A combined theoretical and FT IR spectroscopic approach is used to investigate a synthesis route to the long sought transient species ethenesulfenic acid. The flash vacuum pyrolysis (FVP) of divinyl sulfoxide exhibits elimination of acetylene at a temperature above 500°C as can be seen by gas phase FT IR spectroscopy. Ab initio calculations (MP2/cc-pVTZ, MP2/cc-pVQZ, and CCSD(T)/cc-pVTZ) including a normal coordinate analysis together with consideration of anharmonic effects pave the way for the identification of the corresponding pyrolysis products. Geometries, energies, and so far unknown vibrational frequencies of ethenesulfenic acid and ethanethial S-oxide are calculated and the two species are identified as the main products in this particular gas phase reaction by their characteristic infrared transitions. Experimental and theoretical frequencies are in good agreement. The recorded IR spectra indicate that the precursor is completely converted to products above 800°C, with an approximate ratio of 1:2 for the acid and S-oxide products. The calculations place the sulfenic acid 13.9 kJ/mol higher in energy than the S-oxide. This indicates the presence of kinetically controlled reactions for the simultaneous formation of ethenesulfenic acid and ethanethial S-oxide under FVP conditions.