

## Gas Phase Generation of HCCCS and CCCHS Radicals from Anionic Precursors. The Rearrangement of CCCHS to HCCCS.

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Two neutral radicals with CCC bond connectivity, HCCCS and CCCHS, have been generated by one electron vertical oxidation of precursor anions. The anions were formed in the chemical ionisation source of a VG ZAB 2HF two sector mass spectrometer as follows: (i)  $\text{HCCCH}_2\text{SC}_2\text{H}_5 + \text{O}^- \rightarrow (\text{HCCCS})^- + \text{H}_2\text{O} + \text{C}_2\text{H}_5$ , and (ii)  $\text{Me}_3\text{SiCC}(\text{cyclo-SCH}_2\text{CH}_2\text{S}) + \text{F}^- \rightarrow ^-\text{CCCHS} + \text{Me}_3\text{SiF} + \text{cyclo-SC}_2\text{H}_4$ . Neutralisation of these anions was effected by collision with oxygen and subsequent ionisation of the neutrals to the corresponding cations allowed for their detection using the electric sector of the instrument. This process is known as *neutralisation-reionisation* ( $^-\text{NR}^+$ ) mass spectrometry.  $^-\text{NR}^+$  data indicate that  $\text{HCCCS}^-$  is stable on the time scale of the experiment (*ca.*  $10^{-6}$  sec.), whereas the  $\text{CCCHS}^-$  anion leads to two neutrals CCCHS and HCCCS under the experimental conditions.

These experimental results will be discussed along with theoretical calculations which indicate that the rearrangement of CCCHS to HCCCS can occur by three pathways; concerted H or S rearrangements, or the stepwise H rearrangement process  $\text{CCCHC} \rightarrow \text{CCHCS} \rightarrow (\text{cyclo-C}_3\text{H})=\text{S} \rightarrow \text{HCCCS}$ . Comparison of the *charge reversal* ( $^-\text{CR}^+$ ) and  $^-\text{NR}^+$  spectra of  $(\text{CC}^{13}\text{CHS})^-$  indicates that (at least a part) of the rearrangement involves the S migration pathway. Theoretical data also suggests that H rearrangement should compete with S rearrangement.