Kinetic studies of the reaction of atomic sulfur with acetylene

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Abstract

The rate constant for reaction of sulfur atoms with acetylene was measured. Laser flash photolysis of CS_2 precursor was employed to generate ground-state $S(^3P)$ atoms, which were monitored with time-resolved resonance fluorescence as they reacted with C_2H_2 in a large excess of Ar bath gas. Temperatures from 295 to 1015 and pressures from 10 to 500 mbar were investigated. A pressure-dependence was observed at all temperatures, revealing that adduct formation is the dominant reaction channel. The necessary stability suggests H_2CCS or possibly HCCSH are the products at high temperatures, so that the reaction is spin-forbidden. The fall-off curves may be represented with a broadening factor $F_{cent} = 0.6$, and low and high-pressure limiting rate constants of $k_0 = 1.0 \times 10^{-18} (T/K)^{-3.55} \exp(-1990 \ K/T) \ cm^6 \ molecule^{-2} \ s^{-1}$ and $k_\infty = 2.1 \times 10^{-11} \exp(-11.2 \ kJ \ mol^{-1}/RT) \ cm^3 \ molecule^{-1} \ s^{-1}$, respectively. An entrance barrier to recombination of about 10 kJ mol^{-1} is proposed to arise where the singlet and triplet potential energy curves cross.
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1. Introduction

There is a limited amount of data concerning the gas-phase reactivity of C–S bonds. Details of C–S bond breaking or formation are important in a variety of contexts, including astrochemistry, atmospheric chemistry, diamond deposition and the combustion of sulfur-containing fuels. Sulfur–acetylene chemistry has been proposed as part of a mechanism leading to CS_2 formation in the Claus process [1,2]. The presence of sulfur appears to increase the production of PAHs from coal combustion [3] and nanoparticles from diesel

combustion [4], and sulfur plays a role in the deposition of diamond-like films with acetylene as the carbon precursor [5]. Organo-sulfur compounds have been detected in comets and the interstellar medium [6,7], where the mechanisms for their formation remain unclear.

Recent computational studies indicate several bound intermediates on the triplet and singlet potential energy surfaces for C_2H_2S which could be collisionally stabilized [8,9]. This would yield pressure-dependent kinetics for the overall reaction

$$S(^3P_J) + C_2H_2(+M) \rightarrow products(+M) \qquad (1)$$
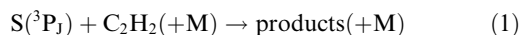
where M represents a collision partner. However, previous experimental studies of this reaction,

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which covered temperatures up to 484 K at fixed pressures of around 300 mbar, did not allow for any pressure dependence for the rate constant k_1 to be revealed [10,11].

Here we present new measurements that span wider ranges of pressure, about 10–500 mbar of Ar, and of temperature, about 300–1000 K. These data reveal that adduct formation is the dominant mechanism and allow some assessment of the thermal stability of these adduct(s). Further, we find that reaction 1 is spin-forbidden and are able to use the pressure dependence of k_1 to investigate the role of intersystem crossing quantitatively, and to compare the low-pressure limit with an RRKM analysis.

2. Methodology

The reagents used were CS_2 (99%, Sigma Aldrich), degassed by freeze–pump-thaw cycles at 77 K, Ar (99.9999%, Air Liquide), used directly, and C_2H_2, degassed and then purified by distillation at 182 K (liquid nitrogen/heptane slush). Gas mixtures were prepared manometrically and stored in glass bulbs.

Sulfur atoms were generated by laser flash photolysis of CS_2 precursor at 193 nm, and monitored by time-resolved resonance fluorescence at 181 nm (^3S–^3P (4s–3p)). Experiments were conducted with a large excess of Ar as a bath gas which served several purposes. It rapidly quenched any excited $S(^1D)$ formed photolytically, it slowed diffusion of S atoms to the reactor walls, it maintained isothermal conditions in the reaction cell and it served as the collision partner M in reaction 1. A general description of the heated reaction cell and details of modifications for S-atom chemistry have been provided previously [12–15]. Briefly, following their pulsed generation, ground-state $S(^3P_J)$ atoms were consumed by reaction with added C_2H_2 or lost by diffusion out of the reaction zone (a volume defined by the intersection of the photolysis and probe beams, each approximately 1 cm across), which was effectively first order. By working under pseudo-first-order conditions with $[C_2H_2] \gg [S]$ we may write

$$d[S]/dt = -k_{ps2}[S][C_2H_2] - k_{diff}[S] = -k_{ps1}[S] \quad (2)$$

where k_{ps2} is the effective second-order rate constant for reaction 1 at a given bath gas density [M]. The pseudo-first-order decay coefficient k_{ps1} was obtained from non-linear least squares fits to exponential decays of S-atom resonance fluorescence, which is proportional to [S]. This fluorescence was excited by a microwave-powered discharge lamp through which flowed a dilution of 0.01% H_2S in Ar at ca. 20 Pa pressure. We used Suprasil quartz optics which block H-atom radiation. Fluorescence was detected with a solar blind

photomultiplier tube operated in the photon counting mode, and signals from 100–8000 decays were accumulated in a multichannel scaler. An example is shown in Fig. 1. Typically around 4 1/e lifetimes were analyzed. Because this decay is first order, knowledge of absolute [S] is not required. The initial value $[S]_0$ was estimated from $[CS_2]$, its absorption cross section at 193.3 nm, the laser photolysis energy F and the beam cross section of 0.6 cm^2, to ensure that pseudo-first-order condition were attained. Most experiments were carried out with $[S]_0$ of the order of 10^{12} molecule cm^{-3}. At room temperature, where the primary reaction was slowest, higher values up to ~10^{13} molecule cm^{-3} were used to verify that secondary chemistry was unimportant. A constant slow flow of reagents ensures each laser pulse encounters a fresh mixture and that products do not accumulate in the reaction zone.

Linear plots of k_{ps1} vs $[C_2H_2]$, such as that shown in Fig. 2, yield the second-order rate constant k_{ps2} as the slope, and its statistical uncertainty. In each experiment $[C_2H_2]$ was varied from zero to a maximum value of the order of 10^{15} molecule cm^{-3}. The small values of F (in the range 0.02–0.1 mJ) and the modest absorption cross section of C_2H_2 at 193.3 nm, $(1.34 \pm 0.05) \times 10^{-19}$ cm^2 molecule^{-1} [16], mean that concentrations of photolytic fragments of C_2H_2 were too small to interfere significantly. The experimental conditions were varied to verify that the observed k_{ps2} were independent of parameters such as F, $[CS_2]$ and $[S]_0$, and the average residence time τ_{res} of gases in the heated reactor before photolysis. This latter variation checks for any thermal decomposition or CS_2–C_2H_2 chemistry, and a dependence was noted at the highest temperatures investigated, ~1015 K. These high-temperature data were therefore plotted as a function of τ_{res} and extrapolated linearly to zero residence time.
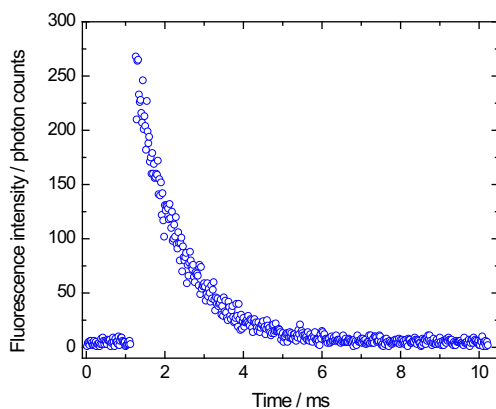

Fig. 1. Example fluorescence signal from S atoms following pulsed photolysis of CS_2 at 1015 K.