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**Gas-phase ion-molecule reactions of methyl-tertiary-butyl-ether
(MTBE) 43rd ASMS Meeting on Mass Spectrometry and Allied Topics:
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ANALYTICAL CHEMISTRY

- 30** TWO HPLC METHODS FOR THE ANALYSIS OF PENTA AZAPENTACOSANE. Gregory A. Turner,* Timothy B. Skinner and Evelyn A. Murrill. Midwest Research Institute, Kansas City, Missouri, 64110.

Pentaazapentacosane (1,19-bis-(ethylamino)-5,10,15-triazanonadecane, BE-4-4-4-4, BE-4x4), a synthetic aliphatic polyamine analog, is being developed as a potential antineoplastic agent, with selective activity against brain tumors, by the National Cancer Institute. The analysis of BE-4x4 is complicated by its high polarity and lack of UV chromophores. Two stability indicating HPLC methods have been developed and validated for the analysis of BE-4x4. An ion-paired C18 reverse-phase system with refractive index detection is suitable for assay and purity analyses of the bulk compound. An alternate method utilizes trifluoroacetic acid as a volatile pairing agent, on a PRP-1 polymeric column equipped with evaporative light scattering detection (ELSD). The latter method offers superior sensitivity (< 0.01 mg/mL) and is particularly suitable for the ongoing stability and other developmental analyses for this compound. Stability results and the response characteristics of the ELSD for this compound will be presented.

- 31** DETERMINATION OF THE REACTION THRESHOLD FOR THE ION-MOLECULE REACTIONS OF CYCLOPROPENYL. Curtiss D. Hanson, Samantha Franck, Michelle D. Hammer, Michaela L. Rich; Department of Chemistry, University of Northern Iowa, Cedar Falls, IA 50614-0423

The $C_3H_3^+$ cation has been extensively studied as a precursor ion to the formation of soot in the pyrolysis of fuels and other hydrocarbons. Studies involving soot nucleation in flames point to an ionic mechanism, versus a neutral free radical mechanism, driving the formation of aromatic hydrocarbons. These studies show that the $C_3H_3^+$ cation is critical to this transformation. Two forms of $C_3H_3^+$ are observed: i) the propargyl isomer, which has been determined to be highly reactive, and ii) an unreactive cyclopropenyl isomer. Because the cyclopropenyl isomer is the predominate isomer (>90%), reactions of the cyclic form are important to an understanding of the pyrolysis process. Direct observation of the gas-phase reactions of $C_3H_3^+$ with conjugated dienes has been accomplished using Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS). This technique permits the determination of both the product distribution and the reaction threshold for these reactions.

- 32** GAS-PHASE ION-MOLECULE REACTIONS OF METHYL TERT-BUTYL ETHER. Scott Peterman and Curtiss D. Hanson, Department of Chemistry, University of Northern Iowa, Cedar Falls, IA 50614-0423.

Methyl tert-butyl ether (MTBE) has recently been introduced as an additive used to increase the octane rating of fuels. MTBE, a petroleum-based non-renewable hydrocarbon has recently been implicated in causing health problems in Alaska and its environmental fate has not been adequately addressed. The environmental impact of MTBE is further complicated by secondary by-products formed by its vapor phase chemistry. Secondary products formed from uncombusted fuel and MTBE in the gas-phase can potentially result in the production of unknown compounds, that if released into the atmosphere unnoticed and without proper identification might cause a great concern to the air pollution in the future. To address the potential impact of the secondary by-products formed from the gas-phase reactions of MTBE, the ion-molecule reactions of MTBE and its reactive fragments have been studied by Fourier transform ion-cyclotron-resonance mass spectrometry.

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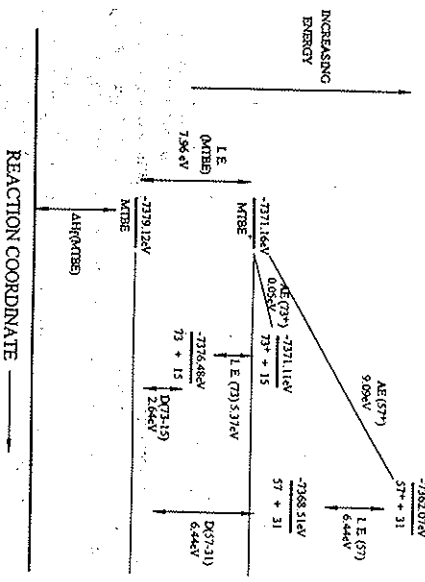
Gas-Phase Ion-Molecule Reactions of Methyl-tert-Butyl Ether (MTBE)

Scott Peterman, Michaela Rich, and Curtiss Hanson
University of Northern Iowa, Cedar Falls, Iowa 50613

The evaluation of Methyl-tert Butyl Ether has been intensively studied since its initial use in the late 1970's. In general, there has been fewer studies concerning the fragment ions formed under combustion conditions. MTBE has been the fastest growing chemical in production during the past decade. Its major use is as an octane inhibitor. Since MTBE is a labile molecule, the energy of combustion does produce chemical reactions that must be recognized. With the health complaints associated with blended gas, the need for an understanding of the chemical reactions occurring from combustion must be understood.

The use of a Fourier transform ion cyclotron resonance mass spectrometer was used for all experimental work. The FT-ICR was chosen due to the ability to model combustion conditions at an ideal rate for observation. All theoretical calculations were done on the Spartan RISC 6000 system calculated at the MP2-6-31g* theory level. Using both methods, a complete picture was provided of the fragmentation patterns and bi- and unimolecular reactions of MTBE.

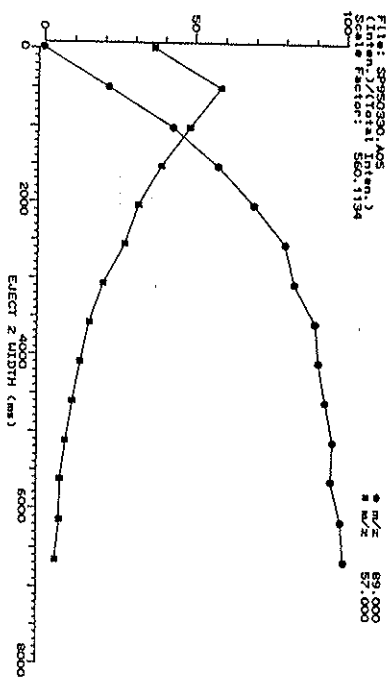
The initial spectrum of MTBE displayed fragmentation at minimal energy into two primary ion, m/z 73 and m/z 57, with no cold molecular ions. Spartan was used to calculate the thermochemical energy relationship for the unimolecular ion decomposition of MTBE.



Because of the lability and the time frame of combustion, the chemical reactions of these fragment ions were studied. Time delays were implemented to distinguish bimolecular reactions occurring. Through this study, a gas-phase acid was determined to be the t-butyl ion, m/z 57. Studies done

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by Gray and Westbrook focused on MTBE in a shock tube experiment, determining that the primary product was the t-butyl radical. The heat of formation for this radical was 6.92 eV, the ion was calculated to be 7.13 eV. Spartan calculations for the ionization energy of the t-butyl ion was determined to be 6.44 eV.



From the delay scan, a rate of proton transfer was calculated to be 3.24×10^{10} cc/(molecules x sec). This rate was compared to similar systems and evaluated to be a strong gas-phase acid. The t-butyl ion also functioned as base. The strength of the ion coupled with the lability of the neutral allowed the ion to abstract an electron from the neutral, causing fragmentation. From this, the formation of the m/z 73 ion was observed. Through labelled experiments, the isomer of this ion was identified.

Collisional activation of the protonated MTBE ion shows the formation of two ions, m/z 57 and m/z 74. The amount of energy imparted on m/z 89 was calculated to be 1.75 eV for the m/z 57 ion, and 2.72 eV for the m/z 74 ion. Spartan calculations gave theoretical values of 1.69 eV and 3.03 eV for the m/z 74.

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