

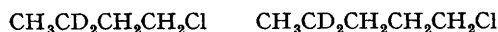
The Course of the Electron Impact-induced Dehydrochlorination of Primary Alkyl Chlorides¹

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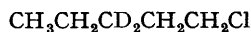
ELECTRON IMPACT-INDUCED dehydration of a series of aliphatic alcohols (n-butyl—n-heptyl alcohol) has been shown² to proceed predominantly (>90%) by a 1,4-elimination process. It is of some mechanistic interest to examine the optimum ring size in other electron impact-induced elimination reactions of which dehydrohalogenation is a particularly important example. This reaction is especially pronounced in chlorobutanes³ but no appropriate isotope labelling experiments have as yet been performed.⁴ In alkyl bromides elimination of a bromine radical far surpasses loss of hydrogen bromide but from the mass spectra of polydeuterated 2-bromobutanes⁵ it was concluded that 1,3-elimination of hydrogen bromide seems to be preferred over other cyclic alternatives.

Since it is known³ that the most intense peak in the mass spectrum of 1-chlorobutane occurs at m/e 56 ($M - \text{HCl}$) and in view of the ready availability of n-butanol (and hence 1-chlorobutane) labelled at specific sites with deuterium⁶ we have investigated the electron impact-induced dehydrochlorination of these latter compounds in order to compare this elimination with the corresponding dehydration reaction.²



(I)

(II)



(III)

In the mass spectrum⁷ of 1-chloro[3,3-²H₂]-butane (I) the peak present at m/e 56 in the unlabelled alkyl chloride was transferred to the

extent of 93% to m/e 57. Thus the dehydrochlorination of 1-chlorobutane occurs almost exclusively in the mass spectrometer by a 1,3-elimination process in marked contrast to the 1,4-elimination of water in n-butanol.²

In view of the extensive documentation now available concerning the greater ease of removal of secondary as opposed to primary hydrogen atoms in electron impact-induced hydrogen rearrangement processes during fragmentation of ethers,⁸ amines,⁹ thioethers,¹⁰ and 2,4-dinitrophenylhydrazones¹¹ it was of interest to extend our dehydrochlorination studies to 1-chloropentane. In this instance both 1,3- and 1,4-elimination could occur by the removal of a secondary hydrogen atom in contrast to 1-chlorobutane where 1,4-elimination must involve abstraction of a primary hydrogen atom.

Quantitative evaluation of the shifts of the m/e 70 ($M - \text{HCl}$) peak of 1-chloropentane in the deuterated analogues (II) and (III) demonstrated that 18% of the hydrogen from C-4 and 72% of the hydrogen from the C-3 position are involved in this dehydrochlorination. Thus, while 1,3-elimination is still the preferred process the reduction to 72% in 1-chloropentane as compared to 93% in 1-chlorobutane again exemplifies the preference for abstracting a secondary over a primary hydrogen atom.⁸⁻¹¹

The most important conclusion to be derived from this study is that the optimum ring size for electron impact-induced dehydration² (six-membered) and dehydrochlorination (five-membered) is different.

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⁷ All mass spectra were obtained using an Atlas CH-4 mass spectrometer operating under the following conditions: reservoir temperature 70°, inlet line 150°, ion source temperature 190° and trap current 10 μ amps.

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⁹ C. Djerassi and C. Fenselau, *J. Amer. Chem. Soc.*, 1965, **87**, 5752.

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