质谱学报 2009 30 (增刊): 12-12 ISSN: 1004-2997 CN: 11-2979/TH

基础研究和新技术

苯撑肼基二硫代碳酸甲酯质子化离子双氢协同迁移的裂解机理研究

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收稿日期 修回日期 网络版发布日期:

摘要 使用碰撞诱导裂解质谱（CID-MS）和泛密函数（DFT）理论计算研究了苯甲撑肼基二硫代碳酸甲酯质子化离子的气相裂解行为。丢失H_2S，CH_3SH 和（NSC）SCH_3是其主要裂解途径。量子化学计算表明，分子中脲基S最容易接受外加质子，形成质子化离子MH-a；该外加质子很容易迁移到亚胺N上，形成异构体MH-b。在碰撞活化下，前驱离子MH-b发生N—N键断裂，伴随着酰胺氢迁移到亚胺氮上，发生（NSC）SCH_3丢失裂解反应；若酰胺氢直接迁移到甲基硫上，则发生CH_3SH丢失反应。若前驱离子MH-a的外加质子迁移到到甲基硫上，则发生CH_3SH丢失反应；若酰胺氢经过甲硫基迁移到脲基S上，则发生H_2S丢失。上述结果证实了该化合物质子化离子的碎裂反应是外加质子和酰胺氢协同迁移的结果。

关键词 协同双氢迁移裂解 CID DFT

分类号

Coordinated Dissociative Proton Transfers in the Fragmentation of Protonated S-methyl Benzenylmethylenehydrazine Dithiocarboxylate

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Abstract The dissociation chemistry of the protonated S-methyl benzenylmethylenehydrazine dithiocarboxylate, PhCH＝N-NHC(＝S)SCH_3 was investigated by CID-MS experiments in combination with density functional theory(DFT) calculations. Eliminations of H_2S, CH_3SH and(NSC)SCH_3 were the three main fragmentation reactions. Calculated results show that thiocarbamide sulfur is the most favored position for protonation. Both the added proton and the thiocarbamide hydrogen shift in turn to the fragment ion in the process of losing(NSC)SCH_3. The thiocarbamide hydrogen migrates to thiocarbamide sulfur concomitantly with H_2S elimination. In the case of CH_3SH elimination, one of the proton/ the thiocarbamide hydrogen migrates to the fragment ion, and the other to the neutral specie. These results indicate that fragmentation of the protonated molecule is viewed as a result of the coordinated migration of both the external proton and the thiocarbamide hydrogen.

Key words coordinated dissociative proton transfers _ CID _ DFT

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