Reaction kinetics of the addition of atomic sulfur to nitric oxide

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(Received 9 June 2004; accepted 23 August 2004)

The reaction of $S(^3P_J)$ with $NO(^2\Pi)$ in an Ar bath gas has been studied by the laser photolysis-resonance fluorescence technique over 300–810 K at pressures from 60 to 800 mbar. The observed second-order rate constants are close to the low-pressure limit. Fitting of Troe's formalism to experiment, with an estimated $F_{\text{cent}} = 0.78 \exp(-T/7445)$ and k_∞ given subsequently, yields $k_0 = (6.2 \pm 0.6) \times 10^{-33} \exp(+ (940 \pm 40)/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. Error limits are $\pm 25\%$. A theoretical analysis of this value suggests that the average energy transferred during collisions between Ar and the excited intermediate is $\langle \Delta E \rangle = -360^{+90}_{-160} \text{ cm}^{-1}$. Over 300–800 K, the high-pressure limit is predicted to be $k_\infty = 2.2 \times 10^{-10} (T/300)^{0.24} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Doublet and quartet adducts between S and NO were characterized via CBS-QB3 theory. The kinetic data can be rationalized with $SNO(^2A')$ as the major product, and an *ab initio* estimate of $\Delta_f H_{298}$ for SNO is $176 \pm 8 \text{ kJ mol}^{-1}$. © 2004 American Institute of Physics. [DOI: 10.1063/1.1806419]

I. INTRODUCTION

Fuel sulfur is known to influence the formation of NO_x during combustion, but mechanistic details of coupling between sulfur and nitrogen chemistry in flames are unknown.^{1–8} It is in this context that we have carried out experimental and computational studies of the reaction

A previous study at room temperature conducted in a CO_2 bath gas demonstrated a pressure-dependent second-order rate constant k_1 .⁹ This indicates that an adduct was formed. An obvious candidate is the sulfur analog of nitrogen dioxide, SNO. This species has been identified in solid Ar matrices by infrared spectroscopy.^{10,11} There have also been two computational investigations of SNO using density functional theory (DFT),^{11,12} the most recent of which identified nine low-lying doublet state isomers. The thermochemistry of ground-state SNO remains unknown. High-temperature shock-tube experiments revealed bimolecular kinetics for reaction (1), and it was determined that the dominant products above 2400 K are $N + SO$.¹³ The reverse of this reaction pathway was suggested by Wendt *et al.* to enhance the formation of prompt NO in flames.²

Here we present results of laser photolysis-resonance fluorescence experiments carried out from 300 to 810 K with argon bath gas pressures from about 60 to 800 mbar. Reaction (1) was found to be close to the low-pressure limit. $S + NO$ is an example of a radical-radical reaction, and therefore, multiple electronic potential-energy surfaces (PES) could be involved. In this case, a total of 12 are possible based on consideration of spin and orbital angular momentum.^{14,15} three each of $^2A'$, $^2A''$, $^4A'$, and $^4A''$. We have applied *ab initio* methods to characterize ground electronic states of structures corresponding to the connectivities

$S-N-O$, $S-O-N$, and $N-S-O$ in both spin manifolds. The PES for addition was analyzed in terms of the energy-transfer mechanism¹⁶

SNO^* represents internally-excited SNO formed by exothermic addition of S to NO. SNO^* may either be stabilized by a collision with a third body M or it may dissociate back to reactants. At the high-pressure limit, $[M] \rightarrow \infty$, the first step (2) is rate controlling, and $k_1 = k_\infty$. This process was quantified via both the statistical adiabatic channel model (SACM)¹⁷ and variational flexible transition state (TS) theory.¹⁸ At the low-pressure limit, the collisional stabilization step (4) becomes rate-controlling, and we may write $k_1 = k_0[M]$, where k_0 is a third-order rate constant. k_0 is analyzed theoretically¹⁶ which, by comparison with experiment, yields information on collisional energy transfer between SNO^* and the Ar bath gas. The computed k_∞ is employed to correct the observations for minor falloff effects and to allow evaluation of falloff at intermediate densities $[M]$. These are the first temperature-dependent investigations of this addition process.

II. EXPERIMENTAL METHOD AND RESULTS

Two sources of NO were employed, commercial ("99.99%" grade from American Gas Group) and our own synthesis.¹⁹ The NO was purified first by trapping at 77 K (liquid N_2) and degassing, which was repeated for several "freeze-pump-thaw" cycles. The NO was then distilled repeatedly from 175 K (methanol slush) and trapped at 77 K until a white solid was obtained. Commercial CS_2 (Aldrich, "99.9+%") was degassed at 196 K (acetone slush). Commercial COS (Matheson) was degassed at 113 K (2-methylbutane/liquid- N_2 slush) and then distilled at about

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230 K. Ar was used directly from the cylinder (99.995%, Air Liquid). Gas mixtures were prepared manometrically in glass bulbs.

The laser photolysis apparatus and general operating procedures have been described elsewhere.^{20–22} Briefly, mixtures of NO and S-atom precursor diluted in an Ar bath gas flowed slowly through a heatable, stainless-steel reaction cell. Actinic radiation entered through one side arm and probe radiation from a resonance lamp through a second side arm, and fluorescence was observed through a third mutually perpendicular side arm. The temperature in the reaction zone, defined by the intersection of the three side arms, was measured with a retractable, sheathed, unshielded thermocouple corrected for radiation errors.²³ Atomic sulfur was generated by two methods: photolysis of CS₂ at 193 nm and photolysis of COS at 248 nm, with pulsed radiation from a Lambda Physik Compex 102 excimer laser. A circular beam (0.9-cm diameter) was defined with an iris. The photolysis rate was 1–2 Hz to allow fresh gas mixtures to enter the reaction zone between pulses. While the absolute concentration of S atoms is not required for the pseudo-first-order kinetic analysis outlined below, as a check, the initial concentration [S]₀ was determined from the laser-pulse energy E_{laser} , the beam area, and the absorption cross sections of the photolytic precursors. For COS at 248 nm and CS₂ at 193 nm, these were taken to be 2.1×10^{-20} and 1.3×10^{-16} cm² molecule⁻¹, respectively.^{24,25} Initially, significant fractions of S(¹D) are produced, but this is rapidly quenched to ground-state S(³P) by collisions with the Ar bath gas and/or COS precursor under our conditions.¹⁵ To confirm this, a few experiments were conducted with $\sim 10^{17}$ molecule cm⁻³ of added CO₂, an efficient quencher of S(¹D) (Ref. 15) with no impact on the observed kinetics.

Around 0.4 mbar of a mixture of 0.1% of H₂S in Ar flowed through a microwave discharge to generate radiation at $\lambda \approx 181$ nm (sulfur (⁴s) ³S → (³p) ³P).²⁶ This radiation was focused through Suprasil quartz optics into the center of the reactor and excited S-atom resonance fluorescence. The time-resolved fluorescence was detected with a solar-blind photomultiplier tube operated in the photon-counting mode with a Suprasil window. This arrangement avoided interference from strong emission from S₂ and/or S₃ in the near UV. Signals following up to 1000 photolysis pulses were accumulated in a multichannel scaler.

We may write

$$d[S]/dt = -(k_1[S][\text{NO}] + k'[S]) = -k_{\text{psl}}[S], \quad (5)$$

where k' accounts mainly for consumption of S by reaction with the precursor. Because the concentration of S is much smaller than that of NO and precursor, pseudo-first-order kinetics are expected. k_{psl} is determined from the nonlinear least-squares fitting of the fluorescence signals to exponential decays. An example is shown in the inset of Fig. 1. A linear plot of k_{psl} versus [NO] at a constant precursor concentration, such as in Fig. 1, has a slope equal to the effective second-order rate constant k_1 . Experiments were carried out to determine the dependence of k_1 on temperature T and [Ar], and to investigate the influence of experimental param-

FIG. 1. Plot of pseudo-first-order rate constant for consumption of S(³P) by NO at 479 K in an Ar bath gas at a total pressure of 816 mbar. The inset shows the fluorescence decay corresponding to the open symbol.

eters such as the laser-pulse energy E_{laser} and the average gas residence time inside the heated cell before photolysis τ_{res} .

Table I summarizes 42 measurements made at five temperatures from 300 to 810 K. At each of these temperatures, we plot k_1 versus [Ar], as shown in Fig. 2, together with linear fits constrained to pass through the origin. Clearly, the kinetics are approximately third-order, with the greatest deviation at 300 K. The slopes of the linear fits yield third-order rate constants k_0 of 12.5, 8.7, 4.2, 2.6, and 2.2×10^{-32} cm⁶ molecule⁻² s⁻¹. A more sophisticated analysis, based on unimolecular rate theory, is presented in Sec. III. There is no major systematic deviation from the best-fit lines as a function of the experimental parameters [S]₀ and τ_{res} , which demonstrates that reaction (1) has been successfully isolated from secondary chemistry and that thermal decomposition of the NO/precursor mixtures was unimportant.

An extrapolation of the shock-tube data of Oya *et al.*, as quoted by Woiki and Roth,¹³ attributed to a direct abstraction down to our highest temperature, yields a rate constant below 10^{-18} cm³ molecule⁻¹ s⁻¹. The Woiki and Roth data extrapolate to an even lower value.¹³ Direct abstraction is therefore negligible in our experiments.

III. QUANTUM CHEMISTRY

Ab initio calculations were made with the GAUSSIAN 98 program suite.²⁷ We applied the complete basis set (CBS-QB3) method of Petersson and co-workers to determine energies.²⁸ This involves calculation of geometry and vibrational frequencies (scaled by 0.99) with Becke's three parameter Lee–Yang–Parr (B3LYP) hybrid density functional and the 6-311G(2d,d,p) atomic basis set. Care was taken to ensure that ground electronic states were located and optimized at this DFT level of theory. Then a sequence of higher-level calculations approximately yields the energy at the CCSD(T) coupled-cluster level of theory extrapolated to the infinite basis set limit. Data for the reactants, ²A'SNO, an alternative isomer ²A'NSO, a transition state connecting them, and a weakly bound isomer ²A'SON, are listed in Table II. The corresponding potential-energy diagram is shown in Fig. 3, and it indicates that NSO is computed to be

about 10 kJ mol^{-1} more stable than SNO. This is a different ordering from that obtained using DFT by Sun *et al.*,¹² but our coupled-cluster calculations should lead to more accurate relative energies than in the prior work. The SON isomer is of a questionable existence. It is predicted to be weakly bound by only about 18 kJ mol^{-1} . At the B3LYP/6-311G(2*d*,*d*,*p*) level of theory, a clear barrier to isomerization, TS1, was located, but with refined energies at the CBS-QB3 level, this barrier disappears. These two calculations are somewhat suspect, however, because of the high degree of spin contamination ($\langle S^2 \rangle$ above 1.6) for SON and TS1. There is a major barrier to isomerization of SNO to NSO. This most stable isomer has not been identified in matrix-isolation experiments, but we speculate that it might play roles in the reactions of NS with O or N atoms with SO.

Data for quartet states are presented for the first time in Table II. With the exception of the very long S–O bond in ^2SON , upon moving to the higher spin multiplicity, the bonds typically lengthen and vibrational frequencies decrease. The quartet manifold is moderately excited with respect to the doublet, with computed adiabatic excitation energies for SNO, NSO, and SON of 224, 222, and 117 kJ mol^{-1} , respectively. Nevertheless, all the quartet states are predicted to be endothermic with respect to $\text{S}(^3P_J) + \text{NO}(^2\Pi)$, and, accordingly, possible quartet contributions to the electronic degeneracy along the reaction coordinate were ignored for the kinetic analysis.

We focus on the most stable isomer of the lower-energy multiplicity, SNO. Based on CBS-QB3 energies, the computed ΔH_0 for reaction (1) is $-189.4 \text{ kJ mol}^{-1}$. An allow-

TABLE I. Summary of experimental measurements for $\text{S}(^3P) + \text{NO} + \text{Ar}$.

<i>T</i> (K)	<i>E</i> _{laser} (mJ)	<i>P</i> (mbar)	[CS ₂] (10 ¹² molecule cm ⁻³)	[NO] _{min} –[NO] _{max} (10 ¹³ molecule cm ⁻³)	[S] ₀ (10 ¹² molecule cm ⁻³)	Residence time <i>τ</i> _{res} (s)	<i>k</i> (10 ⁻¹³ molecule ⁻¹ cm ³ s ⁻¹)	<i>σ_k</i> (10 ⁻¹³ molecule ⁻¹ cm ³ s ⁻¹)
300	0.40	67	8.7	6.83–63.97	1.02	3.4	2.92	0.20
300	0.40	134	10.1	6.93–64.98	1.18	3.4	5.61	0.26
300	0.29	267	3.9	6.20–59.63	0.34	6.8	11.13	0.66
300	0.29	267	19.7	6.28–59.24	1.71	6.8	10.30	0.26
300	0.29	533	9.9	6.18–60.45	0.86	6.9	16.49	0.81
300	0.29	413	10.2	6.39–62.21	0.89	7.1	13.17	0.33
300	0.29	802	5.5	10.68–103.78	0.48	10.4	23.21	1.11
300	0.67	802	5.5	11.16–103.80	1.08	10.4	23.14	0.97
300	0.69	693	4.8	18.43–133.41	0.97	9.0	20.02	0.76
361	312	268	25.8 ^a	39.00–460.90	0.50	7.6	5.57	0.29
361	312	528	38.4 ^a	38.17–245.49	0.74	7.6	10.59	0.56
360	297	803	40.2 ^a	23.72–191.19	0.74	8.7	13.43	0.91
361	297	405	29.5 ^a	18.13–170.54	0.54	5.8	9.37	1.76
361	2.04	665	2.6	22.34–168.49	1.56	7.2	12.03	0.56
360	0.70	209	1.6	34.93–134.07	0.33	4.5	3.57	0.52
360	2.04	209	1.6	34.78–134.24	0.97	4.5	4.09	0.25
360	0.36	808	4.8	31.45–156.47	0.50	8.7	13.21	1.41
360	1.34	807	4.8	31.44–125.41	1.88	8.7	13.16	1.32
360	0.86	413	3.2	64.45–258.35	0.82	11.8	7.33	0.66
360	0.22	543	6.3	42.14–249.45	0.41	11.6	9.10	0.49
361	0.89	141	1.3	110.32–430.18	0.34	5.9	2.65	0.23
360	0.89	276	1.3	44.08–426.16	0.34	5.9	4.75	0.47
361	234	135	29.9 ^a	49.90–359	0.34	3.8	2.07	0.07
481	0.85	822	4.2	19.52–126.15	1.06	8.8	5.39	0.53
481	0.85	820	2.8	68.67–164.99	0.70	11.6	5.10	0.54
481	1.02	668	1.8	31.32–187.51	0.56	9.5	4.34	0.31
481	1.02	670	1.8	31.00–188.97	0.55	9.5	4.06	0.27
481	1.02	541	2.2	37.59–279.19	0.66	11.5	3.44	0.24
481	1.02	424	1.7	30.27–234.16	0.53	6.8	2.61	0.16
480	0.84	292	1.0	56.25–256.40	0.24	6.3	1.62	0.08
480	1.16	140	1.0	39.59–183.45	0.34	4.5	0.96	0.07
479	1.16	816	2.1	35.28–254.48	0.72	6.6	5.07	0.37
481	0.85	440	2.2	20.53–131.02	0.56	4.4	2.99	0.42
669	1.20	907	2.9	290–551	1.01	7.9	2.56	0.24
669	0.33	692	4.3	384–840	0.41	7.9	1.98	0.12
667	0.30	836	5.6	460.5–1227.4	0.49	5.6	2.29	0.10
667	0.30	622	9.6	531.8–2066.9	0.84	9.5	1.74	0.10
809	0.30	824	5.3	444.6–1162.5	0.47	5.2	1.68	0.07
809	0.28	705	3.3	451–908	0.28	5.4	1.35	0.32
809	0.28	389	3.0	331.7–1062.1	0.25	4.9	0.86	0.07
808	1.02	551	1.8	478.5–1346.9	0.54	4.2	1.05	0.10
811	1.02	421	1.7	455.7–1281.2	0.51	4.0	0.71	0.03

^aCOS employed instead of CS₂.

FIG. 2. Plots of effective second-order rate constant k_1 versus $[Ar]$ for the $S(^3P)+NO$ reaction. Panels (a) through (e) correspond to 300, 361, 481, 668, and 809 K. The linear fits are constrained to pass through the origin.

ance for the experimental spin-orbit coupling corrections to the 0-K energies of the reactants (a $+3.4 \text{ kJ mol}^{-1}$ contribution to ΔH_0) and for thermal corrections yields $\Delta H_{298} = -191.1 \text{ kJ mol}^{-1}$. Together with data for S and NO,²⁹ this implies $\Delta_f H_{298}$ for SNO is $176.1 \text{ kJ mol}^{-1}$. The average at-

omization enthalpy error for the CBS-QB3 method is slightly less than 4 kJ mol^{-1} ,²⁸ so we provisionally suggest error limits in this thermochemistry of $\pm 8 \text{ kJ mol}^{-1}$.

In summary, the *ab initio* calculations indicate that the most stable adduct is $^2A'SNO$, with a dissociation energy to

TABLE II. AB INITIO information for the $S(^3P)+NO$ potential energy surface.

Species	$E(\text{CBS-QB3})/\text{a.u.}$	$\langle S^2 \rangle$	Frequencies scaled by 0.99 cm^{-1}	Geometry ^a	Relative enthalpy at 0 K/ kJ mol^{-1b}
$S(^3P)$	-397.657360	2.003			0
$NO(^2\Pi)$	-129.748464	0.753	1969	N-O=1.148	
$SNO(^2A')$	-527.477922	0.768	503, 791, 1647	N-O=1.187, S-N=1.593, SNO=139.6	-189
$NSO(^2A')$	-527.480781	0.765	308, 999, 1176	S-N=1.512, S-O=1.466, NSO=124.7	-197
$SON(^2A')$	-527.412742	1.643	109, 191, 1924	S-O=2.725, O-N=1.136, SON=123.8	-18
TS1 for SON =SNO($^2A'$)	-527.414388	1.643	224i, 87, 1915	N-O=1.393, S-O=2.996, SON=91.2	-23
TS2 for SNO =NSO($^2A'$)	-527.357397	1.227	400i, 126, 1264	S-N=1.481, N-O=2.125, SNO=78.7	+127
$SNO(^4A'')$	-527.392468	3.759	360, 571, 1358	N-O=1.241, S-N=1.717, SNO=119.0	+35
$NSO(^4A')$	-527.396316	3.763	263, 569, 943	S-N=1.775, S-O=1.524, NSO=100.0	+25
$SON(^4A')$	-527.368019	3.761	287, 545, 994	S-O=1.728, O-N=1.225, SON=112.0	+99

^aBond lengths in angstroms and angles in degrees.

^bUncorrected for spin-orbit splitting (see text).

FIG. 3. Potential energy diagram for $S(^3P) + NO$ interaction, showing relative enthalpies at 0 K derived from the CBS-QB3 calculations.

$S + NO$ at 0 K of $E_0 = 186.0 \text{ kJ mol}^{-1}$, and that contributions by the quartet manifold may be neglected. The derived molecular parameters are employed in the kinetic calculations of the next section.

IV. THEORETICAL ANALYSIS OF RATE DATA

Because of the possibility that falloff effects might influence the experimental measurements, we adopted the procedure of (i) derivation of the high-pressure limit k_∞ , (ii) use of preliminary energy-transfer parameters to assess the role of falloff and to correct the experimental data to obtain k_0 (by 14% at room temperature), and (iii) use of k_0 to refine the energy-transfer estimate. Steps (ii) and (iii) were iterated for self-consistency.

The high-pressure limiting rate constant k_∞ was estimated via two approaches. Maergoiz *et al.*³⁰ provide a SACM classical trajectory (CT) treatment on a model valence potential. k_∞ is then given by the expression from phase-space theory and the rigidity factor that accounts for anisotropy in the PES, $f_{\text{rigid}} \approx 0.5$. This calculation leads to

$$k_\infty = 2.2 \times 10^{-10} (T/300)^{0.24} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}. \quad (6)$$

A similar result, smaller by a factor of about 0.6, was obtained via variational microcanonical flexible transition state theory as implemented within the VARIFLEX program of Klippenstein *et al.*³¹ For both approaches, the reaction coordinate for S addition to NO to make SNO was approximated as a

Morse potential ($D = 16035 \text{ cm}^{-1}$, $\beta = 2.347 \text{ \AA}^{-1}$, and $r_e = 1.593 \text{ \AA}$). The electronic degeneracy was assumed to be 2, and α/β was set to the standard value of 0.5.³⁰

At the low-pressure limit, collisional stabilization (4) is rate-limiting. We derive k_0 via Troe's formulation as

$$k_0 = \beta_c Z_{\text{LJ}} F_E F_{\text{anh}} F_{\text{rot}} \frac{\rho_{\text{vib}}(E_0) RT}{Q_{\text{vib}}(\text{SNO})} \frac{Q(\text{SNO})}{Q(\text{S})Q(\text{NO})} \quad (7)$$

and follow the standard notation and procedures given in Ref. 17. The collision rate Z_{LJ} between Ar and SNO is characterized in terms of a Lennard-Jones (LJ) potential. We used $\sigma = 3.47 \text{ \AA}$ and $\epsilon/k = 114 \text{ K}$ for Ar³² and assumed that the values for SNO are similar to those for SO_2 , $\sigma = 4.11 \text{ \AA}$ and $\epsilon/k = 336 \text{ K}$.³³ The data listed in Table II were used to compute partition functions Q and the density of states ρ with a vibrational anharmonicity correction of $F_{\text{anh}} = 1.78$. F_E accounts for the energy dependence of the density of states and is close to 1 (see Table III). The rotational correction F_{rot} was estimated on the assumption of a van der Waals potential and decreased from 67 to 22 as the temperature increased from 300 to 810 K. The decrease in F_{rot} reflects a tightening of the TS as centrifugal barriers move to shorter S–N separations at higher temperatures. Uncertainty in F_{rot} , which depends on the details of the PES for long-range interaction between S and NO, is the greatest source of uncertainty in Eq. (7). Initially, the collision efficiency β_c was set equal to unity to obtain strong-collision rate constants via Eq. (7). These strong-collision rate constants of course overestimate the rate of collisional stabilization of the excited adduct, and comparison with experimental k_0 values indicates that β_c is about 0.5 at room temperature and halves as the temperature is raised. For the more realistic weak-collision model,¹⁷ β_c was derived via the relation

$$\frac{\beta_c}{1 - \sqrt{\beta_c}} = \frac{-\langle \Delta E \rangle}{F_E k T}. \quad (8)$$

Comparison with k_0 measurements (corrected for falloff, see below) is shown on Fig. 4. The best fit is obtained with a temperature-independent value of $\langle \Delta E \rangle = -360 \text{ cm}^{-1}$. Also shown are lines corresponding to $\langle \Delta E \rangle = -520$ and -270 cm^{-1} , respectively, which encompass a $\pm 15\%$ variation in k_0 . Clearly, k_0 here is not very sensitive to the particular value of $\langle \Delta E \rangle$ employed; the range is typical for other reactions with Ar bath gas.¹⁷

We tested SON as a possible final product of reaction (1). We found that the computed k_0 for this reaction could

TABLE III. RRKM parameters for $S + NO + \text{Ar}^a$.

T/K	F_{rot}	S_K	B_K	F_E	β_c	F_{center}	$(k_0 \pm \sigma)/10^{-32} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$
300	67.0	1.50	20.4	1.025	0.50	0.75	14.3 ± 0.7
361	55.2	1.50	17.1	1.030	0.45	0.75	8.9 ± 0.3
481	40.3	1.52	13.1	1.040	0.39	0.73	4.2 ± 0.1
668	27.4	1.56	10.3	1.056	0.32	0.72	2.6 ± 0.1
809	21.7	1.61	9.2	1.068	0.28	0.70	2.1 ± 0.1

^aSee Refs. 17 and 34 for standard notation and details of the calculations. $\langle \Delta E \rangle = -360 \text{ cm}^{-1}$ (see text for the other parameters).

FIG. 4. Plot of low-pressure limiting rate constants for $S(^3P)+NO+Ar$. Symbols: results from Troe fitting to experiment, with 1σ error limits. The solid line is an empirical Arrhenius fit. The dashed line is the result from the statistical adiabatic channel model with $\langle\Delta E\rangle = -360\text{ cm}^{-1}$. The dotted lines correspond to $\langle\Delta E\rangle = -520$ (upper) and -270 cm^{-1} (lower) with k_0 15% above and below the dashed line.

not be reconciled with the measurements, and also note that SON is insufficiently stable to be a sink for S at high temperatures. Even if SON were formed, the *ab initio* results suggest it would easily isomerize to SNO.

At intermediate pressures, the effective second-order rate constant k_1 for the scheme of processes (2)–(4) is controlled by the balance of collisional stabilization of the excited intermediate SNO* and dissociation of this intermediate back to reactants. Rice–Ramsperger–Kassel–Marcus (RRKM) theory provides a framework for analysis of this falloff region, and we employed Troe’s representation of falloff curves¹⁷

$$k_1 = \left(\frac{k_0[M]}{1 + k_0[M]/k_\infty} \right) \times F_{\text{cent}}^{\{1 + [\log_{10}(k_0[M]/k_\infty)/0.75 - 1.27 \log_{10} F_{\text{cent}}]^2\}^{-1}} \quad (9)$$

The broadening parameter F_{cent} was obtained as outlined by Troe³⁴ from $\langle\Delta E\rangle$ and properties of the TS. For this purpose, we assumed the TS was loose so that one of the three frequencies is the stretch of NO, another is the reaction coordinate, and the third (bending) motion can be represented as a rotation.³⁵ Intermediate results and F_{cent} are given in Table III. k_0 was derived via nonlinear least-squares fits of Eq. (9) to experimental k_1 values at each temperature. These fits are shown in Fig. 5, and Table III lists the statistical uncertainty of the fitted k_0 values. The variation of k_0 with temperature is shown in Fig. 4, and may be summarized as

$$k_0 = (6.2 \pm 0.6) \times 10^{-33} \exp(+ (940 \pm 40)/T) \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}, \quad (10)$$

along with

$$F_{\text{cent}} = 0.78 \exp(-T/7445). \quad (11)$$

FIG. 5. Troe fit of the second-order rate constants for $S(^3P)+NO+Ar$ (see text). Lines: falloff fits, symbols: measurements. From top to bottom, the temperatures are 300, 361, 481, 668, and 809 K.

In conjunction with the expression for k_∞ given above, Eq. (6), the effective second-order k_1 can be estimated for a wide range of T and $[Ar]$. Proposed error limits for k_1 derived over 300–810 K from Eqs. (6) and (9)–(11) are twice the rms of the scatter of Fig. 5, that is, $\pm 25\%$.

The only comparable prior data for addition are those obtained by van Roodselaar *et al.* at 298 K with a CO_2 bath gas.⁹ Their third-order rate constant is $5.2 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$, which is 3.6 times larger than our k_0 at 300 K. Presumably, polyatomic CO_2 is a more efficient collisional partner M than Ar. This will permit the falloff effects to occur at lower pressures than for $M=Ar$, and van Roodselaar *et al.* saw significant deviation from third-order behavior at $[CO_2] > 6 \times 10^{18} \text{ cm}^{-3}$.⁹ They employed a Lindemann–Hinshelwood analysis, i.e., Eq. (9) with $F_{\text{cent}}=1$, to derive $k_\infty = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This is an order of magnitude smaller than our estimate, but the neglect of broadening, in fact, makes their value a lower bound.

V. CONCLUSIONS

Experimental determinations of the rate constant for $S+NO$ recombination lie close to the low-pressure limit, in accord with expectations from unimolecular rate theory. The high-pressure limit was assessed via SACM/CT calculations on a standard valence potential which are expressed by phase-space theory with a rigidity factor of 0.5, and microcanonical variational flexible TST, and falloff curves were generated by fitting to experiment. The results can be rationalized in terms of formation of $^2A'$ SNO, whose stability is estimated via *ab initio* calculations. *Ab initio* calculations indicate that NSO is a somewhat more stable isomer than SNO, and that the SON conformation is weakly bound. Kinetic control likely makes SNO the dominant product.

ACKNOWLEDGMENTS

The authors thank Amy Y. Chung, Stephani Eveslage, and Rebecca Lucente for assistance with preliminary experi-

ments. This work was supported by the National Science Foundation (Grant No. CTS-0113606), the Robert A. Welch Foundation (Grant No. B-1174), and the UNT Faculty Research Fund.

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