Theoretical and experimental study of tropylium formation from substituted benzylpyridinium species

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Résumé en anglais: Fragmentation pathways of unsubstituted and substituted benzylpyridinium compounds were investigated using mass-analysed kinetic energy (MIKE) technique in combination with high level of quantum chemical calculations in the gas phase. Fast atom bombardment (FAB) source was used for ionisation of the studied compounds. The formation of both benzylium and tropylium species were investigated. Hybrid Hartree-Fock/Density Functional Theory calculations have been performed to assess the geometries and the energies of the transition states and intermediates. For each cases, different reaction pathways were investigated, and particularly in the case of the formation of tropylium species, the formation of the seven-membered ring before or after the loss of pyridine were studied. The effect of para-methyl and para-methoxy substituents on the activation energy of the rearrangement process to form thermodynamically stable tropylium compounds has been studied. Theoretical calculations showed competition between direct bond cleavage and rearrangement reactions to form benzylium and tropylium compounds, respectively. Experimental results also suggested that the rearrangement process takes place to yield stable tropylium under “soft ionisation techniques”, such as FAB.


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