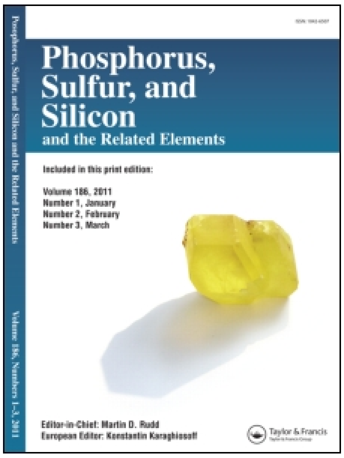

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STUDIES ON THE FRAGMENTATION OF DIALKYL DISULFIDES UPON ELECTRON IMPACT

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STUDIES ON THE FRAGMENTATION OF DIALKYL DISULFIDES UPON ELECTRON IMPACT

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Recent studies on the fragmentation of some organic disulfides upon electron impact in a mass spectrometer have shown two main decomposition routes besides simple bond disconnection: skeletal rearrangements[1-3] and proton transfer[4]. Transposition of the molecular components takes place via loss of one or two sulfur atoms while the carbon skeleton is preserved. Such molecular rearrangements are particularly noticeable in small molecules like dimethyl disulfide. Larger systems show a different fragmentation pattern in which proton transfer to give alkyl hydrodisulfides becomes predominant. The transfer of protons has been shown to proceed by way of intramolecular 1,2 and 1,3 hydrogen shifts from α and β carbons respectively by means of selective deuterium labbeling of diethyl disulfide.[4]

In view of the small number of models reported and the possible operation of other fragmentation mechanisms a study of the mass spectra of a series of eighteen unsymmetrical dialkyl disulfides was undertaken. Unsymmetrical compounds were chosen since either skeletal rearrangements or proton transfers would be different for the participation of each side of the molecule, thus providing twice the amount of information as compared with symmetrical systems. Also the relative intensities of fragments formed by a given mechanism but from unequal parts of the molecule can be qualitatively correlated with the relative energy requirement of the process involved.

The present study led to the following conclusions:

1- Skeletal rearrangements occur to a visible extent only in small molecules in which the energy acquired during the electron impact cannot be dispersed effectively through the molecular backbone. As a consequence skeletal transpositions can be neglected in the majority of cases with the exception of few interesting instances.

2- Proton transfer occur via concerted hydrogen shifts onto one sulfur atom yielding alkyl hydrodisulfides which in turn rearrange further to furnish H_2S_2.

3- While 1,2-hydrogen shifts have been reported by Block et al.[4] these do not become apparent when the ratio of β to α protons is larger than 3:2. 1,3-hydrogen shift predominates in all cases studied and was also shown to take place by selective deuterium labbeling of a model compound so constituted as to provide an unfavorable 1,3 vs. 1,2 hydrogen shift -one β deuterium vs. two α protons.

4- 1,4-hydrogen shift was shown to occur for the first time also via a concerted process by means of labbeling experiments.

5- Gas-phase kinetic studies suggest the intermediacy of four- and five-membered transition states for 1,3- and 1,4- hydrogen shifts respectively.

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