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adiabatic barriers differently than trajectories,⁵⁸ quantum corrections to k_1 and $k_s(E)$ also will influence the proper balance of trajectory calculations for k_1 and $k_a(E)$.

As the above considerations suggest, the structure of eq 6 for k is itself an approximation. The closest derivation of eq 6 is on the basis of a steady-state condition for $C_2H_3^*$ at every total energy E. Even at this level, k_1 in eq 6 should be reformulated as $k_1(E)$ and included in the integral over E. However, more importantly, in the weak collision regime ($\beta < 1$), the buffer gas collisions are not just stabilizing $C_2H_3^*(E)$, but also exciting and deexciting (but not stabilizing) $C_2H_3^*(E)$. The total energy of the metastable vinyl radical is changing up or down by collisions and a master equation is needed to fully describe the dynamics. While considerable work has been done⁵⁹ on approximate analytical solutions for the master equation, the actual situation may be more complex than anticipated. Because of the low moment of inertia for the addition of a light H atom, one might expect that the metastable vinyl radical formed in a collision would be vibrationally hot but rotationally cold. The first few collisions with a buffer gas may involve primarily a redistribution of energy between the rotational and vibrational degrees of freedom.⁶⁰ Trajectory studies on HO_2^{*61} and $HO_2^* + He^{62}$ suggest that both intrinsic non-RRKM behavior in dissociation and energy transfer rates in stabilization are strongly affected by the degree of rotational excitation in the metastable radical. Thus, the master equation solution and the corresponding pressure dependence of the rate constant could be controlled by the competition between collisional reorganization of the internal energy, collisional stabilization, and unimolecular dissociation. The previously mentioned limitations of eq 6 in fitting equally well the entire pressure dependence of the $H + C_2H_2$ rate constant could perhaps be affected by this.

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VI. Conclusions

The main conclusion of this work is that the major differences noticed by other investigators¹⁰ between measured rate constants for the $H + C_2H_2$ recombination reaction and standard RRKM chemical activation theory are not removed by a more accurate calculation of relevant features of the potential energy surface. While reasonable agreement is obtained between theory and experiment for high-pressure isotope effects and the overall shape of the pressure dependence of the rate constant, the calculated magnitude of the high-pressure rate constant is a factor of 10 too high and calculated low-pressure isotope effects tend to be factors of 2 different from experiment. Most likely, the source of these discrepancies lies primarily in approximations to the dynamics and not further errors in the calculated features of the potential energy surface. Trajectory calculations and perhaps even quantum dynamics calculations appear to be needed to identify the dynamical errors.

At the POL-CI level, the ab initio calculations show excellent agreement with experimental values for the equilibrium geometry and normal mode frequencies of acetylene and good agreement with the experimental estimate of the dissociation energy of the vinyl radical. The agreement, especially for the characteristics of acetylene, was superior to that obtained by the only other ab initio study, one done at a UHF level. Both ab initio calculations produce a calculated reaction barrier at the saddle point considerably higher than that inferred from experiment and a heat of formation for the vinyl radical considerably less negative than the experimental estimate. In the POL-CI calculations, the error in the reaction barrier is almost exactly the same as that in the heat of formation, suggesting a systematic displacement of the chemically interesting portion of the surface from that of the H + $C_{2}H_{2}$ asymptote.

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SO(B–X) Bands. Tests of the Effects of SO Decay and Energy Transfer from $O_2(^1\Delta_a)$ on Measured SO Absorption Cross Sections in the $O + CS_2$ Reaction System

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SO is generated by reacting CS_2 vapor with excess O atoms. Decay of SO in the presence of excess O results in essentially quantitative formation of SO₂. Hence, the average [SO] in the absorption cell is given by the difference between measured SO₂ concentrations in the cell with and without addition of NO₂ upstream, and no correction for SO decay is required. Cross sections measured by using O atoms from the reaction of N with NO are in good agreement with those obtained by using O atoms from discharged O2/He mixtures, which shows that formation of $SO(1\Delta)$ by energy transfer from $O_2(1\Delta_g)$ is not a significant source of error in these measurements.

Introduction

In a previous paper¹ absolute absorption cross sections were given for SO between 190 and 235 nm, at a resolution of 0.08 nm (fwhm, triangular slit function). The SO was produced in a fast-flow system by reacting excess O atoms

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with CS_2 , and the concentration of SO in the absorption cell was determined by adding excess NO2 through an inlet jet located near the entrance to the cell and measuring the amount of SO_2 produced by the reaction

$$NO_2 + SO \rightarrow NO + SO_2$$
 (1)

 $k_1 = 1.36 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\text{ref } 2)$

The SO_2 concentration was determined by measuring its absorption spectrum in the 190-235-nm range. Because SO_2 as well as SO was produced in the O + CS_2 reaction, the amount of SO present during a given spectrometer scan was obtained as the difference between two measured SO_2 concentrations, with and without added NO_{2} . This SO concentration was then corrected for loss of SO by recombination inside the 100-cm absorption cell, and the corrected value was used in the conversion from $\ln (I_0/I)$ to cross section. The rate of loss of SO inside the absorption cell was determined in a separate experiment, with CS_2 in excess, by measuring the difference in SO_2 production when NO₂ was added first through the jet near the entrance to the cell and subsequently through a jet close to the exit from the cell. For this purpose the SO_2 concentration was measured at a fluorescence station downstream from the cell, the SO_2 fluorescence being excited by a Cd 228.8-nm resonance lamp. The fluorescence station could not be used to measure $[SO_2]$ when O atoms were in excess because the fluorescence signal was swamped by stray O + SO chemiluminescence.³ The SO absorption cross sections could not be measured with CS_2 in excess because CS_2 itself absorbs very strongly in the wavelength region of interest.⁴

In addition to the cross-section values obtained by scanning over the whole region of interest, cross sections at discrete wavelengths were determined in two ways. First, at wavelengths where SO absorbed much more strongly than SO_2 , the ratio of SO to SO_2 cross sections was determined by measuring the ratio of $\ln I_0/I$ values without and with excess NO_2 added. A measurement of the absolute cross section for SO_2 at the same wavelength then gave a value for the SO cross section. Because some SO_2 was always present as an impurity before NO_2 was added, this method gave a lower limit for the SO cross section at the chosen wavelength. In the second type of measurement, discrete wavelengths were found by trial and error, such that the value of $\ln I_0/I$ did not alter when NO₂ was added. At such wavelengths the absorption cross sections of SO and SO_2 must be equal. At wavelengths where comparison was possible, cross sections obtained from this type of measurement were about 15% smaller than the values obtained from scans over the whole wavelength range. In the present work we have investigated this discrepancy and have concluded that results obtained from the wavelength scans were too large because of the correction for SO decay in the absorption cell.

In the previous study the O atoms were produced by a microwave discharge in O_2/He mixtures. Such a system is known to generate a high yield of metastable $O_2(^1\Delta_g)$ molecules, which readily transfer energy to SO to form $SO(^{1}\Delta).^{5}$ If a significant proportion of the SO in the absorption cell were in the $^{1}\Delta$ state, this would not affect the measurement of total [SO] via reaction 1, but the measured cross sections would be too low because the metastable SO would not contribute to the $B \leftarrow X$ absorption spectrum. In the present work we have tested this possibility by comparing cross sections found by using O atoms obtained from an O_2 /rare gas discharge with those found by using O atoms obtained from the reaction of N atoms with NO. The two sets of measurements agree to within the limits of experimental error from other sources,

which indicates that production of $SO(^{1}\Delta)$ from $O_{2}(^{1}\Delta_{g})$ was not a significant problem in these experiments.

Experimental Section

The apparatus and materials were similar to those used in the previous study, except that the SO_2 fluorescence station was omitted, and a water jacket was provided for temperature control on the absorption cell and on the 30 cm of 20-mm diameter tubing which was interposed between the NO_2 inlet jet and the absorption cell. The results to be discussed here were obtained with the water jacket at 25 ± 2 °C, at total pressures between 1.1 and 1.5 torr (Texas Instruments quartz spiral gauge). In the experiments using O atoms from the reaction of N with NO, Matheson prepurified nitrogen was passed through a microwave discharge powered by a Raytheon PGM-100 microwave generator operation at a power level of 300-400 W, and the resulting stream of partially dissociated N_2 was titrated visually with NO. Nitrogen and helium were dried by passage through a molecular sieve trap at liquid-nitrogen temperature; oxygen and nitric oxide were similarly passed through a silica gel trap immersed in a solid CO₂/alcohol bath. The McPherson Model 218 monochromator was fitted with a grating having 1200 grooves/mm (previously 2400); the monochromator entrance and exit slits were set at 25 μ m, giving a triangular slit function of 0.10-nm width at half-height (previously 0.082 nm). Flowmeter voltages and the output from the lock-in amplifier were taken via a 12-bit A/D converter (Datel MDAS-16) to a Radio Shack TRS-80 microcomputer. Data storage was initiated by a change in the state of a microswitch, operated by a cam mounted on the grating drive, which switched to the on state at 2-nm intervals. The transmitted light signal was sampled at either 60 or 120 points per nanometer, and up to 2500 points were taken per scan. Spectra were plotted from disk files, using an X-Y recorder driven by the computer through two pairs of 8-bit D/A converters. Each pair provided calibrated coarse and fine analog inputs to an operational-amplifier adder, whose output was taken to one of the recorder inputs.

Results and Discussion

Correction for SO Decay. The decay of SO in the absorption cell is expected to occur mainly by^6

$$SO + SO + M \rightarrow S_2O_2 + M$$
 (2)

 $k_2(M=N_2) = 4 \times 10^{-31} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1} (\text{ref } 6)$

$$SO + S_2O_2 \rightarrow S_2O + SO_2 \tag{3}$$

 $k_3 = 3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} (\text{ref } 6)$

together with

$$SO + SO \rightarrow S + SO_2$$
 (4)

 $k_4 = 3 \times 10^{-15} - 8 \times 10^{-15} \text{ cm}^3 \text{ molecules}^{-1} \text{ s}^{-1} \text{ (see ref 1)}$

$$SO + O + M \rightarrow SO_2 + M$$
 (5)

$$k_5(M=He) = 9.8 \times 10^{-34} \text{ cm}^6 \text{ molecule}^{-1} \text{ s}^{-1} (\text{ref } 7)$$

Reaction 4 possibly occurs on the walls rather than in the gas phase; certainly, SO decay in the absence of excess O atoms leads to deposition of a film of sulfur. Such films are readily cleaned off the walls and windows by atomic oxygen, the anticipated products being SO and/or SO₂. In the absence of excess O atoms, SO decay is accompanied mainly by formation of S_2O_2 , together with some S_2O , SO₂, and solid sulfur, and the procedure adopted previously to

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Figure 1. Effect of excess O atoms on SO yield, using O atoms from O_2 /He discharge. The peak at 219.8 nm is the SO (7,0) band; the peaks on either side are due to SO₂. Successive curves are displaced by 0.1 unit on the vertical axis for clarity. Oxygen flows, reading from top to bottom: 190, 126, 78, 35, 20; units: standard cubic centimeters per minute (sccm). Total flow, other gases = 980 sccm; total pressure = 1.40 torr. Unsmoothed data; 400 points per scan.

allow for SO decay in the absorption cell appears correct. However, as Herron and Huie⁶ have noted, a complete interpretation of SO decay kinetics must include the reactions

$$0 + S_2 O_2 \rightarrow SO + SO_2 \qquad (k_6 \text{ not known}) \qquad (6)$$

$$O + S_2 O \rightarrow 2SO \tag{7}$$

 $k_7 \sim 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ (ref 8)}$

Reaction 6 would be expected to be fast, so that with O atoms in excess the steady-state concentrations of S_2O_2 and S_2O are likely to be very small, in which case the only significant product of SO decay in the presence of excess O atoms is SO_2 .

Let the average concentrations of SO and SO₂ in the absorption cell, with no NO₂ introduced, be C_1 and C_2 , respectively; C_1 and C_2 are the quantities which govern ln I_0/I in the two spectra. Upstream from the cell, at the NO₂ inlet, the concentration of SO will be higher $(C_1 + x)$ and that of SO₂ correspondingly lower $(C_2 - y)$. When excess NO₂ is introduced, the SO is converted to SO₂ and the average concentration of SO₂ in the absorption cell then becomes

$$C_3 = C_1 + C_2 + x - y \tag{8}$$

But if the decay of SO gives SO₂ quantitatively, then x and y are equal and the average SO concentration C_1 is simply $C_3 - C_2$, the difference between the SO₂ concentrations with and without NO₂ added. In the previous work the cross sections of the final SO₂ spectrum (Figure 13 of ref 1) were calculated with an allowance of 12% for decay of SO in the absorption cell. Omission of this factor brings the values in the spectrum into good agreement with the values found by measurements at discrete wavelengths.

An experimental test of the foregoing arguments was provided by the observation that, with a given flow of CS_2 , the ratio of SO to SO_2 in the absorption cell was sensitive to the size of the O atom excess. Figure 1 shows values of $\ln I_0/I$ for several scans over a group of peaks near 220 nm for the O + CS_2 reaction flame with excess O atoms and with varying proportions of O_2 in the He/O₂ discharge. Under the conditions of these experiments a major fraction of the O₂ is dissociated to atoms. It is apparent that the central peak of the group, due to SO, diminishes relative to the two SO₂ peaks as the O atom excess is increased. The same effect is observed, albeit to a lesser extent be-



Figure 2. Effect of excess O atoms on SO yield, using O from the reaction of N with NO. The peak at 209.8 nm is the SO (11,0) band; the peak at 210.4 nm is due to SO₂. Excess oxygen atom flows/sccm, from top to bottom: 0, 2.0, 5.0, 12.0, 16.4. Total flow: 1000 sccm; pressure = 1.40 torr. Data smoothed with 5-point running average; 200 points per scan.



Figure 3. Representative results for SO cross sections between 210 and 230 nm. Upper plot, O atoms from discharged O_2 ; lower plot, O atoms from N + NO reaction. Unsmoothed data; 1200 points per scan. [SO]/(molecules cm⁻³) = 1.1×10^{14} (upper plot) and 2.1×10^{14} (lower plot).

TABLE I: Effect of Excess O Atoms on SO Yield for Varying O_2 Flow in O_2/He Discharge^a

O ₂ flow	[SO]	[SO ₂]	sum	SO + NO ₂	
20	1.79	6.45	8.24	8.1	
35	1.62	5.53	7.15	7.9	
78	1.00	7.32	8.32	7.9	
126	0.76	7.31	8.07	8.0	
190	0.44	6.94	7.38	7.6	

^a Units: sccm in column 1; 10^{14} molecules cm⁻³ elsewhere. Columns 2 and 3 result from least-squares fitting of the curves in Figure 1 to standard SO and SO₂ spectra. Column 4 is the sum of columns 2 and 3. Column 5 gives the total SO₂ present (spectra fitted by eye) when excess NO, was added.

cause of the smaller range of atom concentration, when O atoms are obtained from the N + NO reaction and the O atom concentration is varied by altering the flow rate of the NO added to discharged N_2 . This is illustrated in Figure 2 for a composite SO + SO₂ absorption peak near

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Figure 4. Representative results for SO cross sections between 199 and 211 nm. Upper plot, O atoms from discharged O_2 ; lower plot, O atoms from N + NO reaction. Unsmoothed data; 1200 points per scan. [SO]/(molecules cm⁻³) = 1.9×10^{14} (upper plot) and 1.7×10^{14} (lower plot).

210 nm. Our finding the same effect with O atoms from N + NO makes it unlikely that the variations of the $[SO]/[SO_2]$ ratio in Figure 1 could be due to changes in the production of $SO(^{1}\Delta)$. The actual origin of the effect has not been established, but it appears reasonable to attribute it to a sequence of processes such as

$$SO + SO \rightarrow S_2O_2^*$$
 (9)

$$S_2 O_2^* \to SO + SO \tag{10}$$

$$S_2O_2^* + M \rightarrow S_2O_2 + M \tag{11}$$

$$S_2O_2^* + O \rightarrow SO_2 + SO \tag{12}$$

$$S_2O_2 + O \rightarrow SO_2 + SO \tag{6}$$

where steps 9-11 are the microscopic collision processes which together comprise reaction 2, reaction 12 is required to be much faster than reaction 6, and reaction 12 is required to be competitive with reaction 11 when O atoms are in large excess. For each of the scans in Figure 1, the amount of SO_2 present after excess NO_2 had been introduced was measured, and the absorption curves obtained in the absence of NO_2 were fitted by a least-squares procedure to standard SO and SO_2 spectra. The results are shown in Table I. The amount of SO_2 found after adding NO2 is seen to be reasonably constant and in good agreement with the total of $SO + SO_2$ obtained by fitting the curves to a sum of standard SO and SO_2 spectra. Hence, we conclude that the decay of SO in the presence of O atoms does lead to virtually quantitative formation of SO_{2} , and no correction for SO decay is required.

Test for the Effect of $O_2({}^1\Delta_g)$. Numerous spectra were obtained at the same resolution, namely, 0.10 nm, with O atoms from discharged O_2/He and O_2/Ar mixtures, and with O atoms from the reaction of N with NO. Within the (sometimes considerable) experimental uncertainty of the results, absorption cross sections obtained from the two kinds of experiment were in good agreement. Representative examples are shown in Figures 3 and 4. We conclude that, at the current level of precision, $SO(^{1}\Delta)$ is negligible. This is consistent with the observation⁵ that $SO(1\Delta)$ undergoes wall deactivation much more readily than $O_2({}^1\Delta_{\sigma})$. The present cross sections are appreciably lower than those given in Figure 13 of ref 1, which is attributable mainly to the incorrect use of a correction factor for SO decay in ref 1, and in part to the slightly lower resolution of the present experiments.

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Analysis by Gas-Phase Electron Spin Resonance of H, O, OH, and Halogen Atoms in Flames

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A new development of Westenberg and Fristrom's method is proposed to detect, by ESR, labile species in flames. The species extracted by a sampling probe are detected at low pressure ($p = 4 \times 10^{-2}$ torr) after a time of residence in the probe close to 8 ms. H, O, OH, as well as halogen atoms in inhibited flames have been detected with a good signal-to-noise ratio. To account for species destruction in the probe, especially on the NaOH/ HNO₃-treated surface of the probe ($\epsilon = 10^{-3}-10^{-4}$), an extrapolation method to p = 0 is proposed. Mole fraction profiles of H, O, and OH in methanol-air flames stabilized at 80 torr in a flat flame burner were obtained. The results are in relatively good agreement with those calculated by Westbrook and Dryer for methanol flames. In the burned gases, the mole fractions of the species are consistent with the partial equilibrium hypothesis.

Introduction

Microstructure analyses of laminar flames have provided a good way for the study of free-radical and atom elementary reactions occurring in combustion processes. In the past 10 years, the powerful development of the molecular beam sampling technique coupled to an analysis of stable or labile species by modulated beam mass spectrometry has led to a great amount of data in this field. The advantage of mass-spectrometric detection of the beam is that all chemical species in the flame can be monitored. However, with the two procedures of calibration generally used, some difficulties^{1,2} appear, coming

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