directed toward a more complete understanding of the combined effects of phase, dose rate, temperature, and scavenger additives are in progress.

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The Chemiluminescent Reaction of Oxygen Atoms with Sulfur Monoxide at Low Pressures

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The reaction of oxygen atoms with sulfur monoxide results in a visible blue emission, extending into the ultraviolet. The reaction was studied in the low pressure region up to a total pressure of 20 μ where the emission was found to be due to the simple two-body reaction, $SO + O \rightarrow SO_2 + h\nu$, analogous to the two-body reaction of nitric oxide and oxygen atoms. The rate coefficient for this reaction was estimated as 7×10^{-16} cm.^{3}/molecule sec. The SO was produced by reaction with O atoms *via* $COS + O \rightarrow CO + SO$. This reaction could also be used under certain conditions to titrate the oxygen atoms to obtain a quantitative measure of the oxygen atom concentration.

Introduction

In a previous publication[1] a study was made of the light emission from the reaction of nitric oxide with oxygen atoms at low pressure. The light emission was shown to be due to a direct two-body combination

$$NO + O \longrightarrow NO_2 + h\nu \qquad (1)$$

An alternate mechanism for light emission was possible involving a preliminary three-body reaction followed by alternate paths of deactivation or emission

$$NO + O + M \longrightarrow NO_2^* + M \qquad (2)$$

$$NO_2^* + M \longrightarrow NO_2 + M^* \qquad (3)$$

or

$$NO_2^* \longrightarrow NO_2 + h\nu \qquad (4)$$

At high pressures, substantially above 1 mm., this complex mechanism (reactions 2–4) or a similar mechanism may become important: Originally some investigators believed that reaction 1 was not likely and favored the three-body mechanism. The observation of diffuse bands in the observed emission at higher pressures, as well as some dependence on a third body for the intensity of emission, supported this view.[2]

However, the experimental results at low pressures are in agreement with those obtained recently by Johnathan and Doherty,[3] and there can be no doubt that reaction 1 does occur and predominates at least at total pressures substantially below 1 mm.

Light emission also occurs from the reaction of sulfur monoxide with O atoms

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(1) R. R. Reeves, P. Harteck, and W. H. Chace, *J. Chem. Phys.*, **41**, 764 (1964).

(2) H. P. Broida, H. I. Schiff, and T. M. Sugden, *Trans. Faraday Soc.*, **57**, 259 (1961).

(3) G. Doherty and N. Johnathan, *Discussions Faraday Soc.*, to be published.

$$SO + O \longrightarrow SO_2 + h\nu \qquad (5)$$

This reaction is 127 kcal. exothermic, equivalent to a wave length limit of approximately 2300 Å., which corresponds to the observed wave length limit of the emission. The emission visually appears as a strong blue compared to the greenish white NO–O atom emissions. Again an alternate mechanism may be postulated

$$SO + O + M \longrightarrow SO_2^* + M \qquad (6)$$

$$SO_2^* + M \longrightarrow SO_2 + M^* \qquad (7)$$

or

$$SO_2^* \longrightarrow SO_2 + h\nu \qquad (8)$$

As discussed in the previous work, the light emission at very low total pressures, *i.e.*, in the micron region, must be dependent on the third body (M) owing to the primary reaction (6). If no dependence on pressure (or M) is observed under these conditions, then a simple combination *via* reaction 5 must occur and dominate in this region.

The purpose of the present work was to study the reaction of sulfur monoxide and oxygen atoms in order to determine if the light emission was due to the simple combination described by reaction 5 or to a more complex mechanism of the type described by reactions 6–8.

Experimental

The experimental method and equipment used in this work was essentially the same as that used in the previously reported work on the chemiluminescent reaction of nitric oxide and O atoms.[1] In this case, however, a 50-l. spherical reaction vessel was used as shown in Figure 1. A pumping speed of 75–100 l./sec. was easily attained at 5 μ. As in the previous work, there was a negligible consumption of the reactants on the vessel walls or in the gas phase.

The SO was generated by adding carbonyl sulfide to the O atom stream in the reaction tube at a point upstream of the side tube to the 50-l. vessel. The resultant SO–O atom gas mixture was pumped under steady-state conditions with only a small fraction being pumped into the 50-l. system. Conditions were held constant in the reaction tube to assure a constant percentage of reactants being fed into the 50-l. system where no further appreciable consumption of reactants occurred. Variations of pressure in the 50-l. vessel while conditions were held constant in the reaction tube permitted reaction studies at constant percentage of reactants but at different pressures.

A photomultiplier tube placed on the high-pressure input reaction tube (see Figure 1) was used with appropriate filters to monitor the SO–O atom emission at 300–500 μ. In this way, changes in the constituents could be detected as the pressure–intensity values were obtained. This was important because the curves of intensity *vs.* pressure would be altered significantly if the input quantities changed during a run. The relative intensity of light emission from the 50-l. flask was followed using an EMI/US 6256B photomultiplier tube which has a quartz window giving response extending into the ultraviolet. To avoid extraneous light, the emission was generally monitored using a CS7-37 Corning filter. This filter transmitted the light emission only in the 3200- to 3900-Å. region which is also transmitted by the wall of the Pyrex reaction vessel.

Since the phototubes measure the emission intensity of the reaction, it was possible to measure the concentrations of the constituents at any point in the reaction vessel using the following titration method. Experimental conditions were maintained constant such that a steady flow of O atoms was produced. The COS input was then allowed to increase steadily which caused a corresponding increase in the relative intensity of the emission. When enough COS was added, the intensity passed through a maximum, then decreased steadily until ultimately enough COS was added to consume all the O atoms, and no emission could be observed downstream.

In Figure 1 is also shown a side tube attached to the 50-l. vessel. The diameter of this was equal to the reaction tube used at high pressure. Measurements of the emission intensity in the two tubes could be directly compared to obtain the relative light intensity at the different pressures.

The 15-cm. cold trap was cooled with liquid nitrogen to avoid contaminating the diffusion pump. The gas flow was sufficient to avoid any interference between the cold trap and the reaction vessel.

Results and Discussion

COS can react with oxygen atoms in two ways[4]

$$COS + O \longrightarrow CO + SO \qquad (9)$$

and

$$COS + O \longrightarrow CO_2 + S \qquad (10)$$

At room temperature with a total pressure in the millimeter range no CO_2 could be detected by a mass spectrometer located downstream of the reaction zone.[5]

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[4] A. L. Myerson, F. R. Taylor, and P. L. Hanst, *J. Chem. Phys.*, **26**, 1309 (1957).

[5] The ratio k_9/k_{10} has been found to be $>10^3$; therefore, any interference by reaction 10 is negligible: S. Dondes and D. Safrany, private communication.

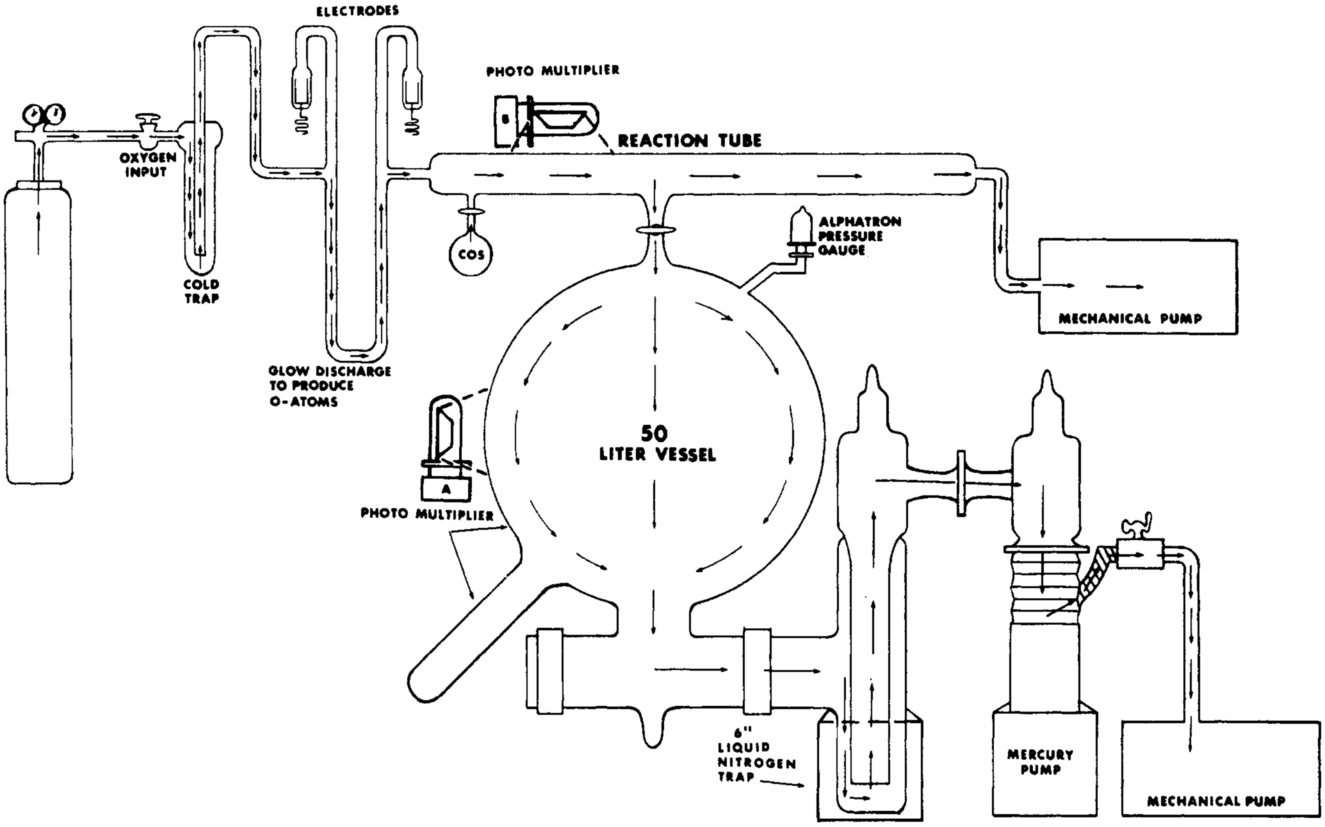

Figure 1. Schematic of apparatus.

Reaction 9 is, therefore, predominating, and it was estimated that the rate coefficient was of the order of 10^{-14} cm.^{3}/molecule/sec. This reaction rate was important to the titration described above. The maximum intensity was attained when the quantity of COS equaled half the O atom concentration, and no emission was observed when the concentrations were equal. Essentially, an O atom was immediately consumed to produce each sulfur monoxide molecule from the COS by reaction 9, and then the light-emitting reaction (5) followed. The emission was readily observed, but no further significant consumption of O atoms occurred since reaction 5 is relatively slow.

The rate of the three-body collision reaction, $SO + O + M \rightarrow SO_2 + M$, was negligible under these conditions. It should be noted that the reactions of CO are sufficiently slow that the CO produced in reaction 9 acted essentially as an inert gas and did not interfere with the measurements reported here. The heats of reaction for a number of the reactions of interest in this study are listed in Table II as derived from the heats of formation given in Table I.

Reactions 9 and 5 are completely analogous to the O atom titration method using the reaction of NO_2 with O atoms.[2] In this case NO is formed, an O atom is consumed (as in (9)), and the unreactive constituent is the O_2 formed instead of CO

$$NO_2 + O \longrightarrow NO + O_2 \tag{11}$$

Table I: Heats of Formation for the Constituents Involved

Molecule	ΔH_f from atoms, kcal./mole
S_2	-83^a
SO	-127^b
S_2O	-189^c
SO_2	-254^d
COS	-340^e
CO_2	-381
CO	-256
O_2	-118

[a] S. W. Benson, "Foundation of Chemical Kinetics," McGraw-Hill Book Co., Inc., New York, N. Y., 1960, p. 663. [b] W. D. McGrath and J. J. McGarvey, *J. Chem. Phys.*, **37**, 1574 (1962). [c] A recent article by R. Hagemann (*Compt. rend.*. **255**, 899 (1962)) gives the heat of formation of S_2O from rhombic sulfur and molecular oxygen as -17 kcal. With this information and an assortment of dissociation energies for S_2, the value $\Delta H_f(S_2O) = -189$ seems reasonable. [d] Calculated from ΔH_f for SO and from reaction 5. [e] Calculated using the value given by Myerson (ref. 4) for reaction 9.

Table II: Heats of Reaction

	Reaction	ΔH (exothermic), kcal./mole[a]
(1)	$NO + O \rightarrow NO_2 + h\nu$	-72
(5)	$SO + O \rightarrow SO_2 + h\nu$	-127
(9)	$COS + O \rightarrow CO + SO$	-43^b
(10)	$COS + O \rightarrow CO_2 + S$	-51^b
(13)	$SO + O_2 \rightarrow SO_2 + O$	-9
(14)	$SO + SO \rightarrow SO_2 + S$	0
(15)	$S + O_2 \rightarrow SO + O$	-9
(16a)	$S_2O + O \rightarrow SO + SO$	-65^c
(18)	$S_2O + S \rightarrow SO + S_2$	-21^c

[a] In some cases values of ΔH are uncertain, but all the reactions are expected to remain exothermic as written. [b] Myerson (ref. 4). [c] These representative exothermic values were estimated from the heats of formation in Table I. The importance lies not in the exact values, but in that the reactions are exothermic as written.

A second O atom is consumed when the NO formed in the fast reaction (11) reacts to give NO_2 plus light emission

$$NO + O \longrightarrow NO_2 + h\nu \qquad (12)$$

Comparison of the two methods gave identical results. A two-step method was used for titration with NO_2 where a maximum light intensity was determined in the first step, and NO was added separately until the corresponding value of intensity was reached in order to obtain the actual rate of flow.[6] This avoided the complications due to $2NO_2 \leftrightarrows N_2O_4$. It should be noted that, in the case of COS, no such dimer is formed, and, in addition, COS is a less corrosive or reactive gas than NO_2 and, therefore, somewhat easier to handle and measure. The titration could be readily made directly in a single step using the disappearance of the blue emission as indicative of the end point with increasing COS flow or using the maximum light intensity as indicative of half the O atoms present, as with NO_2.

The emission was observed as the COS flow rate was varied, which changed the SO concentration directly since reaction 9 was very fast under these conditions. The O atoms remained essentially constant with only slight change due to consumption *via* reaction 9 because the COS was always a small fraction of the O atoms. The resultant emission intensity in the low-pressure reaction vessel was plotted *vs.* the emission intensity in the high-pressure side, and a linear dependency was observed.

The O atom concentration could be varied by varying the power to the glow discharge. A linear dependency also resulted.

With the fraction of reactants constant, the pressure in the 50-l. vessel was permitted to increase by turning off the diffusion pump as described in the previous publication. The emission intensity in the vessel increased with the square of the pressure, or, more specifically, $I = kp^{1.98\pm0.02}$, for a series of nine runs made under different conditions of starting pressure and reactant concentrations. A typical oscillograph plot of intensity *vs.* pressure is given in Figure 2. The data were then plotted as I *vs.* p^2 as also shown in Figure 2. The resulting straight line, typical of many runs, confirms a two-body mechanism.

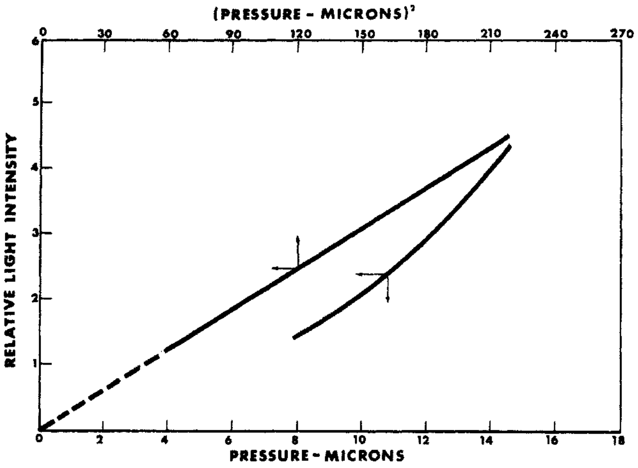

Figure 2. Typical oscillograph plot of intensity *vs.* pressure.

This variation of intensity with the square of the pressure at constant mole fraction was also found when the intensity of emission in the high-pressure reaction tube and in the low-pressure, 50-l. reaction vessel were compared. This comparison was made by simultaneously observing the emission intensities in the high-pressure reaction tube and in a 45-mm. diameter side arm attached to the 50-l. vessel. The intensities varied by more than a factor of 1000 and were found to be proportional to the square of the pressure even over this wide range within 10% or less, or within the experimental error of the measurements. This result adds additional support to the conclusion that the two-body emission reaction (5) occurred.

An estimate was made of the rate of reaction 5 by comparing the maximum light intensity of emission of the NO–O atom reaction observed by adding NO_2 with the maximum obtainable under identical conditions using COS. Except for the complications of photomultiplier sensitivities and transmission of the emission through glass envelopes and filters, the ratio of the rate coefficients would be proportional to the ratio of these

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(6) P. Harteck, R. R. Reeves, and G. G. Mannella, *J. Chem. Phys.*, 32, 632 (1960).

maximum light intensities. Allowing for these factors, a ratio of the rate coefficients of k_5/k_1 was found equal to 25 within a factor 2. Assuming $k_1 = 3 \times 10^{-17}$ cm.^{3}/molecule sec.,[7] then $k_5 = 7 \times 10^{-16\pm0.3}$.

As previously noted, linear dependence on O atom concentration was observed with fixed concentration of COS. However, under the conditions where the SO formed was greater than the remaining O atoms, a displacement of the linear response from the coordinate origin was observed. This was attributed to the reactions of the SO molecules producing additional O atoms by the alternate mechanisms below. Under the experimental conditions normally used, however, no appreciable consumption (or production) of reactants could be observed. The various reactions which may occur under alternate conditions are

$$SO + O_2 \longrightarrow SO_2 + O \quad (13)$$

$$SO + SO \longrightarrow SO_2 + S \quad (14)$$

followed by

$$S + O_2 \longrightarrow SO + O \quad (15)$$

Some sulfur is found in the reaction vessel after long operation lending support to reaction 14. Obviously reaction 15 cannot be very fast, or no sulfur deposit would have been observed.

An alternate path for reaction 14 is not possible

$$SO + SO \longrightarrow S_2O + O \quad (16)$$

since it is a strongly endothermic reaction as can be seen in Table II.

When the system had been operating for some time the 50-l. flask became contaminated in certain areas, and it was observed that an enhanced blue emission occurred in these general areas. This corresponded to a surface-catalyzed excitation of the SO_2 molecule, $SO + O$ surface $SO_2^* \rightarrow SO_2 + h\nu$. A similar excitation had been observed earlier with NO and O atoms which resulted in a catalyzed emission of the NO_2 molecule. Visually, the NO_2-excited emission was reddish in appearance. The areas which catalyzed the excitation and resultant blue emission of SO_2 were also found to be effective in catalyzing the excitation of the NO_2 with the resultant reddish emission. Under these conditions, with only oxygen and O atoms in the system, the emission in the ultraviolet was also observed, which could be attributed to the oxygen Herzberg bands, owing to surface-catalyzed recombination of O atoms to form the excited $O_2A^3\Sigma_u^+$. These catalysis effects yielded spurious results when studying the homogeneous gas-phase reactions, and thorough cleaning of the system was periodically necessary to ensure that such effects were avoided.

The simple two-body reaction mechanism found for the light emission from the nitric oxide–oxygen atom reaction was in contrast to the proposed complex mechanism initiated by a three-body reaction which was more generally expected to be the source of the emission even at low pressures.[1] The present work shows a similar two-body mechanism for the sulfur monoxide–oxygen atom reaction. It certainly appears reasonable to expect this mechanism to occur, not as an exception, but as a relatively common source of light emission in many systems.

Conclusions

The experimental results show a second-order dependence of the emission intensity of the chemiluminescent reaction of sulfur monoxide with O atoms corresponding to reaction 5.

The COS reaction with O atoms can also be used under certain conditions for titration and determination of the oxygen atoms present in a gas stream analogous to the NO_2 titration method.

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(7) A. Fontijn and H. I. Schiff in "Chemical Reactions in the Lower and Upper Atmosphere," Interscience Publishers, Inc., New York, N. Y., 1961, p. 239.