Laser-powered Homogeneous Decomposition of Allyl Chloride

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The continuous wave CO_2 laser-powered homogeneous decomposition of allyl chloride sensitized by sulphur hexafluoride was examined in order to determine the course of reaction in the absence of wall effects. The elimination of heterogeneous processes simplifies the reaction scheme and leads to the formation only of propyne, propadiene, benzene, and at higher conversions, acetylene. The total yield of propyne and propadiene is three times higher than that in conventional pyrolysis.

Recently, the usefulness of the laser-powered homogeneous pyrolysis (LPHP) technique for inducing decomposition of organic compounds which do not themselves absorb i.r. laser radiation has been successfully demonstrated.[1] This technique, in which organic substrates are activated by collisional energy transfer from an unreactive, i.r. radiation absorbing gas, obviates the heterogeneous reactions that may occur on hot reactor walls and thus ensures that decompositions are carried out under strictly homogeneous conditions. In reactions in which an appreciable heterogeneous component is important, even in vessels covered with a carbonaceous film, the technique appears extremely interesting since it can lead to novel reaction products or to altered product distribution.[2,3]

One such reaction, the thermolysis of allyl chloride, is a complex homogeneous and heterogeneous process that yields initially propadiene and hydrogen chloride. The composition of the final products is affected by the conditions under which the thermolysis is performed. In a vessel covered with a carbonaceous film at 370—475 °C the propadiene formed undergoes rapid polymerization.[4] In a Pyrex tube heated at 550 °C hexa-

1,5-diene, cyclohexa-1,3-diene, and benzene are the main products.[5] The same compounds are also produced[6] in a quartz tube heated to 540—725 °C, hexa-1,5-diene being preferred at 540—575 °C, cyclohexa-1,3-diene at 600—630 °C, and benzene along with propylene at temperatures above 630 °C. At still higher temperatures (800—1 200 °C) in a flow system acetylene, ethylene, propylene, butadiene, propyne, and propadiene are formed as well.[7] Although the last reaction was studied over a wide range of conditions in order to find the optimum conditions for the production of propyne and propadiene the total yield of the two compounds was as low as 14%. In these pyrolyses, tars and carbonaceous deposits on the walls are significant products, their amounts increasing with conversion.

In the present investigation the LPHP of allyl chloride was studied using a continuous wave CO_2 laser and sulphur hexafluoride as the inert sensitizer. The LPHP of allyl chloride gives hydrogen chloride (in stoicheiometric amounts), propadiene, propyne, benzene, and at higher conversions acetylene and traces of methane. The material balance is consistent
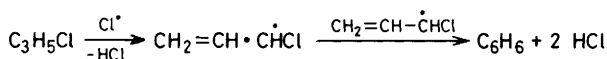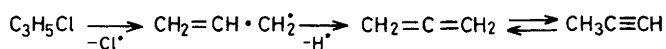
Continuous wave CO_2 laser-powered homogeneous pyrolysis of allyl chloride

Run	SF_6 (mol %)	Total pressure (kPa)	Laser output delivered [a] (W)	Focus [b]	Conversion [c]	Products [d] $CH_3C{\equiv}CH$	$CH_2{=}C{=}CH_2$	C_6H_6
1	53	10.5	4	A	11	0.24	0.18	0.24
					20	0.22	0.14	0.22
					39	0.16	0.12	0.23
2	55	10.6	4	B	10	0.27	0.22	0.26
					27	0.18	0.16	0.24
					46	0.12	0.12	0.25
3	53	12.6 [e]	4	A	16	0	0.17	0.21
					26	0	0.14	0.22
					35	0	0.13	0.21
4	52	10.8	9.5	A	17	0.28	0.10	0.22
					36	0.26	0.10	0.22
					49	0.24	0.09	0.23
5	55	10.6	9.5	B	19	0.25	0.12	0.23
					39	0.24	0.08	0.22
					60	0.19	0.07	0.23
6 [f]	54	10.9	9.5	A	10	0.10	0.18	0.20
					34	0.08	0.10	0.22
					45	0.06	0.10	0.21
7	56	10.5	15	A	25	0.34	0.09	0.21
					50	0.26	0.07	0.22
8	57	79	4	A	14	0.28	0.12	0.26
					33	0.16	0.10	0.20
					48	0.15	0.08	0.18

[a] The amount of laser radiation absorbed by the sample. [b] A, In the middle of the cell; B, at the window. [c] Calculated by following the decrease in absorption of C_3H_5Cl. [d] In mol per mol of C_3H_5Cl decomposed. [e] 2 kPa of helium added. [f] Irradiation chopped with frequency 360 Hz with a 0.37 transmission and 0.63 obscuration wheel driven by a variable d.c. motor.
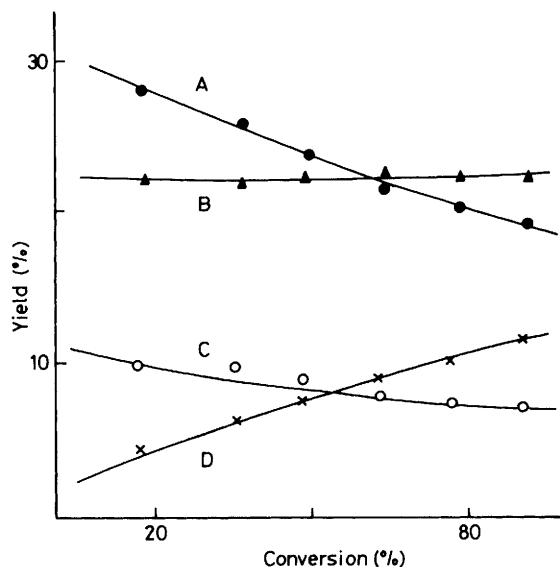
Dependence of the product distribution upon the reaction progress: A, propyne; B, benzene; C, propadiene; D, acetylene

$$C_3H_5Cl \xrightarrow[-Cl^{\bullet}]{} CH_2=CH\cdot CH_2^{\bullet} \xrightarrow[-H^{\bullet}]{} CH_2=C=CH_2 \rightleftharpoons CH_3C\equiv CH$$

$$C_3H_5Cl \xrightarrow[-HCl]{Cl^{\bullet}} CH_2=CH\cdot\overset{\bullet}{C}HCl \xrightarrow{CH_2=CH-\overset{\bullet}{C}HCl} C_6H_6 + 2\ HCl$$

Scheme

with the fact that no other compounds or tar are formed. Representative runs gathered in the Table show that the variation of the laser output from 4 to 15 W and changing the laser beam focus did not noticeably alter the ratio between the main products; the yield of propyne is usually higher than that of propadiene, and the yields of both compounds decrease as the reaction progresses. The yield of benzene in the early stages of reaction is comparable to that of propyne but it is constant during the entire reaction. The only compound whose yield increases as reaction progresses is acetylene. At higher conversions ($>50\%$) traces of methane can also be detected. The product distribution as the reaction progresses is illustrated in the Figure. The higher content of propyne than of propadiene in most runs is apparently related to the known thermal equilibrium between these compounds, propadiene undergoing isomerization at a rate *ca.* 2.3 times faster than propyne.[8-10] The preference of propadiene over propyne in LPHP can be achieved by the addition of helium (run 3) or by chopped radiation (run 6). The first effect is consistent with a lower reaction temperature that results from the high thermal conductivity of helium. The second effect is apparently associated with a shorter dwelling time of propadiene in the reaction zone.

The LPHP of allyl chloride differs remarkably from conventional pyrolyses in the number of products produced. Its mechanism, compared to conventional decomposition, must be substantially reduced in the number of reaction steps. We suggest that reactions in the Scheme take place in the 'wall-less' reactor, and the additional ones suggested previously[5,7] to account for the additional products must occur at the hot vessel walls. The acetylene is most likely produced by decomposition of propyne. Thus LPHP appears to be the best pyrolytic method for preparation of propyne and propadiene from allyl chloride; these compounds are produced in a total yield that is some three times higher than that given by the procedure of Kunichika *et al.*[7]

Experimental

Experiments were carried out with a stainless steel optical cell which was 11 (runs 1—7) or 1.4 cm (run 8) long, had an internal diameter of 2.5 cm, and NaCl windows. The cell was equipped with one needle valve. A continuous wave CO_2 laser constructed in our laboratory and operated at the P(34) line of the $00^{\circ}1 \longrightarrow 10^{\circ}0$ transition was used for the irradiation of gaseous SF_6–C_3H_5Cl mixtures. The output of the laser radiation entering into and transmitted through the cell was measured using a Coherent model 201 power meter. The laser beam was focused with a Ge lens (focal length 25 cm).

In a typical experiment the cell was filled with pre-mixed SF_6 and allyl chloride, and an initial i.r. spectrum was taken. The sample was then irradiated with a laser beam and the extent of the decomposition was followed by periodically taking the i.r. spectrum of the sample. Identification of the products was by i.r.–g.l.c. (Chrom 3; flame ionization) analysis. A Perkin-Elmer model 621 i.r. spectrometer was used to analyse for the concentration of allyl chloride (v_{10} at 1 260 cm^{-1}), propadiene (v_6 at 1 956 cm^{-1}), propyne (v_1 at 3 334 cm^{-1}), benzene (v_{11} at 675 cm^{-1}), acetylene (v_5 at 730 cm^{-1}), and methane (v_4 at 1 306 cm^{-1}). The absorption coefficients were ascertained by measuring the spectra of pure samples.

Sulphur hexafluoride (Montedison; I.E.C. standard), allyl chloride (Fluka, distilled prior to use), acetylene and methane (both Spolek), and propadiene (Koch–Light) were commerical samples. Propyne was prepared by continuous wave CO_2 laser-induced and SF_6-sensitized isomerization of propadiene, the reaction being monitored as in ref. 11.

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