The Course of the Electron Impact-induced Elimination of Hydrogen Sulphide from Aliphatic Thiols*

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ONE, and frequently the most important fragmentation process, subsequent to electron impact, of primary alkanethiols is the loss of hydrogen sulphide from the molecular ion.[1] The qualitative similarity between the mass-spectral behaviour of alcohols and thiols has been noted[2a] and it seemed to us of interest to subject this conclusion to closer scrutiny.

Deuterium-labelling studies[3] of the electron impact-induced dehydration of a series of aliphatic alcohols demonstrated almost exclusive preference ($> 90\%$) for a 1,4-elimination process. By contrast, dehydrochlorination of 1-chlorobutane and 1-chloropentane under electron impact has been shown[4] to proceed preferentially by a 1,3-elimination process. It was thus of some relevance to determine the size of the transition state in the dehydrosulphurization of a typical primary thiol and compare it with the results encountered in aliphatic alcohols and chlorides.

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To this end we have prepared separate samples of pentane-1-thiol labelled respectively with deuterium at the specific α-,β-,γ-, and δ-carbon atoms of the alkyl chain.[5] Calculation† of the shifts in the deuterated analogues of the *m/e* 70 ($M-H_2S$) peak (34% relative intensity) of pentane-1-thiol showed that the elimination of hydrogen sulphide from alkanethiols proceeds mainly (62%) by a 1,4-elimination with the remainder (41%) being supplied by a 1,3-elimination process while hydrogen attached to the α- or δ-carbon atoms is not implicated at all.

On lowering the energy of the incident electrons from 70 to 12 ev the base peak in the spectrum of pentane-1-thiol corresponds to the loss of hydrogen sulphide. Surprisingly the quantitative loss of HDS from the [3,3-$^2H_2$]- and [4,4-$^2H_2$]-derivatives at 12 ev becomes 51% and 44% respectively (*cf.*, 62% and 41% in the case of 70 ev electrons). Thus, an isotope effect, different from that at 70 ev, must be operative at 12 ev.[6] In view of this result the mass spectra of deuterated 1-pentanols[3] and 1-chloropentanes[4] were repeated at 70 and 12 ev and no change in the quantitative retention of deuterium was observed in either of these two classes of compounds at low voltage.

It has been reported[1] that the mass spectra of secondary thiols contain more abundant peaks due to the loss of a sulphydryl radical than of hydrogen sulphide in contrast to the behaviour of primary thiols where $M-SH$ peaks are very small or absent. It should be noted that the loss of a hydroxyl radical in primary alcohols is essentially non-existent.[2b] We have repeated the mass spectrum of pentane-2-thiol at 70 ev and find the relative abundance of the $M-SH$ and $M-H_2S$ peaks to be 12 and 40%, respectively‡ compared to values of 41 and 32%, previously[1] reported. At 12 ev the peak due to the loss of SH was only 16% while that due to the elimination of H_2S had now increased to 100% relative abundance. This discrepancy between our results and those previously obtained prompted us to repeat the mass spectrum of pentane-3-thiol. Under our conditions§ the relative abundance‡ of the peaks due to the loss of SH and H_2S were 35 and 22% respectively (*cf.*, Levy and Stahl[1] who report 85 and 15% respectively) while at 12 ev the elimination of hydrogen sulphide was greater (100% relative abundance) than that (52%) due to the ejection of an SH radical.¶

One may conclude, therefore, that the loss of hydrogen sulphide from secondary thiols is a favoured process even at 70 ev while at lower electron energies (12 ev) it far surpasses the loss of a sulphydryl radical. Our earlier statement[2a] about the qualitative resemblance between aliphatic alcohols and thiols is, therefore, further substantiated. The previous observation[1] of the preference of secondary thiols to eliminate SH rather than H_2S appears to be due, at least in part, to thermal and/or metal-catalyzed effects.§

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† These calculations refer to 70 ev electrons and were complicated by the presence of approximately 10% of a monodeutero-species in both the 1-thio[3,3-$^2H_2$]- and 1-thio[4,4-$^2H_2$]-pentane derivatives. The above results were reached by assuming an equal probability of transfer of deuterium and hydrogen in the loss of hydrogen sulphide from these monodeuterated species. If a complete discrimination against transfer of deuterium is invoked the calculations become 60% and 39% respectively for the loss of HDS from these compounds.

‡ All relative abundance figures have been corrected for ^{13}C isotope contributions.

§ All spectra were recorded with an Atlas CH-4 mass spectrometer operating with the TO-4 ion source and gas cartridge under the following conditions: reservoir temperature 90°, inlet line temperature 150° and source temperature 200°. The low voltage spectra were determined with the draw-out plates of the gas cartridge at zero potential.

¶ Utilizing an all-glass heated (200°) inlet system in conjunction with a CEC model 21-103C mass spectrometer we observed $M-SH$ and $M-H_2S$ speaks of 47 and 25% relative intensity respectively at 70 ev, while at 12 ev these values changed to 20 and 80%, respectively.

[1] E. J. Levy and W. A. Stahl, *Analyt. Chem.*, 1961, **33**, 707.

[2] H. Budzikiewicz, C. Djerassi, and D. H. Williams, "Interpretation of Mass Spectra of Organic Compounds", Holden-Day, San Francisco, 1964, (a) p. 60; (b) p. 33.

[3] W. Benz and K. Biemann, *J. Amer. Chem. Soc.*, 1964, **86**, 2375; S. Meyerson and L. C. Leitch, *ibid.*, p. 2555.

[4] A. M. Duffield, S. D. Sample, and C. Djerassi, *Chem. Comm.*, 1966, 193.

[5] These compounds were prepared according to the conditions of S. Sample and C. Djerassi, *J. Amer. Chem. Soc.*, 1966, **88**, 1937.

[6] S. Meyerson, I. Puskas, and E. K. Fields, *J. Amer. Chem. Soc.*, 1966, **88**, 4974 have observed differences in the quantitative retention of deuterium in the mass spectra of nitroarenes obtained with 70 and 7–8 ev electrons.