11 \pm 0.03) \exp\{-(940 \pm 80/T)\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

4.6. Quantum yields

The quantum yield of 12 for allyl chloride removal in the liquid phase (Table 2) indicates that the liquid undergoes polymerization and we have shown that the rate of removal is consistent with the kinetics of free-radical chain polymerization initiated by light absorption [1]. In the gas phase the quantum yield of about 2 indicates that polymerization is either a minor pathway or non-existent since the primary process probably decomposes one allyl chloride molecule and secondary processes, eqns. (2), (3), (6) and (7), consume others.

The assumption of a quantum yield of unity for the primary process leads to a reasonable accounting for allyl radicals on the basis of the proposed secondary processes. Summation of the quantum yields for products formed by reactions of allyl, counting twice for combination to form hexadiene, gives 0.7, 1.1 and 1.3 allyl radicals per quantum absorbed at 300 K, 341 K and 381 K respectively. Given the crudeness of the quantum yield calculations, these values tend to confirm the validity of the reaction scheme.

4.7. Comparison of photolysis in the three states

Aside from the quantitative treatment made for allyl radical disproportionation and combination, further quantitative treatment of the data does not lead to worthwhile interpretation: the system is too complex and analytical data for compounds containing more than two chlorine atoms or more than six carbon atoms are lacking. Nevertheless a comparison with the solid and liquid phase studies is of interest. When allyl chloride removal is neglected, the summations of the quantum yields obtained are 0.0054 for the solid at 77 K, 0.25 for the liquid at 300 K and 0.48, 0.83 and 1.0 for the gas at 300 K, 341 K and 381 K respectively. The very low product quantum yield in the solid phase photolysis relative to the liquid and gas phase indicates that geminate recombination of radicals formed in the primary process predominates in the solid phase; the quantum yield of 12 for allyl chloride removal relative to 0.25 for the products indicates that polymerization is the predominate mechanism in the liquid phase photolysis; geminate recombination does not occur in the gas phase photolysis, and polymerization, while it may occur, is not important in the gas phase.

Previously [1] we proposed that *cis*- and *trans*-1,3-dichloropropene formed in the solid and liquid phase studies derived from coupling of chloroallyl radical with chlorine atom. The absence of this product in the gas phase

photolysis indicates that this coupling is a cage phenomenon. Cyclopropane and methylacetylene are present in the solid phase photolysis but not in the liquid or gas phase photolysis. This finding reinforces our previous argument [1] that "hot" radicals play a role in the solid photolysis.

Acknowledgment

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