

PHOTOLYSIS OF SO₂ IN THE PRESENCE OF FOREIGN GASES III. QUENCHING OF EMISSION BY FOREIGN GASES

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SUMMARY

The emission yields of SO₂ at 2.0 Torr pressure were measured in the presence of foreign gases at 25°C with incident radiation at 3130 Å. Experiments were performed without and with 0.33 Torr of NO present in order to measure the total and singlet relative emission efficiencies. The foreign gases studied were NO, CO₂, CO, N₂, O₂, N₂O, H₂O, OCS, and thiophene. The main purpose of the study was to extend the quenching gas pressure range beyond that used previously, to see if deviations occurred from the Stern-Volmer quenching plots. Such deviations did occur for the emitting singlet state, ¹SO₂, but not for the emitting triplet state, ³SO₂. It is concluded that ¹SO₂ is neither the state initially produced when the radiation is absorbed, nor the exclusive precursor state to ³SO₂ formation. Relative quenching constants obtained for the singlet and triplet emitting states agree well with previous work. There is no excess ³SO₂ produced over that predicted from Stern-Volmer quenching.

INTRODUCTION

SO₂ can be photoexcited at wavelengths between about 2500 and 3400 Å to give two emitting states, a singlet, ¹SO₂, and a triplet, ³SO₂. The photophysics of the primary process has been well established to be¹⁻³:



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Sidebottom *et al.*⁴ recently found the ${}^1\text{SO}_2$ emission to have a non-exponential decay when excitation was at wavelengths below 2860 Å. Their data were consistent with the hypothesis of one emitting electronic state in which rate constants for loss depend on the vibrational energy. For incident radiation above 2980 Å, the singlet decay was exponential and could be attributed exclusively to low-lying vibrational levels of ${}^1\text{SO}_2$.

Evidence has accumulated, however, that another singlet level of SO_2 (or an isomer) is involved in the photochemistry. Cehelnik *et al.*⁵ required such a state, which they called SO_2^* , to explain CO_2 production in the presence of CO . They proposed that most collisional deactivation of ${}^1\text{SO}_2$ produced this state. These ideas have been corroborated recently in Calvert's laboratory^{6,7}.

${}^1\text{SO}_2$ is known to be quenched by gases other than SO_2 ⁸:



We have considered NO separately because of its special utility to us, as discussed later. If the outlined mechanism is correct, then ${}^1\text{SO}_2$ should follow Stern–Volmer quenching:

$${}^1\text{Q}^{-1} = (k_1 + k_2[\text{SO}_2] + k_5[\text{NO}] + k_6[\text{M}])/k_{1a} \quad (a)$$

where ${}^1\text{Q}$ is the fluorescence emission yield from ${}^1\text{SO}_2$. Thus at constant SO_2 and NO pressures, ${}^1\text{Q}^{-1}$ should vary linearly with the gas pressure of added gas, M .

On the other hand, the possibility exists that SO_2^* is really the state initially formed when radiation is absorbed, and that ${}^1\text{SO}_2$ is produced from it. If so, and if SO_2^* can also be quenched, then the Stern–Volmer plots would deviate from linearity. The possibility that SO_2^* is really the initially formed state is intriguing, since the lifetime of ${}^1\text{SO}_2$ at zero pressure is about 70 times longer than that computed from the integrated absorption coefficient². Previous work has shown no deviation in the Stern–Volmer plots, but all the work was done at relatively low pressures (< 2 Torr). In this paper we extend the pressure range to see if deviations occur.

In order to explain the CO_2 production in the photolysis of SO_2 – CO mixtures, it is necessary that more triplet SO_2 be present than expected from the known quenching constants, *i.e.* there must be an additional source of triplet SO_2 ^{5–7, 9}. Such an effect was also observed in the SO_2 -sensitized phosphorescence of biacetyl, where foreign gases did not completely quench the biacetyl phosphorescence^{10, 11}. In our laboratory we have interpreted these results with additional non-emitting triplet states of SO_2 ^{5, 9, 10} whereas the Calvert group has

postulated an additional source for the emitting ³SO₂ at high gas pressures^{6, 7, 11}. In this paper, therefore, we have extended the quenching measurements using up to one atmosphere pressure of foreign gases to see if there remains a residual emission from ³SO₂.

EXPERIMENTAL

Most of the emission system used has been described in a previous paper¹². The major change was in the detection of the emission signal, which here was mechanically chopped with a 16 slot blade powered by a Princeton Applied Research (PAR) chopper, Model 125, to provide a chopping frequency of 333 Hz. The modulated emission signal passed through a Corning C.S. 0-52 filter to remove wavelengths shorter than 3400 Å before it was detected with an EMI 9558B photomultiplier. The signal voltage was developed across a 10 MΩ resistor, and amplified with a PAR, Model 112, preamplifier (× 100).

The signal was then fed into a PAR (Model 121) Lock-in Amplifier-Phase Detector which was tuned to the chopping frequency. The signal, in phase with the reference signal coming from the mechanical chopper, was read directly on the meter of the lock-in amplifier.

Fluorescence signals were corrected for variations of the intensity of the exciting beam, which was monitored by means of an RCA 935 Photodiode, and for the background signal due to scattered light.

The wavelength used for the irradiation was 3130 Å. For this purpose a 200 W high-pressure Hg arc (Illumination Industries Inc.) was used in conjunction with two 3130 Å interference filters (Baird Atomic Inc.).

Pressure measurements were made with a CD 25 Pace Pressure Transducer Indicator for the 0.01-5 Torr range. A dibutyl phthalate manometer was used for the 2-50 Torr range, and a Wallace and Tiernan absolute pressure gauge for the 50-800 Torr range.

All the following gases used were from the Matheson Company. N₂ (prep. grade), and O₂ (extra dry) were used without further purification. CO (chemically pure grade) was used after passing it through a glass wool trap immersed in liquid N₂. NO (technical grade) was distilled from -186°C into -196°C. N₂O and CO₂ (bone dry) were used after degassing at liquid N₂ temperature. SO₂ (anhydrous) was distilled from -98°C to -130°C.

The OCS was bubbled through a concentrated NaOH solution and then passed through two drying tubes tightly packed with Drierite. The effluent was collected in a U trap immersed in liquid N₂. The OCS was then allowed to distil slowly through a tube tightly packed with Ascarite into a storage bulb. The OCS was then degassed repeatedly at -196°C.

The H₂O used was taken from the tap and used after degassing. Thiophene (Sharpless Chem. Inc.) was purified by gas chromatography with a 10% tricresyl

phosphate on Chromosorb G (N.A.W.) column heated at 100°C, operated with a helium flow rate of 60 cm³/min.

RESULTS

The emission of SO₂ was monitored with incident radiation at 3130 Å so that only low-lying vibrational levels of ¹SO₂ would be involved. Initially the relative emission yield, Q , was examined for 2.00 ± 0.03 Torr of SO₂ in the presence of NO. NO was chosen since it is a known triplet quencher, and small amounts should remove the phosphorescence¹³.

The results are shown in Fig. 1. In the absence of NO, $Q = Q_0 = 59$. Only about 0.1 Torr of NO is required to eliminate the phosphorescence, yielding a relative singlet yield, 1Q_0 , of 23.6. The emission is not further affected until [NO] exceeds 0.4 Torr, at which point further increases reduce the signal due to quenching of ¹SO₂. Thus with 0.33 Torr of NO, ³SO₂ can be removed without significantly reducing ¹SO₂ emission. All additional runs to study the singlet emission alone were carried out with 0.33 ± 0.03 Torr of NO and 2.0 ± 0.03 Torr of SO₂ present.

The Stern–Volmer plot for NO is shown in Fig. 2. Initially, at very low NO pressures, the reciprocal relative emission yield, Q^{-1} , rises with the NO pressure as the triplet emission is quenched, then follows a linear law. However, for pressures

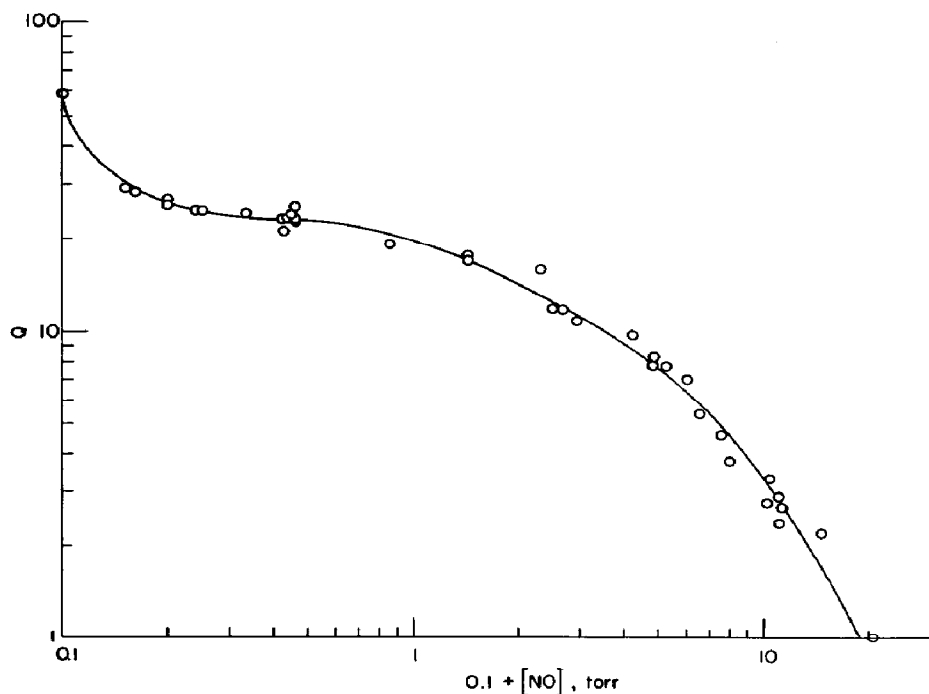


Fig. 1. Log–log plot of the relative emission yield at 25°C vs. $0.1 + [\text{NO}]$ for incident radiation at 3130 Å and $[\text{SO}_2] = 2.0$ Torr.

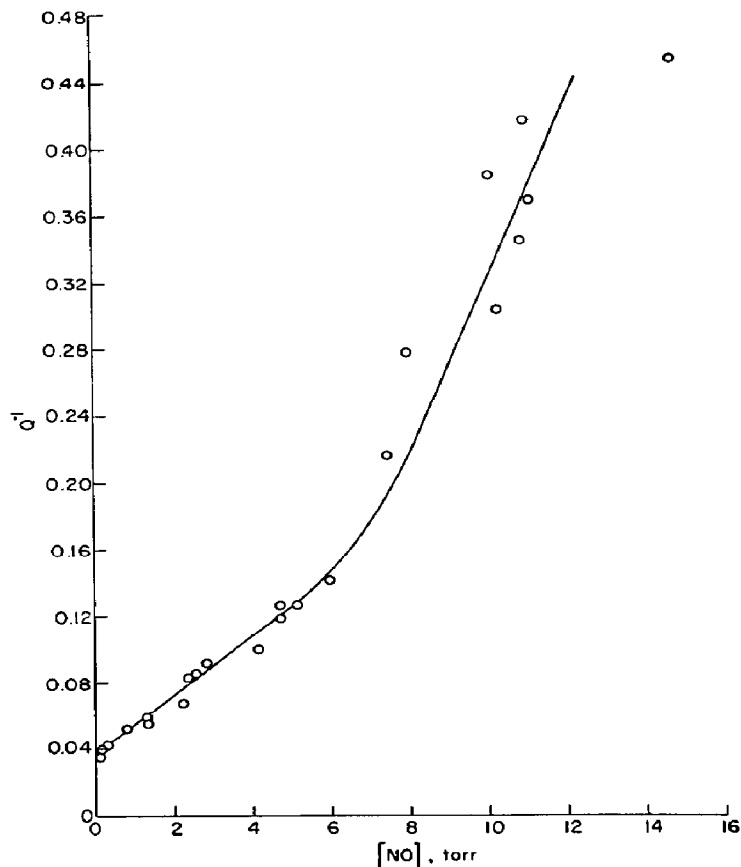


Fig. 2. Plot of reciprocal relative emission yield at 25° C vs. the NO pressure for incident radiation at 3130 Å and [SO₂] = 2.0 Torr.

of NO above about 6 Torr, the emission falls more rapidly than expected from an extrapolation of the low pressure results.

Figures 3–10 show Stern–Volmer plots for 8 different quenching gases, M. In each Figure there is a plot for data obtained in the absence of NO as well as in the presence of 0.33 Torr of NO. The data are plotted as the ratio of the emission yield in the absence of M (Q_0 with NO absent, 1Q_0 with NO present) to that in the presence of M (Q with NO absent, 1Q with NO present). In all cases replicate runs were made.

In the presence of NO, a direct measure is being made of the quenching of the singlet emission from ${}^1\text{SO}_2$. In every case the plot curves upward as the pressure is enhanced. This is particularly marked with CO and N₂ where measurements could be made to relatively high pressures, because these gases are relatively inefficient quenchers. For these gases, the emission at 30 Torr pressure is one-half that expected from an extrapolation of the low pressure asymptotes.

In the absence of NO, the total emission yield from both ${}^1\text{SO}_2$ and ${}^3\text{SO}_2$ is being measured. There is no reason why a Stern–Volmer plot should be obeyed for

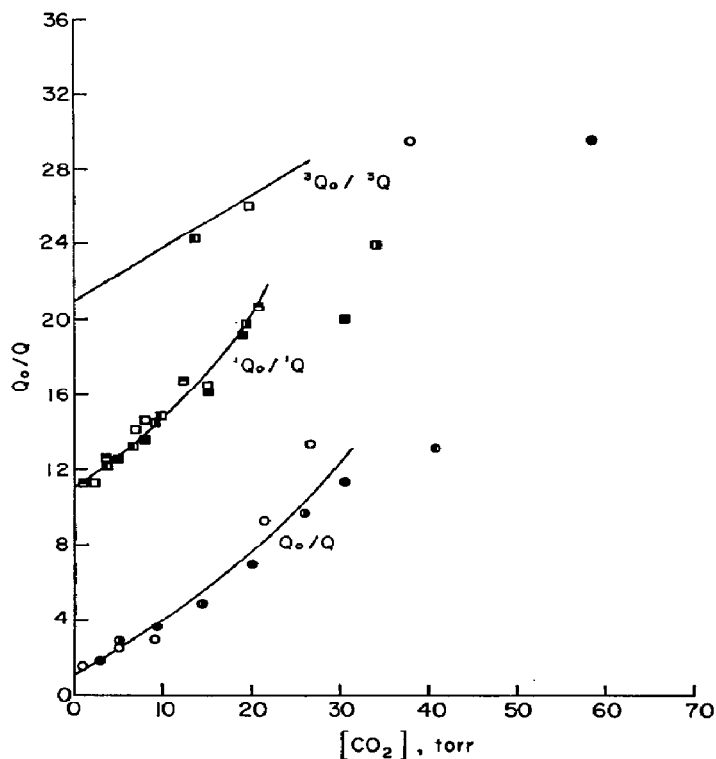


Fig. 3. Plots of the ratio of the emission yield at 25°C in the absence of CO₂ to that in its presence vs. the CO₂ pressure for incident radiation at 3130 Å and [SO₂] = 2.0 Torr. The circles are for data in the absence of NO and correspond to total emission yields. The squares are for data with 0.33 Torr of NO present and correspond to singlet emission yields. The different point notations indicate replicate runs. The triplet yields are computed from the smooth curves passing through the data for Q₀/Q and ¹Q₀/¹Q; the computed curve for ³Q₀/³Q is also shown. The ordinates for ¹Q₀/¹Q and ³Q₀/³Q are displaced for clarity. In all cases the intercept is unity.

a composite emission, but it is convenient to present the data in this way. In fact, if the quenching efficiencies compared to SO₂ are comparable for the two states, the plot will not show the break expected for two-state quenching. Only in the case of thiophene (Fig. 10) is the relative efficiency for the two states markedly different. Thiophene is a very good quencher for ³SO₂, as shown by the fact that only 0.060 Torr of thiophene is needed to completely quench the triplet emission, and the break in the curve is obvious. Again all the curves, except that for H₂O, show the upward curvature as the pressure is increased, although the deviation from linearity is not as marked as when NO is present. For each of the gases except H₂O and thiophene, measurements were made to one atmosphere pressure and in every case the emission was reduced below the limit of detection (Q₀/Q > 100).

Two of the quenching gases gave rise to unique complications. O₂ reacts with NO to produce NO₂. Consequently pressures of O₂ greater than 20 Torr could not be used with NO present. For H₂O at pressures above 12 Torr, the emission signal was not reduced with the addition of more H₂O vapor. This

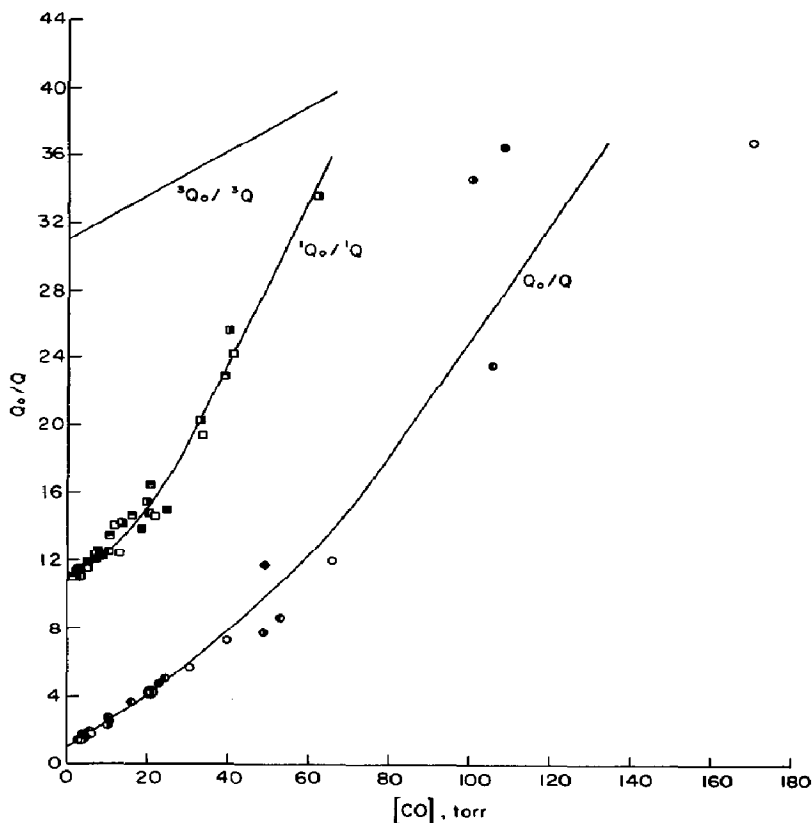


Fig. 4. Plots of the ratio of the emission yield at 25°C in the absence of CO to that in its presence vs. the CO pressure for incident radiation at 3130 Å and [SO₂] = 2.0 Torr. The circles are for data in the absence of NO and correspond to total emission yields. The squares are for data with 0.33 Torr of NO present and correspond to singlet emission yields. The different point notations indicate replicate runs. The triplet yields are computed from the smooth curves passing through the data for Q₀/Q and ¹Q₀/¹Q; the computed curve for ³Q₀/³Q is also shown. The ordinates for ¹Q₀/¹Q and ³Q₀/³Q are displaced for clarity. In all cases the intercept is unity.

residual emission was attributed to light scattering by aerosol formation. This conclusion was supported by the finding that adding an atmosphere of air did not affect the residual signal. In the absence of H₂O vapor, an atmosphere of air completely suppresses the signal.

For thiophene the emission yields in the presence or absence of NO are virtually identical showing that thiophene efficiently removes the triplet emission. For the other seven quenching gases, the triplet yield can be computed from the smooth curves fitting the data for Q₀/Q and ¹Q₀/¹Q. From these curves and the values of Q₀ = 59 and ¹Q₀ = 23.6, the values of ³Q₀/³Q ≡ (Q₀ - ¹Q₀)/(Q - ¹Q) can be computed. These computed curves are shown in Figs. 3-9. They are linear in all cases except possibly for OCS which may show a slight downward trend. Thus the triplet yields follow a simple Stern-Volmer quenching law, whereas the singlet yields do not.

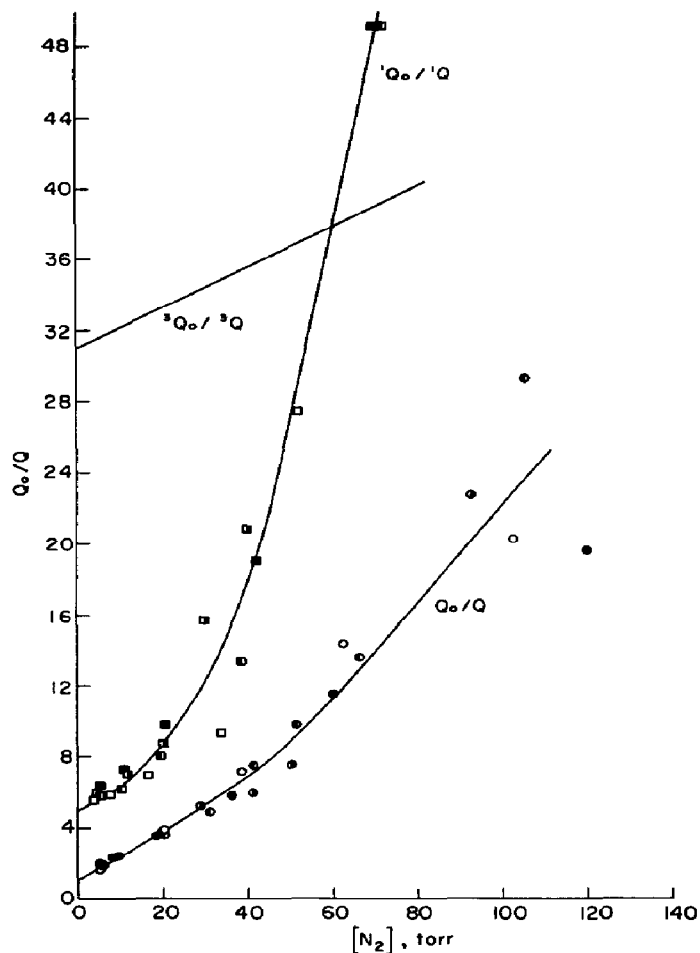


Fig. 5. Plots of the ratio of the emission yield at 25°C in the absence of N_2 to that in its presence vs. the N_2 pressure for incident radiation at 3130 Å and $[SO_2] = 2.0$ Torr. The circles are for data in the absence of NO and correspond to total emission yields. The squares are for data with 0.33 Torr of NO present and correspond to singlet emission yields. The different point notations indicate replicate runs. The triplet yields are computed from the smooth curves passing through the data for Q_0/Q and ${}^1Q_0/{}^1Q$; the computed curve for ${}^3Q_0/{}^3Q$ is also shown. The ordinates for ${}^1Q_0/{}^1Q$ and ${}^3Q_0/{}^3Q$ are displaced for clarity. In all cases the intercept is unity.

DISCUSSION

1SO_2 emission

The deviation from linearity in the Stern-Volmer plots (Figs. 3–10) indicates that the emitting state is not the state which absorbs radiation. Since it is known⁴ that, with incident radiation at 3130 Å, the emission comes from low-lying vibrational levels of 1SO_2 , there are two possible explanations which need to be considered. Either absorption occurs to high vibrational levels of 1SO_2 and the vibrational energy is removed by collision prior to emission, or the absorption is to a different

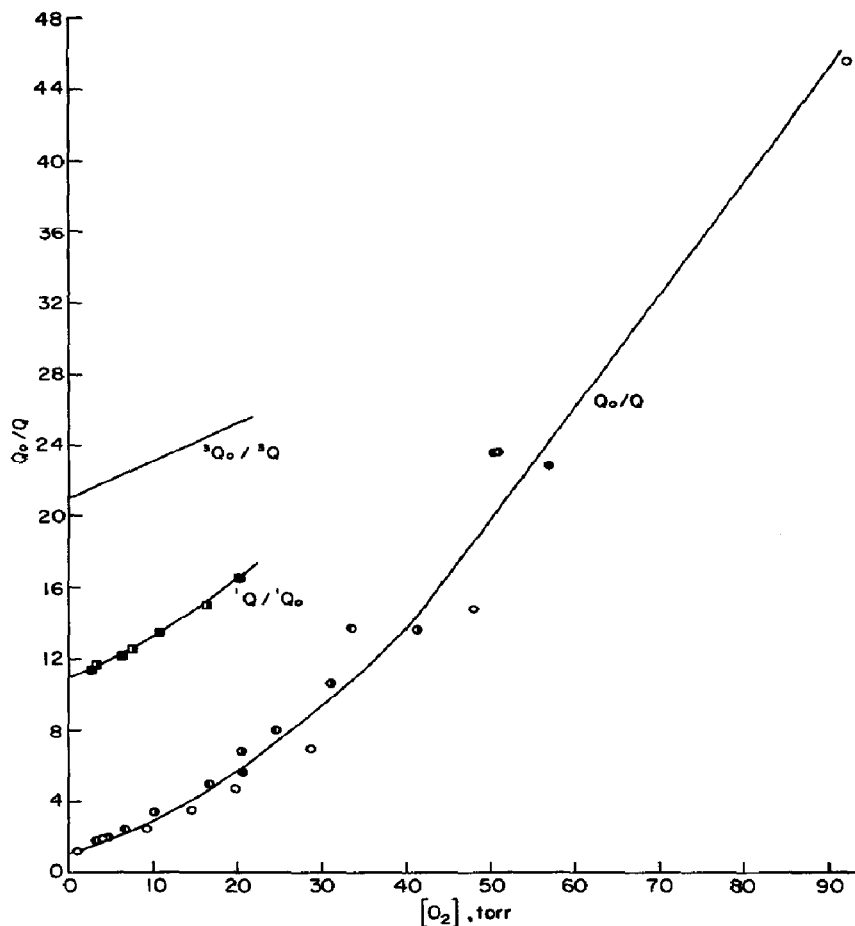


Fig. 6. Plots of the ratio of the emission yield at 25°C in the absence of O₂ to that in its presence vs. the O₂ pressure for incident radiation at 3130 Å and [SO₂] = 2.0 Torr. The circles are for data in the absence of NO and correspond to total emission yields. The squares are for data with 0.33 Torr of NO present and correspond to singlet emission yields. The different point notations indicate replicate runs. The triplet yields are computed from the smooth curves passing through the data for Q_0/Q and ${}^1Q_0/{}^1Q$; the computed curve for ${}^3Q_0/{}^3Q$ is also shown. The ordinates for ${}^1Q_0/{}^1Q$ and ${}^3Q_0/{}^3Q$ are displaced for clarity. In all cases the intercept is unity.

electronic level. In the former case the Stern–Volmer plot should not display two non-zero quenching regions as the pressure is raised. Consequently, the latter explanation must be correct. The simplest mechanism to explain the data is:



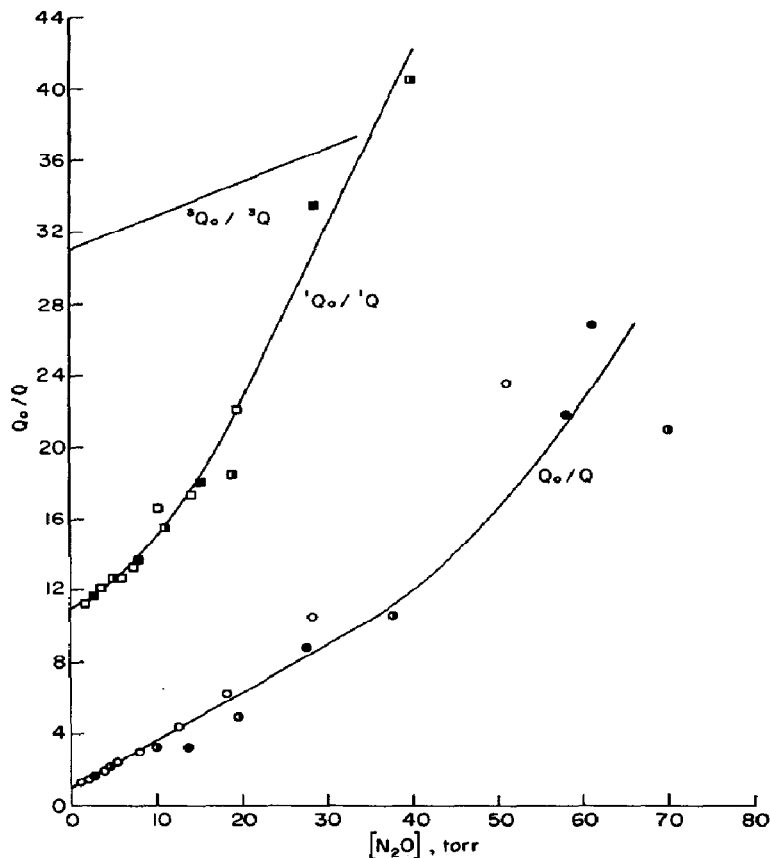


Fig. 7. Plots of the ratio of the emission yield at 25°C in the absence of N_2O to that in its presence vs. the N_2O pressure for incident radiation at 3130 Å and $[SO_2] = 2.0$ Torr. The circles are for data in the absence of NO and correspond to total emission yields. The squares are for data with 0.33 Torr of NO present and correspond to singlet emission yields. The different point notations indicate replicate runs. The triplet yields are computed from the smooth curves passing through the data for Q_0/Q and ${}^1Q_0/{}^1Q$; the computed curve for ${}^3Q_0/{}^3Q$ is also shown. The ordinates for ${}^1Q_0/{}^1Q$ and ${}^3Q_0/{}^3Q$ are displaced for clarity. In all cases the intercept is unity.



The state initially formed by absorption, SO_2^* , has an emission lifetime of about 6×10^{-7} s as computed from the integrated absorption coefficient². Since emission is not seen from SO_2^* , k_8 must be $\geq 10^8$ s⁻¹, which would then give a lifetime of $SO_2^* < 10^{-8}$ s. This value is lower than the 50×10^{-9} s limiting lifetime that could have been seen by Sidebottom *et al.*⁴.

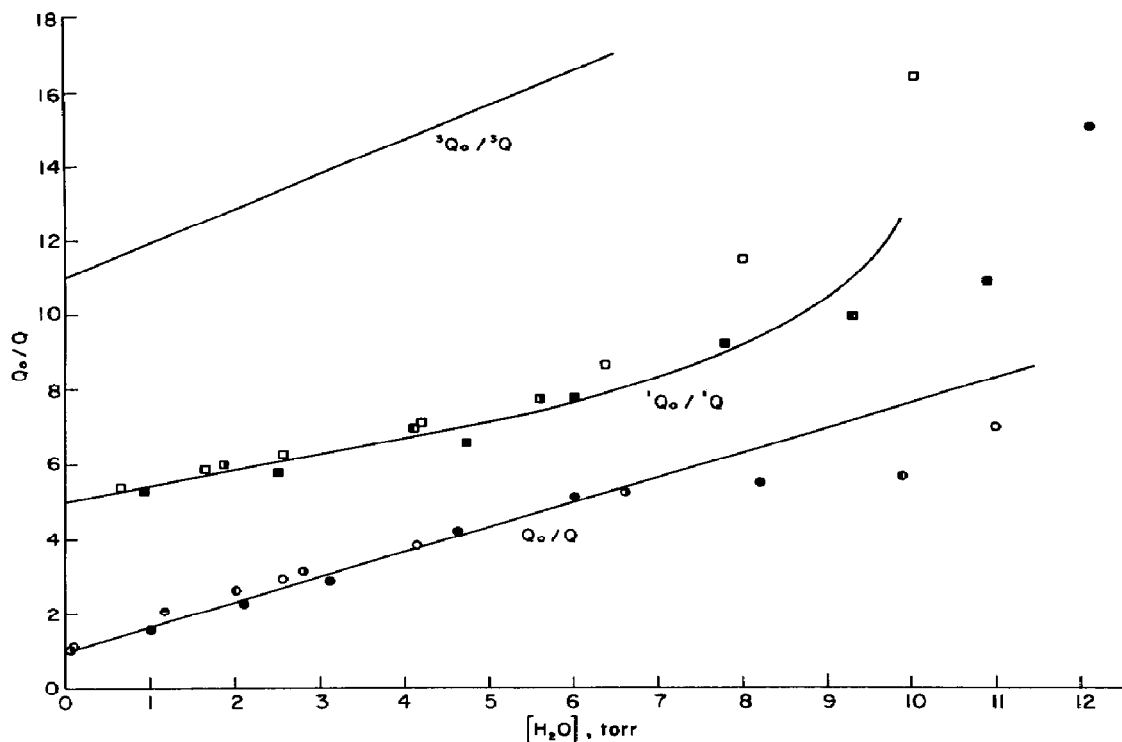


Fig. 8. Plots of the ratio of the emission yield at 25°C in the absence of H₂O to that in its presence vs. the H₂O pressure for incident radiation at 3130 Å and [SO₂] = 2.0 Torr. The circles are for data in the absence of NO and correspond to total emission yields. The squares are for data with 0.33 Torr of NO present and correspond to singlet emission yields. The different point notations indicate replicate runs. The triplet yields are computed from the smooth curves passing through the data for Q₀/Q and ¹Q₀/¹Q; the computed curve for ³Q₀/³Q is also shown. The ordinates for ¹Q₀/¹Q and ³Q₀/³Q are displaced for clarity. In all cases the intercept is unity.

The mechanism predicts the rate law:

$${}^1Q_0/{}^1Q = \frac{(k_{11}k_{-8} + (1 + \alpha)k_6k_8 + k_{11}\beta + k_6k_{11}[M]) [M]}{k_8 \{(1 + \alpha)\beta + k_{-8} \alpha\}} + 1 \quad (b)$$

where $\alpha \equiv (k_9[\text{SO}_2] + k_{10}[\text{NO}])/k_8$

$$\beta \equiv k_1 + k_2[\text{SO}_2] + k_5[\text{NO}]$$

and ¹Q₀ and ¹Q are the singlet emission yields in the absence and presence of quenching gas respectively.

Under our conditions, $\alpha \ll 1$, $\beta \gg k_{-8}$, $k_1 \ll k_2[\text{SO}_2]$, and $k_{11}/k_8 < k_6/\beta$. Thus the limiting low pressure slopes of the Stern-Volmer plots for ¹Q₀/¹Q are approximately equal to k_6/β . From the values of k_6/β , k_6/k_2 can be computed, and they are listed and compared with literature values in Table 1. The uncertainty in these values is ± 10 –20%. Our values for NO and CO₂ are somewhat higher than found by Mettee⁸, but our value for CO₂ is in excellent agreement with that of

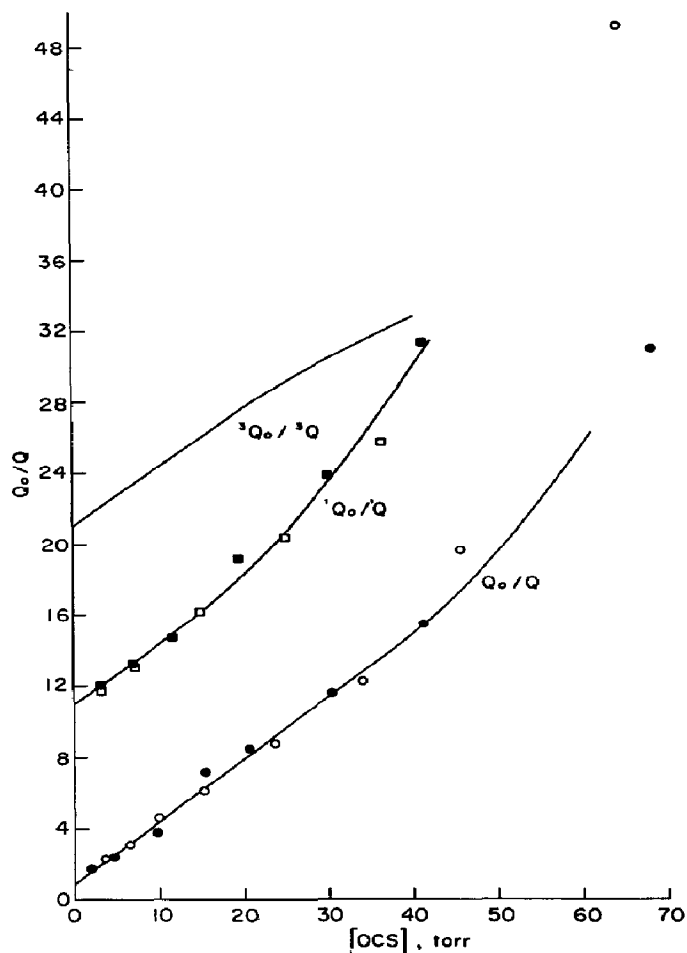


Fig. 9. Plots of the ratio of the emission yield at 25°C in the absence of OCS to that in its presence vs. the OCS pressure for incident radiation at 3130 Å and $[\text{SO}_2] = 2.0$ Torr. The circles are for data in the absence of NO and correspond to total emission yields. The squares are for data with 0.33 Torr of NO present and correspond to singlet emission yields. The different point notations indicate replicate runs. The triplet yields are computed from the smooth curves passing through the data for Q_0/Q and $^1Q_0/^1Q$; the computed curve for $^3Q_0/^3Q$ is also shown. The ordinates for $^1Q_0/^1Q$ and $^3Q_0/^3Q$ are displaced for clarity. In all cases the intercept is unity.

Rao *et al.*¹⁴. For CO and N_2 our results are in excellent agreement with the literature values. For O_2 our value is somewhat high and probably erroneous because of the reaction of NO and O_2 in our system.

$^3\text{SO}_2$ emission

The traditional view is that $^3\text{SO}_2$ is produced from $^1\text{SO}_2$. Since under our conditions the first-order decay processes (reactions 1 and 3) are unimportant, the additional steps needed to explain the $^3\text{SO}_2$ emission are:

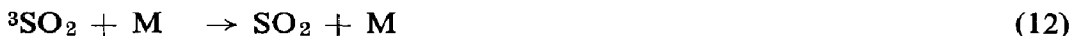


TABLE 1

SUMMARY OF RATE CONSTANT DATA

M	k_6/k_2			k_{12}/k_4		
	This work	Mettee ^a	Calvert	This work	Mettee ^a	Calvert
NO	0.86	0.59	—	~100	64	190 ^d
CO ₂	0.76	0.63	0.73 ^b	0.55	0.31	0.29 ^d
CO	0.32	0.35	—	0.26	0.30	0.22 ^e
N ₂	0.25	0.28	0.29 ^e	0.23	0.27	0.25 ^d
O ₂	0.37	0.27	0.31 ^b	0.42	0.37	0.25 ^d
N ₂ O	0.56	—	—	0.38	—	—
H ₂ O	0.93	—	—	1.8	—	2.28 ^d
OCS	0.72	—	—	0.60	—	—
Thiophene	2.4 2.0 ^f	—	—	≥100	—	—

^a Ref. 8.^b Ref. 14.^c Ref. 15.^d Ref. 13; direct excitation of triplet at 3828 Å.^e Ref. 16; direct excitation of triplet 3828 Å.^f From data with NO absent.

At low pressures the collisional quenching of SO₂* is unimportant, and the approximate rate law for ³SO₂ becomes:

$${}^3\text{Q}_0/{}^3\text{Q} = \frac{(1 + k_6[\text{M}]/k_2[\text{SO}_2]) (1 + k_{12}[\text{M}]/k_4[\text{SO}_2])}{(1 + k_{6a}[\text{M}]/k_{2a}[\text{SO}_2])} \quad (c)$$

Both Mettee⁸ and we have found the Stern–Volmer plot to be satisfied at low quenching gas pressures, so that k_{2a}/k_2 must be similar to k_{6a}/k_6 for each quenching gas for this mechanism to apply. This is highly unlikely. Furthermore the fact that the Stern–Volmer plots for triplet emission do not show the curvature typical of singlet emission excludes the possibility that the triplet state is produced exclusively from the emitting singlet state.

A simple, but not necessarily correct, explanation of the results is that ³SO₂ is produced directly by absorption:



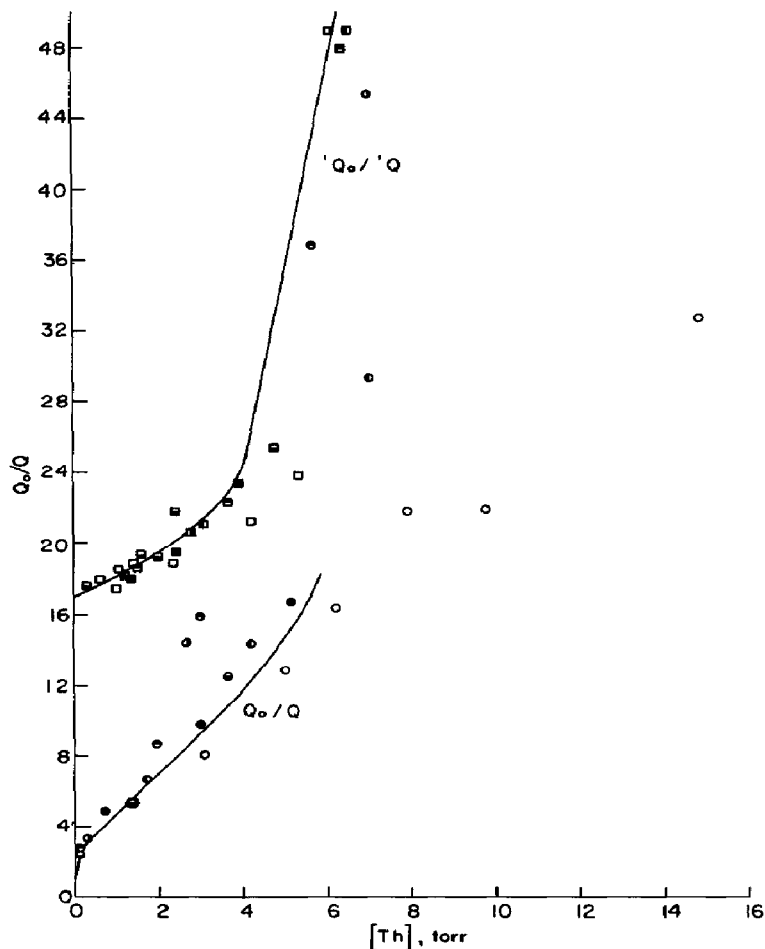


Fig. 10. Plots of the ratio of the emission yield at 25°C in the absence of thiophene to that in its presence vs. the thiophene pressure for incident radiation at 3130 Å and $[\text{SO}_2] = 2.0$ Torr. The circles are for data in the absence of NO and correspond to total emission yields. The squares are for data with 0.33 Torr of NO present and correspond to singlet emission yields. The different point notations indicate replicate runs. The ordinate for ${}^1\text{Q}_0/{}^1\text{Q}$ is displaced for clarity; its intercept is unity.

with the contribution from reactions (2a) and (6a) being negligible. The rate law then becomes:

$${}^3\text{Q}_0/{}^3\text{Q} = 1 + k_{12}[\text{M}]/k_4[\text{SO}_2] \quad (\text{d})$$

A simple straight-line Stern-Volmer plot is predicted in conformance with our findings. The slopes of the plots give $k_{12}/k_4[\text{SO}_2]$, from which k_{12}/k_4 can be computed. The computed values are listed in Table 1. Again the uncertainty is ± 10 –20%. Except for CO_2 , and possibly O_2 , they agree reasonably well with those obtained by Mettee⁸ in the same way, and by Calvert and his coworkers^{13, 16} who directly excited ${}^3\text{SO}_2$ with 3828 Å radiation. As mentioned before, our value

for O₂ is probably unreliable because of the reaction between O₂ and NO. It is not clear why our value for CO₂ is high.

The data for the triplet yields show no excess production of triplet at high pressures. For example, with added nitrogen or CO the Calvert interpretation requires that $^3Q_0/^3Q$ should increase by no more than a factor of two or possibly three. In fact, from our data an increase of at least a factor of 10 is computed.

The lack of excess 3SO_2 production is more dramatically shown by the quenching of the total emission. In every case but with H₂O, which produces an aerosol at pressures > 12 Torr, the total emission Q_0/Q shows the upward curvature as the pressure is raised, but the curvature is less pronounced than that for $^1Q_0/^1Q$. Thus the triplet yield must show less curvature than the singlet yield. For all the quenching gases except H₂O and thiophene, the results were extended to 1 atm pressure and the signal vanished, *i.e.* $Q_0/Q > 100$. Since our value for $Q_0/^1Q = 2.5$, the Calvert interpretation would require that Q_0/Q not increase by more than a factor of 6 and probably less. It is clear that this interpretation is inconsistent with the observations.

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