An experimental and computational study of the reaction of ground-state sulfur atoms with carbon disulfide

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The pulsed laser photolysis/resonance fluorescence technique was used to study the reaction of $S(^3P_J)$ with CS_2 in an Ar bath gas. Over 290–770 K pressure-dependent kinetics were observed and low- and high-pressure limiting rate constants were derived as $k_0 = (11.5 - 0.0133 \text{ T/K}) \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ (error limits $\pm 20\%$) and $k_\infty = (2.2 \pm 0.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Equilibration observed at 690–770 K yields a CS_2 –S bond dissociation enthalpy of $131.7 \pm 4.0 \text{ kJ mol}^{-1}$ at 298 K. This agrees with computed thermochemistry for a spin-forbidden C_{2v} adduct, estimated at the coupled-cluster single double triple level extrapolated to the infinite basis set limit. A pressure-independent pathway, assigned to abstraction, was observed from 690 to 1040 K and can be summarized as $1.14 \times 10^{-10} \exp(-37.0 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with error limits of $\pm 40\%$. The results are rationalized in terms of a computed potential energy surface and transition state theory and Troe's unimolecular formalism. © 2011 American Institute of Physics. [doi:10.1063/1.3644773]

I. INTRODUCTION

Reactions of carbon disulfide have been proposed in mechanisms of sulfur inhibition of nitrogen oxide formation in flames,¹ deposition of diamond from CS_2/H_2 mixtures,² polymerization of CS_2 ,³ and in the Claus process to remove sulfur compounds from natural gas.⁴ In the earliest kinetic study of the reaction of CS_2 with ground state sulfur atoms, $S(^3P_J)$, Basco and Pearson found a pressure dependence at room temperature,⁵ which suggests formation of a stable CS_3 adduct via

where M is a chemically inert bath gas. Its role is to stabilize initially excited CS_3 through collisional energy transfer. An adduct was also invoked to explain isotope exchange between S atoms and CS_2 ,⁶ the rapid quenching of $S(^1D)$ by CS_2 and the energy distribution in the $CS + S_2$ products of the reaction of $S(^1D)$ with CS_2 .⁷ Mass and infrared spectroscopic studies have addressed the existence and properties of carbon trisulfide, where one issue has been whether there is a SSCS chain structure or whether there are three S–C bonds to a central carbon atom, with either D_{3h} or C_{2v} symmetry.^{8,9} At 1260–1820 K, the shock tube experiments by Woiki and Roth¹⁰ yielded bimolecular kinetics ascribed to an alternative abstraction pathway

This reaction was invoked to explain the formation of S_2 in two-photon photolysis of CS_2 .¹¹ The CS_3 potential energy surface (PES) has also been the focus of computational studies, which drew attention to possible roles for intersystem crossing between the triplet and singlet manifolds.^{9,12}

Here, we present new measurements of the kinetics of the reaction of S with CS_2 , over the temperature range 290–1040 K. We observe pressure-dependent kinetics at low temperatures, attributed to channel (1a), equilibrium between formation and dissociation of an adduct at intermediate temperatures, which yields the first measured thermochemistry for CS_3 , and a change in mechanism to the pressure-independent channel (1b) at the high temperature end of the range. The observed thermochemistry is compared to predictions for various candidates on a new computed PES, to show that reaction (1a) proceeds via a spin-forbidden path. The kinetics over the entire range are quantitatively rationalized in terms of the PES.

II. EXPERIMENTAL METHOD

The reaction cell and general operating procedures have been detailed in Ref. 13. Here, carbon disulfide (Aldrich, 99.9+%) was degassed at 196 K (acetone slush) and diluted in a large excess of Ar taken directly from a cylinder (99.995%, Air Liquide). Gas mixtures were prepared manometrically in glass bulbs. Atomic sulfur was generated by pulsed excimer laser photolysis (beam cross section $\sim 0.56 \text{ cm}^2$) of a small fraction of CS_2 at 193 nm at low fluences, below 0.2 mJ cm^{-2} . At this wavelength, the absorption cross section of CS_2 is $1.3 \times 10^{-16} \text{ cm}^2 \text{ molecule}^{-1}$.¹⁴ For estimation of initial atom concentrations, we assume a unit quantum yield for dissociation, although this information is not needed for the kinetic analysis. The ratio of $S(^3P):S(^1D)$ in the products has been reported as 1.6 ± 0.3 .¹⁵ The $S(^1D)$ atoms are expected to be quenched rapidly in our system by collision with the Ar bath gas: the quenching rate constant is $1.4 \times 10^{-11} \text{ cm}^3 \text{ atom}^{-1} \text{ s}^{-1}$,¹⁶ and with $[Ar]$ at over $10^{17} \text{ atom cm}^{-3}$, the collisional lifetime of $S(^1D)$ is less than $1 \mu\text{s}$ which is orders of magnitude shorter than the time scale of the kinetic

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measurements. The ground state sulfur atoms were monitored by time-resolved resonance fluorescence at 181 nm (sulfur (4s) $^3S-(3p)^3P$), excited by a microwave-powered discharge lamp filled with flowing H_2S diluted in Ar (0.1% mole fraction) at a pressure of 0.4 mbar. The optics were made from Suprasil quartz and fluorescence was detected with a solar-blind photomultiplier tube operated in the photon counting mode. Signals from up to 1000 photolysis pulses at each set of conditions were accumulated in a multi-channel scaler and transferred to a computer for analysis.

Following their generation, S atoms are lost mainly by reaction with CS_2 (total second-order rate constant k_1 , which is the sum of k_{1a} and k_{1b}) with a minor contribution from diffusion (k_d), which is found to be effectively first order. This means

$$d[S]/dt = -k_d[S] - k_1[S][CS_2] = -k_{ps1}[S],$$

where k_{ps1} is the effective decay constant under our pseudo-first-order conditions $[S] \ll [CS_2]$. Here, k_{ps1} is obtained by nonlinear least-square fits to the observed fluorescence decays and then plotted against $[CS_2]$ to yield k_1 as the slope. Two examples are shown in Fig. 1. This procedure was repeated at various temperatures (T) and pressures (p). Experimental parameters, such as the residence time in the heated cell (τ_{res}) before photolysis, the concentration $[CS_2]$, and the laser pulse energy (F), were also varied to check there was no influence on the observed kinetics. As discussed below, three temperature regimes were found to exhibit different kinetics. At the highest temperatures, $T > 800$ K, the abstraction pathway (1b) dominates so that the observed $k_1 \approx k_{1b}$. At the lowest temperatures, $T < 660$ K, the addition channel (1a) dominates and $k_1 = k_{1a} + k_{1b}$. Here, k_{1a} was obtained by subtracting k_{1b} (extrapolated down from higher temperatures) from the observed k_1 . This was usually a small correction ($<1\%$) and negligible at room temperature.

At intermediate temperatures, $690 \text{ K} < T < 770 \text{ K}$, reaction (1a) is reversible, i.e., the time scale for decomposition of CS_3 to $CS_2 + S$ is similar to that for addition. Under these conditions biexponential decays of $[S]$ were observed and were interpreted in terms of the mechanism

The first-order rate constants for these five steps at a given $[CS_2]$ and $[Ar]$ are assigned as k_{1a}' , k_{-1a} , k_{1b}' , k_d , and k_2 , where $k_{1a}' = k_{1a}[CS_2]$ and k_{1a} is the effective second-order rate constant for reaction (1a') at a given Ar density, and $k_{1b}' = k_{1b}[CS_2]$. Based on the lower temperature results, k_d was fixed at 10 s^{-1} ; the results were insensitive to the particular value chosen. The remaining four rate constants were determined by nonlinear fitting of the biexponential $[S]$ profile to

FIG. 1. Plot of first-order loss rate of atomic sulfur in the presence of CS_2 (a) at 294 K and 269 mbar total pressure where addition dominates, and (b) at 831 K and 148 mbar total pressure where abstraction dominates. Error bars are 1σ . The insets show an exponential decay of fluorescence signal which corresponds to the filled points.

the corresponding integrated rate law

$$[S] = [S]_0 [(\lambda_1 + k_{-1a} + k_2)e^{\lambda_1 t} - (\lambda_2 + k_{-1a} + k_2)e^{\lambda_2 t}] / (\lambda_1 - \lambda_2), \quad (3)$$

where

$$\begin{aligned} 2\lambda_{1,2} = & -(k_{1a}' + k_d + k_{-1a} + k_2) \pm \{(k_{1a}' + k_d + k_{-1a} + k_2)^2 \\ & - 4(k_{1a}'k_2 + k_2(k_{1a}' + k_{1b}') + k_dk_{-1a} + k_2k_d)\}^{1/2}. \end{aligned}$$

Figure 2 shows an example of a biexponential fluorescence signal and plots of first-order rate constants vs. $[CS_2]$. At a given total density $[M] \approx [Ar]$, k_{1a}' and k_{1b}' increases linearly with $[CS_2]$ and the slopes yield the second-order addition and abstraction rate constants k_{1a} and k_{1b} . The observed first-order dissociation rate constant k_{-1a} should be independent of the concentration of adduct and $[CS_2]$. Here, k_2 allows for diffusion of CS_3 out of the reaction zone (likely to be slow)

FIG. 2. Pseudo-first order rate constants obtained for $S + CS_2$ at 687 K and 573 mbar total pressure, for addition (circles), abstraction (stars), and adduct dissociation (triangles). The inset shows a biexponential decay of the fluorescence signal, plotted logarithmically, which corresponds to the filled points.

and any other processes which consume CS_3 without regenerating S atoms. This channel was found to be minor, with k_2 falling in the range $10\text{--}30\text{ s}^{-1}$.

III. EXPERIMENTAL RESULTS

Table I summarizes 73 kinetic experiments. Below 650 K and above 830 K simple exponential decays were observed, while in the intermediate regime the results come from fitting to the biexponential rate law discussed above. Each experiment was made with five values of $[CS_2]$ approximately evenly spaced; the maximum value of $[CS_2]$ and the corre-

sponding maximum initial $[S]$ is tabulated, along with other experimental parameters. The results are independent of the residence time, which indicates that thermal decomposition and mixing effects were not significant. Within the scatter of the data there is no dependence on the photolysis pulse energy or the initial concentration of atomic S. This shows that secondary chemistry between S and reaction or photolysis products is negligible and that the primary reaction (1) has been isolated from potentially interfering processes.

In the low temperature regime, 290–640 K, k_{1a} exhibits a clear pressure dependence as may be seen in the falloff curves shown in Fig. 3. This behavior is interpreted in terms of an energy transfer mechanism

There is a competition between dissociation of the initially excited CS_3^* back to reactants and collisional stabilization with bath gas molecules M. As $[M]$ tends to zero, this stabilization is rate-limiting and the observed second-order rate constant k_{1a} equals $k_0[M]$, where k_0 is the third-order low-pressure limit rate constant. As $[M]$ tends to infinity, k_{1a} tends to k_∞ , the high-pressure limit, which is equivalent to the rate constant for $S + CS_2$ addition, k_a .

Our data, obtained at intermediate pressures, have been fitted to Troe's falloff expression¹⁷ to obtain the low- and high-pressure limiting parameters,

$$k_{1a} = \left(\frac{k_0[M]}{1 + k_0[M]/k_\infty} \right) F_{\text{cent}}^{\left\{ 1 + \left[\frac{\log_{10}(k_0[M]/k_\infty)}{0.75 - 1.27 \log_{10} F_{\text{cent}}} \right]^2 \right\}^{-1}}. \quad (5)$$

Here, F_{cent} is the broadening factor. Cobos and Troe have analyzed F_{cent} and indicate that for reactants with two degrees of rotational freedom, at 300 K, $F_{\text{cent}} \approx 0.6$.¹⁸ We employ

TABLE I. Summary of measurements of the rate constant k_{1a} for $S + CS_2$ addition, k_{1b} for $S + CS_2$ abstraction and k_{-1a} for CS_3 dissociation.

T (K)	τ_{res} (s)	F (mJ)	P (mbar)	$[CS_2]_{\text{max}}$ (10^{15} molecule cm^{-3})	$[S]_0$ (10^{13} molecule cm^{-3})	$k_{\text{total}} \pm \sigma_{k_{\text{total}}}$ 10^{-13} cm^3 molecule $^{-1} \text{ s}^{-1}$)	$k_{1a} \pm \sigma_{k_{1a}}$ (10^{-13} cm^3 molecule $^{-1} \text{ s}^{-1}$)	$k_{1b} \pm \sigma_{k_{1b}}$ (10^{-13} cm^3 molecule $^{-1} \text{ s}^{-1}$)	$k_{-1a} \pm \sigma_{k_{-1a}}$ (s^{-1})	$K_c / 10^{-16}$ cm^3 molecule $^{-1}$
294	5.1	0.06	269	1.73 ± 0.09	1.57	9.99 ± 0.32	9.99 ± 0.32			
294	1.4	0.06	17	1.04 ± 0.05	0.98	1.34 ± 0.07	1.34 ± 0.07			
294	3.6	0.06	81	1.70 ± 0.08	1.54	5.83 ± 0.35	5.83 ± 0.35			
295	4.6	0.06	144	0.97 ± 0.05	0.80	7.47 ± 0.20	7.47 ± 0.20			
295	4.6	0.10	144	0.97 ± 0.05	1.49	7.81 ± 0.35	7.81 ± 0.35			
295	3.9	0.06	45	1.10 ± 0.06	0.91	3.52 ± 0.14	3.52 ± 0.14			
295	3.9	0.10	45	1.10 ± 0.06	1.69	3.77 ± 0.12	3.77 ± 0.12			
295	6.5	0.04	805	0.87 ± 0.04	0.52	14.30 ± 0.52	14.30 ± 0.52			
295	5.8	0.04	604	0.97 ± 0.05	0.58	13.50 ± 0.66	13.50 ± 0.66			
295	5.1	0.04	422	1.04 ± 0.05	0.62	12.40 ± 0.26	12.40 ± 0.26			
415	5.8	0.06	848	0.62 ± 0.03	0.55	13.90 ± 1.53	13.87 ± 1.53	0.03^a		
415	5.9	0.06	693	0.76 ± 0.04	0.67	12.50 ± 0.33	12.47 ± 0.33	0.03^a		
416	2.7	0.04	426	2.96 ± 0.15	1.55	10.90 ± 1.04	10.87 ± 1.04	0.03^a		
416	1.1	0.04	83	1.48 ± 0.07	0.85	4.17 ± 0.09	4.14 ± 0.09	0.03^a		
418	1.6	0.03	28	1.37 ± 0.07	0.64	2.28 ± 0.07	2.25 ± 0.07	0.03^a		
418	3.2	0.03	147	1.63 ± 0.08	0.74	5.91 ± 0.20	5.88 ± 0.20	0.03^a		
418	4.8	0.03	292	2.06 ± 0.10	0.91	8.18 ± 0.19	8.15 ± 0.19	0.03^a		

TABLE I. (Continued.)

T (K)	τ_{res} (s)	F (mJ)	P (mbar)	$[\text{CS}_2]_{\text{max}}$ (10^{15} molecule cm^{-3})	$[\text{S}]_0$ (10^{13} molecule cm^{-3})	$k_{\text{total}} \pm \sigma_{k_{\text{total}}}$ (10^{-13} cm^3 molecule $^{-1}$ s $^{-1}$)	$k_{1a} \pm \sigma_{k_{1a}}$ (10^{-13} cm^3 molecule $^{-1}$ s $^{-1}$)	$k_{1b} \pm \sigma_{k_{1b}}$ (10^{-13} cm^3 molecule $^{-1}$ s $^{-1}$)	$k_{-1a} \pm \sigma_{k_{-1a}}$ (s $^{-1}$)	$K_c / 10^{-16}$ cm 3 molecule $^{-1}$
420	5.9	0.09	817	1.54 ± 0.08	1.94	13.00 ± 1.43	12.97 ± 1.43	0.03^a		
420	8.2	0.09	586	1.38 ± 0.07	1.76	11.50 ± 1.71	11.47 ± 1.71	0.03^a		
542	4.5	0.05	841	2.45 ± 0.12	1.57	10.90 ± 0.38	10.58 ± 0.38	0.32^a		
542	3.7	0.05	706	1.49 ± 0.07	1.01	10.40 ± 0.45	10.08 ± 0.45	0.32^a		
543	0.5	0.06	28	1.88 ± 0.09	1.48	1.42 ± 0.06	1.10 ± 0.06	0.32^a		
543	0.9	0.06	71	2.18 ± 0.11	1.68	2.79 ± 0.13	2.47 ± 0.13	0.32^a		
543	1.5	0.06	141	2.95 ± 0.15	2.17	4.55 ± 0.28	4.23 ± 0.28	0.32^a		
543	2.9	0.06	281	0.66 ± 0.03	0.56	7.37 ± 0.15	7.05 ± 0.15	0.32^a		
545	4.8	0.05	560	2.11 ± 0.11	1.54	9.46 ± 0.26	9.13 ± 0.26	0.33^a		
545	3.5	0.05	405	1.53 ± 0.08	1.16	8.33 ± 0.62	8.00 ± 0.62	0.33^a		
545	2.9	0.05	280	2.25 ± 0.11	1.63	7.70 ± 0.33	7.37 ± 0.33	0.33^a		
644	2.9	0.02	143	1.59 ± 0.08	0.47	3.24 ± 0.26	2.09 ± 0.26	1.15^a		
685	3.4	0.05	812	3.02 ± 0.15	1.80		5.97 ± 0.39	1.75 ± 0.11	433 ± 36	13.79
685	2.9	0.05	684	2.55 ± 0.13	1.57		5.74 ± 0.14	1.65 ± 0.07	301 ± 28	19.07
685	2.8	0.05	534	2.47 ± 0.12	1.52		5.02 ± 0.34	1.28 ± 0.08	551 ± 43	9.11
686	3.5	0.04	833	1.44 ± 0.07	0.78		5.58 ± 0.20	2.40 ± 0.19	471 ± 34	11.85
686	3.6	0.04	701	1.51 ± 0.08	0.82		5.18 ± 0.14	1.91 ± 0.15	463 ± 51	11.19
686	2.8	0.04	409	1.93 ± 0.10	1.01		4.20 ± 0.15	2.19 ± 0.12	229 ± 26	18.34
686	2.3	0.04	279	1.56 ± 0.08	0.84		3.11 ± 0.11	2.07 ± 0.13	417 ± 38	7.46
686	2.4	0.04	570	2.15 ± 0.11	1.28		5.19 ± 0.18	1.98 ± 0.14	307 ± 44	16.91
686	2.1	0.04	408	1.60 ± 0.08	0.99		4.11 ± 0.12	2.45 ± 0.12	245 ± 29	16.78
686	1.4	0.04	267	2.07 ± 0.10	1.24		3.70 ± 0.13	1.33 ± 0.08	199 ± 18	18.59
687	2.6	0.05	573	1.73 ± 0.09	1.31		4.70 ± 0.13	1.90 ± 0.08	169 ± 21	27.81
687	0.3	0.05	29	1.18 ± 0.06	0.94		0.52 ± 0.02	1.25 ± 0.08	279 ± 24	1.86
687	0.6	0.05	73	1.45 ± 0.07	1.14		1.40 ± 0.05	2.12 ± 0.11	402 ± 36	3.48
687	0.8	0.05	140	1.67 ± 0.08	1.29		2.09 ± 0.07	1.63 ± 0.10	325 ± 53	6.43
687	1.1	0.05	273	1.40 ± 0.07	1.10		3.23 ± 0.16	1.50 ± 0.08	221 ± 29	14.62
726	2.6	0.03	147	3.80 ± 0.19	1.33		1.51 ± 0.11	1.92 ± 0.11	823 ± 74	1.83
726	2.6	0.03	275	3.74 ± 0.19	1.31		2.65 ± 0.26	1.73 ± 0.09	746 ± 92	3.55
727	3.2	0.03	810	1.22 ± 0.06	0.61		3.88 ± 0.15	2.88 ± 0.13	567 ± 64	6.84
727	3.3	0.03	670	1.25 ± 0.06	0.63		3.67 ± 0.12	2.63 ± 0.12	772 ± 96	4.75
728	2.6	0.04	411	2.00 ± 0.10	1.05		3.17 ± 0.14	2.87 ± 0.14	726 ± 70	4.37
728	2.7	0.04	268	1.83 ± 0.09	0.97		2.01 ± 0.17	2.63 ± 0.10	589 ± 72	3.41
728	1.7	0.04	140	1.31 ± 0.07	0.72		1.17 ± 0.08	2.85 ± 0.12	523 ± 37	2.24
729	0.5	0.03	28	0.67 ± 0.03	0.31		0.30 ± 0.03	2.34 ± 0.14	584 ± 78	0.51
729	1.3	0.03	69	1.65 ± 0.08	0.71		0.79 ± 0.05	2.62 ± 0.16	431 ± 53	1.83
729	1.8	0.03	147	2.41 ± 0.12	0.99		1.01 ± 0.09	1.96 ± 0.10	455 ± 40	2.22
729	3.6	0.03	548	2.76 ± 0.14	1.06		3.66 ± 0.17	3.56 ± 0.18	708 ± 76	5.17
729	1.7	0.03	264	1.32 ± 0.07	0.55		2.35 ± 0.08	3.50 ± 0.10	528 ± 42	4.45
733	0.4	0.04	29	0.96 ± 0.05	0.51		0.20 ± 0.02	2.36 ± 0.12	494 ± 50	0.40
733	0.7	0.04	73	1.83 ± 0.09	0.93		0.59 ± 0.03	2.47 ± 0.10	673 ± 60	0.88
751	1.8	0.04	283	3.45 ± 0.17	1.69		1.91 ± 0.06	2.97 ± 0.13	1360 ± 118	1.40
771	1.8	0.04	289	3.41 ± 0.17	1.67		1.74 ± 0.25	3.56 ± 0.17	1499 ± 142	1.16
831	2.7	0.04	320	1.48 ± 0.07	0.80			4.58 ± 0.22		
831	2.4	0.04	148	1.31 ± 0.07	0.72			4.19 ± 0.16		
831	1.9	0.04	64	1.03 ± 0.05	0.57			4.88 ± 0.39		
835	0.4	0.06	35	1.02 ± 0.05	0.94			5.13 ± 0.17		
835	0.6	0.06	73	1.64 ± 0.08	1.46			5.31 ± 0.13		
835	1.0	0.06	151	2.73 ± 0.14	2.27			5.06 ± 0.11		
933	1.5	0.05	303	1.02 ± 0.05	0.82			9.34 ± 0.45		
933	1.0	0.05	159	0.79 ± 0.04	0.65			10.30 ± 0.42		
933	0.8	0.05	79	0.64 ± 0.03	0.53			10.90 ± 0.67		
933	0.3	0.05	32	0.41 ± 0.02	0.34			9.67 ± 0.26		
1037	0.5	0.06	73	0.84 ± 0.04	0.80			15.50 ± 1.39		
1037	0.8	0.06	143	1.31 ± 0.07	1.22			16.80 ± 0.75		
1037	0.3	0.06	35	0.52 ± 0.03	0.51			17.10 ± 0.65		

^aExtrapolated from the Arrhenius fit to the k_{1b} results at 685–1037 K and subtracted from the observed k_{total} to yield k_{-1} .

FIG. 3. Falloff curves for $S + CS_2$ with fits to the Troe formalism (see text). Error bars are $\pm 1\sigma$.

this value here. The fits to experimental data are shown in Fig. 3, and the corresponding low- and high-pressure limiting rate constants k_0 and k_∞ are summarized in Table II. The temperature dependence of the low-pressure limit k_0 is shown in Fig. 4, and k_0 shows a typical decrease with temperature. A simple linear fit over 300–730 K may be expressed as

$$k_0 = (11.5 - 0.0133 T/K) \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}.$$

Considering the scatter of points about this line, we assign error limits of $\pm 20\%$. The high-pressure limit k_∞ shows

TABLE II. Low- and high-pressure limiting rate constants derived from falloff behavior in $S + CS_2 + Ar$, and the corresponding collision efficiency β_c .

T / K	$k_0 / 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$	$k_\infty / 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	β_c
295	7.4	2.4	0.33
417	6.1	2.6	0.39
543	4.5	2.8	0.42
686	2.7	1.7	0.37
729	1.45	1.7	0.22

FIG. 4. Temperature dependence of the low-pressure limiting rate constant for $S + CS_2 + Ar$. Solid line: empirical fit; dotted line: fit to Troe's unimolecular formalism (see text).

no consistent variation with temperature (see Table II) and can be summarized by the mean of $k_\infty = 2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with error limits of $\pm 0.6 \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

In the middle temperature regime, where equilibration is observed over 690–770 K, the kinetics remain pressure-dependent and the k_{1a} results fit well when included with the lower temperature results (see Fig. 4 and Table II). This provides some validation of the more complex kinetic analysis, Eq. (3), that was applied. This analysis also yields the dissociation rate constant k_{-1a} which is listed in Table I. The ratio $k_{1a}/k_{-1a} = K_c$ is converted to the equilibrium constant K_{eq} (relative to a standard state of 10^5 Pa for unit activity). K_{eq} is plotted in van't Hoff form in Fig. 5, along with a minor correction for the temperature-dependence of ΔH and ΔS . This correction to $\ln K_{eq}$, $(\Delta S_{298} - \Delta S_T)/R + (\Delta H_T - \Delta H_{298})/RT$, is based on theoretical results for the vibrational frequencies of the adduct (see below) and is approximately equal to 0.15 here. We estimated S_{298} for S, CS_2 , and CS_3 to be 167.8, 237.9, and $291.9 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively. A “Third Law”

FIG. 5. van't Hoff plot of equilibrium constant for S atom addition to CS_2 , constrained to pass through the computed intercept of $\Delta S_{298}/R$.

FIG. 6. Arrhenius plot for $S + CS_2$ abstraction channel. Open circles (1σ error bars) and solid line: present work; solid circles: Woiki and Roth (Ref. 10); dashed line: transition state theory for TS-5 (see text).

analysis relies on the separately computed theoretical $\Delta S_{298} = -113.8 \text{ J K}^{-1} \text{ mol}^{-1}$ to fix the intercept as $\Delta S_{298}/R$, and the slope of the best fit line is then $-\Delta H_{298}/R$. Noting the scatter in K_{eq} , we allow for up to a factor of 2 error in K_{eq} to obtain $\Delta H_{298} = -131.7 \pm 4.0 \text{ kJ mol}^{-1}$ for addition of S to CS_2 . The corresponding bond dissociation enthalpy (BDE) at 0 K is $128.0 \pm 4.0 \text{ kJ mol}^{-1}$. Use of 298 K enthalpies of formation of 277.2 and $116.7 \text{ kJ mol}^{-1}$ for S and CS_2 ,¹⁹ respectively, leads to an enthalpy of formation of $262.2 \text{ kJ mol}^{-1}$ at 298 K. The recent revision of $\Delta_f H_{298}(S^3P)$ to $279.5 \text{ kJ mol}^{-1}$ by Nagy *et al.*²⁰ implies $\Delta_f H_{298}(CS_3) = 264.5 \text{ kJ mol}^{-1}$.

The data from $T \geq 685 \text{ K}$ yield information about the abstraction rate constant k_{1b} , either alone ($T \geq 830 \text{ K}$) or from modeling the mixed addition and abstraction mechanism (over 685–770 K). These results are plotted in Arrhenius form in Fig. 6 and a weighted fit is

$$k_{1b} = (1.14 \pm 0.23) \times 10^{-10} \times \exp(-37.0 \pm 1.3 \text{ kJ mol}^{-1}/RT) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1},$$

where the uncertainties are $\pm 1\sigma$ in the Arrhenius parameters. Consideration of the covariance leads to 1σ statistical uncertainties of $\sim 20\%$. Combination in quadrature with a 5% allowance for potential systematic errors leads to 95% confidence limits of $\pm 40\%$ for k_{1b} .

IV. COMPUTATIONAL ANALYSIS

The PES for the $S + CS_2$ system was initially explored with density functional theory (DFT) (B3LYP) and the 6–311G(2d,d,p) basis set. Then the geometries and harmonic vibrational frequencies of minima and transition states (TSs) were computed with coupled-cluster theory, at the UCCSD(T)/aug-cc-pV(T+d)Z level, where “tight d” basis functions were included for sulfur.²¹ Figure 7 shows the geometries of stationary points, and the Cartesian coordinates and frequencies are listed in Table IS of the supplementary information.²² Then, further single-point energy calculations at the UCCSD(T)/aug-cc-pV(Q+d)Z and UCCSD(T)/aug-cc-pV(5+d)Z levels of theory were made at these geometries.

FIG. 7. (a) CCSD(T)/aug-cc-pV(T+d)Z geometries of triplet minima and transition states in the S + CS₂ system. (b) CCSD(T)/aug-cc-pV(T+d)Z geometries of singlet minima and transition states in the S + CS₂ system.

The total (Hartree-Fock plus correlation) energies for each species were extrapolated to the infinite or complete basis set (CBS) limit in three ways. We used an exponential fit²³ through the three CCSD(T)/aug-cc-pV(n+d)Z energies as a function of n , with $n = 3-5$, respectively, and a two-point $1/n^3$ extrapolation²⁴ for $n = 4$ and $n = 5$, and for $n = 3$ and $n = 4$. All the coupled-cluster calculations were carried out with the MOLPRO suite,²⁵ and the results are summarized in Table IIS in the supplementary information.²² Also shown there are several minor corrections. Core-valence electron correlation effects were evaluated with the cc-pwCvTZ basis set²⁶ and CCSD(T) theory, and the same basis set was employed to compute scalar relativistic corrections at the CISD level of theory as the sum of mass-velocity and Darwin terms.

The contribution of spin-orbit splitting in triplet atomic sulfur is included via an empirical correction of $-2.35 \text{ kJ mol}^{-1}$ to the energy of S.²⁷ Harmonic frequencies are used to estimate the vibrational zero-point energy (ZPE).

The total energy for each species at 0 K is derived as the sum of the CCSD(T) energy extrapolated to the CBS limit, the scalar relativistic term, the core-valence correlation correction, and the vibrational ZPE. Table III lists the contributions of each term to the energy relative to the reactants, which at 0 K is equivalent to the relative enthalpy. It may be seen that the contributions of the scalar relativistic and core-valence terms are typically of the order of 1 kJ mol^{-1} and of opposite signs, so in most cases they make only modest contributions to the relative enthalpy. Two exceptions are TS-8 and

FIG. 7. (Continued.)

$S(^1D)$, where the core-valence difference from the reactants exceeds 3 kJ mol^{-1} . TS-8 is the transition state for addition of $S(^1D)$ to the C atom in CS_2 , a process not directly relevant to the present experiments. Because of orbital degeneracies the single-reference methods employed are not in fact appropriate for $S(^1D)$, and the computed excitation energy relative to $S(^3P)$ of 130 kJ mol^{-1} is in poor accord with the experimental value of 110 kJ mol^{-1} . The latter value is used in the PES diagram. Inspection of Table III shows that relative energies at the CCSD(T)/aug-cc-pV(Q+d)Z level are approaching those obtained with the larger basis set, and so the extrapolations to the complete basis set limit are not large. The pairwise $1/n^3$ T-Q extrapolations are on average 0.4 kJ mol^{-1} below those at the Q-5 level, with a rms deviation of 0.9 kJ mol^{-1} . Thus in larger systems, the computationally less-demanding T-Q evaluations may be sufficient for some purposes. The two-point Q-5 extrapolation scheme yields values on average 1.2 kJ mol^{-1} above results from the three-point T-Q-5 exponential extrapolation, with a rms deviation of 1.4 kJ mol^{-1} . Here, we employ the average of these two extrapolation methods and allow for an uncertainty of $\pm 2 \text{ kJ mol}^{-1}$ to cover

differences arising from details of what extrapolation scheme is chosen. We note that Feller and Peterson applied roughly similar methods to a large set of molecules and found mean absolute errors in atomization energies of around 3 kJ mol^{-1} ,²⁸ which is probably a reasonable estimate of the overall uncertainty in the results here.

The corresponding PES is drawn in Fig. 8. Triplet species that arise from spin-conserving interactions of $S(^3P)$ with CS_2 are connected with solid lines. The most stable triplet species, labeled as IM-3, is bound by $\sim 10 \text{ kJ mol}^{-1}$ at 0 K and cannot account for the adduct observed to be bound by $\sim 128 \text{ kJ mol}^{-1}$ at 0 K. Accordingly, singlet species, in principle arising from $S(^1D) + \text{CS}_2$ interactions, were also investigated and are shown with dotted lines in Fig. 8. It may be seen that the singlet intermediate IM-6 is predicted to be bound by $130.1 \pm 3 \text{ kJ mol}^{-1}$ is the most plausible candidate for the adduct.

For CS_2 the equilibrium bond length is computed to be $1.562 \times 10^{-10} \text{ m}$, which compares well with an experimental value of $1.554 \times 10^{-10} \text{ m}$.²⁹ The computed C_{2v} geometry for CS_3 has a unique S–C distance of $1.603 \times 10^{-10} \text{ m}$ and two other S–C distances of $1.748 \times 10^{-10} \text{ m}$, and the

TABLE III. Computed energies relative to S + CS₂, in kJ mol⁻¹.

Species	CCSD(T) AV(T+d)Z	CCSD(T) AV(Q+d)Z	CCSD(T) AV(5+d)Z	ZPE	Scalar relativity	Core- valence correlation	Two-point T-Q extrapolation ^a	Two-point Q-5 extrapolation ^a	Three-point T-Q-5 extrapolation ^a	T-Q + corrections ^b	Q-5 + cor- rections ^b	T-Q-5 + correc- tions ^b
S(³ P)+CS ₂	0	0	0	0	0	0	0	0	0	0	0	0
S(¹ D)+CS ₂	127.9	125.5	124.7	0	0.0	3.3	126.0	126.3	126.7	129.3	129.5	130.0
³ S ₂ +CS	27.6	22.3	20.0	-6.1	-0.8	1.3	20.8	19.8	20.7	15.2	14.2	15.1
¹ S ₂ +CS	101.1	94.7	92.0	-6.3	-0.8	2.1	92.4	91.4	92.5	87.4	86.3	87.5
IM-1	10.8	6.2	5.1	0.0	0.0	-0.3	5.3	6.3	7.2	5.0	6.0	6.9
IM-2	-1.4	-7.1	-8.6	-1.3	0.0	-0.5	-8.9	-7.8	-6.7	-10.7	-9.6	-8.6
IM-3	4.3	-5.8	-9.5	0.4	0.8	-0.8	-10.8	-11.0	-9.1	-10.3	-10.5	-8.6
IM-4	12.2	2.3	-1.4	-0.1	0.9	-0.6	-2.6	-2.8	-1.0	-2.5	-2.7	-0.9
IM-5	-50.6	-56.6	-58.3	0.7	-0.2	0.7	-58.6	-57.8	-56.7	-57.4	-56.6	-55.5
IM-6	-116.1	-127.1	-131.3	2.9	0.8	-1.4	-132.8	-133.3	-131.3	-130.5	-131.1	-129.1
IM-7	-60.4	-72.7	-77.4	2.2	1.1	-1.1	-79.3	-80.0	-77.8	-77.1	-77.8	-75.6
IM-8	-13.2	-28.7	-35.4	1.8	0.9	-0.5	-37.7	-40.1	-37.4	-35.4	-37.8	-35.1
Adduct-1	-5.9	-6.1	-6.1	0.3	-0.1	-0.2	-3.9	-3.9	-3.8	-3.8	-3.8	-3.8
Adduct-2	93.3	87.2	84.4	-5.2	-0.5	1.9	85.1	83.9	85.0	81.2	80.1	81.2
Adduct-3	21.7	16.7	14.6	-5.5	-0.6	1.2	15.5	14.7	15.6	10.6	9.8	10.6
TS-1	47.7	44.9	43.9	-1.2	-0.5	0.0	45.3	45.2	45.7	43.5	43.4	43.9
TS-2	53.2	50.8	49.9	-0.9	-0.5	0.1	51.4	51.3	51.7	50.2	50.0	50.5
TS-3	24.6	15.2	11.5	-1.0	1.1	-1.2	10.7	9.9	11.5	9.6	8.8	10.5
TS-4	15.8	9.8	7.2	-0.8	0.3	-0.7	7.7	6.8	7.9	6.5	5.6	6.7
TS-5	55.6	48.9	46.0	-4.2	-0.6	0.9	46.4	45.3	46.5	42.4	41.4	42.5
TS-6	47.2	37.8	34.3	-1.6	0.7	-0.3	33.3	33.0	34.7	32.2	31.8	33.5
TS-7	63.0	56.6	53.8	-4.7	-0.5	1.0	54.2	53.3	54.4	50.1	49.1	50.3
TS-8	57.3	57.5	57.7	1.6	-0.8	3.9	60.1	60.2	60.1	64.8	64.9	64.9
TS-9	-48.1	-54.4	-56.4	0.3	0.0	-0.2	-56.7	-56.0	-54.9	-56.6	-56.0	-54.8
TS-10	-50.3	-61.3	-65.8	0.9	0.8	-1.0	-66.9	-68.1	-66.2	-66.2	-67.5	-65.5
TS-11	61.0	49.0	44.4	-0.2	0.5	-0.2	42.5	41.9	44.1	42.6	42.0	44.2

^aIncludes empirical spin-orbit correction for S(³P).^bCorrections are for vibrational ZPE, scalar relativistic effects, and core-valence electron correlation.

separation of the latter two S atoms is 2.163×10^{-10} m. This separation is similar to the S-S distance in HSSH,³⁰ 2.056×10^{-10} m, and is consistent with a single S-S bond in the molecule. Based on the performance with CS₂, we suggest un-

FIG. 8. Potential energy diagram for S + CS₂ showing triplet (solid line) and singlet (dotted line) stationary points computed via CCSD(T)/CBS theory (see text). Experimental energy used for S(¹D).

certainties of around 0.01×10^{-10} m in the CS₃ bond lengths. The computed harmonic frequencies of CS₂ of 395 (2, Π_u), 666 (Σ_g), and 1549 (Σ_u) cm⁻¹ compare well with the experimental fundamental transitions of 397 (2), 658, and 1535 cm⁻¹, respectively.³¹ Anharmonicity is therefore minor here. For CS₃, the predicted harmonic frequencies are 274 (B₂), 392 (B₁), 405 (A₁), 575 (A₁), 590 (B₂), and 1250 (A₁) cm⁻¹. The last two values are close to the observed fundamentals of 570 and 1263 cm⁻¹.⁸ An alternative argument that anharmonicity does not make a significant contribution to the binding in the adduct IM-6 is that the data in Table III show that ZPE mostly cancels between the adduct and the fragments (Δ ZPE ~ -3 kJ mol⁻¹). Therefore, potential application of typical scale factors of around 0.95–1 to account for anharmonicity would change the BDE by less than 0.2 kJ mol⁻¹.

We also focus on TS-5 because it is the highest barrier along the most favorable spin-allowed path connecting S + CS₂ to CS + S₂. The enthalpy at 0 K is 41.9 kJ mol⁻¹ relative to S + CS₂. With reference to Fig. 7(a), the S-S and two S-C separations are 1.915×10^{-10} m, 2.263×10^{-10} m, and 1.560×10^{-10} m, respectively, and the S-S-C and S-C-S angles are 108.9° and 121.2°. The harmonic vibrational frequencies are 369i, 1191, 677, 240, 98 (A') and 98 (A'') cm⁻¹. The A'' mode corresponds to out-of-plane twisting of the TS. A rigid scan as a function of twist angle was performed with

density functional theory, which indicated that the barrier to rotation is 9.8 kJ mol^{-1} relative to the *cis*-configuration, and that there is a *trans*-configuration of the TS 5.2 kJ mol^{-1} less stable than the *cis*-form. Approximate reduced moments of inertia for torsion were calculated about an axis connecting the centers of mass of the two rotating groups. Here, the *cis*- and *trans*-configurations of the TS have $I_{\text{red}} = 1.96 \times 10^{-46}$ and $6.56 \times 10^{-47} \text{ kg m}^2$, respectively. Assuming that the torsional force constant remains the same, the corresponding harmonic oscillator value is 169 cm^{-1} at the *trans*-configuration, where the moment of inertia is smaller. These data were employed in the CT- $C\omega$ method of Ellingson *et al.*³² to estimate the partition functions for this torsional mode of TS-5. Below about 700 K the results differ little from treating torsion as a harmonic oscillator.

V. DISCUSSION

At room temperature, the low-pressure limit $k_0 = (8.3 \pm 2.8) \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ derived by Basco and Pearson⁵ from their experiments with Ar and N_2 bath gas agrees with our value in Table II.

The pressure independence we observed at $T \geq 830 \text{ K}$ is consistent with a bimolecular abstraction reaction k_{1b} and our results are compared with the shock-tube data of Woiki and Roth¹⁰ in Fig. 6. An extrapolation of our Arrhenius fit passes through the shock-tube data, which indicates excellent accord between the two data sets. The activation energy of 37 kJ mol^{-1} is similar to the lowest computed barrier height on the triplet surface, TS-5 in Fig. 8, which is 41.9 kJ mol^{-1} at the CCSD(T)/CBS level of theory. However, these quantities are not precisely equivalent. A quantitative comparison comes from evaluation of the rate constant for passage over this barrier via canonical transition state theory (TST). Aside from the torsional frequency in the TS discussed above, all internal modes were treated as harmonic oscillators. The CCSD(T) data yield $k_{\text{TST}} = 7.7 \times 10^{-15} (T/\text{K})^{1.42} \exp(-5000 \text{ K}/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over 298–2000 K. As seen in Fig. 6, there is moderate accord with the measurements. The magnitude of k_{1b} is reproduced although the activation energy is high, as is the pre-exponential factor. In other words, the computed enthalpy and entropy of the TS are both too high and these errors largely cancel. It may be that a more sophisticated analysis of the TS would lead to a smaller entropy, but given the accuracy of the computed enthalpy change for channel (1a) it is not clear that better calculations would reduce the barrier height significantly. It is likely that other reaction pathways passing through TS-2 and TS-7 make a small contribution to the total reactivity. It is also possible that multiple intersystem crossings (ISC) contribute to the net loss of triplet S atoms at high temperatures. For example, ISC between reactants and the singlet surface in the region of IM-5 could be followed by a second ISC between IM-7 and $\text{CS} + {}^3\text{S}_2$, with no barrier higher than the endothermicity of the overall reaction. This might account for the extra reactivity at ~ 700 – 1000 K beyond that involving TS-5. All these pathways lead to the same products, CS + triplet S_2 .

The assignment of C_{2v} CS_3 (IM-6) as the product of the pressure-dependent reaction of S with CS_2 is based here on

close accord between the computed bond strength and that observed. This species was initially proposed as the global minimum on the CS_3 PES by Froese and Goddard who made MP4/6-31G(d) calculations.¹² Very recently the products of reaction (1a) were studied by Ma *et al.*, who used matrix-isolation and infrared spectroscopy to reach the same conclusion, based on comparison with DFT frequencies and intensities.⁹ This singlet product means that the dominant pathway below about 700 K is spin-forbidden, which can account for the modest value of the high-pressure limit k_∞ of $\sim 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. k_∞ is two orders of magnitude smaller than for a typical spin-allowed bimolecular process and because it is proportional (via the pre-exponential Arrhenius A factor) to the probability for triplet-singlet ISC, this probability is around 0.01. There are few well-characterized spin-forbidden systems for comparison. We note that the A factor for $\text{O} + \text{SO}_2$ recombination is of a similar magnitude to the present k_∞ , at $6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,³³ and the high-pressure limiting dissociation kinetics of N_2O (Ref. 34) imply, via the equilibrium constant, an A factor for $\text{O} + \text{N}_2$ recombination of $9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ which is an order of magnitude smaller. In the latter case Olschewski *et al.* rationalized the ISC probability in terms of the spin-orbit splitting in atomic oxygen, which is a measure of the spin-orbit coupling between singlet and triplet PESs at the point of ISC.³⁵ It may be possible to extend this analogy to the other two systems, where the greater spin-orbit coupling in sulfur is consistent with the higher probability of ISC. In the $\text{S} + \text{H}_2\text{S}$ system, where ISC occurs with an interaction between *two* sulfur atoms, an ISC probability of 0.2 was found to fit the observed kinetics.³⁶

The negligible temperature dependence of k_∞ suggests there is no significant barrier to the overall reaction (1a). Based on the PE diagram this rules out initial participation of the triplet intermediate IM-1 because this species is connected to the reactants via a significant barriers of $\sim 44 \text{ kJ mol}^{-1}$. IM-3 and IM-4 are accessible over lower barriers of 6–10 kJ mol^{-1} .

A question is where does ISC occur when IM-6 is formed? One possibility is along a pathway where S atoms add to the central C atom in CS_2 . We have investigated the energies of the singlet and triplet states along a C_{2v} path defined by optimizing the singlet molecular geometry of IM-5 at a series of fixed C–S distances, at the B3LYP/6-311G(2d,d,p) level of density functional theory. The results are shown in Fig. 9(a). It may be seen that there is an ISC point at $r(\text{C}–\text{S}) \sim 1.9 \times 10^{-10} \text{ m}$, so that an approaching triplet S atom could transition to the singlet surface there. However, in terms of Fig. 8, the approaching S atom would first have to overcome an energy barrier of $\sim 40 \text{ kJ mol}^{-1}$ associated with TS-1. Such a barrier is inconsistent with our measurements. A second pathway was investigated at the same density functional level. We scanned partially optimized structures corresponding to dissociation of triplet IM-3 by extension of the S–S bond, and singlet energies were evaluated at these structures as well. The results are plotted in Fig. 9(b) and reveal an ISC point at $r(\text{S}–\text{S}) \sim 2.4 \times 10^{-10} \text{ m}$. The geometry of this structure is detailed in Fig. 10, where the singlet and triplet surfaces have the same energy which is $\sim 1 \text{ kJ mol}^{-1}$ below

FIG. 9. Relaxed scans showing B3LYP/6-311G(2d,d,p) energies for triplet (solid points) and singlet (open points) states along possible CS₂-S path ways. (a) Geometries from dissociation of singlet IM-5 maintaining C_{2v} symmetry, corresponding to interaction of S with the central C atom in CS₂. (b) Geometries from dissociation of triplet IM-3 maintaining C_s symmetry, corresponding to interaction of S with a terminal S atom in CS₂.

that of separated ³S + CS₂ (neglecting any changes in vibrational zero-point energy or spin-orbit splitting). This pathway corresponds to attack by a triplet S atom at a terminal S atom in CS₂ roughly perpendicular to the S-C-S structure, initially via the triplet ad-1 region shown in Fig. 8, followed by ISC to the singlet IM-7 species which easily isomerizes to the more stable IM-6 via the low-barrier TS-10. This ISC point, in Fig. 10, has not been optimized to the minimum energy ISC point, but already shows there is a pathway with essentially no barrier.

At the low-pressure limit, addition kinetics will be independent of the probability of ISC. In terms of Eq. (4), a quasi-equilibrium is set up between S, CS₂, and excited CS₃^{*}, and the concentration of CS₃^{*} is independent of the rates of the forward and reverse steps k_a and k_{-a} . We have assessed the low-pressure limiting rate constant k_0 for the addition (1a)

FIG. 10. Intersystem crossing point located with B3LYP/6-311G(2d,d,p) theory, where singlet and triplet energies are equal.

via Troe's unimolecular formalism,¹⁷ which yields

$$k_0 = Z_{\text{LJ}} \beta_c \frac{\rho_{\text{vib}}(E_0)RT}{Q_{\text{vib}}(\text{CS}_3)} \frac{Q(\text{CS}_3)}{Q(\text{S})Q(\text{CS}_2)} F_E F_{\text{anh}} F_{\text{rot}}, \quad (7)$$

where the terms have their usual meanings. The CCSD(T) data were used for the molecular properties of CS₃, together with a threshold energy for adduct dissociation of $E_0 = 130 \text{ kJ mol}^{-1}$. The Lennard-Jones collision rate between excited adduct molecules and the bath gas, $Z_{\text{LJ}} \approx 4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, was derived with σ and $\varepsilon/k_B T$ parameters for CS₃ of 5.0 Å and 425 K. These CS₃ parameters were assumed to be somewhat larger than estimated values for CS₂. Parameters for Ar are 3.47 Å and 114 K. The F_E and F_{anh} terms were derived in the standard way and are ~ 1.1 and 1.235, respectively.¹⁷ Here, F_{rot} was assessed via the ratio I^+/I which corresponds to the ratio of moments of inertia of the stretched, dissociating molecule to the ground state. We assumed that the critical structure for dissociating CS₃ is the ISC geometry shown in Fig. 10. The rotational constants at the ISC point are 9.32, 1.47, and 1.27 GHz, while the values for IM-6 are 6.65, 2.67, and 1.90 GHz. The ratio of the two largest moments of inertia in each species yields $I^+/I = 1.645$.³⁷ In turn this yields $F_{\text{rot}} \approx 1.6$ via the analysis of Troe.¹⁷ Strong-collision rate constants (which correspond to deactivation of initially excited CS₃^{*} at every collision with the bath gas³⁸) were derived via the above expression 7 by setting the collision efficiency β_c equal to 1. The ratio of the observed weak-collision k_0 to the theoretical strong-collision values yields the collisional efficiencies listed in Table II. These efficiencies may be related to the average energy transferred per collision between CS₃^{*} and the Ar bath gas, $-\langle \Delta E \rangle_{\text{all}}$, via the result¹⁷

$$\frac{\beta_c}{1 - \sqrt{\beta_c}} = \frac{-\langle \Delta E \rangle_{\text{all}}}{F_E RT}. \quad (8)$$

Figure 4 shows k_0 derived when $-\langle \Delta E \rangle_{\text{all}} = 2.8 \text{ kJ mol}^{-1} \times (T/298 \text{ K})^{0.7}$. This expression ranges from 2.8 up to 5.1 kJ mol⁻¹ across the experimental temperature range and leads to reasonable agreement with the measured k_0 . These values of $-\langle \Delta E \rangle_{\text{all}}$ lie within typical ranges.³⁸ These energy transfer parameters in effect absorb all uncertainty in the theoretical unimolecular analysis and, therefore, are not to be considered as very precise. In particular, uncertainty in details of the long-range S + CS₂ interaction and ISC region mean that the rotational F_{rot} term is probably the least well-defined contribution to the unimolecular rate via Eq. (7). Nevertheless, reasonable choices of parameters are seen to be able to

rationalize the magnitude of the low-pressure limiting recombination rate constant.

VI. CONCLUSIONS

A change in mechanism is demonstrated for the reaction of S atoms with CS₂. At low temperatures, pressure-dependent spin-forbidden addition is the dominant pathway and can be rationalized via Troe's unimolecular formalism. As the temperature is raised, equilibration can be observed directly and, hence, the bond strength in the adduct is deduced. By comparison with CCSD(T) *ab initio* calculations this allows firm identification of the adduct among several candidates, an assignment in accord with the IR/matrix isolation experiments of Ma *et al.* At higher temperatures still the kinetics switch to pressure-independent and can largely be rationalized in terms of a spin-allowed abstraction pathway to make CS + ³S₂. The present results in this regime are in accord with the shock tube study of Woiki and Roth.

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