to react for a period of Δt . During this time, the local concentrations reach the values $c_A(x,\Delta t)$ and $c_B(x,\Delta t)$, and the change of the concentration of both reactants is

$$\Delta c(x,\Delta t) = c_{\mathbf{A}}(x,0) - c_{\mathbf{A}}(x,\Delta t) = c_{\mathbf{B}}(x,0) - c_{\mathbf{B}}(x,\Delta t)$$
(13)

which can be calculated from

$$\Delta c(x,\Delta t) = c_{\rm B}(x,0)F/(F-1) - c_{\rm B}(x,0)/(F-1) \quad (14)$$

where

2

$$F = \frac{c_{\rm A}(x,0)}{c_{\rm B}(x,0)} \exp\{[c_{\rm A}(x,0) - c_{\rm B}(x,0)]k\Delta t\}$$
(15)

Equations 14 and 15 are obtained from the integrated rate equations of reaction 1. In case of complex reaction mechanisms, the system of differential rate equations must be solved numerically.¹⁰ The concentrations $c_i(x,\Delta t)$ at the end of the reaction step are the initial values for the next diffusion step.

Conclusions

Figure 1b-d shows a few examples of the large number of computer simulations we have carried out. Our results indicate that second-order rate constants in the range of 10^3-10^8 M⁻¹ s⁻¹ can be determined by diffusion competition, if the initial concentrations of A and B are in the range of 10^{-4} - 10^{-7} M. A tube length of L = 8 cm is sufficient for the end effects to be negligible for several thousands of seconds. As the examples in the figures

(10) Szamosi, J.; Kristyan, S. J. Comput. Chem. 1984, 5, 186.

indicate, for different rate constants, large differences in the concentration profiles arise already after less than 15 min.

In an actual experiment, a sliding cell¹¹ arrangement can be used, which is routinely employed for the determination of diffusion coefficients. After the initiation of the diffusion-reaction process, the concentration profiles at several different times can be established with a position-scanning spectrophotometer.¹² By use of these profiles, the partial derivatives in eq 6 can be calculated with the Savitsky-Golay method.¹³ Then, with the knowledge of the diffusion coefficients, eq 6 yields the desired rate constant. The calculated rate constant is unaffected by the small distortion of the initial concentration profiles caused by the sliding of the cells at t < 0, since the distortions are rapidly self-corrected by the system.

In general, the limitations of the diffusion competition method are given by the accuracy of the experimental values of $c_i(x,t)$, from which the partial derivatives in eq 6 must be computed. Clearly, the uncertainty of the calculated rate constant k increases as the difference $\partial c_i / \partial t - D_i (\partial^2 c_i / \partial x^2)$ approaches the uncertainty of the product $c_A c_B$.

Acknowledgment. This work was partially supported by the R. A. Welch Foundation and the Organized Research Fund of UTA. Acknowledgment is made to the donors of the Petrolum Research Fund, administered by the American Chemical Society, for additional support.

(12) Tanigaki, M.; Kondo, K.; Harada, M.; Eguchi, W. J. Phys. Chem. 1983, 87, 586 and references therein.

Falloff Curves of the Recombination Reaction $O + SO + M \rightarrow SO_2 + M$ in a Variety of **Bath Gases**

C. J. Cobos,[†] H. Hippler, and J. Troe^{*}

Institut für Physikalische Chemie der Universität Göttingen, D-3400 Göttingen, West Germany (Received: October 25, 1984)

The recombination reaction $O + SO + M \rightarrow SO_2 + M$ has been studied at room temperature by laser flash photolysis in a variety of 13 bath gases M. By variation of the pressure between 0.2 and 200 bar, major parts of the falloff curves were observed. A limiting high-pressure rate coefficient of $k_{rec,\sigma} = 5.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and limiting low-pressure rate coefficients of $k_{rec,0}/[\text{Ar}] = 5.1 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ and $k_{rec,0}/[\text{N}_2] = 7.7 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ were obtained. A theoretical analysis of these data and SO₂ dissociation results suggests that excited electronic states of SO₂ contribute with a factor of 5-20 to the low- and high-pressure ranges of the reaction. Average energies transferred per collision $\langle \Delta E \rangle$ are derived from the low-pressure rate coefficients. For M = Ar, $\langle \Delta E \rangle$ probably does not markedly depend on the temperature between 300 and 5000 K. The indirectly derived $\langle \Delta E \rangle$ values from this work correspond to recently directly measured values after laser excitation.

Introduction

Recent experiments from our laboratory have demonstrated that energy transfer of the vibrationally highly excited triatomic molecules CS_2^{1-3} and $SO_2^{3,4}$ can be measured directly. For these molecules there is a strong mixing of relatively low-lying electronic states such that, by absorption of UV photons, vibrationally highly excited molecules in the electronic ground state can be produced. Their stepwise loss of energy in collisions⁵ can be monitored by "hot" UV absorption spectroscopy.6-8

It appears important to compare the derived information on energy transfer with more indirect results from thermal unimolecular reaction studies. There are two ways to do this: (i) analysis of the absolute values of the low-pressure dissociation or recombination rate coefficients, (ii) measurement and analysis of relative collision efficiencies of a series of bath gases including sufficiently "strong" colliders. For CS_2 and SO_2 the first approach meets some difficulties. As a consequence of the strong mixing of electronic

0022-3654/85/2089-1778\$01.50/0 © 1985 American Chemical Society

⁽¹¹⁾ Claesson, S. Nature (London) 1946, 158, 824.

⁽¹³⁾ Savitzky, A.; Golay, M. J. E. Anal. Chem. 1964, 36, 1627.

[†]On leave from the Instituto de Investigaciones Fisicoquimicas Teóricas y Aplicadas (INIFTA), La Plata, Argentina.

⁽¹⁾ J. E. Dove, H. Hippler, H. J. Plach, and J. Troe, J. Chem. Phys., 81, (1) J. E. Dove, H. Hippler, and J. Troe, J. Chem. Phys., in press.
 (2) J. E. Dove, H. Hippler, and J. Troe, J. Chem. Phys., in press.
 (3) M. Heymann, H. Hippler, and J. Troe, J. Chem. Phys., in press.
 (4) H. Hippler, D. Nahr, and J. Troe, J. Chem. Phys., in press.

⁽⁵⁾ J. Troe, J. Chem. Phys., 77, 3485 (1982).

⁽⁶⁾ H. Hippler, K. Luther, J. Troe, and R. Walsh, J. Chem. Phys., 68, 323 (1978)

⁽⁷⁾ H. Hippler, J. Troe, and H. J. Wendelken, J. Chem. Phys., 78, 5351 (1983).

⁽⁸⁾ M. Heymann, H. Hippler, and J. Troe, J. Chem. Phys., 80, 1853 (1984).

Recombination Reaction $O + SO + M \rightarrow SO + M$

states, there is a major contribution of excited electronic states to thermal dissociation and recombination.⁹ Since the properties of these states are still badly characterized, their presumably large contribution can only be estimated with large uncertainties. In order to analyze the absolute values of the rate coefficients, all available spectroscopic information have to be combined with dissociation and recombination data over wide temperature and pressure ranges. Unfortunately, for CS₂ the recombination has not been accessible at all; thermal dissociation data in the lowpressure limit¹⁰ alone did not allow² for a reliable analysis. In the absence of recombination studies also no relative collision efficiency measurements are available. Before our present study, the situation for SO₂ was not much better. After many years with controversial results^{11,12} for SO₂ low-pressure dissociation, only recently could the source of the discrepancy be traced.¹³ The few available results^{14,15} for the recombination

$$O + SO(+M) \rightarrow SO_2(+M) \tag{1}$$

differed by about a factor of 5; relative collision efficiency measurements were not available.

After more unsuccessful attempts¹⁶ to study the recombination $S + CS(+M) \rightarrow CS_2(+M)$, in the present work we concentrated on the SO_2 recombination (1). We succeeded not only in measuring the low-pressure rate coefficient of reaction 1 in a large variety of bath gases but we also were able to measure the full falloff curve up to the high-pressure limit. In this way, not only an analysis of relative collision efficiencies but also of the contributions of excited electronic states to the absolute values of the rate coefficients has become possible.

Experimental Technique

The recombination (1) of oxygen atoms and SO radicals was studied after laser flash photolysis of SO₂ at 193 nm. The photolysis laser was an ArF excimer laser (Lambda Physik EMG 200) delivering 10-ns pulses of 100 mJ cm⁻² pulse energies. At 193 nm, SO₂ photolysis proceeds by the spin-allowed process¹⁷⁻¹⁹

$$SO_2(X^1A_1) + h\nu \rightarrow SO_2(\tilde{C}^1B_2) \rightarrow O(^3P) + SO(X^3\Sigma^-)$$
 (2)

The subsequent recombination (1) was followed by monitoring the SO₂ light absorption at 302 nm. Absorption measurements employed a Xe–Hg high-pressure arc lamp (Hanovia 200W) as a light source, a monochromator (Zeiss M4Q III), a photomultiplier (RCA 1P28), and an oscilloscope (Tektronix 7633). Experiments using other analysis wavelengths, such as 265.5, 275.5, 306, and 313 nm, gave results identical with those at 302 nm.

Our high-pressure photolysis cell made from stainless steel has been described earlier.^{20,21} It used an arrangement where photolysis light beams traversed the cell perpendicularly through two sets of 20-mm-thick quartz windows. In this cell there was a minimum of dead volume. The perpendicular geometry assured the absence of stray laser light in the analysis system.

Usually 0.7 torr of SO_2 in the presence of a bath gas were

(9) I. W. M. Smith, Int. J. Chem. Kinet., 16, 423 (1984).

- (10) H. A. Olschewski, J. Troe, and H. Gg. Wagner, Ber. Bunsenges. Phys. Chem., 70, 1060 (1966).
- (11) H. A. Olschewski, J. Troe, and H. Gg. Wagner, Z. Phys. Chem. (Frankfurt and Main), 44, 173 (1965).
- (12) D. C. Astholz, K. Glänzer, and J. Troe, Proc. Int. Symp. Shock Tubes Waves, 11th, 1977, 232 (1978).
- (13) H. J. Plach and J. Troe, Int. J. Chem. Kinet., 16, 1531 (1984).
 (14) C. J. Halstead and B. A. Thrush, Proc. R. Soc. London, Ser. A, 295, 363 (1966).
- (15) S. Takahashi, Mem. Def. Acad., Math., Phys., Chem., Eng. (Yokosuka, Jpn.), 10, 369 (1970). S. Miyazaki and S. Takahashi, Ibid., 11, 307 (1971).
- (16) J. E. Dove, H. Hippler, and J. Troe, unpublished results.
 (17) A. Freedman, S. C. Yang, and R. Bersohn, J. Chem. Phys., 70, 5313
- (1979). (18) G. Black, R. L. Sharpless, and T. G. Slanger, Chem. Phys. Lett., 90, 55 (1982).
- (19) M. Kawasaki, K. Kasatani, and H. Sato, Chem. Phys., 73, 377 (1982).
- (20) A. E. Croce de Cobos and J. Troe, Int. J. Chem. Kinet., 16, 1519 (1984).
- (21) A. E. Croce de Cobos, H. Hippler, and J. Troe, J. Phys. Chem., 88, 5083 (1984).



Figure 1. Falloff curve for the recombination $O + SO + Ar \rightarrow SO_2 + Ar$.



Figure 2. Falloff curve for the recombination O + SO + N_2 \rightarrow SO_2 + $N_2.$



Figure 3. Falloff curve for the recombination $O + SO + C_3F_8 \rightarrow SO_2 + C_3F_8$.

photolyzed at temperatures near 300 K. We studied the bath gases He, Ne, Ar, Kr, Xe, H₂, D₂, N₂, CO₂, CH₄, CF₄, SF₆, and C₃F₈. The bath gas pressures ranged from 0.2 to 200 bar (in some cases). The gases used were of highest available commercial purity. No further purification appeared necessary.

The recombination of SO₂ always followed pseudo-second-order rate laws. The corresponding second-order rate coefficients $k_{\rm rec}$ were derived from a second-order plot of the absorption signals. Since these signals were small, they could be evaluated from the expression

$$\frac{I_0}{\Delta I(t)} - \frac{I_0}{\Delta I(t=0)} \simeq \frac{k_{\text{rec}}t}{(\ln 10)\epsilon l}$$
(3)

where I_0 is the intensity of the incident analysis light, I(t) is the intensity of the transmitted analysis light, $\Delta I(t) = I(\infty) - I(t)$,

TABLE I: Second-Order Rate Coefficients for the Different Bath Gases

			$k_{\rm rec}/10^{-11}$ cm ³ molecule ⁻¹ s ⁻¹												
[]	M]/bar	He	Ne	Ar	Kr	Xe	N ₂	H ₂	D ₂	CO ₂	CH4	CF ₄	SF ₆	C ₃ F ₈	
	0.2	0.24		0.16		0.18	0.21			1.1		1.0	1.3	1.4	_
	0.5	0.35	0.26	0.34		0.25	0.66	2.8	2.5	2.3	0.73	1.9	2.3	2.3	
	1	1.3	0.54	1.1	1.0	1.5	1.3	3.6	3.6	2.4	2.8	3.1	2.9	3.6	
	2	1.6	1.3	1.4	1.2	2.1	1.6	4.1	4.1	3.1	3.8	3.6	2.9	3.8	
	3	2.0	1.3				1.8				4.0	3.8	3.6	4.8	
	5	2.0	2.1	2.2	2.5	2.7	2.9	4.2	4.7	4.0	4.5	4.3	4.8		
	10	2.3		2.9			3.6								
	25	3.7		3.1			3.8								
	50			3.8			4.3								
	100			4.3			4.7								
	200			4.9			4.9								

l is the optical path length of 2 cm, and ϵ is the SO₂ absorption coefficient. In all experiments it was found that $I(\infty) = I(t=0)$. Up to 200 bar of bath gas pressure we did not notice any changes in the effective SO₂ absorption coefficient at 302 nm of $\epsilon = 61$ L mol⁻¹ cm⁻¹ (for the spectral width of our analysis system of 0.7 nm (fwhm)). The 302-nm wavelength was chosen in order to give a maximum transmitted light intensity with 0.7 torr of SO_2 in the reaction vessel.

Experimental Results

Our experimental second-order rate coefficients $k_{rec,0}$ for the various bath gases used are summarized in Table I. Each value is the average of about four experiments. A graphical representation of our experiments for the bath gases Ar, N_2 , and C_3F_8 is given in Figures 1-3. When compared to the curve for the other triatomic molecules like NO2,²² INO,²³ ClNO,²⁴ O3,²⁰ and HO₂,²¹ the falloff curves are shifted markedly toward low pressures such that deviations from third-order behavior are pronounced already at pressures below 1 bar. The high-pressure limits are approached at comparably low pressures. An explanation for this behavior is given in the quantitative analysis of rate coefficients below.

Although a major part of the falloff curves was measured in our work, an accurate extrapolation to the limiting low- and high-pressure rate coefficients ($k_{rec,0}$ and $k_{rec,\infty}$, respectively) could not be done without the help of theory. As in our earlier work we employed the technique of reduced falloff curves^{25,26} by which $k_{\rm rec}/k_{\rm rec,\infty}$ is expressed in terms of the Lindemann-Hinshelwood expression and additional strong-collision and weak-collision broadening factors. This analysis involves an iteration: preliminary analysis of limiting low- and high-pressure rate coefficients in order to determine the adequate broadening factors and a final fit. As described in more detail in ref 21, we followed the procedure and obtained the full curves included in Figures 1-3. They are characterized by center broadening factors of, e.g., $F_{cent}(M=Ar)$ $\simeq 0.58 \pm 0.1, F_{cent}(M=N_2) \simeq 0.55 \pm 0.1, \text{ and } F_{cent}(M=C_3F_8)$ $\simeq 0.76 \pm 0.1.$

The experiments with these three bath gases lead to a limiting high-pressure rate coefficient of $k_{rec,\infty} = 5.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ s^{-1} . Limiting low-pressure rate coefficients are, e.g., for the bath gases Ar and N₂, $k_{rec,0}/[Ar] = 5.1 \times 10^{-31}$ cm⁶ molecule⁻² s⁻¹ and $k_{rec,0}/[N_2] = 7.7 \times 10^{-31}$ cm⁶ molecule⁻² s⁻¹. Low-pressure rate coefficients for the other bath gases are included in Table II. The estimated uncertainty for $k_{rec,\infty}$, because of uncertainties of the extrapolation and data scattering, is about $\pm 20\%$. The corresponding uncertainty of $k_{rec,0}$ is about ±40% in most cases.

Our low-pressure rate coefficient for M = Ar of 5.1×10^{-31} cm⁶ colecule⁻² s⁻¹ agrees better with the old value of 8.8×10^{-31} cm⁶ molecule⁻² s⁻¹ obtained by Halstead and Thrush¹⁴ than with that by Takahashi and co-workers¹⁵ of $(1.6-2.0) \times 10^{-31}$ cm⁶ molecule⁻² s⁻¹. These two results were obtained at low pressures

(25) J. Troe, J. Phys. Chem., 83, 114 (1979)

TABLE II: Experimental Low-Pressure Rate Coefficients for the **Different Bath Gases**

М	$(k_{\rm rec,0}/[M])/10^{-31}$ cm ⁶ molecule ⁻² s ⁻¹	М	$(k_{\rm rec,0}/[{\rm M}])/10^{-31}$ cm ⁶ molecule ⁻² s ⁻¹
He	6.4	D,	70
Ne	4.5	cō,	42
Ar	5.1	CH₄	44
Kr	6.0	CF₄	40
Xe	6.5	SF	49
N_2	7.7	C ₁ F ₈	62
н	70	5 8	

with the discharge flow technique.

Discussion

Mechanism. Besides reaction 1, the following reactions and their possible influence on our measurements should be considered:

$$O + O(+M) \rightarrow O_2(+M) \tag{4}$$

$$O + SO_2(+M) \rightarrow SO_3(+M)$$
(5)

$$O + SO_2 \rightarrow SO + O_2 \tag{6}$$

$$SO + SO \rightarrow S_2 + O_2$$
 (7a)

$$\Rightarrow S_2 O + O \tag{7b}$$

$$SO + SO(+M) \rightarrow S_2O_2(+M)$$
(8)

The rate coefficients of reaction²⁷ 4, the spin-forbidden recombination^{28,29} 5, and reaction³⁰⁻³² 7c are sufficiently well-known. From their rate coefficients one estimates that these reactions cannot contribute markedly to our observations. Similarly, the endothermic processes 6, 7a, and 7b are probably not important under our conditions. There exists only controversial information about the rate coefficient of reaction 8. In recent measurements³³ SO radicals were produced in a flow system via the reaction OCS + O. Then, the disappearance of the SO radicals was monitored by mass spectroscopy. From a simulation of the presumed mechanism, $k_8/[N_2] = 4.4 \times 10^{-31} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ was deduced. However, an absolute calibration of SO and S₂O₂ signals apparently was difficult. If k_8 were really so large, reaction 8 would have interfered with our measurements of reaction 1. However, there are several arguments against a marked participation of

(33) J. T. Herron and R. E. Huie, Chem. Phys. Lett., 76, 322 (1980).

⁽²²⁾ J. Troe, Ber. Bunsenges. Phys. Chem., 73, 144 (1969).

 ⁽²³⁾ H. van den Bergh and J. Troe, J. Chem. Kinet., 8, 501 (1976).
 (24) H. Hippler and J. Troe, Int. J. Chem. Kinet., 8, 501 (1976).

⁽²⁶⁾ J. Troe, Ber. Bunsenges. Phys. Chem., 87, 161 (1983). R. G. Gilbert, K. Luther, and J. Troe, *ibid.*, 87, 177 (1983).

⁽²⁷⁾ D. L. Baulch, D. D. Drysdale, J. Duxbury, and S. Grant, "Evaluated Kinetic Data for High Temperature Reactions. Vol. 3: Homogeneous Gas Phase Reactions of the O2-O3 System, the CO-O2-H2 System, and of Sulphur-containing Species", Butterworths, London, 1976. (28) D. C. Astholz, K. Glänzer, and J. Troe, J. Chem. Phys., 70, 2409

⁽¹⁹⁷⁹⁾

⁽²⁹⁾ D. C. Baulch, R. A. Cox, R. F. Hampson, Jr., J. A. Kerr, J. Troe, and R. T. Watson, J. Phys. Chem. Ref. Data, 9, 295 (1980).
(30) C. J. Halstead and B. A. Thrush, Photochem. Photobiol., 4, 1007

^{(1965).}

⁽³¹⁾ K. H. Hoyermann, H. Gg. Wagner, and J. Wolfrum, Ber. Bunsenges. Phys. Chem. 71, 603 (1967).

⁽³²⁾ R. J. Donovan, D. Husain, and P. T. Jackson, Trans. Faraday. Soc., 65, 2930 (1969).

reaction 8. The absorption coefficient of S_2O_2 in the spectral region 240-340 nm is ten to one hundred times larger than that of SO₂.^{34,35} If there would have been an appreciable formation of S_2O_2 , this should have given absorption-time profiles which led to different apparent rate coefficients at different wavelengths. Also, the final absorption levels should have differed from the preflash levels. This was not observed. If nevertheless the absorption signals were attributed to S_2O_2 formation, a rate coefficient of $k_8 \simeq 10^{-9} \pm 0.5$ cm³ molecule⁻¹ s⁻¹ would have been derived at 200 bar of N₂. This value would be anomalously large. Earlier conclusions on k_8 from ref 30 and 36 as well as a theoretical estimate, which we made in the present work using the formalism described below, suggested values of $k_8/[N_2] \simeq 10^{-33}$ cm⁶ molecule⁻² s⁻¹. Therefore, we believe that reaction 8 has not contributed markedly to our observed absorption profiles.

The previous discussion supports the experimental evidence of a simple recombination mechanism governed predominantly by reaction 1. In the following we analyze the properties of the derived recombination rate coefficients, i.e., absolute values and dependence on the nature and on the concentration of the bath gases M.

Analysis of $k_{rec,0}$ and $k_{rec,\infty}$. A theoretical analysis of the limiting low- and high-pressure recombination rate coefficients $k_{rec,0}$ and $k_{\rm rec,\infty}$ was performed in terms of statistical unimolecular rate theory. For $k_{rec,\infty}$, we used the simplified statistical adiabatic channel model of ref 37 which leads to

 $k_{\text{rec},\infty} =$

$$K_{\rm c}^{-1} \frac{kT}{h} \frac{Q^*_{\rm cent} F^*_{\rm AM} \Pi Q^*_{j} \Pi Q^*_{\rm m}}{\sigma^* Q_{\rm vib \ rot}} \exp\left(-\frac{\Delta H^{\rm o}_0 + \Delta E_{\rm 0z}}{kT}\right)$$
(9)

For $k_{\rm rec,0}$, we employed the expression

 $k_{\rm rec,0} =$

$$K_{\rm c}^{-1}\beta_{\rm c}Z_{\rm LJ}[\mathbf{M}] \frac{\rho_{\rm vib,h}(E_0)kT}{Q_{\rm vib}}F_{\rm anh}F_{\rm E}F_{\rm rot} \exp\left(-\frac{\Delta H^{\bullet}_0 + \Delta E_{0z}}{kT}\right)$$
(10)

from ref 38. For the notation, the reader is referred to ref 37 and 38. The calculation is straightforward leading to a maximum possible value of $k_{rec,\infty} = 3.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ in the phase space limit for $\alpha/\beta \gtrsim 1$, which is markedly lower than the experimental value of 5.3×10^{-11} cm³ molecule⁻¹ s⁻¹. A similar effect is observed with $k_{rec,0}$: the apparent collision efficiencies β_c , obtained by comparing eq 10 with the experiments, exceed unity, e.g., $\beta_c = 3.0$, 2.9, and 25.2 for M = Ar, N₂, and C₃F₈. Anomalously high β_c values were also obtained in our analysis of SO₂ decomposition rates.¹³ For M = Ar, we obtained $\beta_c = 0.52, 0.25,$ and 0.20 at T = 3000, 4000, and 5000 K, respectively. The results of this analysis of the thermal dissociation data in the low-pressure range and of recombination data in the low- and high-pressure range can only be rationalized by assuming a major contribution of excited electronic states to the dissociation-recombination kinetics. So far, eq 9 and 10 were calculated for the electronic ground-state $X^{1}A_{1}$ only. The comparison with the experiments given above indicates that the contribution from excited electronic states to $k_{rec,0}$ is at least one order of magnitude larger than that of the ground state. This contribution, therefore, in SO₂ exceeds by far the role of excited electronic states evaluated in ref 9 for the NO_2 and HNO_3 systems.

Since the excited electronic states of SO₂ are much less well-known than the ground state, it is not too easy to apply eq 9 and 10 to these states as well. In the following a tentative analysis is made on the basis of the available information. It should be emphasized that this analysis is very preliminary indeed and

TABLE III: Contribution of the Different Electronically Excited

state	$\frac{E_0 - T_0}{\text{kcal}}$ $\frac{1}{\text{mol}^{-1}}$	α/β	$\frac{k_{ m rec, \infty}}{10^{-11}}$ cm ³ molecule ⁻¹ s ⁻¹	$(k_{ m rec, \infty}Q_{ m el}^{-1}Q^{*}_{ m bend}^{-1})/$ 10 ⁻¹² cm ³ molecule ⁻¹ s ⁻¹
¹ A ₁	130.5	0.30 0.42 0.55	0.771 1.98 2.84	1.99 2.09 2.14
${}^{1}A_{2}$	50.6	0.30 0.42 0.55	0.786 1.40 2.21	1.67 1.64 1.64
³ A ₂	55.3	0.30 0.42 0.55	2.43 4.35 6.74	1.68 1.65 1.64
³ B ₂	55.3	0.30 0.42 0.55	1.92 3.62 6.26	1.60 1.63 1.63

^a $Q_{\rm el}$ is the SO₂ electronic partition function and $Q^{*}_{\rm bend}$ is the pseudopartition function of the disappearing bending mode.

TABLE IV:	Contribution	of the	Different	Electronically	Excited
States to km	. 0/[N2]			-	

state	$E_0 - T_0/\text{kcal} \\ \text{mol}^{-1}$	F _{rot}	$ ho_{vib,h}/\ (kcal\ mol^{-1})^{-1}$	$(k_{rec,0}^{SC}/[N_2])/$ 10 ⁻³¹ cm ⁶ molecule ⁻² s ⁻¹
¹ A ₁	130.5	34.4	479.2	1.95
${}^{1}A_{2}$	50.6	17.0	394.5	1.06
${}^{3}A_{2}$	55.3	16.8	467.4	3.85
${}^{3}B_{2}^{-}$	55.3	16.1	927.2	15.1

should be considered to be semiquantitative only. The SO_2 molecule, below the dissociation energy into ground state SO and O fragments, possesses^{35,39} the excited electronic states ${}^{1,3}B_1$, ${}^{1,3}B_2$, and $^{1,3}A_2$. These electronically excited states are mixed and coupled to highly vibrationally excited levels of the electronic ground state.^{35,40} Association of O and SO radicals, therefore, will populate a mixture of excited electronic states and the electronic ground state. Collisional stabilization in this mixture of electronic states will finally lead to an exclusive population of the electronic ground state at low energies. Temporary trapping of SO₂ molecules near the minima in excited electronic states, however, does not appear to be inconceivable.

We apply eq 9 and 10 to the states ${}^{1}A_{2}$, ${}^{3}A_{2}$, and ${}^{3}B_{2}$ which are correlated with the ground states of O and SO. The other states may contribute as well, in particular at the low-pressure limit where collisional stabilization is rate determining. However, we do not consider them here. For the ¹A₂ state, spectroscopic information is available.⁴¹ The ³B₂ states are believed to be close to the ³B₁ state (with $T_0 = 74.7$ kcal mol⁻¹),⁴² whereas information on the ³A₂ states is still controversial.⁴³⁻⁴⁵ We assume for simplicity that the ${}^{3}A_{2}$ and ${}^{3}B_{2}$ states are all located close to the energy $T_0 = 75.2$ kcal mol⁻¹. We use molecular parameters as given for the corresponding ${}^{1}A_{2}$ and ${}^{1}B_{2}$ states, see Appendix. It was assumed in our work that the electronically excited ${}^{3}B_{2}$ state has an asymmetric structure similar to the ${}^{1}B_{2}$ state (ref 52 and references cited). The individual values of $k_{rec,\infty}$ for the various excited electronic states depend most strongly on the ratio of the looseness parameters α and the Morse parameter β . We varied α over the "normal" range 0.7-1.3 Å⁻¹. From the stretching force

⁽³⁴⁾ A. Wallance Jones, J. Chem. Phys., 18, 1263 (1950).
(35) J. Heicklen, N. Kelly, and K. Partymiller, Rev. Chem. Intermed., 3, 315 (1980)

⁽³⁶⁾ K. Chung, J. G. Calvert, and J. W. Bottenheim, Int. J. Chem. Kinet., 7, 161 (1975).

⁽³⁷⁾ J. Troe, J. Chem. Phys., 75, 226 (1981).

⁽³⁸⁾ J. Troe, J. Chem. Phys. 66, 4752 (1977).

⁽³⁹⁾ F. C. James, J. A. Kerr, and J. P. Simons, Chem. Phys. Lett., 25, 431 (1974).

⁽⁴⁰⁾ H. Watanabe, S. Tsuchiya, and S. Koda, J. Phys. Chem., 87, 906 (1983).

 ⁽⁴¹⁾ Y. Hamada and A. J. Merer, Can. J. Phys., 52, 1443 (1974).
 (42) J. C. D. Brand, V. T. Jones, and C. di Lauro, J. Mol. Spectrosc., 45,

^{404 (1973).}

⁽⁴³⁾ L. H. Hillier and V. R. Saunders, Mol. Phys., 22, 193 (1971). G.
L. Bendazzoli and P. Palmieri, Int. J. Quantum Chem., 9, 537 (1975). P.
Phillips and E. R. Davidson, J. Comput. Chem., 4, 337 (1983).
(44) J. B. Snow, D. C. Hovde, and S. D. Colson, J. Chem. Phys., 76, 3956

^{(1982).}

⁽⁴⁵⁾ K. E. J. Hallin, Y. Hamada, and A. J. Merer, unpublished results cited in ref 35 and 44.

М	T^a	Z_{LJ}^{b}	$k_{\rm rec,0}/[{ m M}]^c$	$k_{\rm rec,0}^{\rm SC}/[{ m M}]^d$	β _c ^e	$k_{\rm rec,0}^{\rm SC}/[{\rm M}]({\rm cor})^{f}$	$\beta_{\rm c}({\rm cor})^{g}$	$-\langle \Delta E \rangle^h$
He	300	4.16	6.4	27.3	0.23	7.10	0.09	27
Ne	300	2.53	4.5	16.7	0.27	4.34	0.10	31
Ar	300	2.96	5.1	19.3	0.26	5.02	0.10	31
	3000	5.50	0.18	0.35	0.051	0.91	0.020	58
	4000	6.05	0.059	0.23	0.026	0.60	0.0098	38
	5000	6.53	0.031	0.16	0.019	0.42	0.0073	37
Kr	300	2.83	6.0	18.5	0.32	4.81	0.12	39
Xe	300	3.05	6.5	20.1	0.32	5.23	0.12	39
N_2	300	3.35	7.7	21.9	0.35	5.69	0.14	47
H_2	300	7.79	70	50.7	1.4	13.2	0.53	410
D_2	300	5.59	70	36.5	1.9	9.46	0.74	1100
CO ₂	300	3.69	42	24.3	1.7	6.32	0.66	740
CH₄	300	4.75	44	31.3	1.4	8.14	0.54	430
CF4	300	3.32	40	21.8	1.8	5.67	0.71	950
SF ₆	300	3.81	49	24.9	2.0	6.47	0.76	1250
$C_3 \check{F}_8$	300	4.22	62	28.3	2.2	7.29	0.85	2200

^{*a*} In K. ^{*b*} In 10⁻¹⁰ cm³ molecule⁻¹ s⁻¹. ^{*c*} In 10⁻³¹ cm⁶ molecule⁻² s⁻¹, experimental values. ^{*d*} In 10⁻³¹ cm⁶ molecule⁻² s⁻¹. ^{*c*} Apparent $\beta_c = k_{rec,0}/k_{rec,0}^{SC}$. ^{*f*} In 10⁻³⁰ cm⁶ molecule⁻² s⁻¹, corrected by multiplication with scaling factor 2.7. ^{*s*} $\beta_c(cor) = k_{rec,0}/k_{rec,0}^{SC}(cor)$. ^{*h*} In cm⁻¹.

constant in the ¹B₂ state of $f_{\rm RC} = 4.17$ mdyn Å⁻¹, for the ³B₂ state one estimates $\beta = 2.3$ Å⁻¹, similar to the value $\beta = 2.4$ Å⁻¹ obtained for the electronic ground state. Therefore, identical α/β values of 0.3–0.55 were tried for the different electronic states. Table III shows our resulting rate coefficients $k_{\rm rec,\infty}$ for the various electronic states involved. For equal α/β values, we nearly found

$$k_{\rm rec,\infty} \simeq g(k_{\rm rec,\infty})_{\rm X}$$
 (11)

where $(k_{\text{rec},\infty})_X$ is the contribution from the electronic ground states and g is the number of electronic states participating in the reaction. Changes of the effective α/β values for the different electronic states would lead to modifications of eq 11 such as indicated in Table III. With g = 8 and $\alpha/\beta \simeq 0.3$ corresponding to $\alpha \simeq 0.7$ Å⁻¹, the experimental value is reproduced.

The contribution of various excited electronic states to the low-pressure rate coefficient $k_{rec,0}$ can differ considerably from that to the high-pressure rate coefficient $k_{rec,w}$. Whereas different electronic multiplicities and partition functions Q^*_m of disappearing oscillators are predominantly responsible for different contributions of electronic states to $k_{rec,\infty}$, different rotational factors F_{rot} , densities of states $\rho_{\text{vib,h}}(E_0)$, and electronic multiplicities are of dominant importance in $k_{rec,0}$. Changes in α/β , unlike the influence on $k_{rec,\infty}$, are of negligible importance. Table IV shows the different factors in $k_{rec,0}$ for the considered electronic states. Apparently, the role of excited triplet states again is dominant. The derived $k_{rec,0}$ values are about one order of magnitude larger than for the ground-state alone. A comparison with the experimental results for the presumably "nearly strong" collider C₃F₈ leads to $\beta_c \simeq 2.2$. At present it does not appear possible to decide whether the additional factor of two to three, which is required to reconcile the analysis with the experiments, has to be sought in the properties of the considered electronic states or in the additional contribution from the other states which correlate with electronically excited fragments.

The present analysis of $k_{\rm rec,0}$ and $k_{\rm rec,\infty}$ has shown that the large number of low electronically excited states has a very pronounced effect on the recombination and dissociation rates of SO₂. We have estimated about one order of magnitude contributions. A more precise characterization would require a better knowledge of the properties of all excited states below the ground-state dissociation energy.

Energy-Transfer Properties from Collision Efficiencies β_c . Due to the complicated contribution of excited electronic states, the determination of collision efficiencies β_c from the absolute values of $k_{\text{rec},0}$ appears presently impossible. However, our present relative collision efficiency measurements for a variety of bath gases do allow us to obtain a fairly reliable estimate. we base the following analysis on the expression⁴⁶

$$\frac{\beta_{\rm c}}{1 - \beta_{\rm c}^{1/2}} \simeq \frac{-\langle \Delta E \rangle}{F_{\rm E} k T} \tag{12}$$

and assume⁴⁷ that $\beta_c \simeq 0.8$ for the strongest collider C_3F_8 . Equation 12 is exact for exponential collision models. It is nearly exact for other collision models.⁴⁶ The uncertainty in the strong collision limit produces an uncertainty in the derived $\langle \Delta E \rangle$ values such as given by eq 12, i.e., a 20% uncertainty in $k_{rec,0}^{SC}$ corresponds to the same uncertainty in the $\langle \Delta E \rangle$ values of weak colliders. Table V includes strong collision rate coefficients $k_{rec,0}^{SC}$ as calculated before, apparent collision efficiencies β_c based on this calculation, and collision efficiencies $\beta_c(cor)$ scaled down by a factor of 2.6 in order to force $\beta_c(M=C_3F_8)$ to a value of 0.85. The same scaling factor was applied to the SO₂ dissociation results from ref 13 which were converted into a recombination data via the equilibrium constants from ref 38. Using the same scaling factor assumes that only temperature-independent factors in $k_{rec,0}$, such as densities of states and multiplicities, should be modified in our treatment of excited electronic states.

For the bath gas Ar, within the estimated uncertainties of the experiments and the analysis of about a factor of 2, our measurements indicate a practically temperature-independent average energy transferred per collision of $\langle \Delta E \rangle \simeq -40$ cm⁻¹ in the range 300-5000 K. (Some weak temperature dependencies, of course, cannot be ruled out.) This result does agree with our recent direct measurements for excited toluene,⁴⁸ CS₂, and SO₂³ which were, however, restricted to much narrower temperature ranges.

The derived absolute values of $\langle \Delta E \rangle$ at room temperature for the inefficient colliders correspond well to our recent direct measurements after laser excitation.^{3,4} For the present system, the marked changes in β_c and $\langle \Delta E \rangle$ values in the series of monatomic, diatomic, and polyatomic bath gases are worth noticing. Also, the efficiencies of H₂ and D₂ compared to the bath gas N₂ are surprisingly large. Since O + H₂ and SO + H₂ are slow reactions under our conditions we cannot explain this effect by side reactions. A more detailed comparison of the present indirect determinations of $\langle \Delta E \rangle$ and the direct measurements after laser excitation will be given in ref 3 and 4.

Acknowledgment. Financial support of this work by the Deutsche Forschungsgemeinschaft (SFB 93 "Potochemie mit Lasern") is gratefully acknowledged. C.J.C. thanks the Consejo Nacional de Investigaciones Científicas Y Técnicas de la República Argentina for a foreign exchange fellowship. exchange fellowship.

Appendix. Molecular Parameters

The vibrational frequencies employed in the calculations are as follows:

 $SO_2(^1A_1)$: 1151.4, 517.7, and 1361.8 cm^{-1.49}

⁽⁴⁶⁾ J. Troe, J. Chem. Phys., 66, 4745 (1977).

⁽⁴⁷⁾ H. Hippler, C. Schippert, and J. Troe, Int. J. Chem. Kinet., Symp. No. 1, 27 (1975).

⁽⁴⁸⁾ H. Hippler, J. Troe, and H. S. Wendelken, J. Chem. Phys., 78, 6709 (1983).

 $SO_2(^1A_2)$: 800, 300,⁵⁰ and 600 cm⁻¹ (estimated as in ref 51). $SO_2(^{3}A_2)$: 800, 300, and 600 cm⁻¹, transferred from the $^{1}A_2$ state. $SO_2({}^{3}B_2)$: the frequencies for this electronic state were taken to be similar to those corresponding to the asymmetric ${}^{1}B_{2}$ state (960, 377, and 211 cm^{-1.52}

SO: 1148.2 cm^{-1.53}

The following values were used for the rotational constants: $SO_2({}^1A_1)$: A = 2.0274, B = 0.3442, and C = 0.2935 cm^{-1.54} $SO_2(^1A_2)$: the values A = 1.0660, B = 0.3892, and C = 0.2851cm⁻¹ were calculated with the structural parameters of ref 41. $SO_2(^{3}A_2)$: A = 0.9978, B = 0.3909, and C = 0.2809 cm⁻¹, calculated with the molecular parameters given in ref 45. $SO_2({}^{3}B_2)$: A = 1.1579, B = 0.3422, and C = 0.2641 cm⁻¹, cal-

culated with the molecular parameters given in ref 52.

Phys., 76, 4893 (1982).
(52) A. R. Hoy and J. C. D. Brand, Mol. Phys., 36, 1409 (1978).
(53) M. W. Chase, Jr., J. L. Curnutt, J. R. Downey, Jr., R. A. McDonald,
A. W. Syverud, and E. A. Valenzuela, J. Phys. Chem. Ref. Data, 11, 695 (1982).

(54) A. Barbe, C. Secroum, P. Jouve, B. Duterage, N. Monnantevil, J. Bellet, and G. Steenbeckeliers, J. Mol. Spectrosc., 55, 319 (1975).

SO: $B = 0.72082 \text{ cm}^{-1}.^{53}$

The bond energy at 0 K for the ground state of SO_2 was calculated from the enthalpies of formation of SO,53 O,53 and SO_2 ⁴⁹ $\Delta H^{\circ}_0 = 130.5$ kcal mol⁻¹. The excitation energies of the electronically excited states used are $T_0({}^1A_2) = 79.9$ kcal mol⁻¹⁴¹ and $T_0({}^3A_2) = T_0({}^3B_2) = 75.2$ kcal mol^{-1,44,45} For the ground electronic state the Morse parameter $\beta = 2.4 \text{ Å}^{-1}$ was calculated with the force constant of the dissociating bond, $f_{\rm RC}$, = 10.34 mdyn Å^{-1,55} Similar β values were used for the electronically excited states (see text).

The same Lennard-Jones parameters $\sigma = 4.1$ Å and $\epsilon/k =$ $328.5k^{56}$ were employed for all electronic states of SO₂. For the bath gases, the Lennard-Jones parameters given in ref 48 were used, and the corresponding collision frequencies were calculated by means of reduced collision integrals.48,57

Registry No. SO₂, 7446-09-5; SO, 13827-32-2; O, 17778-80-2; He, 7440-59-7; Ne, 7440-01-9; Ar, 7440-37-1; Kr, 7439-90-9; Xe, 7440-63-3; H₂, 1333-74-0; D₂, 7782-39-0; N₂, 7727-37-9; CO₂, 124-38-9; CH₄, 74-82-8; CF₄, 75-73-0; SF₆, 2551-62-4; C₃F₈, 76-19-7.

One-Electron Redox Reactions Involving Sulfite Ions and Aromatic Amines

P. Neta and Robert E. Huie*

Chemical Kinetics Division, Center for Chemical Physics, National Bureau of Standards, Gaithersburg, Maryland 20899 (Received: November 5, 1984)

The one-electron oxidation of aromatic amines by the SO_3^- radical and of sulfite and bisulfite ions by aromatic amine radical cations has been investigated. p-Phenylenediamine (PDA) and N,N,N',N'-tetramethyl-p-phenylenediamine (TMPD) were oxidized by SO_3^- with rate constants of 5.0×10^7 and 5.2×10^8 M⁻¹ s⁻¹, respectively, in basic solutions. Protonation of the amine reduced the rates considerably ($k = 4.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for PDA at pH 5.25; $k = 8.2 \times 10^6 \text{ M}^{-1} \text{ s}^{-1}$ for TMPD at pH 4.5). With aniline and N,N-dimethylaniline (DMA), the reverse reaction was observed. DMA⁺ radical reacted with $SO_3^{2^-}$ with $k = 9.9 \times 10^8$ M⁻¹ s⁻¹ and with HSO_3⁻ with $k < 5 \times 10^5$ M⁻¹ s⁻¹. Aniline radical cation also oxidized SO₃²⁻ rapidly ($k = 4 \times 10^9$ M⁻¹ s⁻¹) and HSO₃⁻ less rapidly ($k = 4.8 \times 10^6$ M⁻¹ s⁻¹). The aniline neutral radical reacted too slowly to be measured with either. A secondary product was observed in acid solution of TMPD with an absorption maximum at 455 nm. This was ascribed to a reaction between the SO_3^- and TMPD⁺ radicals.

In earlier publications from this laboratory, we have reported rate constants for the reactions of sulfite radicals and peroxysulfate radicals produced by the pulse radiolysis of aqueous sulfite and sulfite/oxygen solutions.^{1,2} In addition, some rate constants for the oxidation of sulfite and bisulfite by free radicals were reported. We have now extended this work to reactions involving aromatic amines.

The oxidation of aromatic amines by radicals produced by pulse radiolysis in water has been reported.³⁻⁵ The hydroxyl radical adds to the aromatic ring, and the adduct, in a few microseconds, dissociates to give the radical cation.^{3,4} The sulfate radical, SO_4^{-1} , reacts by direct electron transfer to give the radical cation. Hexacyanoferrate(III) has been used to oxidize many aromatic amines to their cation radicals.⁶ Equilibrium constants have been derived for the radical formation from several aromatic diamines

and diimines which, coupled with the two-electron redox potential, give one-electron potentials for the diamines.⁷ These potentials have been found to correlate with the rate of photographic development of silver halides by several *p*-phenylenediamines in the presence of sulfite.8

This study has been prompted also by a desire to understand the autoxidation of SO_2 in aqueous solution, including the effects of added organic compounds and the possible chemical transformation of these organic compounds during autoxidation. SO₃⁻ and SO_5 are key radicals in the autoxidation of SO_2 , and their chemistry must be understood before SO₂ autoxidation is understood.

In this paper we report rate constants for the oxidation of aromatic amines by SO3⁻ and SO5⁻, rate constants for the oxidation of sulfite and bisulfite by aromatic amine radicals, and evidence for a reaction between the sulfite radical and an amine radical cation. In addition, the reaction of NH_2 with sulfite has

⁽⁴⁹⁾ JANAF Thermochemical Tables, Natl. Stand. Ref. Data Ser., Natl. Bur. Stand., No 37 (1971).
 (50) R. J. Shaw, J. E. Kent, and M. F. O'Dwyer, J. Mol. Spectrosc., 82,

^{1 (1980).}

⁽⁵¹⁾ S. Kimel, D. Feldmann, J. Laukemper, and K. H. Welge, J. Chem.

⁽⁵⁵⁾ S. Saito, J. Mol. Spectrosc., 30, 1 (1969).

⁽⁵⁶⁾ F. M. Mourits and F. H. A. Rummens, Can. J. Chem., 55, 3007 (1977).

⁽⁵⁷⁾ R. C. Reid, J. M. Prausnitz, and T. K. Sherwood, "The Properties of Gases and Liquids", 3rd ed, McGraw-Hill, New York, 1977.

Huie, R. E.; Neta, P. Chem.-Biol. Interact., in press.
 Huie, R. E.; Neta, P. J. Phys. Chem. 1984, 88, 5665.
 Rao, P. S.; Hayon, E. J. Phys. Chem. 1975, 79, 1063.
 Holcman, J.; Sehested, K. J. Phys. Chem. 1977, 81, 1963.

⁽⁵⁾ Steenken, S.; Neta, P. J. Phys. Chem. 1982, 86, 3661.

⁽⁶⁾ Corbett, J. F. J. Chem. Soc. B 1969, 207.

 ⁽⁷⁾ Tong, L. K. J.; Glesmann, M. C. Photogr. Sci. Eng. 1964, 8, 319.
 (8) Tong, L. K. J.; Bishop, C. A.; Glesmann, M. C. Photogr. Sci. Eng. 1964, 8, 326.