The Course of the Electron Impact-induced Elimination of Hydrogen Fluoride from Primary Alkyl Fluorides

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THE electron impact-induced dehydration of aliphatic alcohols has been shown[1] to involve almost exclusive preference ($> 90\%$) for a 1,4-elimination process. Subsequently we have demonstrated by deuterium labelling that dehydrochlorination[2] of 1-chlorobutane and 1-chloropentane proceeded predominantly (93% and 72% respectively) by a 1,3-elimination and that dehydrosulphurization[3] of pentane-1-thiol occurred mainly (62%) by 1,4-elimination, the remainder (41%) being 1,3. It has also been observed[4] that in 2-bromobutanes the expulsion of hydrogen bromide appeared to occur by 1,3-elimination but quantitative estimates were precluded owing to complications arising from the intense peak in the mass spectra of these compounds associated with the loss of a bromine radical. As 1-fluorobutane shows an intense peak at m/e 56, ($\Sigma_{29} = 14{\cdot}8\%$ at 70 ev and $43{\cdot}7\%$ at 12 ev) in its mass spectrum due to the loss of hydrogen fluoride we have prepared deuterated analogues of this compound in order to determine the optimum ring in this elimination.

The loss of the elements of DF from 1-fluorobutanes specifically labelled with deuterium[†] at all positions of the alkyl chain at 70 and 12 ev is summarized in Table 1.

It is evident from Table 1 that a substantial isotope effect[6] discriminating against deuterium must be operating and most importantly that five- and six-membered transition states are preferred in

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[†] 1-Fluoroalkanes labelled specifically with deuterium were prepared from the corresponding deuterated 1-bromobutanes and 1-bromohexanes (ref. 5) (in excess of 95% isotopically pure) by reaction with an excess of sodium fluoride in ethylene glycol at 100° for 48 hr. Samples for mass spectrometry were purified by gas-phase chromatography using a 10 ft. × ¼ in. 20% Apiezon column.

the dehydrofluorination. This result should be contrasted with the electron impact-induced dehydration[1] of n-butanol (>90% by 1,4-elimination) and the dehydrochlorination[2] of 1-chlorobutane (93% by 1,3-elimination) thus demonstrating the enormous effect of the hetero-atoms on the preferred ring size for elimination.

TABLE 1

Percentage loss of deuterium fluoride from deuterated analogues of 1-fluorobutane‡

	70 ev	12 ev
1-Fluoro-[1,1-$^2H_2$]butane	0%	2%
1-Floruo-[2,2-$^2H_2$]butane	8%	10%
1-Fluoro-[3,3-$^2H_2$]butane	31%	35%
1-Fluoro-[4,4,4-$^2H_3$]butane	39%	41%

In view of the known preference for abstraction of secondary (methylene) over primary (methyl) hydrogen atoms in mass-spectrometric fragmentations of chlorides,[2] ethers,[7] amines,[8] and thioethers[9] we considered it important to extend our studies to 1-fluoroalkanes of more than four carbon atoms so that the intermediacy of larger ring sizes (notably six-membered) involving methylene hydrogen atoms in the elimination of hydrogen fluoride could be evaluated.

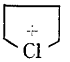
The results summarized in Table 2 show that the dehydrofluorination of 1-fluorohexane proceeds mainly (74%) at 70 ev by a seven-membered-ring intermediate, while at lower electron voltage (12 ev) this value becomes 52%. This decrease must correspond to either a different isotope effect[6] or varying site-specificity for hydrogen abstraction at lower electron voltages. Little or no isotope effect[6] apparently operates in the 70 ev electron impact-induced dehydrofluorination of labelled 1-fluorohexanes (97% DF loss accounted for in Table 2) in contrast to the situation in the corresponding 1-fluorobutanes (78% DF loss accounted for in Table 1).

TABLE 2

Percentage loss of deuterium fluoride from deuterated 1-fluorohexanes‡

	70 ev	12 ev
1-Fluoro-[3,3-$^2H_2$]hexane	2%	5%
1-Fluoro-[4,4-$^2H_2$]hexane	21%	25%
1-Fluoro-[5,5-$^2H_2$]hexane	84%	52%
	97%	

The loss of HF from 1-fluorohexane yields an ion (m/e 84) of low abundance (Σ_{29} 0·4%) compared to 1-fluorobutane (m/e 56, Σ_{29} 14·5%). A comparison of the dehydrohalogenation of 1-fluorohexane and 1-chlorohexane is, however, not completely relevant since the two compounds fragment in different fashions and the dehydrohalogenation is a minor process in contrast to the situation in the butyl halides. Thus loss of 29 mass units from the molecular ion of 1-chlorohexane (formation of ion *a*, m/e 91)[10] generates the most abundant ion in this compound's mass spectrum while in the corresponding fluoro-compound such an ethyl elimination produces an ion (m/e 75) of only 4% relative abundance.


a, m/e 91

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‡ All mass spectra were determined with an Atlas CH-4 mass spectrometer using a TO-4 ion source (200°) and gas cartridge. The low-voltage spectra correspond to nominal ev values and were determined with the draw-out plates of the gas cartridge at zero potential. The values quoted are considered reliable to ± 2%.

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