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Photochemistry of 3-halopropenes in argon matrices

A. J. Barnes and S. Holroyd
Department of Chemistry and Applied Chemistry, University of Salford, Salford M5 4WT, U.K.

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Abstract—The photochemistry of 3-chloropropene, 3-bromopropene and 3-iodopropene in argon matrices was investigated using infrared spectroscopy to determine the major products. The primary product was found to be the allene–hydrogen halide complex, with propyne and cyclopropyl halides being produced by secondary photolysis of the allene.

INTRODUCTION

Although the photochemistry of halogenated alkanes has been studied extensively, few studies of the photochemistry of halogenated alkenes have been reported. The photolysis at 254 nm of 3-chloropropene in the liquid (300 K) and solid (77 K) phases has been studied by Phillips and Volman [1, 2]. In the liquid phase photolysis, the major products were polymeric compounds and in both phases a number of chlorinated C_3 and C_6 compounds were produced. Hydrocarbon products were 1,5-hexadiene (liquid phase only), propene, cyclopropane (solid phase only), allene, propyne (solid phase only), ethane, ethene and methane. Gas phase photolysis of 3-chloropropene produced more than 15 products, including propene, allene and propyne, with 1,5-hexadiene as the major product [3]. Similar products were found in the pyrolysis of 3-halopropenes [4]. These studies have all been interpreted in terms of a free radical mechanism, with the primary process being the generation of allyl radicals. The allyl radical was not observed in the ESR spectrum of u.v.-irradiated solid 3-chloropropene [2], but it was found after photolysis of dilute 3-chloropropene in methanol [5]. The allyl radical has also been found after u.v.-irradiation of 3-halopropenes at 4 K [6] or flash photolysis of a number of allyl compounds in the gas phase at ambient temperature [7].

A study of the u.v. photolysis of iodoalkanes in argon matrices, using i.r. spectroscopy and gas liquid chromatography to determine the products, found that under these conditions the alkene–hydrogen iodide complex was the major product [8], in contrast to ESR studies which had shown the presence of alkyl radicals [6, 9]. Irradiation of chloroalkanes in argon matrices similarly led to the alkene–hydrogen chloride complexes [10]. Recently, photolysis of fluoroalkenes in argon matrices has been shown to give alkyne–hydrogen fluoride complexes [11]. The vacuum u.v. photolysis of propene in low temperature matrices also gave products (allene, propyne, ethene, methane) consistent with a molecular elimination mechanism [12]. In the present work, the photochemistry of the 3-halopropenes in argon matrices was investigated using i.r. spectroscopy to determine the major products.

EXPERIMENTAL

The 3-halopropenes were obtained from B.D.H. Ltd and distilled under vacuum prior to use. Matrix samples were prepared by mixing the 3-halopropene and argon matrix gas in the desired proportions using standard manometric techniques. The mixture was deposited on an alkali halide window cooled to *ca.* 20 K using an Air Products Displex closed-cycle refrigerator. Photolysis was carried out using a Philips medium pressure mercury arc with a water filter to minimise heating of the matrix. Infrared spectra were recorded on a Perkin–Elmer 225 spectrophotometer, calibrated using standard gases.

RESULTS AND DISCUSSION

Infrared spectra of each of the 3-halopropenes (chloro-, bromo- and iodo-) in argon matrices, at matrix to solute (M/S) ratios between 700 and 250, were recorded before and after u.v. irradiation, photolysis times of up to $3\frac{1}{2}$ h being used. For 3-bromopropene, prominent new absorptions appeared at 2439 and 850/844 cm^{-1} after only 1 h of photolysis (Fig. 1), whereas for 3-chloropropene or 3-iodopropene only weak to medium intensity bands were obtained after 2–3 h of photolysis. The absorption maxima of the 3-halopropenes in dilute carbon tetrachloride solution were found to be 228 nm (Cl), 243 nm (Br) and 260 nm (I). Assuming that the absorption maxima are not shifted drastically by the matrix environment, the absorption bands for the chloro and iodo compounds fall in regions where the emission of a medium pressure mercury lamp is low, whereas the absorption of the bromo compound is close to a weak maximum in the emission curve.

Each of the 3-halopropenes gave two bands in the corresponding hydrogen halide stretching region after photolysis. For 3-chloropropene these bands, at 2736 and 2696 cm^{-1}, can be readily identified as due to the allene–hydrogen chloride and propyne–hydrogen chloride complex respectively. Both complexes have previously been studied in argon matrices, the HCl stretching frequencies being reported at 2737 and 2698 cm^{-1} [13]. The corresponding hydrogen bromide and hydrogen iodide complexes have not been reported, but the similarities of the relative wavenumber shifts (HCl 0.047 and 0.060; HBr 0.047

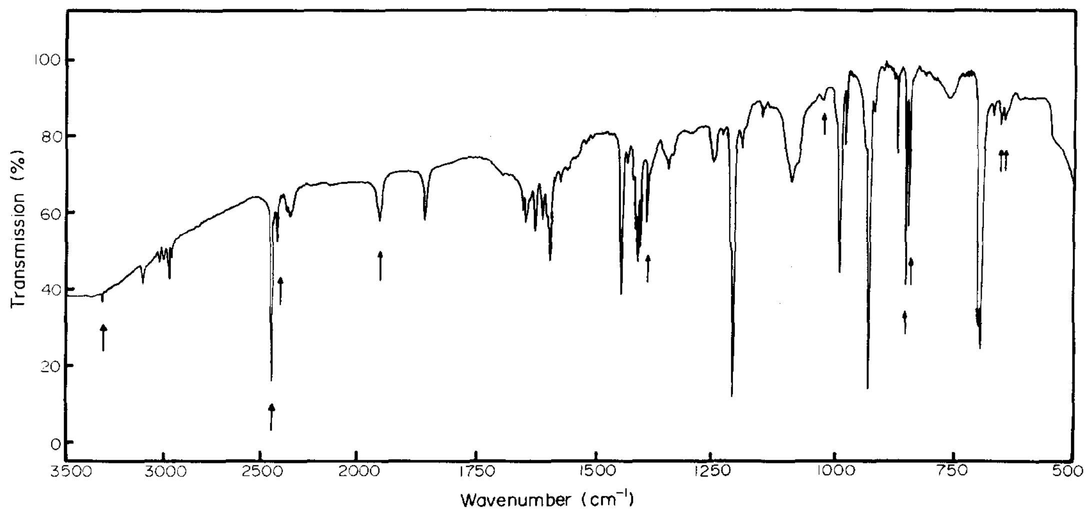

Fig. 1. Infrared spectrum of 3-bromopropene in an argon matrix (M/S = 300) after photolysis for 1 h. The arrows mark product absorptions.

and 0.061; HI 0.038 and 0.056) confirm the assignment to allene–hydrogen halide and propyne–hydrogen halide complexes. Many of the other absorptions appearing after photolysis can be assigned to either allene or propyne. The most intense bands of allene in an argon matrix are at 1956, 1390, 839 and 355 cm^{-1} [14]. Photolysis of each of the 3-halopropenes gave rise to bands around 1950, 1390 and 840 cm^{-1} which can be assigned to either allene–hydrogen halide complexes or uncomplexed allene (355 cm^{-1} was below the spectral range studied). Similarly, the most prominent bands of propyne in an argon matrix are at 3324, 1247, 630 and 332 cm^{-1} [14]. Photolysis of the 3-halopropenes gave rise to bands around 3315 and 640 cm^{-1} which can be assigned to complexed and uncomplexed propyne.

After a short period of photolysis, the bands due to allene were dominant with only weak bands due to propyne. As the period of photolysis was extended, the relative intensity of the propyne bands increased. This observation suggests that allene is the primary product in the photolysis of the 3-halopropenes and that propyne arises from secondary photolysis of the allene. CHAPMAN[15] has reported that u.v. irradiation of allene in an argon matrix produces cyclopropene and propyne. In the present work, no conclusive evidence was found for the presence of cyclopropene. The most intense bands of cyclopropene in the gas phase are at 2983, 1044, 1011 and 570 cm^{-1}, with similar wavenumbers in a xenon matrix [16]. The band appearing at *ca.* 1025 cm^{-1} after photolysis of the 3-halopropenes could be due to a cyclopropene mode, perturbed by complex formation with the hydrogen halide, but there was no evidence of the 570 cm^{-1} band nor of a band in the hydrogen halide stretching region due to a cyclopropene-hydrogen halide complex. WALSH[17] has discussed the kinetics and mechanism of the isomerisation of allene to propyne via cyclopropene in the gas phase and found that the conversion of allene to cyclopropene is the rate determining step. This may account for the concentration of cyclopropene in the present experiments being too low to detect.

The photolysis product absorptions remaining to be identified are weak bands at 1296, 1026 and 812 cm^{-1} from 3-chloropropene and at 1025 cm^{-1} from 3-bromopropene. The 1026 cm^{-1} band could be due to cyclopropane, which gives a strong band at this wavenumber in an argon matrix, but there was no evidence of a band near 865 cm^{-1}, where cyclopropane has an intense absorption. The 1296, 1026 and 812 cm^{-1} absorptions all coincide with strong bands of cyclopropyl chloride in an argon matrix. The other intense bands of cyclopropyl chloride at 1443, *ca.* 1420 and 765 cm^{-1}, would be difficult to observe because they are very close to the C–H deformation or C–Cl stretching absorptions of the 3-chloropropene. Cyclopropyl bromide in the gas phase has a strong band at 1026 cm^{-1} [18], thus allowing a similar assignment to be made for the 1025 cm^{-1} band arising from the photolysis of 3-bromopropene. The bands attributed to cyclopropyl halides grew in intensity relative to the allene bands as the photolysis proceeded. The cyclopropyl halides thus appear to be a secondary product, possibly arising from recombination of allene and the hydrogen halide via a cyclopropene intermediate (thus accounting for the failure to observe cyclopropene). CRISTOL, LEE and NOREEN[19] have reported the formation of cyclopropyl chloride and bromide from the photosensitised rearrangement of 3-chloro- and 3-bromopropene.

The bands observed after the photolysis of the 3-halopropenes are summarised in Table 1.

CONCLUSIONS

Photolysis of 3-chloropropene, 3-bromopropene or 3-iodopropene in argon matrices led primarily to the

Table 1. Summary of-absorptions (cm^{-1}) appearing after photolysis of 3-halopropenes in argon matrices

Cl	Br	I	Assignment
3314 (w)	3314 (w)	3316 (w)	Propyne–HX CH stretch
2736 (s)	2439 (vs)	2165 (w)	Allene–HX HX stretch
2696 (m)	2404 (m)	2123 (vw)	Propyne–HX HX stretch
	1952 (w)	1953 (w)	Allene } C=C=C as. str.
1948 (vw)	1947 (m)		Allene–HX } C=C=C as. str.
~1390 (vw)	1389 (m)	1389 (w)	Allene(–HX) CH_2 scissors
~1296 (w)			Cyclopropyl X CH def.
1026 (w)	1025 (vw)		Cyclopropyl X CH_2 wag
851 (s)	850 (vs)	846 (m)	Allene–HX } CH_2 wag
844 (m)	844 (s)	842 (w)	
		839 (vw)	Allene } CH_2 wag
812 (w)			Cyclopropyl X CX def.
648 (vw)	652 (m)		
640 (w)	643 (w)	640 (vw)	Propyne–HX } CH bend
~634 (sh)	~635 (sh)	635 (w)	
		628 (m)	Propyne } CH bend

production of an allene–hydrogen halide complex. Secondary photolysis of the allene gave the propyne–hydrogen halide complex and probably also the cyclopropyl halide. Some uncomplexed allene and propyne were also observed.

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