Kinetics Studies of the Reaction of Atomic Sulfur with Acetylene

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The reaction

\[ \text{S} \left( ^3P_j \right) + \text{C}_2\text{H}_2 \left( + M \right) \rightarrow \text{products} \left( + M \right) \]

is of potential importance in a variety of applications, including combustion of sulfur-containing fuels, astrophysics and diamond deposition. Previous measurements have covered temperatures up to 484 K and do not show any pressure dependence, although a variety of potential bound intermediates are possible (1,2). The observed activation energy was well below the endothermicity for formation of, for example, HCCS + H or CCSH + H (3).

Ground-state sulfur atoms were generated by pulsed photolysis of CS2 precursor at 193 nm, and monitored by time-resolved resonance fluorescence at 181 nm, in the presence of excess C2H2 in an Ar bath gas. Experiments were conducted over 295 – 1015 K and at pressures from 10 to 400 torr, and these wide ranges enabled observation of pressure-dependent kinetics. By application of Troe’s formalism, the observed low-pressure limit can be expressed as \(1.1 \times 10^{-30} T^{-5.1} \exp(-2800 / T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}\) and the high-pressure limit is approximately \(4.6 \times 10^{-11} \exp(-13.5 \text{ kJ mol}^{-1} / RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}\).

These results are discussed in terms of recently computed potential energy surfaces for singlet and triplet interactions between S and C2H2 (3,4), using RRKM theory and analysis of possible intersystem crossing. A singlet adduct is the most likely product.

References
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