# The Chemiluminescent Reactions of Atomic Oxygen with Carbonyl Sulfide and Hydrogen Sulfide[1]

by **A. Sharma, J. P. Padur, and P. Warneck**

*GCA Corporation, Bedford, Massachusetts 01730* *(Received July 15, 1966)*

The chemiluminescence intensity in the reactions $O + COS$ and $O + H_2S$ was studied in a flow system as a function of reaction time and reactant concentrations. In the initial stage of the reactions, the intensity increases linearly with time, the slope being proportional to the concentration of COS or $H_2S$ and to the square of atomic oxygen concentration. A kinetic analysis shows that these results are consistent with the notion that the reaction responsible for the emission in both cases is reaction 7, $O + SO \rightarrow SO_2 + h\nu$. From the relative intensities, the rate of SO formation in the $H_2S$ reaction was found to be 1.85 times greater than that in the COS reaction. In the 400–800-$\mu$ pressure region studied here, reaction 7 was found to be pressure dependent. The associated emission rate was determined at 800 $\mu$ by comparison with the air-afterglow reactions as $k_7 = 5.7 \times 10^{-15}$ cc/molecule sec. The consumption of SO radicals by reactions other than reaction 7 is discussed together with intensity–time profiles for the later stages of the $O + COS$ reaction.

## Introduction

Mass spectrometric investigations by Liuti, Dondes, and Harteck[2a] and in this laboratory[2b] have shown that the first step in the reaction of oxygen atoms with carbonyl sulfide is the formation of SO radicals

$$O + COS \longrightarrow CO + SO \qquad (1)$$

The rate constant for this process has been determined.[2b] The reaction of oxygen atoms with hydrogen sulfide has also been found to produce SO radicals,[3] but the mechanism for this reaction is more complex than the first one. From mass spectrometer observations, Liuti, Dondes, and Harteck[3] suggest

$$O + H_2S \longrightarrow OH + SH \qquad (2)$$

$$O + OH \longrightarrow O_2 + H \qquad (3)$$

$$H + H_2S \longrightarrow H_2 + SH \qquad (4)$$

$$O + SH \longrightarrow SO + H \qquad (5)$$

where the last two reactions constitute a chain. The chain cannot be long since the ratio of SO production to $H_2S$ consumption is only about 0.5. The reactant consumption ratio, $O:H_2S$, is only slightly greater than unity and a bimolecular rate law is obeyed. Liuti, *et al.*, have also considered the step

$$O + H_2S \longrightarrow H_2 + SO \qquad (6)$$

but ruled it out as a major contributing reaction on the basis of the isotope scrambling observed in the products when atomic oxygen was treated with a mixture of $H_2S$ and $D_2S$.

The chemiluminescence associated with these reactions has also been investigated.[4-8] A comparative

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[1] Supported by the National Aeronautics and Space Administration.

[2] (a) G. Liuti, S. Dondes, and P. Harteck, presented at the 152nd National Meeting of the American Chemical Society, New York, N. Y., 1963; (b) J. O. Sullivan and P. Warneck, *Ber. Bunsenges. Physik. Chem.*, **69**, 7 (1965).

[3] G. Luiti, S. Dondes, and P. Harteck, *J. Am. Chem. Soc.*, **88**, 3212 (1966).

[4] A. Sharma, J. P. Padur, and P. Warneck, *J. Chem. Phys.*, **43**, 2155 (1965).

[5] A. G. Gaydon, "The Spectroscopy of Flames," Chapman and Hall, Ltd., London, 1957.

[6] L. Hermann, J. Skrich, and M. Grenat, *J. Quant. Spectry. Radiative Transfer*, **2**, 215 (1962).

[7] C. J. Halstead and B. A. Thrush, *Nature*, **204**, 992 (1964).

[8] T. R. Rolfes, R. R. Reeves, and P. Harteck, *J. Phys. Chem.*, **69**, 849 (1965).

study[4] has shown that the emission spectra from the reactions of oxygen atoms with carbonyl sulfide, hydrogen sulfide, and carbon disulfide and the $SO_2$ afterglow spectrum are nearly identical, featuring similar intensity distributions. These observations suggest that the emitter and the process leading to the formation of the emitter are the same in all four cases of chemiluminescence. Evidence is mounting that the reaction responsible for the emission is

$$O + SO \longrightarrow SO_2 + h\nu \qquad (7)$$

as was originally suggested by Gaydon.[5] Hermann, *et al.*,[6] observed that the short-wavelength cutoff of the $SO_2$ afterglow near 2400 A coincides with the onset of the dissociation continuum in the $SO_2$ absorption spectrum. Halstead and Thrush[7] found that the $SO_2$ afterglow intensity is directly proportional to the product of oxygen atom and SO radical concentrations. Most recently, Rolfes, Reeves, and Harteck[8] studied the light emission from the reaction of O atoms with COS at low total pressures and compared it with the $O + NO_2$ reaction resulting in the air–afterglow emission involving radiative combination of atomic oxygen with nitric oxide. Their results indicate that at low pressures, the two reactions are analogous and that reaction 7 proceeds *via* a simple two-body combination mechanism.

The present work set out to derive additional evidence for the occurrence of reaction 7 by studying the time dependence of the chemiluminescent intensity in the reactions of atomic oxygen with COS and $H_2S$ for various initial reactant concentrations. From such experiments, the rate of SO production associated with reactions 1 and 2 could be determined. The rate for reaction 7 was also determined. In addition, intensity profiles were obtained for the later stage of the reaction of oxygen atoms with COS to explore the possibilities of SO loss reactions.

## Experimental Section

The conventional fast-flow system employed a cylindrical reactor of 1.9-cm i.d. Atomic oxygen was produced by microwave discharge. Either a 99:1 argon–oxygen mixture or pure oxygen was discharged. The second reactant entered the reactor *via* an inlet provided with several radially oriented holes. The inlet could be moved along the reactor axis by means of a friction drive. Observations were made downstream of the mixing point using a 1P28 photomultiplier tube connected to a Victoreen microammeter. The chemiluminescent emission was viewed through a quartz window mounted on the side of the reactor. A collimating slit system was interposed so that a spatial resolution of about 7 mm was obtained. The corresponding time resolution was 0.7 msec for linear flow rates around 10 m/sec.

Capillary flowmeters were used to measure volume flow rates of the individual gaseous components: argon, oxygen, carbonyl sulfide, and hydrogen sulfide. The concentrations of these constituents at the mixing point were determined from the fraction of the total flow rate and the prevailing total pressure measured with a McLeod gauge. The total pressure was held at 800 $\mu$ unless stated otherwise. Atomic oxygen concentrations were determined by gas titration, using the procedure described by Harteck, *et al.*[9] This is a two-step method. Oxygen atoms are first titrated with $NO_2$ to determine the maximum intensity corresponding to the titration half-point. The $NO_2$ is then replaced by NO to determine the NO flow corresponding to the same intensity value. The accuracy of this method is not as good as the direct titration with $NO_2$, but the complications due to the $2NO_2 \rightleftharpoons N_2O_4$ equilibrium in measuring $NO_2$ flow rates are avoided.

## Results and Discussion

*Dependence of Intensity on Time and Concentration.* To investigate the time dependence of the chemiluminescence intensity, the photomultiplier currents were recorded as a function of the reactant inlet position and the reaction time was calculated from the distance between inlet position and observation point and the prevailing linear flow rate of the gas mixture in the reactor. The introduction of both COS and $H_2S$ gave emission intensities whose increase with time was linear so long as the reaction times were reasonably short and the employed concentrations were moderate. Figure 1 demonstrates this observation for the reaction of oxygen atoms with COS in a plot of intensities *vs.* time for three initial COS concentrations. Only the highest COS concentration produces a nonlinear intensity–time dependence at reaction times greater than 8 msec. Figure 1 also shows that the intensities extrapolate to zero at a common origin beyond the point of reactant introduction. This is primarily due to the limited spatial resolution of the collimating slit system, although back diffusion can also contribute to the effect.

The linearity of intensity with time for short reaction times permits the use of the initial slope of the intensity–time profile as a measure of the reaction rate. The variation of the initial slope with oxygen atom concen-

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[9] P. Harteck, R. R. Reeves, and G. G. Manella, *J. Chem. Phys.*, 32, 632 (1960).

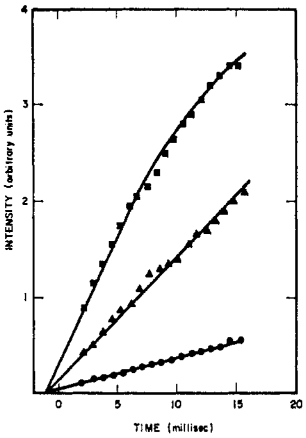

Figure 1. Chemiluminescence intensity *vs.* reaction time in the system O + COS for three initial COS pressures: ●, 7.6 $\mu$; ▲, 20.6 $\mu$; ■, 35 $\mu$; the average O atomic pressure was 9.5 $\mu$.

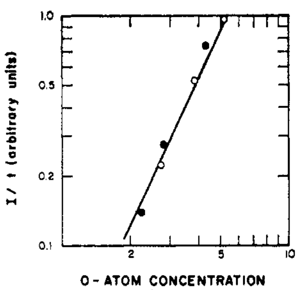

Figure 2. Initial slope of intensity–time profile as a function of O atom concentration for the systems: ●, O + COS; ○, O + $H_2S$.

tration for the reactions with either COS or $H_2S$ is shown in Figure 2 using a logarithmic plot presentation. The concentrations of COS and $H_2S$, respectively, were held constant in these experiments. The intensities for the $H_2S$ reaction actually were brighter than those shown in Figure 2 by about a factor of 2, but these data points were adjusted to fall onto the same line as the COS data, so that the equivalence of the dependence on oxygen atom concentration in both cases is more clearly demonstrated. The slope of the straight line in Figure 2 is $S = 2.08$, indicating that the chemiluminescence intensity is proportional to the square of the oxygen atom concentration.

Figure 3 shows, in a similar fashion, the variation of the initial slope of the intensity–time profile with COS concentration and $H_2S$ concentration, respectively. Data from several runs performed on different days were used in this plot and corrected for the observed oxygen atom concentration, making use of the $(O)^2$ law. Here again, the data indicate a brighter chemiluminescence for the $H_2S$ reaction when compared with the emission from the reaction with COS. However, both plots yield straight lines with nearly identical slopes. The averaged value for the two slopes, $S = 1.1$, indicates a first-order concentration dependence for carbonyl sulfide and hydrogen sulfide.

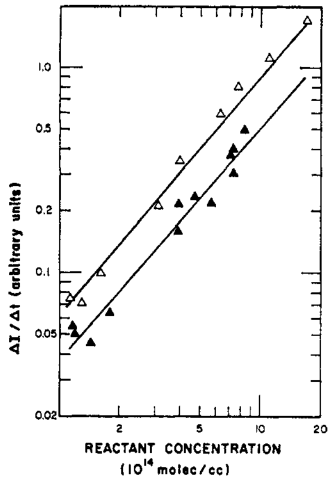

Figure 3. Initial slope of intensity–time profile as a function of COS (▲) and $H_2S$ (△) concentrations.

In addition to these experiments in which the total pressure was 800 $\mu$, a set of experiments was carried out for the O + COS reaction at a total pressure of only 330 $\mu$. It was established that, at the lower pressure, the intensity dependence on reaction time and initial reactant concentrations was the same as that at 800 $\mu$, but the over-all intensity was found to be about three times smaller. While this result indicates a pressure dependence of reaction 7 (in contrast to the observation by Rolfes, *et al.*[8]), it has not been possible to study this effect in detail because the flow rate could not be adequately controlled in the present apparatus. However, the measured rate of reaction 7 reported below also indicates a pressure effect and the discussion of this point will be deferred.

The results summarized in Figures 1–3 can be interpreted in terms of reaction 7 if it is taken into account that, for sufficiently short reaction times, the consumption of the initial reactants is still negligible. With this condition, the SO concentration is a linear function of reaction time, at least in the initial stage of the reaction where the destruction of SO radicals by reaction 7 or other follow-up reactions is not yet significant. For the reaction of atomic oxygen with carbonyl sulfide, the initial rate of SO radical production is

$$\frac{\Delta[\mathrm{SO}]}{\Delta t} = k_1[\mathrm{O}][\mathrm{COS}]$$

and the increase of intensity, $\Delta I$, produced by reaction 7 in the time interval, $\Delta t$, is correspondingly

$$\frac{\Delta I_1}{\Delta t} = k_7[\mathrm{O}]\frac{\Delta[\mathrm{SO}]}{\Delta t} = k_7k_1[\mathrm{O}]^2[\mathrm{COS}] \qquad (\mathrm{A})$$

The right-hand side of this equation represents the initial slope of the intensity–time profile. A similar expression is derived also for the reaction of oxygen atoms with hydrogen sulfide

$$\frac{\Delta I_2}{\Delta t} = k_7[\mathrm{O}]\frac{\Delta[\mathrm{SO}]}{\Delta t} = k_7k_x[\mathrm{O}]^2[\mathrm{H_2S}] \qquad (\mathrm{B})$$

where $k_x$ denotes the rate constant for SO production in the over-all mechanism of the O + $H_2S$ reaction. $k_x$ is not to be identified with the rate constant for reaction 5, even though this reaction may be the principal generator of SO radicals. Instead, $k_x$ is proportional to $k_2$ by a factor which depends on the number of chains involving reactions 4 and 5.

Equations A and B predict a linear relationship with initial COS or $H_2S$ concentration and a quadratic one for the atomic oxygen concentration. This is in agreement with the relationship found in the present experiments. Alternatively, the present results can be used to demonstrate that the chemiluminescence intensity is proportional to the product of the concentrations of atomic oxygen and SO radicals, as required if reaction 7 is the predominant light-emitting process. These results, therefore, are in good agreement with the data reported by Halstead and Thrush[7] and by Rolfes, *et al.*[8] It is also significant that the analysis of the present data refers to the very early stage in the reactions because mechanisms can be suggested which lead to the observed concentration dependence but feature different chemiluminescent reactions. However, such mechanisms would require the buildup of an intermediate concentration (such as SO), so that initially the chemiluminescence intensity could not be a linear function of time. The observed concentration dependences and linearity with time taken together constitute strong evidence in favor of assigning reaction 7 as the principal chemiluminescent reaction.

*Determination of the Rate Constant $k_x$.* It has been noted above that the reaction of atomic oxygen with $H_2S$ produces a brighter chemiluminescence than the reaction with COS under similar conditions. This fact can now be explained by the difference of the associated rates for SO formation. As eq A and B show, the ratio of the initial slopes obtained for the intensity–time profiles in the two reactions is given by

$$\frac{\Delta I_2/\Delta t}{\Delta I_1/\Delta t} = \frac{k_x}{k_1}\,\frac{[\mathrm{H_2S}]}{[\mathrm{COS}]}\,\frac{[\mathrm{O}]_2^2}{[\mathrm{O}]_1^2} \qquad (\mathrm{C})$$

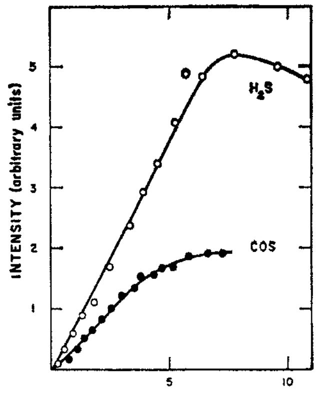

Figure 4. Intensity *vs* flow rate of COS (●) and $H_2S$ (○) at constant O atom concentration.

where $[\mathrm{O}]_1$ and $[\mathrm{O}]_2$ refer to the initial oxygen atom concentrations prevailing in the COS and $H_2S$ experiments, respectively. According to eq C, the ratio of the rate constants, $k_x/k_1$, can be obtained directly from Figure 2, where the data are corrected for the varying initial oxygen atom concentrations. Since the logarithmic plot in Figure 2 yields parallel lines, $k_x/k_1$ is represented simply by the ratio of the $\Delta I/\Delta t$ values for identical COS and $H_2S$ concentrations. The averaged ratio of rate constants obtained from these data is $k_x/k_1 = 1.85$.

In the region where the dependence of intensity on reaction time is still linear, the right-hand side of eq C also represents the ratios of intensities at any time, *t*. An experiment was performed in which the chemiluminescence intensity close to the mixing point (at $t \approx 1$ msec) was recorded as a function of the COS and $H_2S$ flow rates. The results, shown in Figure 4, are appropriately corrected for the difference of oxygen atom concentration in the two cases. Since for small reactant flows the reactant concentrations are proportional to the measured flow rates, the observed linear increase of intensities for moderate flow rates again verifies the first-order concentration dependence discussed above. The ratio of the slopes in Figure 4 is

$$\frac{\Delta I_2/\Delta[\mathrm{H_2S}]}{\Delta I_1/\Delta[\mathrm{COS}]} = \frac{k_x}{k_1} = 1.85$$

in excellent agreement with the average value found above. Applying the previously determined value for the rate constant of the O + COS reaction, $k_1 = 0.91 \times 10^{-14}$ cc/molecule sec,[2b] one obtains the absolute value $k_x = 1.70 \times 10^{-14}$ cc/molecule sec. It should be emphasized again that this rate constant refers only to that portion of the O + $H_2S$ reaction which leads to the formation of the SO radicals.

The present value for $k_x$ is smaller by a factor of 6 than that inferred from the mass spectrometric data reported by Liuti, *et al.*:[3] $k_x = 1 \times 10^{-13}$ cc/molecule sec. The resulting discrepancy is not easily explained, since the experimental conditions concerning flow rates, reactant concentrations, etc., in both investigations are rather similar. Thus, one would expect the same reaction mechanism to hold in both cases. One possibility for the disagreement may be due to a difference in the wall conditions. In the mechanism indicated in the Introduction, the production of SO proceeds rapidly only if the HS radicals are not easily removed at the wall. The enhancement of HS consumption at the wall by adverse conditions in the present experiments therefore may have reduced the SO production to the observed level.

*Determination of the Rate Constant $k_7$.* The rate constant associated with the reaction 7 was determined by comparing the light emission from the O + COS reaction with that produced in the air–afterglow reaction

$$O + NO \longrightarrow NO_2 + h\nu \qquad (8)$$

The relative spectral intensity distribution for reaction 7 was previously determined in this laboratory.[4] The emission lies mainly in the violet and ultraviolet portion of the spectrum. Fontijn, Meyer, and Schiff[10] have determined the spectral intensity distribution for reaction 8 and have shown that it is centered in the red and near infrared. Both emissions overlap in the 3800–5200-A wavelength region. An interference filter was therefore employed in the comparison experiment to limit the radiation seen by the photomultiplier to the region of overlap. The filter featured a transmission maximum near 4100 A and a band width of 75 A. The fraction of radiation registered by the photomultiplier–filter combination compared to the total integrated emission from each reaction was determined from the known spectral response of the phototube, the transmission characteristics of the filter, and the relative spectral intensity distributions for both reactions. The evaluation of the comparison experiment requires only the ratio of the two fractions, which was found to be $f_8/f_7 = 0.029$, where the subscripts refer to reactions 8 and 7, respectively.

The introduction of nitric oxide to the gas flow containing oxygen atoms results in an emission intensity which is time independent, whereas it has been shown above that the introduction of carbonyl sulfide produces an intensity which increases linearly with time. In the first case, the intensity is given by

$$I_8 = k_8[O][NO]$$

and in the second case by eq A. With the provision that the oxygen atom concentration remains constant the combination of both equations yields

$$k_7 = \frac{k_8[NO]\Delta I_1/\Delta t}{k_1[O][COS]I_8} \qquad (D)$$

or when the total intensities, $I_1$ and $I_8$, are replaced by the equivalent photomultiplier currents, $i_1$ and $i_8$

$$k_7 = \frac{f_8 k_8[NO]\Delta i_1/\Delta t}{f_7 k_1[O][COS]i_8}$$

The following individual rate constants were employed in the evaluation of eq D: $k_1 = 0.91 \times 10^{-14}$ cc/molecule sec, given by Sullivan and Warneck,[2b] and $k_4 = 6.4 \times 10^{-17}$ cc/molecule sec, determined by Fontijn, Meyer, and Schiff.[10]

Figure 5 shows the results of the comparison experiments. The photomultiplier currents registered upon admixture of either NO or COS to a discharged argon–oxygen mixture are plotted as a function of reaction time. From the slope of the current–time profile for the O–COS reaction, one obtains $\Delta i_1/\Delta t = 330 \times 10^{-7}$ A/sec, whereas $i_8 = 0.085 \times 10^{-7}$ A. The prevalent concentrations of nitric oxide, carbonyl sulfide, and atomic oxygen are given in the legend. With these data, eq D yields the rate constant associated with reaction 7: $k_7 = 5.7 \times 10^{-15}$ cc/molecule sec. This value is about 8 times greater than the rate constant estimate of Rolfes, Reeves, and Harteck[8] for pressures around 10 $\mu$. The discrepancy is greater than the combined experimental error in both determinations. The fact that the present result, obtained at a higher pressure, is much larger indicates again a pres-

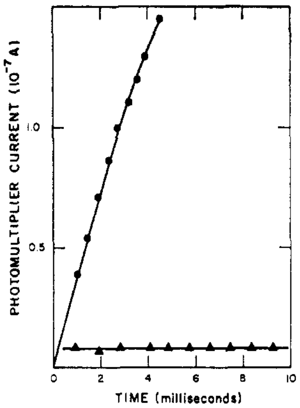

Figure 5. Intensity–time profile for O + COS (●) and O + NO (▲). Concentrations in molecules per cubic centimeter are $[COS]_0 = 4.2 \times 10^{14}$, $[NO]_0 = 5 \times 10^{14}$, and $[O]_0 = 1.65 \times 10^{14}$.

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(10) A. Fontijn, C. B. Meyer, and H. I. Schiff, *J. Chem. Phys.*, **40**, 64 (1964).

sure effect, thereby substantiating the data presented earlier in this paper. However, the increase in the emission rate is insufficient for a reaction that occurs solely by third-body association. Apparently, reaction 7 can proceed both as a two-body and as a three-body association reaction, with the former being predominant at lower pressures and the latter becoming important as the pressure is increased. This interpretation is consistent with the results by Rolfes, *et al.*,[8] Halstead and Thrush,[9,11] and the present data. Thus, reaction 7 should proceed mainly as a two-body reaction at pressures below 100 $\mu$, whereas at 800 $\mu$ pressure, the predominant reaction would be

$$O + SO + M \longrightarrow M + SO_2 + h\nu \qquad (7M)$$

From the above data, one obtains the corresponding third-body rate constant: $k_{7M} = k_7/[M] = 2.2 \times 10^{-31}$ cc$^2$/molecule$^2$ sec. This value is only one-fourth as large as the over-all third-body association rate constant found by Halstead and Thrush[11] for the reaction

$$O + SO + M \longrightarrow SO_2 + M \qquad (9)$$

which presumably includes reaction 7M and was studied in $SO_2$ afterglow experiments. Most significant for the O + COS reaction is the result that, under the present experimental conditions, reactions 7 and 9 combined are as rapid as the precursor reaction 1, so that these reactions are effective SO loss processes. This aspect of the reaction will now be discussed.

*SO Radical Consumption.* The importance of the SO losses in the O + COS reaction has been recognized previously. Rolfes, *et al.*,[8] considered the reactions

$$SO + SO \longrightarrow SO_2 + S \qquad (10)$$

$$SO + O_2 \longrightarrow SO_2 + O \qquad (11)$$

and the occurrence of reaction 10 was suggested also by the mass spectrometer observations of Sullivan and Warneck.[2b] On the other hand, Halstead and Thrush[11] argued for an alternative explanation of these results in terms of reaction 9 in combination with a reaction of SO with COS. While the present experiments could provide no detailed information on the individual SO loss reactions, it was of interest to investigate the intensity–time profiles in the later stage of the O + COS reaction for comparison with profiles calculated on the basis that reaction 9 is the major SO loss reaction. The rate coefficient $k_9 = 8.3 \times 10^{-31}$ cc/molecule sec given by Halstead and Thrush was used in the calculations.

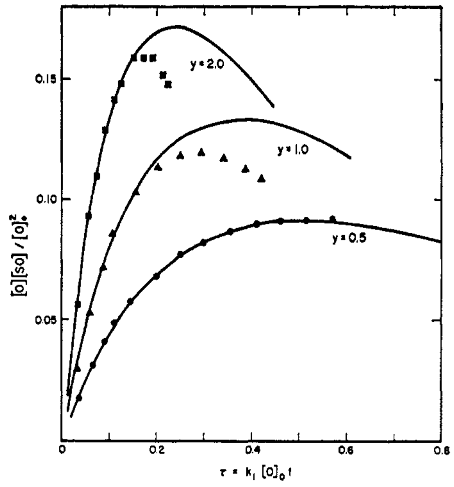

Figure 6. Intensity–time profile for the system O + COS for different initial concentration ratios $y = [COS]_0/[O]_0$. Experimental data: ●, 0.57; ▲, 0.93; ■, 1.9. Calculated results are shown by solid lines.

The results of this experiment are shown in Figure 6. Intensities were calculated by numerical integration of the pertinent differential equations and are plotted in the form $[SO][O]/[O]_0^2$ *vs.* the reaction parameter $\tau = k_1[O]_0t$ for several initial reactant concentration ratios $y = [COS]_0/[O]_0$. The experimental data points were obtained with 650 $\mu$ of pure oxygen instead of the argon–oxygen mixtures, so that a higher initial oxygen-atom concentration could be realized. A common scaling factor was applied to the experimental intensity data to facilitate the comparison.

Figure 6 demonstrates a fairly good agreement between the calculated and observed intensity profile for $y = 0.5$. Marked deviations occur in the later stage of the reaction for the higher initial [COS]/[O] concentration ratios, thus indicating the consumption of SO by reactions occurring in addition to reaction 9. The observed increase in the deviations with increasing COS concentration points to the importance of either reaction 10 or the reaction of SO with COS as suggested by Halstead and Thrush.[11] Reaction 11 would not explain the observed behavior. These results, therefore, lead to the conclusion that, despite its comparatively fast rate, reaction 9 alone is insufficient to explain the observed intensity profiles. It should be noted, however, that the fast rate deduced previously[2b] for reaction 10 cannot be upheld.

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(11) C. J. Halstead and B. A. Thrush, *Photochem. Photobiol.*, **4**, 1009 (1965).