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 CS₂ precursor was employed to generate ground-state S(^3)P atoms, which were monitored with time-resolved resonance fluorescence as they reacted with C₂H₂ 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 H₂CCS or possibly HCCSSH are the products at high temperatures, so that the reaction is spin-forbidden. The fall-off curves may be represented with a broadening factor F̃ = 0.6, and low and high-pressure limiting rate constants of k₀ = 1.0 × 10⁻¹⁸ (T/K)^3.55 exp(−1990 K/T) cm⁴ molecule⁻² s⁻¹ and k∞ = 2.1 × 10⁻¹¹ exp(−11.2 kJ mol⁻¹/RT) cm⁴ molecule⁻² 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 CS₂ 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 C₂H₂S which could be collisionally stabilized [8,9]. This would yield pressure-dependent kinetics for the overall reaction

\[ \text{S}^1(\text{P}_\text{J}) + \text{C}_2\text{H}_2(+\text{M}) \rightarrow \text{products}(+\text{M}) \]  

where M represents a collision partner. However, previous experimental studies of this reaction,
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 \( \text{Ar} \), 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 \( \text{CS}_2 \) (99%, Sigma Aldrich), degassed by freeze–pump–thaw cycles at 77 K, \( \text{Ar} \) (99.9999%, Air Liquide), used directly, and \( \text{C}_2\text{H}_2 \), 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 \( \text{CS}_2 \) precursor at 193 nm, and monitored by time-resolved resonance fluorescence at 181 nm (\( ^1\text{S} \to ^3\text{P} \) (4 strife 3 strife)). Experiments were conducted with a large excess of \( \text{Ar} \) as a bath gas which served several purposes. It rapidly quenched any excited \( ^1\text{D} \) 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 pulse generation, ground-state \( ^3\text{P}_0 \) atoms were consumed by reaction with added \( \text{C}_2\text{H}_2 \) 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 \( \text{[C}_2\text{H}_2] \ll \text{[S]} \) we may write

\[
\frac{d[\text{S}]}{dt} = -k_{\text{ps2}}[\text{S}][\text{C}_2\text{H}_2] - k_{\text{diff}}[\text{S}] = -k_{\text{ps1}}[\text{S}]
\]

where \( k_{\text{ps2}} \) is the effective second-order rate constant for reaction 1 at a given bath gas density \( [M] \). The pseudo-first-order decay coefficient \( k_{\text{ps1}} \) 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% \( \text{H}_2\text{S} \) in \( \text{Ar} \) 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 l/e lifetimes were analyzed. Because this decay is first order, knowledge of absolute \([\text{S}]\) is not required. The initial value \([\text{S}]_0\) was estimated from \([\text{CS}_2]\), 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 \([\text{S}]_0\) of the order of \( 10^{12} \) molecule \( \text{cm}^{-3} \). At room temperature, where the primary reaction was slowest, higher values up to \( \sim 10^{15} \) molecule \( \text{cm}^{-3} \) 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 \( k_{\text{ps1}} \) vs \( \text{[C}_2\text{H}_2] \), such as that shown in Fig. 2, yield the second-order rate constant \( k_{\text{ps2}} \) as the slope, and its statistical uncertainty. In each experiment \([\text{C}_2\text{H}_2]\) was varied from zero to a maximum value of the order of \( 10^{15} \) molecule \( \text{cm}^{-3} \). The small values of \( F \) (in the range 0.02–0.1 mJ) and the modest absorption cross section of \( \text{C}_2\text{H}_2 \) at 193.3 nm, \((1.34 \pm 0.05) \times 10^{-19} \) \text{cm}^2 \text{molecule}^{-1} \[16\], mean that concentrations of photolytic fragments of \( \text{C}_2\text{H}_2 \) were too small to interfere significantly. The experimental conditions were varied to verify that the observed \( k_{\text{ps2}} \) were independent of parameters such as \( F \), \([\text{CS}_2]\) and \([\text{S}]_0\), and the average residence time \( \tau_{\text{res}} \) of gases in the heated reactor before photolysis. This latter variation checks for any thermal decomposition or \( \text{CS}_2 \)-\( \text{C}_2\text{H}_2 \) chemistry, and a dependence was noted at the highest temperatures investigated, \( \sim 1015 \) K. These high-temperature data were therefore plotted as a function of \( \tau_{\text{res}} \) and extrapolated linearly to zero residence time.

![Fig. 1. Example fluorescence signal from S atoms following pulsed photolysis of CS2 at 1015 K.](image-url)
3. Results and discussion

Data from 94 experiments are summarized in Table S1 of the Supplemental material. The $k_{ps2}$ values were found to be independent of the initial radical concentrations, indicating successful isolation of the elementary reaction 1 from secondary processes such as S-atom reaction with the products of the primary reaction 1. There is a clear dependence of $k_{ps2}$ on [Ar], as shown in Fig. 3. This is consistent with a Lindemann–Hinshelwood mechanism of the form

$$S + C_2H_2 \xrightarrow{k_a} \text{adduct} \xrightarrow{k_b} \text{adduct} + M \quad (3)$$

After formation of an initially excited adduct with rate constant $k_{ps2}$, there is competition between redissociation of the excited adduct ($k_{a}$) and stabilization by collision with the bath gas M ($k_{b}$). At the limit of low pressure, the collisional stabilization is rate-limiting and $k_{ps2} = k_0 [M]$ where $k_0$ is the third-order low-pressure limit rate constant. At the limit of high pressure all adducts are stabilized, initial addition is rate-limiting, and $k_{ps2} = k_{\infty}$ which defines the second-order high-pressure limit rate constant. Interpolation between these two regimes is carried out via Troe’s formalism [17]

$$k_{ps2} = \frac{k_0 [M]}{1 + k_0 [M]/k_\infty} \times F_{\text{ent}}(1 + 10^{(0.75 - 1.27 \log_{10} F_{\text{ent}})})^{-1} \quad (4)$$

The fits are shown in Fig. 3 and the results for the limiting values in Table 1. The scatter on Fig. 3 for the rate constants at 298 K seems large in part because of the small range of $k_1$ accessible close to the high-pressure limit, which occurs at relatively low pressures at low temperatures. A broadening factor $F_{\text{ent}} = 0.6$ was selected, as appropriate for atom + linear reactant [18]. The listed uncertainties of the low-pressure limit and the extrapolated high-pressure limit in Table 1 are purely statistical and are based on the covariance matrix for the sensitivity of the fit to the parameters. We comment that the uncertainty in $k_{\infty}$ is particularly large at 1015 K because the reaction is not far from the low-pressure limit at the highest temperature and the minor fall-off is weakly sensitive to $k_{\infty}$.

The nature of the adduct is explored with reference to the computational studies of Woon and Leonori et al. [8,9], who investigated the triplet and singlet surfaces using coupled cluster theory and W1 theory, respectively. We have plotted their results on the same axes in Fig. 4. This potential energy diagram shows that bimolecular products are too endothermic to play a role here, but that candidate adducts are triplet $^3$CHCHS and singlet c-CHCHS, c-SCCH$_2$, H$_2$CCS and HCCSH. Drawings of these structures are provided in the Supplemental material. The fact that we still observe a pressure dependence at 1015 K indicates that the addition products of reaction 1 must be thermodynamically stable at this temperature. Further, the decays of S atoms remain exponential down to the baseline, with no evidence of a back reaction. This situation can be contrasted to the analogous reaction of O atoms with C$_2$H$_2$, where bimolecular products such as CO + CH$_2$ and H + HCCO are favored. We consider the equilibrium

$$S + C_2H_2 \rightleftharpoons \text{adduct} \quad (5)$$

The concentration equilibrium constant $K_c$ equals $[\text{adduct}]/([S][C_2H_2])$. We define stability here as sufficient to act as a sink for at least half the initial S atoms, and with $[S]_0 << [C_2H_2]$, this implies $K_c > 1/[C_2H_2]$. We evaluate this limit using the median [C$_2$H$_2$] in our experiments, and evaluate $K_c$ for the different possible adducts from the partition functions Q and the dissociation enthalpy $\Delta H_0$, using the input data in Table S2 of the Supplementary material:

$$K_c = \frac{Q(\text{adduct})}{Q(S)Q(C_2H_2)} \exp \left(\frac{\Delta H_0}{RT}\right) \quad (6)$$

The results are compared in Fig. 5. It may be seen that the triplet adduct is insufficiently stable to account for adduct formation even at room temperature, while only H$_2$CCS (ethenethione, the sulfur analog of ketene) and possibly HCCSH (ethynethiol) are stable enough to yield adducts long-lived under our conditions at ~1015 K. Reaction 1 is therefore spin-forbidden.

We now test whether assignment of H$_2$CCS as the dominant product is consistent with our observations via Rice–Ramsperger–Kassel–Marcus (RRKM) theory. The probability of intersystem crossing (ISC) between triplet and singlet surfaces factors equally into the formation and
dissociation paths in Eq. (3). Because these paths create a pre-equilibrium at the low-pressure limit, this probability does not influence $k_0$. We set the threshold energy $E_0$ for dissociation of H$_2$CCS to S($^3$P) + C$_2$H$_2$ equal to $\Delta H_0$ for dissociation, \(304 \text{ kJ mol}^{-1}\) computed by Leonori et al. [9], plus 10 kJ mol$^{-1}$ to reflect a barrier $E_0$ observed at the high-pressure limit for recombination (see below). We assume the reaction rate to be negligible below this energy threshold and employ Troe’s unimolecular formalism [17] for the dissociation of the adduct:

$$k_{0,\text{diss}}/k_c = \frac{Z_{W}}{Q_{\text{vib}}(H_2CCS)} \frac{\rho_{\text{vib}}(E_0)}{RT} \frac{F_{\text{E}}F_{\text{anh}}F_{\text{rot}}}{\exp\left(\frac{-E_0}{RT}\right)}$$

(7)
Table 1
Results of Troe fitting of S + C2H2 measurements with Fcen fixed at 0.6.

<table>
<thead>
<tr>
<th>Temperature/ K</th>
<th>Low-pressure limit rate constant $k_0$ $\times 10^{10}$ cm$^3$ molecule$^{-2}$ s$^{-1}$</th>
<th>Collision efficiency $\beta_c$</th>
<th>High-pressure limit rate constant $k_\infty$ $\times 10^{-11}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>296</td>
<td>2.09 ± 0.42</td>
<td>0.101</td>
<td>2.13 ± 0.16</td>
</tr>
<tr>
<td>366</td>
<td>3.07 ± 0.49</td>
<td>0.089</td>
<td>5.68 ± 0.66</td>
</tr>
<tr>
<td>459</td>
<td>4.98 ± 0.53</td>
<td>0.105</td>
<td>11.0 ± 1.0</td>
</tr>
<tr>
<td>720</td>
<td>5.49 ± 0.43</td>
<td>0.110</td>
<td>31.4 ± 2.1</td>
</tr>
<tr>
<td>1013</td>
<td>2.47 ± 0.58</td>
<td>0.074</td>
<td>141 ± 63</td>
</tr>
</tbody>
</table>

* Statistical uncertainty is 2σ.

Because $K_c$ (Eq. (6)) is the ratio of addition to dissociation rate constants $k_{0,\text{add}}/k_{0,\text{diss}}$, and $E_0 - \Delta H_0 = E_b$, we may write

$$k_{0,\text{add}}/\beta_c = Z_{LJ} \frac{\rho_{\text{coll}}(E_0) \, RT}{Q_{\text{coll}}(\text{H}_2\text{CCS})} \times \frac{Q(\text{H}_2\text{CCS})}{Q(S)Q(C_2H_2)} F_E F_{\text{anh}} F_{\text{rot}} \times \exp \left(-\frac{E_b}{RT} \right)$$

(8)

where the symbols have their usual meanings. $\beta_c$ represents the collisional efficiency of the Ar bath gas. $Z_{LJ}$ is the Lennard–Jones rate constant, based on $\sigma$ and $\varepsilon/k_B T$ parameters for Ar and H$_2$CCS of 3.47 Å and 114 K, and 4.35 Å and 300 K, respectively (the latter values are a guess, based on values for C$_2$H$_2$ and H$_2$S. $Z_{LJ}$ is not very sensitive to the particular numbers.) $Q$ is the partition function, $\rho$ is the density of states, and the $F$ terms are corrections for the energy dependence of the density of states, vibrational anharmonicity and angular momentum effects. The ratio of the two largest moments of inertia at the geometry at the crossing point relative to those of H$_2$CCS yield $I'/I = 1.05$ which contributes to $F_{\text{rot}}$. $\beta_c$ was initially chosen to fit Eq. (8) to the experimental $k_0$ points and is listed in Table 1. The associated average energy transferred per collision with Ar was found to be approximately represented as $-<\Delta E>_{\text{coll}} = 400$ (T/298 K) J mol$^{-1}$ which is within typical values for other reactions [19]. The corresponding temperature dependence of $k_0$ can be summarized as $k_0 = 1.0 \times 10^{-18}$ (T/K)$^{3.55}$ exp($-1990$ K/T) cm$^3$ molecule$^{-2}$ s$^{-1}$ and is compared to experiment on Fig. 6. At moderate temperatures the recombination rate constant increases with temperature because of the barrier to be overcome, while at high temperatures the most important factor is the decrease in collisional efficiency with increasing temperature. Similar behavior was seen in the spin-forbidden addition of O atoms to SO$_2$ [20].

The high-pressure limit for reaction 1 is plotted in Arrhenius form in Fig. 7, and a weighted fit can be expressed as

$$k_\infty = (2.1 \pm 0.7) \times 10^{-11} \exp(-11.2$$

$$\pm 1.2 \text{ kJ mol}^{-1}/(\text{RT}) \text{cm}^3\text{molecule}^{-1} \text{s}^{-1}$$

(9)

where the uncertainties are ±2σ in the Arrhenius parameters. The earlier measurements [10,11] should correspond to this high-pressure limit and are also plotted there. They lie a factor of ca. 2 larger than the present results, which might reflect an influence of secondary chemistry in the prior work. $k_\infty$ corresponds to the rate constant for formation of initially excited adducts in the scheme shown in Eq. (3) and is proportional to the probability of ISC. The rate constant is $\sim 4 \times 10^{-10}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ for the spin-allowed addition of singlet S(1D) to acetylene [9], which tells us the collision rate between S atoms and C$_2$H$_2$, so we may estimate the ISC probability for S(3P) addition per collision as ca. 5%. This probability is in the range of values proposed for other spin-forbidden addition reactions of S(3P), such as $\sim 1\%$ for S + CS$_2$ [21] and $\sim 20\%$ for S + H$_2$S [22].

The temperature dependence in Eq. (7) suggests the presence of an energy barrier to S(3P) addition, so we have explored some of the geometries where ISC may occur. We used B3LYP/6-311G(2d,p) density functional theory implemented with the Gaussian 09 program [23] to evaluate singlet energies as S was brought towards C$_2$H$_2$ from the side, in a C$_{2\text{V}}$ geometry. The other geometry parameters were allowed to relax as a function of $r$, the distance between S and the center of C$_2$H$_2$. The singlet and triplet energies were calculated at these same geometries using the CBS-QB3 method (excluding zero-point vibrational energy) [24], and the results are plotted as a function of $r$ in Fig. 8. As expected from prior work where there is no barrier to formation of thirene [9] and the triplet analog is significantly endothermic [8], the long-range singlet potential is attractive while the triplet potential is repulsive, so there is a crossing, which we locate at $r = 2.47 \times 10^{-10}$ m. The energy here (excluding zero point energy) is 11.4 kJ mol$^{-1}$ above the ground state reactants, which becomes 9.7 kJ mol$^{-1}$ after correction for zero-point energy changes. This is
fortuitously close to the observed activation energy in Eq. (9). These are not formally identical quantities but the accord suggests the temperature dependence can be rationalized in terms of an ISC-induced barrier. This analysis does not rule out the existence of other ISC regions elsewhere on the PES. For example, in the analogous reaction of triplet O atoms with C$_2$H$_2$, exothermic fragmentation rather than stabilization is observed, with the major products being H + HCCO and CO + CH$_2$ in triplet and singlet states. Formation of $^1$CH$_2$ is spin-forbidden and a recent analysis \cite{25} suggests the overall fraction of collisions leading to CO + $^1$CH$_2$ is $7 \pm 3\%$, which is higher than might be expected given the weak spin–orbit coupling of oxygen. Unlike reaction 1, there is a strongly bound, long-lived triplet HCCO adduct which allows for multiple trajectories to explore an ISC region leading to ketene.
4. Conclusions

New pressure-dependent measurements show that adduct formation is the dominant mechanism even at the highest temperatures explored, ~1015 K. A combination of potential energy information from the literature with the necessary thermal stability to account for the observations suggests H₂CCS is the likely candidate at the highest temperatures, although HCCSH might also play a role. The reaction is spin-forbidden and the high-pressure limit can be rationalized in terms of a 5% probability for intersystem crossing and a ca. 10 kJ mol⁻¹ barrier to recombination, which is consistent with our initial exploration of triplet-singlet curve crossing. The low-pressure limit is rationalized via RRKM theory and reasonable energy transfer parameters.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.proci.2014.05.079.

References