Dissociative Electron Attachment to Trifluoromethanesulfonic Anhydride: A Candidate Precursor for Electron-Induced Superacid Formation in EUV Resist Materials

Filipe Ferreira da Silva,*[a] M. Mendes,[a] Diogo Sequeira,[a] Rodrigo Rodrigues,[a] Fabian Holzmeier,[b] Oddur Ingólfsson[c]

[a] CEFITEC, NOVA University Lisbon, 2829-516 Caparica, Portugal;
[b] imec, Kapeldreef 75, 3001 Leuven, Belgium;
[c] Department of Chemistry, University of Iceland, Science Institute, Dunhagi 3, 107 Reykjavík, Iceland

The ionizing nature of extreme ultraviolet (EUV) radiation generates cascades of low-energy secondary electrons that can play an important role in the chemical transformations underlying chemically amplified resist operation.[1,2] In such systems, efficient generation of a strong acid is essential for amplification of the lithographic response. Recent studies of dissociative electron attachment (DEA) to molecular photoacid generators have demonstrated that low-energy electrons can strongly influence acid-generation pathways and may provide opportunities for tailoring the sensitivity of EUV resist materials.[2,3]

Motivated by our recent investigation of DEA to pentafluorophenyl triflate,[3] we explore trifluoromethanesulfonic anhydride (triflic anhydride, Tf_2O) as a possible molecular precursor for electron-induced superacid generation. The high symmetry of Tf_2O, with two equivalent trifluoromethylsulfonyl groups, provides an attractive molecular architecture in which electron attachment may promote selective fragmentation and formation of the highly stabilized trifluoromethanesulfonate anion. Previous gas-phase studies have established negative-ion chemistry of triflic anhydride and determined the electron affinity of the trifluoromethanesulfonate ion,[4] providing an important foundation for the present investigation.

Here, we report a systematic study of dissociative electron attachment to trifluoromethanesulfonic anhydride in the gas phase over the low energy range. The observed negative ion yields and their energy dependence are analysed in terms of the temporary negative ion resonances and the thermochemical thresholds of the accessible fragmentation pathways.

Particular attention is given to pathways leading to ($CF_3SO_3^-$), the conjugate base of triflic acid, (CF_3SO_3H), a prototypical superacid. The results are discussed in the context of molecular design strategies for EUV resist materials and the possibility of exploiting electron-induced fragmentation of highly symmetric fluorinated precursors as a route towards controlled superacid generation and enhanced sensitivity in EUVL resist chemistry.

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* Corresponding author: f.ferreiradasilva@fct.unl.pt; phone I +351 212 948 576