Kinetics Studies of the Reaction of Atomic Sulfur with Acetylene

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The reaction

$$S\ (^3P_J) + C_2H_2\ (+ M) \rightarrow \text{products}\ (+ M)$$

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 CS_2 precursor at 193 nm, and monitored by time-resolved resonance fluorescence at 181 nm, in the presence of excess C_2H_2 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 $1.1 \times 10^{-30}\ T^{-5.1}\ \exp(-2800 / T)$ cm^6 molecule^{-2} s^{-1} and the high-pressure limit is approximately $4.6 \times 10^{-11}\ \exp(-13.5\ \text{kJ mol}^{-1} / RT)$ cm^3 molecule^{-1} s^{-1}.

These results are discussed in terms of recently computed potential energy surfaces for singlet and triplet interactions between S and C_2H_2 (3,4), using RRKM theory and analysis of possible intersystem crossing. A singlet adduct is the most likely product.

References

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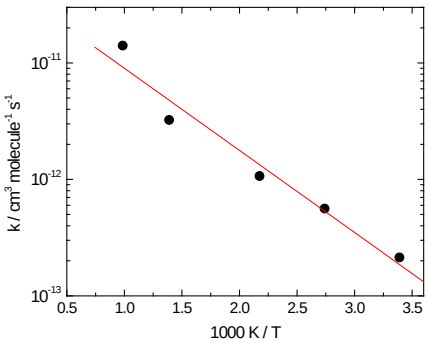

High-pressure-limiting rate constant for S + C_2H_2