

NEUTRAL CUMULENE OXIDE CCCCCO IS ACCESSIBLE BY ONE-ELECTRON OXIDATION OF [CCCCO]⁻ IN THE GAS PHASE.

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Theoretical calculations at the CCSD(T)/aug-cc-pVDZ//B3LYP/6-31G* level of theory indicate that (i) doublet [CCCCO]⁻ is a stable species which should undergo collision-induced Franck-Condon vertical oxidation [under neutralisation-reionisation conditions (⁻NR⁺)] to produce both triplet CCCCCO (ground state) and singlet CCCCCO, (ii) some of the CCCCCO species formed (particularly the triplet) should be stable for the microsecond duration of the NR experiment, whereas others will be energised (particularly the singlet) and should decompose to form CCC and CO. The [CCCCO]⁻ radical anion has been formed in the ion source of the mass spectrometer by the reaction $\text{CH}_3\text{OCH}_2\text{C}+\text{C}-\text{CO}-\text{CH}(\text{CH}_3)_2 + \text{O}^{\cdot-} \rightarrow [\text{CCCCO}]^{\cdot-} + \text{CH}_3\text{O}^{\cdot} + (\text{CH}_3)_2\text{CH}^{\cdot}$. The ⁻NR⁺ spectrum of [CCCCO]⁻ shows a recovery signal at *m/z* 64 corresponding to ionised CCCCCO, together with a pronounced peak at *m/z* 36 (CCC⁺) produced by ionisation of CCC (formed by the reaction $\text{CCCCO} \rightarrow \text{CCC} + \text{CO}$). The experimental observations are in agreement with the predictions of the theoretical study.