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Kinetic Study by EPR of the Production and Decay of $SO(^1\Delta)$ in the Reaction of $O_2(^1\Delta_g)$ with $SO(^3\Sigma^-)$

W. H. BRECKENRIDGE* AND TERRY A. MILLER

Bell Telephone Laboratories, Incorporated, Murray Hill, New Jersey 07974

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The existence of the reaction of $O_2(^1\Delta_g)$ with ground-state $SO(^3\Sigma^-)$ to produce $SO(^1\Delta)$ and ground-state $O_2(^3\Sigma_g^-)$ has been confirmed using a fast-flow system and electron paramagnetic resonance detection of all four species. A kinetic study of this reaction has resulted in the determination of the absolute value of the rate constant: $(2.12\pm0.22\times10^8)$ liter mole$^{-1}\cdot$sec.$^{-1}$ The reaction is therefore faster, by an order of magnitude, than any quenching process by a neutral species yet reported for $O_2(^1\Delta_g)$ in the gas phase, reaction or deactivation. The rapid rate is in rough accord with predictions derived from observations of similar *atomic* processes by other workers, indicating that the reactive process probably involves simple spin-allowed transfer of electronic energy in which a resonance situation is approximated. The mechanism for the decay of the $SO(^1\Delta)$ produced in the reaction has also been determined. It is shown that $SO(^1\Delta)$ is heterogeneously deactivated to $SO(^3\Sigma^-)$ at the reaction vessel walls with an efficiency about four orders of magnitude greater than that observed for deactivation of $O_2(^1\Delta_g)$ to $O_2(^3\Sigma_g^-)$. Such a high wall deactivation efficiency may explain the spectroscopic observations by other workers of $SO(^3\Sigma^-)$ but not the expected $SO(^1\Delta)$ in the pyrolysis products of ethylene episulfoxide.

I. INTRODUCTION

The reactivity of the first electronically excited state of oxygen, $O_2(^1\Delta_g)$, has recently come under scrutiny for a variety of reasons. For example, reactions of this particular low-lying level of O_2 are implicated in many organic oxidations,[1] in upper atmosphere[2] and air pollution[3] chemistry, and in biological processes.[4] Kinetic measurements of reaction and physical deactivation of $O_2(^1\Delta_g)$ have been obtained by several techniques.[5] One of the later and more promising of these is the use of electron paramagnetic resonance for detection of $O_2(^1\Delta_g)$ in a fast-flow system.[6,7]

It has been postulated[8] that electronically excited $SO(^1\Delta)$, observed by EPR when the products of a microwave discharge in oxygen are mixed with carbonyl sulfide, is produced by the novel direct reaction of $O_2(^1\Delta_g)$ with ground-state $SO(^3\Sigma^-)$ to yield ground-state $O_2(^3\Sigma_g^-)$ and $SO(^1\Delta)$. This reaction provides an ideal candidate for quantitative kinetic study by electron paramagnetic resonance in that all four species can be detected by EPR. There is also reason to believe that the rate of the reaction is unusually high compared to the rates of most reactions of $O_2(^1\Delta_g)$.

The reaction is formally similar both to electronic energy-transfer processes of atoms[9] and to the well-known spin-exchange reactions of electronically excited, complex organic molecules.[10–12] It is of interest, then, to see if the reaction, which involves only simple diatomic species of low energy, can be understood in terms of the current conceptions of these two rather different types of processes. The hope was entertained that such knowledge might increase our general understanding of the important phenomenon of electronic energy transfer.

In this work we have confirmed the existence of the proposed reaction and present here the results of EPR experiments which have resulted in the determination of the rate constant. We have also determined the mechanism of quenching of $SO(^1\Delta)$ and measured its rate.

II. EXPERIMENTAL

The method of measurement of rates of chemical reactions using fast-flow techniques with EPR detection has become common enough[6,13,14] that we need describe the apparatus only briefly, with emphasis on those aspects of our equipment and procedures which differ from that reported by others. In essence, the method depends on the measurement, by EPR, of the concentration of a reactant as a function of the distance (and thus, at constant velocity, the time) over which the reactant has been in contact with a reactive gas in the flow tube. Conditions whereby the concentration of reactive gas is approximately constant are usually employed so that the measured decay is pseudo-first-order.

The basic flow apparatus is shown in Fig. 1. The flow tube was quartz, 22-mm i.d.; the quartz section of the tube surrounded by the EPR cavity was 36-mm i.d. A tight-fitting Teflon sleeve could be inserted into the main flow tube to cover the working region surface just to the edge of the cavity. The movable injector tube (quartz, 10-mm i.d.) was coated with a thin layer of inert grease (Halocarbon Products Corporation) to facilitate easy movement through the O-rings. The mixing inlet consisted of 10 evenly spaced 0.5-mm holes in the end of the injector. Volume flow rates of gases were controlled by means of precision needle valves and measured by timing the filling of a calibrated volume connected to a halocarbon oil manometer (Halocarbon Products Corporation, oil No. 13–21). Total pressure in the flow tube was measured with an identical manometer connected near the cavity or a calibrated Texas Instruments precision pressure gauge.

The rf discharge region shown in Fig. 1 consisted of two external Al foil electrodes and an HgO film

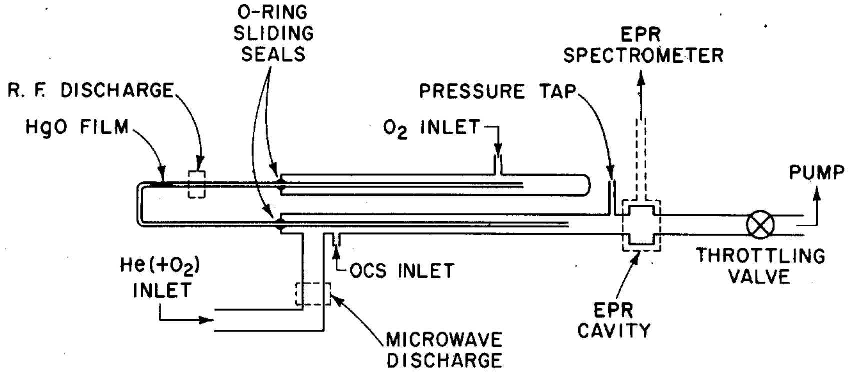

FIG. 1. Schematic diagram of experimental apparatus.

downstream which was heated to remove oxygen atoms efficiently. The injector U-tube was securely fastened to a mount which moved smoothly along parallel tracks, and it was shown that the position of the injector could be changed without disturbing the efficiency of the discharge for producing $O_2(^1\Delta_g)$.

Oxygen atoms were produced by passing helium containing small amounts of oxygen ($\sim$1%) through the microwave discharge operated at low power. The extremely small amounts of $O_2(^1\Delta_g)$ produced by this procedure were negligible compared to the $O_2(^1\Delta_g)$ produced by the rf discharge with pure O_2 flowing through the injector. Excess carbonyl sulfide could be added downstream of the microwave discharge to produce $SO(^3\Sigma^-)$ by the well-known reaction,[15]

$$O(^3P)+OCS\rightarrow CO+SO(^3\Sigma^-). \qquad (1)$$

It was possible, therefore, to vary continuously the point at which a stream containing only $O_2(^1\Delta_g)$ ($\sim$5%) and $O_2(^3\Sigma_g^-)$ was added to the main flow, which contained small amounts of $SO(^3\Sigma^-)$ in helium.

The EPR spectrometer used in these studies has been described previously.[16] The Varian V-4535 large sample access cavity operated in the TE_{01n} mode. The transition $J=1$, $K=1\rightarrow 2$, $M=0\rightarrow -1$ was used for the measurement of $SO(^3\Sigma^-)$. The absolute concentration of $SO(^3\Sigma^-)$ was determined by calibrating the magnitude of the EPR signal using two separate methods:

(i) Titration of SO by NO_2,[17]

(ii) Comparison with the magnitude of an EPR signal from known pressures of NO, using the calculated theoretical intensity ratio for the two transitions.[18]

The two methods were in excellent agreement, and the average of the two values was taken as the final calibration factor. Detection of $SO(^1\Delta)$ was carried out using the $J=2$, $M=-1\rightarrow 0$ transition. The concentration of $SO(^1\Delta)$ was calculated from the observed signal strength and the theoretical ratio of intensity to the calibrated SO transition. See Appendix I for the details of the theoretical calculations. The species $SO(^1\Delta)$ and $SO(^3\Sigma^-)$ were always measured under exactly the same experimental conditions.

$O_2(^1\Delta)$ was monitored by means of the $J=2$, $M=-1\rightarrow 0$ transition. The EPR signal strength was calibrated by observing the difference in signal height of a strong $O_2(^3\Sigma_g^-)$ EPR line when the rf discharge was on and off, assuming all of the missing $O_2(^3\Sigma_g^-)$ to be converted to $O_2(^1\Delta_g)$. This procedure has been shown by other workers to be satisfactory.[6,7]

Matheson Company helium (uhp), oxygen (uhp), sulfur dioxide (anhydrous), nitric oxide (technical), nitrogen dioxide, and carbon monoxide (C.P.) were used without further purification. Carbonyl sulfide (Matheson) and carbon disulfide (Baker Analyzed Reagent) were freeze pumped several times before use.

Before the main study was initiated the rate of Reaction (1) was measured because of its relevance to the projected experiments and because the determination allowed some estimate of the accuracy and reliability of the apparatus. The procedure used was quite similar to that of Westenberg and De Hass.[15] Our value for the rate constant at 297°K, $k_1=(7.2\pm 0.4)\times 10^6$ liter mole$^{-1}\cdot$sec^{-1}, is within the range of values (20% variation) reported in four other separate studies.[15,19]

III. RESULTS

A. General Observations

The experiments indicate that when $^1O_2$ in O_2 is added by means of the injector to the main flow of helium containing SO, the concentration of $^1O_2$ decreases regularly as the position of $^1O_2$ injection (distance Z) from the EPR cavity is increased, but the concentration of SO remains approximately constant. [For convenience, $O_2(^1\Delta_g)$ and $SO(^1\Delta)$ are hereafter in the text designated $^1O_2$ and ^1SO, respectively, while $O_2(^3\Sigma_g^-)$ and $SO(^3\Sigma^-)$ are designated simply O_2 and SO.] As $^1O_2$ decreases, an increase in ground-state O_2 concentration is observed, showing that the major process responsible for the decay of $^1O_2$ involves net deactivation and not chemical consumption of $^1O_2$. The presence of ^1SO is also detected when and only when the $^1O_2$

is added to the SO–helium stream. Surprisingly, the magnitude of the observed ^1SO signal appears to *decrease* in approximately the same fashion as the $^1O_2$ signal as the distance Z is increased. Careful measurements showed that at a fixed total pressure the ^1SO concentration is proportional to the product of the concentrations of $^1O_2$ and SO.

The decay of $^1O_2$ was first order, and the rate of the $^1O_2$ quenching was directly proportional to the concentration of SO (see Fig. 2 for typical rate plots). These are precisely the conditions expected for pseudo-first-order decay of $^1O_2$ in the presence of a sufficient excess of quenching agent. However, the concentration of SO was always at least 4 times *less* than that of $^1O_2$.

B. Proposed Mechanism

We believe the following mechanism best accounts for our results and will present quantitative evidence which supports this contention:

$$O_2(^1\Delta_g)+SO(^3\Sigma^-)\xrightarrow{k_2}O_2(^3\Sigma_g^-)+SO(^1\Delta), \qquad (2)$$

$$SO(^1\Delta)\xrightarrow{k_3}SO(^3\Sigma^-), \qquad (3)$$

where Reaction (3) represents an apparent first-order deactivation of ^1SO which is fast compared to Reaction (2) ($k_3 \gg k_2[^1O_2]$). The mechanism implies that for any fixed point along the flow tube (i.e., at any time after an initial transient), steady-state conditions would dictate the concentrations fo ^1SO and SO:

$$-d[SO]/dt=d[^1SO]/dt=0=k_2[SO][^1O_2]-k_3[^1SO], \qquad (A)$$

$$[^1SO]=k_2[SO][^1O_2]/k_3, \qquad (B)$$

$$F=k_2/k_3=[^1SO]/[SO][^1O_2]. \qquad (C)$$

As long as the flow velocity is sufficiently high, so that there is no appreciable decay of $^1O_2$ over the detection region (~2.5 cm), the relation (C) should be satisfied for all the measurements made at the detection cavity, irrespective of injector distance Z or the flow velocity (for the velocities used here.) The constancy of F over the distance Z was confirmed in 20 kinetic experiments in which the variation of F with Z was of the order of 5% only, even when the concentration of $^1O_2$ varied with Z by a factor of greater than 2. Evidence that Eq. (C) is satisfied over wide ranges of $^1O_2$ and SO concentrations (and flow velocities) is shown in Figs. 3 and 4. The slopes of the two plots are identical, as predicted by Eq. (C).

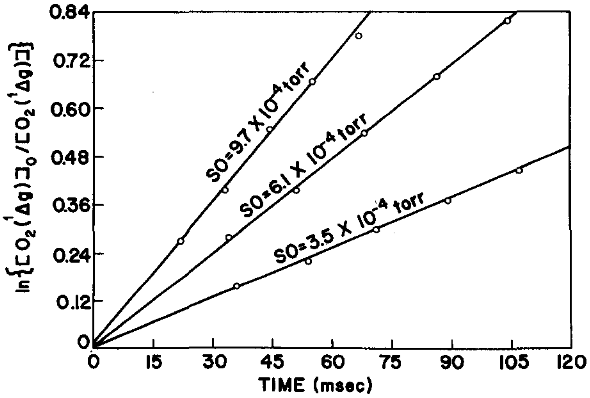

FIG. 2. Typical plots of first-order decay of $O_2(^1\Delta_g)$ in the presence of $SO(^3\Sigma^-)$. The ordinates were normalized in the standard fashion[6,13] to injector position $Z=0$.

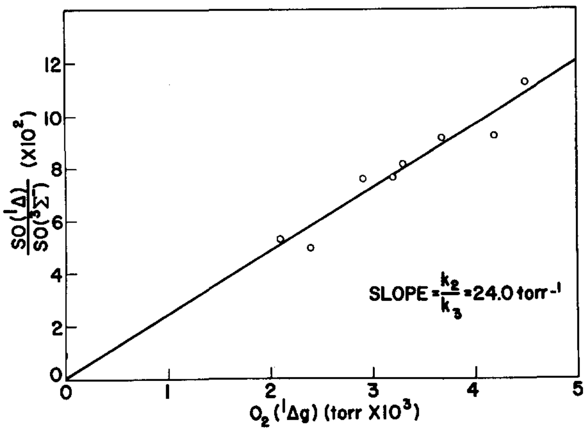

FIG. 3. plot of $SO(^1\Delta)/SO(^3\Sigma^-)$ vs $O_2(^1\Delta_g)$. Total pressure is 0.45±0.03 torr. Flow velocities varied from 300 to 750 cm/sec.

The postulated mechanism is consistent with the observations and allows an adequate explanation of the somewhat unusual conditions whereby the decay of one reactant in a bimolecular reaction is pseudo-first-order even though the decaying reactant is in large excess over the other reaction partner. The existence of Reaction (2) has therefore been confirmed. The probable identity of Reaction (3) will be discussed below. This has no important bearing on the determination of k_2, however, and it is convenient at this point to discuss the kinetic measurements in detail.

C. Kinetic Measurements

For each experiment the concentrations of $^1O_2$, SO, and ^1SO were measured as a function of Z with both discharges operating. The concentration of $^1O_2$ was then determined as a function of Z with the microwave discharge off, in order to correct for any deactivation of $^1O_2$ on the walls or by OCS. The correction was negligible except for conditions of low flow rate and low concentration of SO, where decay due to wall deactivation became a nonnegligible part of the total decay rate (but always less than 10% of the total rate). In separate experiments, it was shown that the rates of deactivation of $^1O_2$ by OCS, CO, or SO_2 [possibly formed in small amounts by reaction of

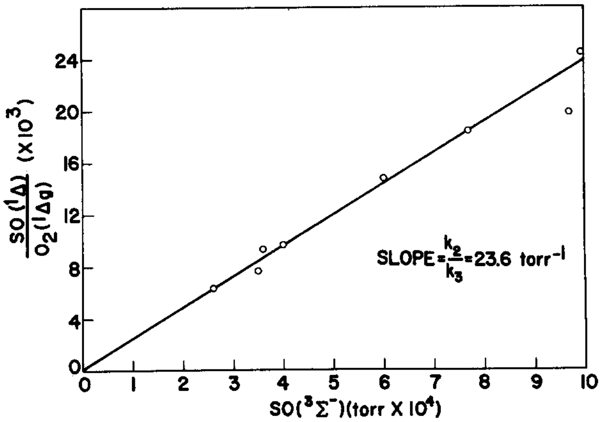

FIG. 4. A plot of $SO(^1\Delta)/O_2(^1\Delta_g)$ vs $SO(^3\Sigma^-)$. Total pressure 0.45±0.03 torr. Flow velocities varied from 300 to 750 cm/sec.

$O(^3P)$ with SO] were negligible for all conditions employed. Upper limits for the rate constants are shown in Table I. There were sometimes slight variations with Z of the measured SO concentrations. The variations were usually less than 10%, however, and the concentration of SO used in calculating k_2 for each experiment was taken as the average of the values determined over Z.

Examples of $^1O_2$ decay plots are shown in Fig. 2. A collection of rate constant data determined over a wide range of conditions is shown in Table II. Corrections due to back diffusion and viscous pressure drop, each estimated[20] to be only 2%–6%, were ignored because of the approximate cancelling tendency of the two effects under these particular conditions. Within the observed experimental error, there was no difference in the average values of k_2 determined with and without the Teflon sleeve in place in the reaction tube. The reported value is therefore,

$$k_2=(2.12\pm0.22)\times10^8 \text{ liter mole}^{-1}\cdot\text{sec}^{-1} \ (297°\text{K}),$$

where the uncertainty is the rms deviation from the mean of the values in Table II.

Because of the complexity of producing two unstable molecules and measuring their reaction rate, we were particularly concerned about the avoidance of systematic errors in the determination of k_2. The most likely error would result from the fact that SO is produced and measured at fixed points, so that there could have been appreciable gradients in the SO concentration along the flow tube. A *large* gradient is obviously ruled out by the linearity of the decay plots.

Auxiliary experiments and other considerations lead us to believe that *any* gradient is probably negligible. There are two main possible conditions which could produce gradients. (i) The reaction of $O(^3P)$ with OCS is not brought sufficiently to completion at the outer injector positions. The procedure followed, however, was to add OCS until the $O(^3P)$ concentration measured at the cavity was decreased to a level which would require that >95% of the oxygen atoms be converted to SO at the injector point at greatest distance from the detection region. (ii) The second possibility is that the concentration of SO was being depleted down the flow tube by some chemical reaction. An experiment was performed in which SO was made by passing a small amount of SO_2 diluted with helium through the rf discharge. A flow of oxygen in the main flow tube was controlled so that the He/O_2 mixture beyond the injector point was at approximately the same total pressure and composition as that of the kinetic measurements. The decay of SO observed at the cavity, with maximum variation of the injector distance and a flow rate smaller than any used in the later experiments, was less than 10%. This indicated that the following reactions were occurring to a negligible extent:

$$SO+O_2\xrightarrow{k_4}SO_2+O(^3P), \tag{4}$$

$$SO+SO\xrightarrow{k_5}SO_2+S(^3P). \tag{5}$$

Upper limits for the rate constants, shown in Table I, are consistent with those determined by Halstead and Thrush.[21] Also observations by Westenberg and De Haas[15] show that there is no decay of SO under comparable conditions of reaction time and excess OCS.

As a further check on the possibility of systematic error, semiquantitative measurements of k_2 were made under different conditions with SO obtained from different sources. These other reaction conditions were not as convenient or as dependable as the method used for the more accurate measurements, but independent measures of k_2 were provided. In one set of experiments, SO produced in the SO_2/He discharge described above was added through the injector to discharged oxygen containing $^1O_2$ (in the main flow tube). The variation of $^1O_2$ with injector distance

TABLE I. Values and upper limits of rate constants for various reactions measured in this work.

Reaction	Rate constant (liter mole⁻¹·sec⁻¹)
$O(^3P)+OCS\rightarrow CO+SO(^3\Sigma^-)$	$(7.2\pm0.4)\times10^6$
$O_2(^1\Delta_g)+OCS\rightarrow$quenching	$<2\times10^5$
$O_2(^1\Delta_g)+CO\rightarrow$quenching	$<2\times10^5$
$O_2(^1\Delta_g)+SO_2\rightarrow$quenching	$<1\times10^6$
$SO+O_2\rightarrow SO_2+O(^3P)$	$<5\times10^4$
$SO+SO\rightarrow SO_2+S(^3P)$	$<3\times10^7$

led to a value of $k_2 = (1.5\times 0.8)\times 10^8$ liter mole^{-1}·sec^{-1}. In another series of measurements, either CS_2 or OCS was added through the injector to discharged oxygen containing $^1O_2$ and large amounts of $O(^3P)$. By estimating the SO concentration profile as a function of injector distance it was possible to calculate k_2 from the $^1O_2$ decay: $k_2 = (1.8\pm 0.8)\times 10^8$ liter mole^{-1}·sec^{-1}.

D. Identification of Reaction (3)

Reaction (3) must be a fast reaction under the conditions of our measurements which efficiently converts ^{1}SO to SO. Perhaps the most obvious reaction is a collisional deactivation process involving one of the gases present. Deactivation by O_2 is ruled out because the O_2 pressure could be varied by a factor of greater than 2 without any marked effect on the quantity F, defined in the relation (C). Deactivation by SO, $^1O_2$, or ^{1}SO itself can also be eliminated by the very constancy of F. Because any CO present should be approximately proportional to the amount of SO, deactivation by CO is also considered unlikely. The OCS concentration probably varied by at least a factor of 2 over the course of these experiments, so that deactivation by OCS, or for that matter any impurity in the OCS, is not the process responsible. Deactivation by He should be slow and certainly not faster than deactivation by O_2, and no decrease in F was noted when the pressure of helium was doubled. Therefore, homogeneous deactivation of ^{1}SO is apparently *not* the process which produces the fast rate of Reaction (3).

TABLE II. Summary of measurements of the rate constant k_2 at 297°K for the reaction: $O_2(^1\Delta_g)+SO(^3\Sigma^-)\rightarrow O_2(^3\Sigma_g^-)+SO(^1\Delta)$.

Flow tube surface	Pressure (torr)	Velocity (cm/sec)	[SO] (torr)	k_2 (liter mole^{-1}·sec^{-1})
Quartz	0.44	350	6.4×10^{-4}	2.21×10^8
Teflon	0.34	580	7.3	1.98
Teflon	0.34	720	3.8	2.08
Teflon	0.41	300	6.9	2.37
Quartz	0.45	540	10.2	2.07
Teflon	0.33	570	3.9	1.77
Teflon	0.70	450	7.8	2.26
Quartz	0.44	450	8.1	1.91
Quartz	0.44	370	4.2	1.98
Teflon	0.45	390	2.7	2.23
Teflon	0.38	330	3.8	2.33
Quartz	0.75	400	7.4	2.22
Teflon	0.46	390	10.2	2.49
Teflon	0.46	340	3.7	1.96
Quartz	0.45	540	10.5	1.78
Teflon	0.39	750	10.2	2.43
Teflon	0.33	580	8.8	1.79
Quartz	0.44	360	6.2	2.25
			Av	$(2.12\times 0.22)\times 10^8$

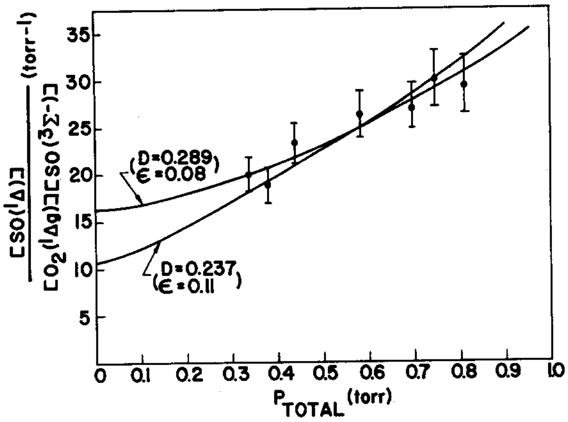

FIG. 5. Variation of $F=[SO(^1\Delta)][O_2(^1\Delta_g)]^{-1}[SO(^3\Sigma^-)]^{-1}$ with total pressure. The error bars represent the variation of several determinations at each pressure. The two solid lines were calculated using the Semenov equations[30] and values of D which were 10% higher and 10% lower than the value of D obtained by the methods of Appendix II. The values of ϵ were selected so that predicted values of F at the midpoint of the pressure variation, 0.58 torr, were approximately equal to the median value of F over this pressure range.

Radiative decay of SO($^1\Delta$) at a rate fast enough to satisfy the requirements for Reaction (3) would imply a radiative lifetime for SO($^1\Delta$) of less than 2×10^{-3} sec ($\approx 1/k_3$). Although the comparable $^1\Delta_g$ state of O_2 has a radiative lifetime of $\approx 3\times 10^{+3}$ sec,[22] a sufficiently short radiative lifetime for SO($^1\Delta$) is not entirely impossible. In O_2, electric dipole transitions between the $^1\Delta_g$ (and $^1\Sigma_g^+$) and $^3\Sigma_g^-$ states are forbidden because of nuclear exchange symmetry. The transition is therefore via a magnetic dipole mechanism which also requires a perturbation (presumably spin–orbit coupling) that mixes π states into the wavefunctions.[23] In SO the nuclear exchange symmetry is absent and electric dipole transitions are allowed, assuming again that mixing of π states occurs. The admixture of π states is likely enhanced, though not greatly, by the heavier sulfur atom is SO. These combined effects probably reduce the radiative lifetime of SO($^1\Delta$) compared to $O_2(^1\Delta_g)$ by something like 10^4–10^5,[24] giving a lifetime of the order of 0.03–0.3 sec. As the estimate depends critically on unknown mixing coefficients and transition moments, we readily admit its possible inaccuracy.

However, the radiative lifetime of the $^1\Sigma^+$ state of NF, which is isoelectronic with O_2 but not homonuclear, has reacently been measured.[25] The same sort of enhancement of this transition (save the heavy-atom effect which probably accounts for less than a factor of 10) relative to the transition in the homonuclear O_2 would be expected. The reported radiative lifetime of NF($^1\Sigma^+$) is 0.16 sec. The radiation from the $^1\Delta$ state of NF was seen but no lifetime reported.[25] Presumably the $^1\Delta$ state is longer lived because of its lower transition frequency. Assuming the frequency

TABLE III. Measurements of $F\{[SO(^1\Delta)][O_2(^1\Delta_g)]^{-1}[SO(^3\Sigma^-)]^{-1}\}$ for flow tube sections (in the EPR cavity) of different surface-to-volume ratios. The factors F_{36} and F_{22} (the values of F measured in tubes of 36- and 22-mm i.d.) are, respectively: 16.1 ± 0.9 and 9.2 ± 0.6, in units of torr^{-1}. Total pressure was 0.41 torr. The theoretical value of F_{36}/F_{22} for (*c*) was calculated using the equations of Semenov[a] to estimate the effect of partial diffusional control. The uncertainty in this estimate represents an assumed 10% uncertainty in both the calculated diffusion coefficient and the measured value of k_2

	F_{36}/F_{22}
Predicted	
(a) For radiative decay	1.00
(b) From ratio of diameters only	1.64
(c) Entry *b* corrected for diffusion considerations	1.95 ± 0.15
Experimental	1.75 ± 0.15

[a] N. N. Semenoff, Acta Physicochim. URSS **18**, 93 (1943).

factor and heavy-atom effect roughly cancel[26] for $SO(^1\Delta)$, we would obtain by extrapolation of the NF data a lifetime for $SO(^1\Delta)$ in the range suggested above by purely theoretical considerations. Thus it does not appear that radiative decay of $SO(^1\Delta)$ is fast enough to account for the observed reaction (3).

Nevertheless we searched for emission in the reaction zone using a PbS detector and filter with maximum sensitivity in the 10 000–20 000-Å region. In no case was any emission found which coincided with the production and decay of $SO(^1\Delta)$, though emission was observed from what we believe to be the long-wavelength tail[27] of the SO_2 afterglow produced in the $O(^3P)$–OCS reaction zone. It is probable that emission from $SO(^1\Delta)$ would have been observed if the radiative half-life were really less than 2×10^{-3} sec.[28]

The only obvious possibility remaining for Reaction (3) is heterogeneous deactivation of ^1SO at the walls of the detection section of the flow tube. Elementary considerations show that the wall deactivation efficiency ϵ would have to be greater than 0.01 to account for the observed ^1SO concentrations. It can be shown, using estimates of the diffusion coefficient of a trace of ^1SO in a 50% He/O_2 mixture (see Appendix II), that the conditions in the detection section of the flow tube at a total pressure of 0.5 torr are intermediate between the "kinetic" and "diffusion-controlled" cases of wall reactions.[29] Therefore, in this pressure region the quantity F should show some positive dependence on total pressure, an effect which is in fact observed.

The solutions of the differential equations which describe the general case of a wall reaction in a cylindrical vessel have been given by Semenov.[30] The mathematical treatment involves Bessel functions and is complex, but results suitable for the treatment of our conditions are presented in graphical form.[30] Given the diffusion coefficient D, the rate constant k_2, and the radius of the detection section, it is possible to determine from these solutions the value of the wall deactivation efficiency ϵ which is consistent with the observed value of F. The expected dependence of F on total pressure can then be calculated.

The variation of F with total pressure is shown in Fig. 5. The two solid lines were calculated using the Semenov equations and values of D which were 10% higher and 10% lower than the value of D obtained using the method outlined in Appendix II. The ϵ values were selected so that the predicted F values at the midpoint of the pressure variation, 0.58 torr, were equal to approximately the median value of F over this pressure range. The important point to note is that the observed *variation* over this range of total pressure is consistent with the calculated variation. Because of the appreciable scatter of the F data and because of the approximations involved in the calculation of the diffusion coefficients, however, the data fit certainly cannot be taken as absolute proof that Reaction (3) is wall deactivation. Also, the Semenov equations are strictly valid only for static conditions, although laminar flow is unlikely to alter drastically the calculated pressure dependence.

Rather more conclusive evidence that Reaction (3) is in fact heterogeneous deactivation was obtained by varying the surface-to-volume ratio of the portion of the flow tube inside the detection cavity. Two flow tubes, differing only in the diameter of the section contained in the EPR cavity, were freshly cleaned with 10% HF to produce surface conditions as similar as possible. Several measurements of F were than made in each tube under the same conditions. If Reaction (3) is surface deactivation, then to a first approximation F should vary directly with the diameters of the tubes,[29] (i.e., a surface reaction in the "kinetic" region involving no diffusional control.) However, for a surface reaction whose rate is completely controlled by diffusion to the wall, dependence of F on approximately the *square* of the ratio of the diameters would be expected.[29] The dependence of F on the tube diameter for this intermediate case, then, should be between these two extremes. The results, shown in Table III, certainly reveal a large dependence of F on cell diameter, and the magnitude of the experimental ratio confirms the prediction. The ratio c was calculated using the Semenov equations[30] to estimate the effects of partial diffusional control. These experiments show that Reaction (3) is definitely heterogeneous deactivation of $SO(^1\Delta)$ at the flow tube wall with an efficiency ϵ of approximately 0.1.

Because of the heterogeneity of Reaction (3), the average concentration of ^1SO is lower in the upstream section of the reaction tube, where the radius is smaller, and the concentration of SO is therefore always slightly *higher* upstream than in the detection region. Because $[^1SO]$ is small relative to $[SO]$, the corrections to the measured rate constants were always less than 6%.

The rate constants reported in Table II have been so corrected. The active portion of the EPR cavity was situated at the downstream end of the larger diameter section of the flow tube and calculations using the above value of ϵ indicated that there was sufficient time for the new steady-state concentration of ^{1}SO to be established in the 3-cm region between the end of the smaller diameter section and the beginning of the actual detection region under all flow conditions used. The failure to observe any apparent difference in the values of k_1 measured with and without the Teflon sleeve in place would also imply that the rate of deactivation of ^{1}SO on Teflon is no more than a factor of 2 less than that on quartz.

E. Wall Deactivation Efficiencies

In view of the importance of SO($^1\Delta$) wall deactivation in this study, it was thought to be of general interest to determine the wall deactivation efficiencies of quartz and Teflon for $^1O_2$. Apparent first-order decay of $^1O_2$ was measured at very low flow rates (~100 cm/sec) by varying the injector position at which an $^1O_2/O_2$ mixture was added to a stream of helium in the main flow tube. The rates of the possible interfering reactions,

$$O_2(^1\Delta_g)+O_2(^1\Delta_g)\rightarrow O_2(^1\Sigma_g^+)+O_2(^3\Sigma_g^-),$$

$$O_2(^1\Delta_g)+O_2(^3\Sigma_g^-)\rightarrow O_2(^3\Sigma_g)+O_2(^3\Sigma_g^-),$$

are negligible under the conditions of measurement.[5,31] Measured values of wall deactivation efficiencies are shown in Table IV, along with various determinations by other workers.

TABLE IV. Measured wall deactivation efficiencies (probabilities of deactivation per wall collision) for $O_2(^1\Delta_g)$ and SO($^1\Delta$).

Species	Wall material	Efficiency
$O_2(^1\Delta_g)$[a]	Quartz	$(1.5\pm0.4)\times10^{-5}$
$O_2(^1\Delta_g)$[a]	Teflon	$(1.6\pm0.5)\times10^{-5}$
$O_2(^1\Delta_g)$[b]	Quartz	4×10^{-5}
$O_2(^1\Delta_g)$[c]	Pyrex	2.3×10^{-5}
$O_2(^1\Delta_g)$[d]	Pyrex	$(1.2\text{–}2.3)\times10^{-5}$
SO($^1\Delta$)[a]	Quartz	~0.1
SO($^1\Delta$)[a]	Teflon	>0.05

[a] This work.

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The difference of three to four orders of magnitude in the efficiencies for $^1O_2$ and ^{1}SO is striking, but it should be emphasized that $^1O_2$ is exceptionally stable to wall deactivation for an electronically excited molecule. For instance, the value of ϵ for $O_2(^1\Sigma_g^+)$ is approximately 0.01.[32] Also, the fact that ^{1}SO is polar may play some role here. Interestingly, the increasing efficiencies of wall deactivation for $O_2(^1\Delta_g)$, $O_2(^1\Sigma_g^+)$, and SO($^1\Delta$) appear to parallel the known (and estimated) rates of purely radiative decay for these species.

IV. DISCUSSION

A. Reaction of $^1O_2$ with SO

Our results allow us to conclude that $^1O_2$ is rapidly quenched by SO and that Reaction (2) is a major pathway in this reactive process. Because we measure only the decay of $^1O_2$, the possibility that the measured rate includes some contribution from other mechanistic routes cannot strictly be ruled out, however. For instance, if vibrationally excited SO were formed in some fraction of the reactive collisions of $^1O_2$ with SO, vibrational relaxation by He, O_2, or the flow tube wall could be fast enough[9,33] to satisfy the observed steady-state conditions. Careful attempts to detect vibrationally excited SO as a product of Reaction (2) were unsuccessful, but a small steady-state population of SO($v=1$) could have been below our limits of detection. Because of the observed low rates of physical deactivation of $^1O_2$ by species like SO_2, OCS, O_2,[31] H_2O,[31] and even NO and NO_2,[34] however, we believe that any path in the reaction of $^1O_2$ with SO other than Reaction (2) is likely to be quite minor. Higher rates of deactivation by compounds such as aliphatic amines have been reported,[35] but the rate enhancement in these cases appears to be a result of very low ionization potentials, allowing substantial mixing of charge-transfer states in the collision complex and thus facilitating the singlet–triplet multiplicity change. There is no reason to believe that such an effect could be important in the case of SO, which has an ionization potential of 10.6 eV.[36]

Reaction (2) is faster by an order of magnitude than any quenching process by a neutral species yet reported for $^1O_2$ in the gas phase, reaction *or* deactivation,[5,6,31,35,37] and several orders of magnitude faster than simple physical deactivation by most molecules.[31] We believe that the fast rate is indicative of the unique reaction path and interpret the reaction as a spin-allowed transfer of electronic energy in which energy resonance is approximated.[9] The reactive process, therefore, is essentially a spin exchange involving the lowest singlet and triplet states of two diatomic molecules with the same electronic configuration, conforming perfectly to an allowed process in terms of the Wigner spin rules. In order to discuss this view in any detail, it is necessary to make some estimate of the electronic energy of ^{1}SO. This energy has not been determined spectroscopically but Colin[38] has pointed out that the energy difference between SO and ^{1}SO must be approximately 6350 cm^{-1}. Thus, Reaction (2) is about 1600 cm^{-1} exothermic.

Absolute rate measurements have recently become available for similar types of electronic exchange re-

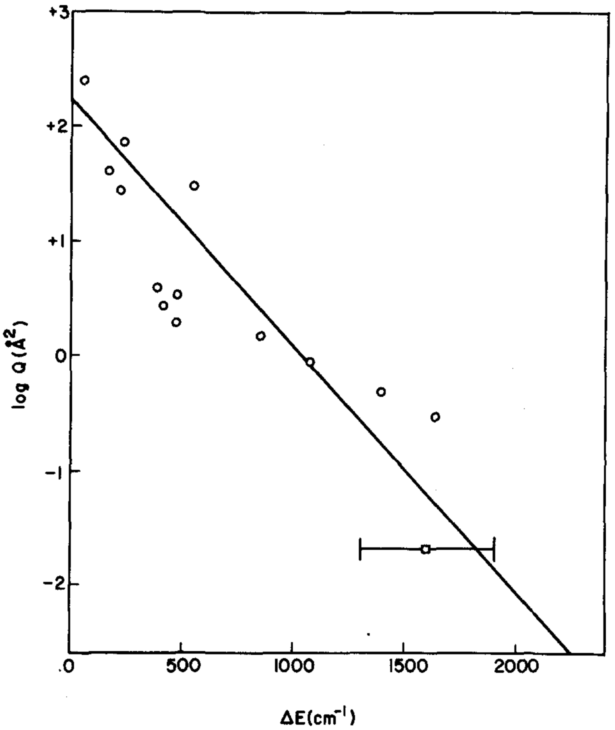

FIG. 6. Plot of the logarithm of the cross sections of atomic reactions involving electronic energy exchange against the energy discrepancy from perfect resonance. (The plot of Callear[9] has been revised to include recent results.[39]) The square represents our measured cross section for reaction (2), with the error bars indicating an uncertainty of 300 cm^{-1} in the electronic energy of $SO(^1\Delta)$.

actions involving excited atoms, of which the most comprehensive appear to be those of Krause and coworkers.[39] Cross sections Q for such processes have shown[9,39] to correlate roughly with ΔE, the energy discrepancy from perfect resonance in the general reaction,

$$A^*+B\rightarrow A+B^*+\Delta E,$$

where A* and B* are excited states of A and B. One such correlation is presented in Fig. 6, where the $\log Q$-vs-ΔE plot of Callear has been revised to include later results.[39,40] It can be seen that the measured cross section of 0.02 Å² for Reaction (2) is certainly of the right order of magnitude for the approximate correlation. This interpretation of Reaction (2) is consistent with the evidence that $^1O_2$ is generally so remarkably resistant to physical deactivation and is also quite inert chemically[7] for an electronically excited molecule. That is, no unusually strong interaction is required to explain the fast rate of reaction of $^1O_2$ with SO.

Triplet-to-singlet energy-transfer processes involving complex organic molecules on first consideration seem analogous to Reaction (2). The available evidence[10,11] indicates that rates for these reactions approach gas-kinetic collision frequencies for reactions with $\Delta E \sim 0$. Efficient vibronic coupling and the greater likelihood of attractive chemical interactions (as evidenced by correlations of rates with acceptor electrophilicities[11,12]) are the likely explanations for such high efficiencies. Because the rate of Reaction (2) is in semiquantitative agreement with predictions based only on experiments involving near-resonant electronic energy transfer in *atoms*, these factors are apparently of little importance for this reaction.

It is quite interesting to note that apparently the only $^1O_2$ quenching reactions, even in solution, reported to have higher rate constants than Reaction (2) may occur by a mechanism similar to the one proposed here. Foote *et al.*[4] have found that carotenoids quench $^1O_2$ nondestructively at a rate which is close to diffusion controlled and believe this could explain the efficient protection of chlorophyll from photobleaching which is provided by β-carotene. These workers suggest, with some justification from the observed sharp increase in quenching rate with the number of conjugated double bonds in polyenes, that the deactivation occurs readily because the lowest triplet states of carotenoids may lie slightly below the $^1O_2$ electronic energy of 22.5 kcal/mole. Thus spin-allowed transfer of electronic energy could take place in a near-resonant situation. Because in addition there is the likelihood of greater attractive interaction of $^1O_2$ with a complex molecule like β-carotene, and the possibility of efficient vibronic coupling, it is not surprising that the reaction occurs at almost every collision, even if the resonance is not exact. Our studies of Reaction (2) certainly show that such an energy-transfer process for $O_2(^1\Delta_g)$ can take place at a rapid rate even with a simple molecule like SO in the gas phase and thus provide indirect support to the Foote mechanism.

It appears, then, that extremely efficient deactivation of $^1O_2$ may require species with electronically excited states at levels less than 23 kcal/mole above the ground state. Very few molecules possess such low-lying excited states, but the discovery (or design) of such molecules could be important in the inhibition of photo-oxidation processes.

In view of this, we have considered the possibility that Reaction (2) might have some importance in the chemistry of polluted atmospheres. Because of the low deactivation rates for normal atmospheric gases,[31] Reaction (2) could be considered a possible quenching process for $^1O_2$ in atmospheres heavily polluted with sulfur oxides. Quite high concentrations of about 1 ppm SO would be required, however, to increase the rate beyond that which is set by deactivation by O_2.[31]

The observation of the very high wall deactivation efficiency for ^1SO helps clarify several experimental results concerning the mechanism of SO formation in the thermal decomposition of ethylene episulfoxide. Hartzell and Paige[41] reported mass spectroscopic evidence of the formation of SO in the pyrolysis of ethylene episulfoxide. Rodson and Sauers[42] have also established that SO is formed in the thermal decomposition of ethylene episulfoxide and propose that it should be formed in a singlet state. Further experiments have suggested that the decomposition produces initially only ethylene and SO. If this is correct, conservation of spin would require that SO be formed in a singlet state, since the triplet state of ethylene is energetically inaccessible.

Saito,[43,44] however, has carried out experiments in which ethylene episulfoxide is pyrolyzed in a quartz tube and the decomposition products pumped through a microwave spectrometer. He readily observed the spectrum of SO($^3\Sigma^-$), but reports that when a similar experiment was performed using EPR detection, no SO($^1\Delta$) spectrum could be observed. Because spin-allowed homogeneous decomposition of the episulfoxide would require SO to be formed in its singlet state, Saito proposed that the decomposition must occur only heterogeneously at the wall where spin-conservation considerations may have no validity. We believe that our experiments show that homogeneous decomposition of the episulfoxide forming SO($^1\Delta$) could well have taken place in Saito's experiments, because any SO($^1\Delta$) thus formed would likely have been quenched to SO($^3\Sigma^-$) by wall collisions before it could have been detected spectroscopically.

APPENDIX I: CALCULATION OF RELATIVE CONCENTRATIONS OF SO($^2\Delta$) AND SO($^3\Sigma^-$) FROM THEIR EPR SIGNALS

The absolute concentration of SO($^1\Delta$) in the spectrometer cavity can be obtained from its EPR signal strength by using Eqs. (1) and (2) of Ref. 18 to show that

$$N(^1\Delta\mathrm{SO})/N(S_p)=S(^1\Delta\mathrm{SO})Q(^1\Delta\mathrm{SO})/S(S_p)Q(S_p), \tag{A1}$$

where S is the EPR signal strength and Q is a function depending on, among other things, g values, partition functions, transition moments, etc. S_p is any standard paramagnetic species undergoing electric dipole transitions whose concentration can be independently measured and its Q value calculated. S_p is usually taken to be NO since NO is the only stable molecule with electric dipole EPR transitions.

However, we have shown[18] that the absolute concnetration of ground-state SO($^3\Sigma^-$) can be related to its EPR signal via an equation like (A1) with S_p being NO. Since SO($^3\Sigma^-$) was always present in our system, it was convenient to choose S_p to be SO($^3\Sigma^-$) and measure the concentrations of SO($^1\Delta$) relative to the calibrated SO($^3\Sigma^-$) signal. Because of the very low concentrations of SO($^1\Delta$), it was impossible experimentally to make separate corrections for slight power and/or modulation broadening as was done for SO($^3\Sigma^-$).[18] The procedure used, therefore, was to measure the ratio of the SO($^1\Delta$) and SO($^3\Sigma^-$) signal strengths and assume that the correction factors were the same for both signals. The method of measuring height times width squared was used,[18] but for the SO($^1\Delta$) signals of extremely low signal to noise, it was sometimes necessary to measure the ratio of peak hights only and then multiply by the width-squared ratio determined at higher concentrations of SO($^1\Delta$). Neither of these procedures introduces *any* error as long as the relaxation processes between Zeeman levels are the same for both states. While the processes are probably not exactly the same, any significant difference seems highly unlikely.

Thus the problem of determining $N(^1\Delta\mathrm{SO})$ reduces to calculating Q', where, in the notation of Ref. 18,

$$Q'=\frac{Q(^1\Delta\mathrm{SO})}{Q(^3\Sigma^-\mathrm{SO})}=\left[\frac{Z(^1\Delta\mathrm{SO})}{Z(^3\Sigma^-\mathrm{SO})}\right]\left[\frac{g_{\mathrm{eff}}(^1\Delta\mathrm{SO})}{g_{\mathrm{eff}}(^3\Sigma^-\mathrm{SO})}\right]\times\left[\frac{\exp(-E(^1\Delta\mathrm{SO})/kt)}{\exp(-E(^3\Sigma^-\mathrm{SO})/kt)}\right]^{-1}\left[\frac{\mu(^1\Delta\mathrm{SO})_{ij}}{\mu(^3\Sigma^-\mathrm{SO})_{ij}}\right]^{-2}. \tag{A2}$$

In writing Eq. (A2), one has assumed both species share an equilibrium rotational temperature and that this temperature is high compared to the rotational energies of either. For practical purposes the ratio of the Z's is just the ratio of the degeneracy factor, two for the Λ doublets of the $^1\Delta$ state and three for the triplet structure of the $^3\Sigma^-$ state. $g_{\mathrm{eff}}(^3\Sigma^-\mathrm{SO})$, $\mu(^3\Sigma^-\mathrm{SO})_{ij}$, and the energy exponential have been given in Ref. 18 for the $K=J=1$, $M_J=0\leftrightarrow M_J'=-1$, $K=2$, $J=1$ transition. For SO($^1\Delta$), g_{eff} can be taken as equal to its theoretical case (a) value of $\frac{2}{3}$, and the energy exponential as unity. The value of $\mu(^1\Delta\mathrm{SO})_{ij}$ in the direction of the electric field for the transition involved has been given by Carrington, Levy, and Miller[45] as

$$|\mu(^1\Delta\mathrm{SO})_{ij}|^2=\{\Lambda^2/4[J(J+1)]^2\}\times\mu_0^2[J(J+1)-M(M+1)], \tag{A3}$$

where $\Lambda=2$ for the $^1\Delta$ state and μ_0 is the permanent electric dipole moment of the $^1\Delta$ state. Because for the observed lines the two Λ-doublet transitions are superimposed in SO($^1\Delta$), the right-hand side of (A3) should be multiplied by another factor of 2. Thus for the observed line with $J=2$, $M=-1$, and $M+1=0$, we obtain

$$|\mu(^1\Delta\mathrm{SO})_{ij}|^2=\tfrac{1}{3}\mu_0^2. \tag{A4}$$

There have been two determinations[46,47] of μ_0 for SO($^1\Delta$), which agree within experimental error. We take a weighted average (based on the reported uncertainties) and use $\mu_0=1.37$ D.

Using these values we obtain

$$\frac{N(^1\Delta\mathrm{SO})}{N(^3\Sigma^-\mathrm{SO})}=Q'\frac{S(^1\Delta\mathrm{SO})}{S(^3\Sigma^-\mathrm{SO})}=0.260\frac{S(^1\Delta\mathrm{SO})}{S(^3\Sigma^-\mathrm{SO})}. \tag{A5}$$

Using Eqs. (A5) and (3) of Ref. 18 (and the NO calibration described therein) we have obtained absolute concentrations of SO($^1\Delta$) from its EPR signals.

APPENDIX II: CALCULATION OF THE DIFFUSION COEFFICIENT OF A TRACE OF SO($^1\Delta$) IN A 50% He/O_2 MIXTURE

The diffusion coefficient D for a trace of SO($^1\Delta$) diffusing into a 50% He/O_2 mixture was calculated by estimating the diffusion coefficients of SO($^1\Delta$) in pure helium and in pure oxygen, and applying the experimentally confirmed relation,[48]

$$D_{i-\mathrm{mix}}^{-1}=\sum_{j\neq i} X_j D_{ij}^{-1},$$

where j is one component of a multicomponent mixture, X_j is the mole fraction of that component, i is the trace component, and D_{ij} is the binary diffusion coefficient for i and j. The D_{ij} were calculated with the approximate equation of Chapman,[49,50] using the following collision diameters: $\sigma_{\mathrm{He-SO}}=3.2$ Å; $\sigma_{\mathrm{O_2-SO}}=3.6$ Å. The resulting value of D is 0.26 cm^2/sec at 760 torr and 297°K.

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[*] Present address: Department of Chemistry, University of Utah, Salt Lake City, Utah 84112.

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