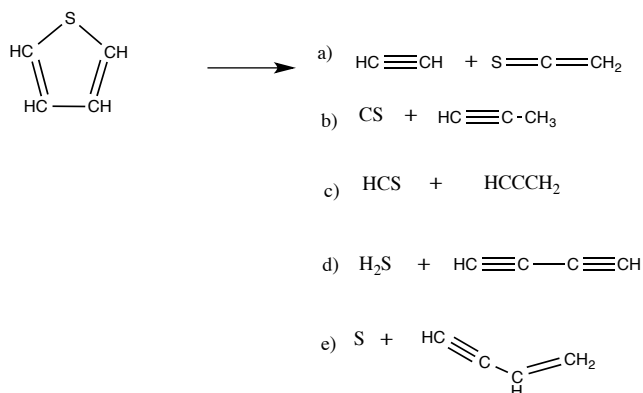


We are studying the unimolecular decomposition of petroleum relevant molecules; diethyl sulfide, dimethyl disulfide, dimethyl disulfide, ethanethiol, thiophene and methylthiophene. We will be the first to establish direct evidence rather than indirect evidence of radical intermediates formed during thermal decomposition. The initial steps of decomposition will be crucial in interpreting the subsequent reaction steps that follow. All experiments use a hyperthermal nozzle configured to matrix isolation infrared absorption and vacuum ultraviolet photoionization mass spectroscopies. These techniques allow for thermal tuneability (298-1700 K) and sensitive detection of intermediate species such as radicals. In addition to experimental studies, the thermal decomposition mechanisms of sulfur species will be investigated theoretically using density function and ab initio quantum chemical techniques.

From the date of last report fall 2017, we have completed and published the complete thermal decomposition of thiophene. Scheme 1 depicts the five product channels for the unimolecular thermal decomposition of thiophene.

Scheme 1: Unimolecular Pathways for thermal decomposition of the thiophene



This study involved the collection of PIMS data at the University of Colorado and Matrix Isolation IR data at Middlebury college. The PIMS data (Figure 1) were collected for several different temperatures and the optimum decomposition temperature was identified and used for IR studies. Authentic IR spectra were taken for room temperature thiophene and heated thiophene (1500 K). In addition, authentic IR spectra were obtained for thermal decomposition products acetylene, methylacetylene, propargyl radical, hydrogen sulfide and 1,3-butadiyne. A sample of the IR spectra taken for thiophene study is depicted in Figure 2. All experiential data was supported by ab initio and density functional calculations.

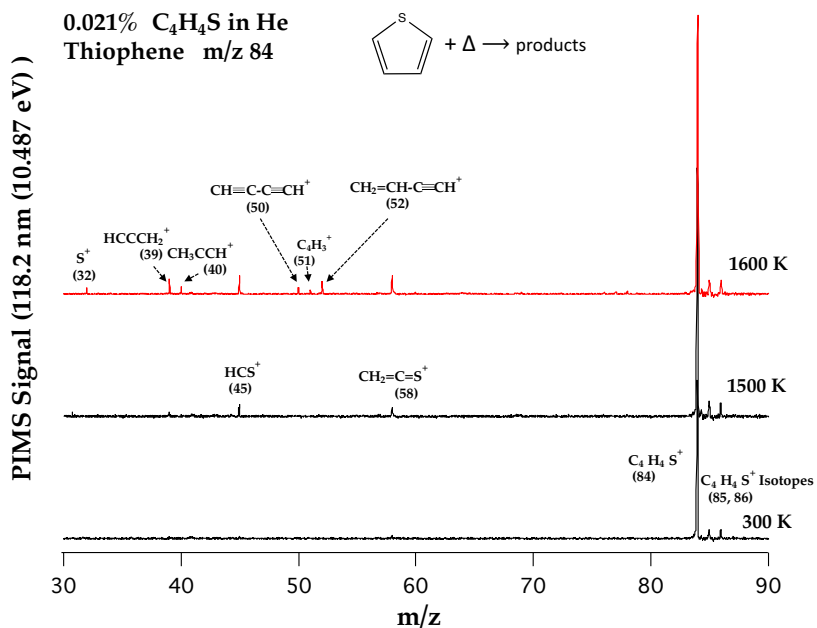


Figure 1: PIMS spectra of the decomposition products of thiophene in a high temperature microreactor. The bottom trace is the mass spectrum that results when thiophene (0.021 % C₄H₄S in He) transits the reactor at room temperature (300 K)

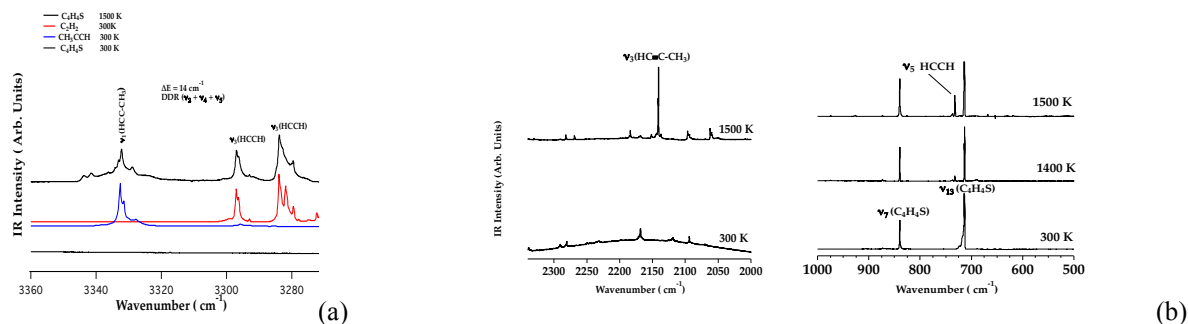


Figure 2. (a) Matrix IR absorption spectra from 3360 to 3270 cm⁻¹ of room temperature C₄H₄S (bottom trace) and authentic samples of HCCH (red spectrum) and CH₃CCH (blue spectrum). The top trace is the IR spectrum resulting from heating 0.021 % C₄H₄S/Ne mixture to 1500 K. Intense IR bands of the pyrolysis products HCCH (ν₃) and CH₃CCH (ν₁) are observed. (b) Vibrational bands for pyrolysis products HCCH (ν₅) and CH₃CCH (ν₃) in the IR region of 2300 cm⁻¹ to 2000 cm⁻¹ and 1000 cm⁻¹ to 500 cm⁻¹.

Matrix isolation IR spectra were collected for both dimethyl sulfide and dimethyl sulfide. Room temperature spectra were obtained for both compounds and fundamental modes for each molecule have been assigned.