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A Kinetic Study of the Recombination Reaction $\text{Na} + \text{SO}_2 + \text{Ar}$

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The recombination of atomic sodium, $\text{Na}(3^2\text{S})$, with SO_2 has been investigated at 787 K, in a bath of Ar at pressures from 1.7 to 80 kPa. Na was generated by pulsed excimer laser photolysis of NaI vapor at 308 nm and monitored by time-resolved resonance absorption of the D lines at 589 nm under pseudo-first-order conditions. The measured pseudo bimolecular rate constants lie in the third-order and falloff regions and were fitted well by using either a Lindemann mechanism or an empirical RRKM expression. The parameters are discussed in the text. The low-pressure limit is about $(2.4\text{--}2.7) \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$. By use of RRKM theory, combined with a lower limit based on the absence of any observed equilibration, the Na- SO_2 bond energy is estimated as $190 \pm 15 \text{ kJ mol}^{-1}$. Extrapolation to the high-pressure limit yields $k_\infty \approx (1\text{--}3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, in accord with a harpoon model for electron transfer to form an ionic adduct.

1. Introduction

There have been several recent investigations of recombination reactions of sodium atoms, for example with O_2 ¹⁻⁴ and OH .⁵ In all these studies the measurements have been made in the low-pressure third-order regime, and it has been assumed that the high-pressure limit is gas kinetic.^{3,4} The purpose of the study presented here is to check this assumption experimentally.

The reaction

is selected because molecular beam experiments demonstrated that alkali metals form long-lived collision complexes with SO_2 ,⁶ and the NaSO_2 adduct is known as an ion-pair species from matrix isolation studies.⁷ This adduct has also been the subject of an *ab initio* investigation⁸ and is a dominant product in lean flames containing sodium and sulfur.⁹ The greater number of vibrational degrees of freedom in this adduct, as compared to e.g. NaO_2 , is expected to lower the falloff pressure region to an experimentally accessible range. Here we present measurements on reaction 1 in the third-order and falloff regions and extrapolate the data to the high-pressure limit.

A second area of interest with this class of reaction is the bond energy of the adduct formed. We quantify this in two ways, by fitting the third-order rate constant to an RRKM expression and by setting a lower limit from the absence of observed equilibration.

2. Experimental Technique

The concentration of atomic sodium, $\text{Na}(3^2\text{S})$, is monitored by time-resolved atomic resonance absorption spectroscopy following its generation by pulsed UV photolysis of sodium iodide

vapor in the presence of a large excess of SO_2 . The main components of a new experimental system are now described.

High-Temperature Reactor. The reactor is based on a six-way stainless steel cross, and a schematic diagram of the apparatus is shown in Figure 1 (two unused side arms are not shown). The intersection of the three cylinders forms a roughly cubic region, about 2 cm on a side. Each side arm is 11 cm long with a 2.2-cm i.d. The inner 7 cm of each side arm is wrapped in nichrome resistance heating wire, electrically insulated with ceramic beads. The reactor is housed in a thermally insulating box, 20 cm on a side, made of 2.5-cm-thick alumina boards (Zircar Products ZAL-50). The terminal 1.5 cm of each side arm outside the insulation is water-cooled, and connections to the end of each side arm are by standard ISO NW25 KF fittings. The intersection region of the side arms defines the reaction zone, where transient species are generated and detected. A combustion boat containing solid NaI is placed in a heated side arm of the reactor. NaI vapor is entrained by the gas flow and swept through the reaction zone.

An Omega CN 3910 KC/S temperature controller monitors the reactor temperature with a sheathed type K (chromel/alumel) thermocouple inside the insulating box and operates a solid-state relay to control the current through the heating wire (maximum power 650 W at 115 V). This arrangement provides a temperature stability of about $\pm 1 \text{ K}$, from room temperature up to about 900 K. A second sheathed type K thermocouple can be slid to the center of the reaction zone to monitor the gas temperature, which is displayed on an Omega DP 285 readout. A separate moveable radiation shield was employed in preliminary experiments, to test for possible radiation errors in the thermocouple measurements. We found that, for the conditions used in this work, such errors are less than 2 K and are therefore neglected.

Optical System. A Questek 2110 XeCl excimer laser provides pulses of radiation (308 nm, fwhm duration 15 ns) for photolysis of the NaI vapor. The UV beam is diverged slightly with a concave mirror before entering the reactor through a Vycor window. The maximum intensity incident on the window is about 10 mJ cm^{-2} . The actinic intensity, and thus the initial Na concentration $[\text{Na}]_0$, is varied by changing the excimer gas fill and by placing neutral density filters in the UV beam. $[\text{Na}]$ in the reaction zone is monitored by resonance absorption of the CW radiation from a hollow cathode lamp (the unresolved doublet at 589.0 and 589.6 nm, $\text{Na}(3^2\text{S}) \rightarrow \text{Na}(3^2\text{P}_{3/2,1/2})$), approximately focused into a parallel beam perpendicular to the photolysis ra-

(1) Marshall, P.; Narayan, A. S.; Fontijn, A. *J. Phys. Chem.* **1990**, *94*, 2998.

(2) Husain, D.; Marshall, P.; Plane, J. M. C. *J. Chem. Soc., Faraday Trans. 2* **1985**, *81*, 301.

(3) Silver, J. A.; Zahniser, M. S.; Stanton, A. C.; Kolb, C. E. In *Proceedings of the 20th Symposium (International) on Combustion*; The Combustion Institute: Pittsburgh, 1984; p 605.

(4) Plane, J. M. C.; Rajasekhar, B. *J. Phys. Chem.* **1989**, *93*, 3135.

(5) Husain, D.; Plane, J. M. C.; Xiang, C. C. *J. Chem. Soc., Faraday Trans. 2* **1984**, *80*, 1619.

(6) Ham, D. O.; Kinsey, J. L. *J. Chem. Phys.* **1968**, *48*, 939.

(7) Milligan, D. E.; Jacox, M. E. *J. Chem. Phys.* **1971**, *55*, 1003.

(8) Ramondo, F.; Bencivenni, L. *Mol. Phys.* **1989**, *67*, 707.

(9) Steinberg, M.; Schofield, K. *Prog. Energy Combust. Sci.* **1990**, *16*, 311.

Figure 1. Schematic diagram of the high-temperature reactor.

diation. At the exit of the reactor the resonance radiation is spectrally isolated, first with an interference filter (Oriel, centered at 590 nm, fwhm 10 nm) and then by focusing onto the entrance slit of an Oriel 77250 monochromator employed at a resolution of 2 nm.

Electronics. The intensity of the resonance light transmitted through the reaction zone, I , is measured with a Hamamatsu IP28 photomultiplier tube, operated at 700–900 V (Thorn EMI PM28RA supply). The output is amplified (Thorn EMI C632-A1) and captured in a computer-controlled digital oscilloscope (Rapid Systems R402). The maximum signal sampling rate is 0.5 MHz, and 2048 time channels are used. Data collection is initiated by a trigger pulse from a digital delay/pulse generator (Stanford Research Systems DG535) which controls the timing in each experiment. The digital oscilloscope is triggered before the excimer laser to permit measurement of the steady transmitted light intensity in the absence of Na, I_0 , as well as the variation of I with time after the laser pulse. This sequence is repeated up to 100 times, at 1 Hz, and the signals are averaged to suppress random noise. The data are then transferred to an IBM XT-compatible computer for storage and analysis.

Gas Handling. Experiments were performed with a large excess of argon bath gas, to ensure thermalization of photolytically generated Na and to increase the heat capacity of the gas mixture so that the temperature remains constant during reaction. Gas mixtures flow slowly through the reactor so that a fresh sample reaches the reaction zone before each photolysis pulse (repetition rate 1 Hz), to avoid the accumulation of reaction products. The average residence time of the gas before photolysis is τ_{res} . The time taken to sweep gas out of the reaction zone is long compared to the reaction time scale (typically 1 ms), which makes the reactor kinetically equivalent to a static system.

Ar (Linde 99.997%) is used directly from the cylinder. SO_2 (J.T. Baker, 99.96%) is purified by three freeze–pump–thaw cycles at 77 K. Mixtures are prepared on a Pyrex vacuum line by adding about 100 kPa of Ar to 0.01–0.6 kPa of SO_2 in a bulb and then stored for several hours to allow for thorough mixing before use. Pressures are measured with a capacitance manometer system (MKS Instruments Type 226A) and gas flows set with mass-flow controllers (MKS Instruments Types 1159A and 1159B). The mass-flow controllers are calibrated against a Teledyne-Hastings HBM-1A bubble meter. Typical flow rates used are from 100 to 1000 sccm of Ar plus 0–50 sccm of mixtures of SO_2 in Ar. These flows are combined and then transferred to the reactor through a stainless steel tube. We find that $[\text{SO}_2]$ in the reactor takes 30–60 min to stabilize at the start of an experiment, which we attribute to adsorption onto the walls of the reactor and the connecting line, similar to that noted by Plane and Saltzman in the case of HCl .¹⁰

Figure 2. Plot of the pseudo-first-order decay coefficient for Na as a function of $[\text{SO}_2]$ in Ar bath gas. $T = 787$ K and $P = 6.0$ kPa.

Data Analysis. The method of analyzing the data for I as a function of time has been described before.^{1,2} $[\text{Na}]_0 \ll [\text{SO}_2]$ (see below) which ensures pseudo-first-order kinetics for the decay of $[\text{Na}]$. Thus

$$[\text{Na}] = [\text{Na}]_0 \exp(-k_{\text{psl}}t) \quad (2)$$

where t is the time after the photolysis pulse and k_{psl} is the pseudo-first-order decay coefficient. Equation 2 is combined with the Beer–Lambert Law to yield an expression for the time-resolved transmitted light intensity

$$I = I_0 \exp[-\epsilon l [\text{Na}]_0 \exp(-k_{\text{psl}}t)] \quad (3)$$

where ϵ is the absorption coefficient of Na and l is the absorption path length. We estimate $l = 1.9$ cm here and use $\epsilon = 1.25 \times 10^{-12}$ cm² molecule⁻¹. I_0 is measured as described above, and then k_{psl} and the quantity $A = \epsilon l [\text{Na}]_0$ are obtained from about 2000 $I(t)$ points by nonlinear least-squares fitting.^{2,11} The validity of the Beer–Lambert law for the unresolved Na D-line doublet has been demonstrated for $I > 0.6I_0$.¹² For some decays the initial absorption was larger than this, and in these cases analysis was begun once I had increased to $0.6I_0$. $[\text{Na}]_0$ was obtained by extrapolation back to zero time. The absolute value of $[\text{Na}]_0$ is unnecessary for a first-order analysis but can be derived from A . Preliminary experiments suggested that a reasonable estimate of the uncertainty in the derived k_{psl} is $\sigma_{k_{\text{psl}}}/k_{\text{psl}} \approx 5\%$.

k_{psl} is given by

$$k_{\text{psl}} = k_{\text{ps2}}[\text{SO}_2] + k_{\text{diff}} \quad (4)$$

k_{ps2} is the pseudo-second-order rate constant for reaction 1, and k_{diff} accounts for the loss of Na by processes other than reaction 1, primarily diffusion out of the reaction zone. k_{psl} is measured for typically six values of $[\text{SO}_2]$, from 0 to $[\text{SO}_2]_{\text{max}}$. k_{ps2} , together with its uncertainty $\sigma_{k_{\text{ps2}}}$, is derived from the slope of a plot of k_{psl} versus $[\text{SO}_2]$ (see Figure 2), using the algorithm of Irvin and Quickenden.¹³ This algorithm incorporates both $\sigma_{k_{\text{psl}}}$ and $\sigma_{[\text{SO}_2]}$. The dominant contributions to $\sigma_{[\text{SO}_2]}$ are the uncertainties in the gas flows. These are estimated from the scatter in the calibration plots prepared for the flow controllers and are combined to yield a total $\sigma_{k_{\text{ps2}}}$. As in earlier work, the estimated uncertainty of the temperature T is $\sigma_T/T = 2\%$.¹⁴

3. Results and Discussion

Twenty-two measurements of k_{ps2} were made at $T = 787 \pm 16$ K and are summarized in Table I. The total pressure P was varied from 1.7 to 80 kPa, corresponding to a variation of the total density $[M]$ (effectively $[\text{Ar}]$) by a factor of about 50. $[\text{Na}]_0$ was

(10) Plane, J. M. C.; Saltzman, E. S. *J. Chem. Phys.* **1987**, *87*, 4606.

(11) Marshall, P. Ph.D. Thesis, University of Cambridge, 1985.

(12) Husain, D.; Plane, J. M. C. *J. Chem. Soc., Faraday Trans. 2* **1982**, *78*, 163.

(13) Irvin, J. A.; Quickenden, T. I. *J. Chem. Educ.* **1983**, *60*, 711.

(14) Marshall, P.; Fontijn, A. *J. Chem. Phys.* **1986**, *85*, 2637.

TABLE I: Summary of Rate Constant Measurements for Na + SO₂ + Ar

<i>P</i> , kPa	[M] ≈ [Ar], 10 ¹⁷ cm ⁻³	<i>τ</i> _{res} , s	[Na] ₀ , 10 ¹¹ cm ⁻³	[SO ₂] _{max} , 10 ¹³ cm ⁻³	<i>k</i> _{ps2} ± σ _{kps2} , 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹
1.67	1.53	0.5	2.2	14	3.32 ± 0.10
2.33	2.15	0.3	1.4	13	4.24 ± 0.17
2.36	2.17	0.6	1.7	25	5.31 ± 0.22
3.60	3.31	2.0	2.2	22	7.85 ± 0.40
6.00	5.52	1.6	1.9	17	12.2 ± 0.7
9.84	9.05	0.7	1.5	8.8	20.5 ± 0.5
9.84	9.05	0.7	3.0	8.8	18.8 ± 0.7
12.3	11.3	1.7	2.2	4.8	20.3 ± 0.8
20.0	18.4	1.8	1.6	20	33.3 ± 1.4
25.7	23.7	1.8	1.9	10	37.3 ± 1.2
25.9	23.8	1.8	1.7	6.3	32.9 ± 0.5
25.9	23.8	7.0	3.8	15	30.5 ± 1.3
32.7	30.1	1.8	1.5	7.5	47.5 ± 1.8
33.3	30.7	0.9	1.9	3.7	54.6 ± 2.6
33.9	31.2	0.9	1.0	3.9	61.4 ± 2.6
40.0	36.8	1.8	1.6	6.5	51.8 ± 3.5
46.7	42.9	1.6	1.0	1.4	39.4 ± 2.4
46.7	42.9	1.6	1.7	3.0	53.0 ± 3.8
47.3	43.6	6.4	1.8	7.2	48.2 ± 2.1
53.6	49.3	1.8	1.1	6.6	63.0 ± 5.8
66.7	61.3	2.3	1.6	2.9	69.5 ± 6.0
80.0	73.6	2.2	1.1	2.7	84.1 ± 8.5

Figure 3. Plot of pseudo-second-order rate constant for Na + SO₂ against [Ar]. The straight line corresponds to a linear least-squares fit to the first eight points.

varied from 1.0×10^{11} to 3.8×10^{11} cm⁻³, which was always much less than [SO₂] to ensure pseudo-first-order conditions. There was no significant influence of [Na]₀ on the *k*_{ps2} values which demonstrates that neither photolysis nor reaction products affected the observed kinetics. Reaction 1 was therefore isolated from any interfering processes. NaBr was also tried as a photolytic precursor for Na but, despite a literature value for its absorption cross section at 308 nm similar to NaI,¹⁵ no Na was detected even at higher temperatures. There was no consistent variation of *k*_{ps2} with *τ*_{res}, which was varied by a factor of about 10, an observation which shows that thermal decomposition of the SO₂ was insignificant. For a given actinic intensity [Na]₀ increased with *τ*_{res} which indicates that the heated gas did not reach equilibrium with the solid NaI. The vapor pressure of NaI at 787 K corresponds to 1.2×10^{12} cm⁻³,¹⁶ which is therefore an upper limit to the [NaI] actually employed.

Preliminary experiments showed that even at very large [Na]₀, not used for kinetic measurements, about 30% of the resonance light was transmitted. Presumably it passed around the photolysis region in the reactor. A correction was therefore subtracted from *I* and *I*₀ before analysis, the effect of which was to increase *k*_{ps1} slightly (by less than 5%).

Figure 4. Lindemann plot of reciprocal pseudo-second-order rate constant for Na + SO₂ against reciprocal [Ar].

Figure 3 is a plot of *k*_{ps2} versus [M]. At [M] < 10¹⁸ cm⁻³ third-order behavior is observed, where *k*_{ps2} ∝ [M]. Figure 3 also shows the best weighted linear fit to the first eight points. The intercept is $(1.7 \pm 3.4) \times 10^{-13}$ cm³ molecule⁻¹ s⁻¹ (statistical uncertainties in fitted parameters are quoted as ±1σ), which is therefore insignificantly different from zero. The lack of any significant true bimolecular reaction between Na and SO₂ is consistent with the thermochemistry: the channel Na + SO₂ → NaO + SO is endothermic by 276 ± 42 kJ mol⁻¹ at 0 K.¹⁷ At [M] > 10¹⁸ cm⁻³ a linear extrapolation of the low-pressure data lies above the measured *k*_{ps2} values, which shows that these measurements are in the falloff region.

These observations can be interpreted in terms of a simple Lindemann mechanism.¹⁸ An initial excited adduct is formed, which can either decompose back to reactants or be stabilized by collision with the bath gas:

In the low-pressure limit, process 6 is rate-limiting and third-order kinetics are predicted (*k*₀ is the third-order rate constant):

$$k_{ps2,0} = k_0[M] = k_5 k_6[M]/k_{-5} \quad (7)$$

At the high-pressure limit, second-order kinetics are expected:

$$k_{ps2,\infty} = k_{\infty} = k_5 \quad (8)$$

The observed pseudo bimolecular rate constant for Na consumption according to this mechanism is

$$k_{ps2}(\text{Lindemann}) = k_0[M]/\{1 + k_0[M]/k_{\infty}\} \quad (9)$$

Equation 9 is fitted to our data by plotting 1/*k*_{ps2} versus 1/[M], and the results are shown in Figure 4. There is a good fit to our observations, with *k*₀ = $(2.4 \pm 0.2) \times 10^{-29}$ cm⁶ molecule⁻² s⁻¹ and *k*_∞ = $(1.2 \pm 0.2) \times 10^{-10}$ cm³ molecule⁻¹ s⁻¹.

The Lindemann mechanism is known to predict too sharp a falloff of *k*_{ps2} with [M],¹⁸ and a more realistic empirical expression for *k*_{ps2} used in the NASA rate constant compilations¹⁹ is also tested here:

$$k_{ps2}(\text{NASA}) = k_{ps2}(\text{Lindemann}) \times 0.6^{[1 + (\log k_0[M]/k_{\infty})^2]^{-1}} \quad (10)$$

This expression is based on an RRKM analysis where the energy

(17) Chase, M. W., Jr.; Davies, C. A.; Downey, J. R., Jr.; Frurip, D. J.; McDonald, R. A.; Syverud, A. N. *JANAF Thermochemical Tables*, 3rd ed.; *J. Phys. Chem. Ref. Data* **1985**, *14* (Suppl. No. 1).

(18) Robinson, P. J.; Holbrook, K. A. *Unimolecular Reactions*; Wiley-Interscience: London, 1972; Chapter 1.

(19) DeMore, W. B.; Molina, M. J.; Sander, S. P.; Golden, D. M.; Hampson, R. F.; Kurylo, R. F.; Howard, C. J.; Ravishankara, A. R. *Chemical Kinetics and Photochemical Data for Use in Stratospheric Modeling*. Evaluation Number 8; JPL Publication 87-41; Jet Propulsion Laboratory: Pasadena, 1987.

(15) Davidovits, P.; Brodhead, D. C. *J. Chem. Phys.* **1967**, *46*, 2968.

(16) Cogin, G. E.; Kimball, G. E. *J. Chem. Phys.* **1948**, *16*, 1035.

Figure 5. Extrapolation of measured k_{ps2} for $\text{Na} + \text{SO}_2$ (solid circles) to higher densities, showing low- and high-pressure limits from the NASA RRKM expression (see text). The solid curve corresponds to the NASA fit. The dashed curve corresponds to a Lindemann fit.

dependence of step 6 is taken into account. A nonlinear least-squares fit of our data to the form of eq 10 yields $k_0 = (2.7 \pm 0.2) \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ and $k_{\infty} = (2.8 \pm 0.5) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This fit is shown in Figure 5, where it is extrapolated to high $[\text{M}]$. Both the Lindemann and NASA parameterizations describe our observations equally closely, with root-mean-square deviations of 14% from the experimental data. Allowing for potential systematic errors, we estimate 2σ confidence limits of $\pm 20\%$ for these fits. The latter pair of parameters are expected to be somewhat more meaningful and are therefore selected for further analysis.

The only previous investigation of the kinetics of reaction 1 was by Bawn and Evans in the 1930s using the diffusion flame technique.²⁰ The average of their two estimates of k_{ps2} at 511 K and 0.5 kPa of N_2 is $2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which is an order of magnitude larger than a pressure extrapolation of the present work. However, the kinetics were too fast to measure quantitatively with their apparatus,²⁰ and k_{ps2} for reaction 1 probably decreases with increasing temperature.¹⁻⁵

Low-Pressure Limit and Na-SO₂ Bond Energy. Other recombination reactions of atomic Na^{1-5} have been analyzed in terms of Troe's RRKM formalism.^{21,22} Here we couple his expression with the equilibrium constant to derive an expression for the low-pressure third-order recombination rate constant

$$k_0 = \beta_c Z_{LJ} \{ \rho(E_0) RT / Q_{\text{vib}}(\text{NaSO}_2) \} \times F_E F_{\text{anh}} F_{\text{rot}} Q(\text{NaSO}_2) / [Q(\text{Na}) Q(\text{SO}_2)] \quad (11)$$

where $\rho(E_0)$ is the vibrational density of states of NaSO_2 at the threshold energy E_0 for NaSO_2 dissociation to $\text{Na} + \text{SO}_2$. Q is the partition function. F_E , F_{anh} , and F_{rot} are factors to account for the energy dependence of $\rho(E_0)$, for the effects of vibrational anharmonicity, and for centrifugal barriers. We estimate these quantities as 1.20, 1.37, and 7.6, respectively. We take the structure and vibrational frequencies of NaSO_2 from the ab initio study by Ramondo and Bencivenni.⁸ $\beta_c Z_{LJ}$ is the weak-collision stabilization rate constant, which we set at the reasonable value of $2.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Selection of $E_0 = 170 \text{ kJ mol}^{-1}$

gives agreement with the measured k_0 . We assume an uncertainty of a factor of 2 in the non- E_0 -dependent terms of eq 11, which leads to an estimated uncertainty of $\pm 35 \text{ kJ mol}^{-1}$ in E_0 . These limits are large because E_0 is weakly dependent on k_0 and varies as approximately $k_0^{0.2}$.

There is another way to use our data to quantify E_0 , similar to that employed to investigate the Na-O_2 bond energy.¹ No evidence for the reverse reaction (-1) was seen; i.e., all the Na was apparently consumed in the experiments, and at equilibrium $[\text{Na}] \approx 0$. On the assumption that at least 50% of the Na was removed by reaction with SO_2 at the lowest nonzero concentrations employed, $6 \times 10^{12} \text{ cm}^{-3}$, we set a lower limit to K_c of about $1.7 \times 10^{-13} \text{ cm}^3$. If one uses statistical mechanics to calculate K_c , this result implies $E_0 > 172 \text{ kJ mol}^{-1}$.

Ramondo and Bencivenni provide an ab initio estimate for the dissociation energy of NaSO_2 to ions of $D_e = 643 \text{ kJ mol}^{-1}$.⁸ We use their scaled ab initio frequencies for NaSO_2 and SO_2^- to adjust D_e for zero-point vibrational energies and employ experimental values for the ionization potential of Na, $495.8 \text{ kJ mol}^{-1}$,¹⁷ and the electron affinity of SO_2 , $106.8 \pm 0.8 \text{ kJ mol}^{-1}$,²³ to derive $E_0 = 250 \text{ kJ mol}^{-1}$.

Combination of the two experimental estimates suggests that $E_0 \approx 190 \pm 15 \text{ kJ mol}^{-1}$. The magnitude of the difference from the ab initio value is similar to that noted in the analysis of the Na-O_2 bond, but with a different sign.¹ That bond is slightly stronger ($E_0 > 230 \text{ kJ mol}^{-1}$) than the Na-SO_2 bond investigated here. A reasonable estimate of the uncertainty in ab initio E_0 values for these ionic adducts is thus at least $\pm 50 \text{ kJ mol}^{-1}$. k_0 for reaction 1 is about 40 times faster than the analogous reaction with O_2 ,¹⁻⁴ mainly because the density of states at the threshold of dissociation is larger for reaction 1. Our estimated E_0 for reaction 1 is in excellent accord with a very recent determination of $E_0 = 197 \pm 20 \text{ kJ mol}^{-1}$ from flame modeling by Steinberg and Schofield.⁹

High-Pressure Limit. k_{∞} is gas kinetic, indicating that adduct formation proceeds at close to every collision of Na with SO_2 and that there is little energy barrier to association. This is in qualitative accord with molecular beam experiments by Ham and Kinsey, who found large reactive cross sections for the collisions of K and Cs with SO_2 , leading to formation of long-lived complexes.⁶ A simple harpoon model²⁴ calculation for electron transfer from Na to SO_2 shows that the $\text{Na}^+ \text{SO}_2^-$ configuration is favored for separations of up to 0.36 nm. At 787 K, the corresponding rate constant for ion-pair formation is $4.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This compares well with our estimates of $(1-3) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, depending on the extrapolation method employed. For the reaction $\text{Na} + \text{O}_2$ this type of calculation yielded a k_{∞} of about $1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$,³ which is smaller because of the lower electron affinity of O_2 .

Alternative calculations of k_{∞} for $\text{Na} + \text{O}_2$ employed a long-range attractive potential of the form $V(r) = -C_6/r^6$, and yielded k_{∞} values of about $(6-7) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.^{3,4} A similar result is obtained for reaction 1. Using the polarizabilities of Na and SO_2 , we calculate the maximum impact parameter which leads to collision, as described previously.²⁵ The result is 0.52 nm, which corresponds to a rate constant of $8.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This is an overestimate and suggests that the harpoon model may be a better predictor for k_{∞} in these recombinations which form ionic adducts.

4. Conclusions

Kinetic measurements of the association of Na with SO_2 over a wide range of pressure can be fitted using Lindemann theory or an empirical RRKM expression. The low-pressure behavior is consistent with an Na-SO_2 bond energy of about 190 kJ mol^{-1} , which is in accord with recent flame modeling. The experimental data lie in the third-order and falloff regions. Extrapolations show

(20) Bawn, C. E. H.; Evans, A. G. *Trans. Faraday Soc.* **1937**, *33*, 1580.

(21) Troe, J. J. *J. Phys. Chem.* **1979**, *83*, 114.

(22) Troe, J. J. *J. Chem. Phys.* **1981**, *75*, 226.

(23) Nimlos, M. R.; Ellison, G. B. *J. Phys. Chem.* **1986**, *90*, 2574.

(24) Magee, J. L. *J. Chem. Phys.* **1940**, *8*, 687.

(25) Rogowski, D. F.; Marshall, P.; Fontijn, A. *J. Phys. Chem.* **1989**, *93*, 1118.

that the high-pressure limiting rate constant is gas kinetic, which is consistent with a simple harpoon model of electron transfer.

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Kinetic and Thermochemical Study of the $\text{SiH}_3 + \text{HBr} \rightleftharpoons \text{SiH}_4 + \text{Br}$ and $\text{SiH}_3 + \text{HI} \rightleftharpoons \text{SiH}_4 + \text{I}$ Equilibria

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The reactions between SiH₃ and HI (2) and SiH₃ and HBr (5) have been studied by excimer laser flash photolysis coupled with photoionization mass spectrometry over the temperature range 295–550 K, giving $k_2 = 7.3 (\pm 2.8) \times 10^{-12} \exp[2.0 (\pm 1.4) \text{ kJ mol}^{-1}/RT]$ and $k_5 = 1.2 (\pm 0.4) \times 10^{-12} \exp[0.7 (\pm 1.2) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The reverse of reaction 5 was also studied by using excimer laser flash photolysis/resonance fluorescence over the temperature range 298–483 K, giving $k_{-5} = 1.6 (\pm 0.6) \times 10^{-10} \exp[-18.0 (\pm 1.3) \text{ kJ mol}^{-1}/RT] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The enthalpy change for reaction 5, $\Delta H^\circ_{f,298}$, was calculated from $k_5(T)/k_{-5}(T)$ using second law $[-18.4 (\pm 1.8) \text{ kJ mol}^{-1}]$ and third law $[-17.4 (\pm 1.6) \text{ kJ mol}^{-1}]$ techniques, and these values were then employed to provide a recommended value for $\Delta H^\circ_{f,298}$ for SiH₃ of 200.5 (± 2.5) kJ mol⁻¹. The SiH₃–H bond enthalpy at 298 K was also determined, 384.1 (± 2.0) kJ mol⁻¹. The determinations of $k_2(T)$ were combined with literature values of $k_{-2}(T)$ in an additional third law determination of the SiH₃ heat of formation. The result, $\Delta H^\circ_{f,298} = 200.8 (\pm 3.4) \text{ kJ mol}^{-1}$, is of reduced accuracy but in complete accord with the recommended value based on the study of reaction 5. The latter determination also provides a reconciliation of formerly disparate literature values for this heat of formation. The reactivity of SiH₃ is compared to that of the alkyl radicals with both HI and HBr.

Introduction

SiH₃ is one of several hydride intermediates (Si_xH_y) involved in the formation of silicon-containing thin films that are produced by chemical, plasma, and laser vapor deposition processes.^{1–4} Its role in film-growth mechanisms, while still essentially unknown, is expected to be important because this radical is one of the most abundant free-radical species reaching the surface-growth sites from the radical-producing processes occurring above the substrates.^{3,4}

In spite of the obvious interest in the chemical behavior of SiH₃, there still exists a paucity of knowledge of the chemical kinetics of this radical. In addition, its thermochemical properties are still not firmly established. The heat of formation of SiH₃ continues to have an uncertainty of $\approx 8 \text{ kJ mol}^{-1}$ on the basis of recent determinations.^{5–8} The lack of kinetic information is due largely to experimental factors. SiH₃ is difficult to produce directly under controlled conditions, and the radical, until recently, has also been difficult to detect at the low concentrations required for quantitative chemical kinetic studies. It has no known fluorescence spectrum, preventing its detection by the well-developed and sensitive laser-induced fluorescence technique.

Most studies of the kinetics of SiH₃ have relied on indirect chemical sources of this intermediate, such as the reaction^{9–13}

There is a recent exception. Loh et al.¹⁴ have used the photolysis of SiH₃Br at 193 nm as a source of SiH₃ for kinetic studies. However, the desired photodecomposition, to SiH₃ + Br, is a minor ($\approx 10\%$) channel.¹⁵

TABLE I: Determinations of the SiH₃ Heat of Formation and the SiH₃–H Bond Energy (Energies in kJ mol⁻¹)^a

authors	DH ^o ₂₉₈ (SiH ₃ –H)	ΔH ^o _{f,298} (SiH ₃)
Doncaster, Walsh ^{5a} (1981)	378 (±5)	194 (±6) ^b
Boo, Armentrout ⁶ (1987)	386.6	203 (±7)
Berkowitz, Greene, Cho ^{7a} (1987)	≤389.5 ^b	≤205.8 (±5) ^{7b}
current study		
reaction 5, second law	384.6 (±1.8)	201.0 (±2.8)
reaction 5, third law	383.6 (±1.6)	200.0 (±2.6)
reaction 2, third law	384.6 (±2.7)	200.8 (±3.4)
recommended ^c	384.1 (±2.0)	200.5 (±2.5)

^a Uncertainty limits are those reported by the authors. ^b This is the slightly revised heat of formation reported in ref 5b that is based on the same experiments.^{5a} ^c Average of second and third law determinations by using kinetic data of reaction 5.

Recently, sensitive detection methods have been adapted and used to detect SiH₃ in quantitative kinetic studies. They include

- (1) Jasinski, J. M.; Meyerson, B. S.; Scott, B. A. *Annu. Rev. Phys. Chem.* **1987**, *38*, 109.
- (2) *Plasma, Ion and Laser Assisted Chemical Processing of Electronic Materials*; NSF Workshop, San Diego, Feb 1987, Report.
- (3) Robertson, R.; Hils, D.; Chatham, H.; Gallagher, A. *Appl. Phys. Lett.* **1983**, *43*, 544.
- (4) Robertson, R.; Gallagher, A. *J. Appl. Phys.* **1986**, *59*, 3402.
- (5) (a) Doncaster, A. M.; Walsh, R. *Int. J. Chem. Kinet.* **1981**, *13*, 503.
- (b) Walsh, R. *Acc. Chem. Res.* **1981**, *14*, 246.
- (6) Boo, H. B.; Armentrout, P. B. *J. Am. Chem. Soc.* **1987**, *109*, 3549.
- (7) (a) Berkowitz, J.; Greene, J. P.; Cho, H. *J. Chem. Phys.* **1987**, *86*, 1235. (b) Berkowitz, J. *Acc. Chem. Res.* **1989**, *22*, 413.
- (8) Johnson III, R. D.; Tsai, B. P.; Hudgens, J. W. *J. Chem. Phys.* **1989**, *91*, 3340.
- (9) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1985**, *89*, 1752.
- (10) Krasnoperov, L. N.; Chesnokov, E. N.; Panfilov, V. N. *Chem. Phys.* **1984**, *89*, 297.

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