

## PHOTOLYSIS OF SO<sub>2</sub> IN THE PRESENCE OF FOREIGN GASES. V. SENSITIZED PHOSPHORESCENCE OF BIACETYL

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### SUMMARY

SO<sub>2</sub> was irradiated in the presence of biacetyl at 3020 Å and 25°C. The SO<sub>2</sub>-sensitized phosphorescence of biacetyl was monitored both in the absence and presence of N<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub>O, and thiophene. The results show that two triplet states of SO<sub>2</sub> must be involved to explain the yields of biacetyl phosphorescence. Neither of these states has the properties of the emitting triplet state of SO<sub>2</sub> (<sup>3</sup>B<sub>1</sub> or <sup>3</sup>SO<sub>2</sub>). In particular, neither of the two SO<sub>2</sub> triplets is quenched by N<sub>2</sub>, CO, CO<sub>2</sub>, or N<sub>2</sub>O. One of the states, SO<sub>2</sub>\*\*<sub>1</sub>, is quenched by H<sub>2</sub>O, but not by thiophene, whereas the reverse is true for the other state, SO<sub>2</sub>\*\*<sub>2</sub>. The emitting <sup>3</sup>SO<sub>2</sub> state is quenched by all six gases, and very markedly by thiophene.

The state SO<sub>2</sub>\*\*<sub>2</sub> is rapidly quenched by biacetyl and accounts for the sensitized phosphorescence at low biacetyl pressure. At higher biacetyl pressures (~ 1 Torr), its phosphorescence is enhanced because of quenching of SO<sub>2</sub>\*\*<sub>1</sub>. The SO<sub>2</sub>\*\*<sub>1</sub> state has the same properties as the triplet state responsible for chemical reaction between photoexcited SO<sub>2</sub> and CO.

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### INTRODUCTION

The primary photophysical processes which occur when SO<sub>2</sub> is excited into the absorption band centered at about 3000 Å have been studied extensively. The details of the primary process have been examined through lifetime measurements of emission as well as fluorescence and phosphorescence yields during steady-state exposure<sup>1–13</sup>. It is now well established that the phosphorescent state, <sup>3</sup>SO<sub>2</sub>, is the same state that is produced by irradiation at longer wavelengths into the

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forbidden band, *i.e.* the  $^3B_1$  state<sup>14-16</sup>. This state can undergo first-order decay processes or be quenched by collision.



where M is any other gas present in the system. The steady-state concentration for  $^3SO_2$  is then given by:

$$[^3SO_2] = \alpha I_a / (k_1 + k_2[SO_2] + k_3[M]) \quad (4)$$

where  $I_a$  is the absorbed intensity, and  $\alpha$  is the fraction of  $I_a$  that produces  $^3SO_2$ . For direct irradiation into the long wavelength forbidden band,  $\alpha = 1$ . However, for radiation  $\sim 3000 \text{ \AA}$  (into the allowed band),  $\alpha < 1$  and, in general, may be a complex function of the gas pressures.

Wampler *et al.*<sup>12</sup> flash photolyzed  $SO_2$  in the presence of other gases with a 2662  $\text{\AA}$  laser pulse, measured the  $^3SO_2$  triplet emission intensity, extrapolated it to zero time, and thus measured  $\alpha$ . They found  $\alpha$  to be dependent on the ratio  $[M]/[SO_2]$  for M =  $O_2$ ,  $N_2$ , Ar, CO, and  $CO_2$ . On the other hand, Stockburger *et al.*<sup>13</sup> examined the steady-state emission with incident irradiation at 3130  $\text{\AA}$ , and found that  $[^3SO_2]$  obeyed simple Stern-Volmer kinetics for several quenching gases in conformance with Mettee's earlier results<sup>5</sup>. The quenching gases included  $N_2$ , CO, and  $CO_2$ . Thus they concluded that  $\alpha$  must be insensitive to the ratio  $[M]/[SO_2]$ . These seemingly contradictory results may both be correct, since at 2662 and 3130  $\text{\AA}$  the precursor state to  $^3SO_2$  may be different. In fact, the photochemical results from our laboratory require such an interpretation<sup>17</sup>.

Photochemical studies in the presence of foreign gases have been undertaken in a number of laboratories. Dainton and Ivin<sup>18,19</sup> have studied the photolysis of  $SO_2$  in the presence of several paraffins and olefins. Timmons<sup>20</sup> has re-examined the photolysis of  $SO_2$  in the presence of alkanes and has also added CO. Allen and coworkers<sup>21,22</sup> have looked at the  $SO_2-O_2$  system. In our laboratory, extensive studies have been made with  $C_2F_4$ , CO, and thiophene as added gases<sup>17,23,24</sup>.

None of the photochemical studies can be explained by a mechanism involving only the two emitting excited states of  $SO_2$ . Thus Cehelnik *et al.*<sup>17,23</sup> postulated two new non-emitting states, a singlet, designated  $SO_2^*$ , and a triplet, designated  $SO_2^{**}$ , to account for the majority of the photochemical products. Two new states were needed since the triplet quenchers NO and biacetyl could reduce the extent of photochemical reaction, but not eliminate reaction completely.

Recently, Wampler *et al.*<sup>25</sup> have re-examined the formation of  $CO_2$  in 3130  $\text{\AA}$  irradiated mixtures of  $SO_2$  and CO. They concluded that an excess triplet yield is necessary to explain the data, but they felt that this excess triplet could still be  $^3SO_2$  rather than  $SO_2^{**}$ . We feel their interpretation to be unsound for reasons stated in the preceding paper<sup>17</sup>. Nevertheless, it is desirable to obtain

spectroscopic evidence for the postulated non-emitting states. Since they do not emit, direct emission studies are not possible. However, one of the states, SO<sub>2</sub>\*\*<sup>3</sup>, is readily quenched by biacetyl and perhaps can sensitize the phosphorescence of biacetyl.

The technique of using triplet SO<sub>2</sub> to sensitize biacetyl phosphorescence has been used extensively in Calvert's laboratory at relatively low pressures of SO<sub>2</sub>, biacetyl, and quenching gas, *M*<sup>7,8,26,27</sup>. These data were all interpreted in terms of sensitization by only one state of SO<sub>2</sub>, the emitting triplet, <sup>3</sup>SO<sub>2</sub>.

We decided to extend the biacetyl-SO<sub>2</sub> studies to higher pressures of biacetyl and quenching gases in order to see if SO<sub>2</sub>\*\*<sup>3</sup> can sensitize the biacetyl emission. These studies were performed at 3020 Å and 25°C and are reported here. At about the time our studies were undertaken, similar studies were made in Calvert's laboratory<sup>25,28</sup>. Most of their studies used incident radiation at 2875 Å and with CO, N<sub>2</sub>, and CO<sub>2</sub> as quenching gases<sup>28</sup>. Again they found that an excess triplet yield of SO<sub>2</sub> was required to explain the data. They attribute this yield to <sup>3</sup>SO<sub>2</sub> exclusively. Our data reported here go to higher pressures of both biacetyl and quenching gas and include N<sub>2</sub>, CO, CO<sub>2</sub>, N<sub>2</sub>O, H<sub>2</sub>O, and thiophene as quenching gases. Where the data from the two laboratories overlap, the agreement is good. The purpose of the experiments is to critically examine if the sensitization of biacetyl triplet can be explained solely by <sup>3</sup>SO<sub>2</sub>, or whether other triplet states of SO<sub>2</sub> are required.

#### EXPERIMENTAL

All gases were supplied by Matheson Gas Products. Sulfur dioxide (anhydrous) was degassed twice at -196°C and then distilled at -95°C. The fraction volatile at -95°C, but condensable at -130°C, was collected and placed in a dark storage bulb. Immediately before use, SO<sub>2</sub> was degassed again at -130°C.

Nitrogen (research grade) was used without further purification. Manufacturer's analysis showed < 1 ppm oxygen impurity.

Since all grades of commercially available carbon monoxide contain significant amounts of oxygen impurity (200 ppm in Air Products research grade CO), the following purification procedure was developed. Several atmospheres of CO (chemically pure) were condensed in a cooled (-196°C) U trap filled with glass wool. The pressure was quickly reduced to 30 Torr. The residual CO was then allowed to pass into a 3 l storage bulb which contained 5 Torr of biacetyl. The mixture was photolyzed overnight with a medium pressure mercury arc lamp. During this time all of the oxygen was chemically removed. Immediately before use the gas was passed slowly through a cold (-196°C) U trap filled with glass wool to remove unreacted biacetyl and other condensable products.

The CO<sub>2</sub> (bone dry) was degassed repeatedly at -196°C, and used without further purification. The N<sub>2</sub>O was passed through an Ascarite-packed tube and then thoroughly degassed at -196°C.

Biacetyl (J. T. Baker Co., suitable for photosensitizer use grade) was used without further purification after having been degassed first at  $-196^{\circ}\text{C}$  and then at  $-95^{\circ}\text{C}$ . Samples were stable if kept in a light-tight storage bulb. Immediately before use, the biacetyl was degassed again and then distilled into the cell at the lowest possible temperature needed to achieve the desired pressure.

Thiophene (Sharpless Chemical Inc.) was purified by gas chromatography using a 20 ft long column packed with 10% tricresyl phosphate on Chromosorb G (N.A.W.). The column temperature was  $100^{\circ}\text{C}$ , with a helium flow rate of  $60\text{ cm}^3/\text{min}$ . The thiophene was then distilled into the vacuum line, through a tube packed tightly with Ascarite and Drierite, and repeatedly degassed first at  $-196^{\circ}\text{C}$  and finally at  $-130^{\circ}\text{C}$ .

De-ionized water was degassed repeatedly at  $-95^{\circ}\text{C}$ , and used without further purification.

All experiments were carried out in a mercury-free high-vacuum line fitted with Teflon stopcocks. Pressures above 3 Torr were measured with Wallace and Tiernan absolute pressure indicators while pressures below 3 Torr were achieved by volume expansion. The geometry of the optical quartz cell is shown in Fig. 1. The total cell volume was  $\sim 30\text{ cm}^3$  with the fluorescent volume being  $\sim 1.5\text{ cm}^3$ .

The  $\text{SO}_2$ -biacetyl-foreign gas mixtures were irradiated at  $3020\text{ \AA}$ . Biacetyl phosphorescence intensity readings were taken directly from the instrument meter (in  $\mu\text{A}$ ) of a Farrand Mark I spectrofluorometer. Slits were used which gave  $50\text{ \AA}$  dispersion in both the exciting and analyzing monochromators. The intensity of the biacetyl phosphorescence band at  $5100\text{ \AA}$  was divided by the intensity of the second-order reflection of the incident beam. This eliminated errors due to fluctuations in the incident beam intensity. At low biacetyl pressure, the absorption by

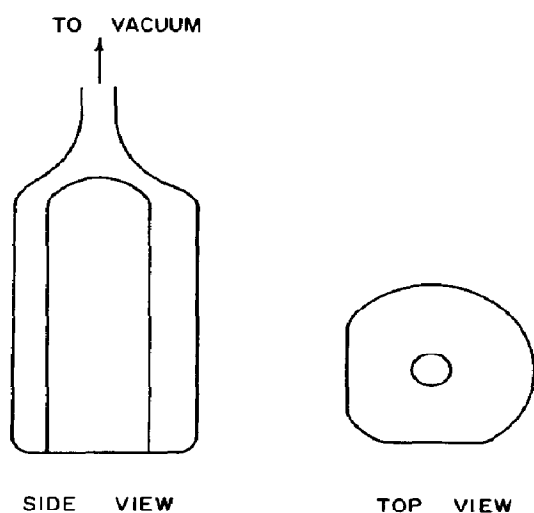


Fig. 1. Optical quartz cell used for the  $\text{SO}_2$ -sensitized phosphorescence of biacetyl.

biacetyl was negligible. However, for biacetyl pressures  $> 5$  Torr, the observed emitted intensity at 5100 Å contained a contribution from the directly absorbing biacetyl molecule. At each pressure this contribution was determined in the absence of SO<sub>2</sub> and subtracted from the observed ratio with SO<sub>2</sub> present to obtain the intensity due to energy transfer only. The correction was always less than 10%.

## RESULTS

All our studies were carried out at 25°C, with incident radiation at 3020 Å. This wavelength was used because it corresponds to the minimum in the biacetyl absorption and minimizes complications due to biacetyl absorption when SO<sub>2</sub>-biacetyl mixtures are irradiated.

Experiments were carried out in which mixtures of SO<sub>2</sub> and biacetyl were irradiated at 3020 Å, and the biacetyl phosphorescence at 5100 Å was monitored. This phosphorescence will give a measure of triplet SO<sub>2</sub> if the triplet biacetyl is removed only by emission and/or first-order internal conversion steps. In order to check this requirement the following experiments were done: biacetyl was irradiated with 4358 Å radiation to produce low-lying vibrational levels of the triplet, <sup>3</sup>B<sub>0</sub>, which emits the phosphorescence. Then SO<sub>2</sub>, or a quenching gas, or mixtures of them, were added to test their effect on the emission intensity. If 1 Torr of biacetyl was irradiated, the addition of 3 Torr of SO<sub>2</sub>, N<sub>2</sub>, or CO enhanced the

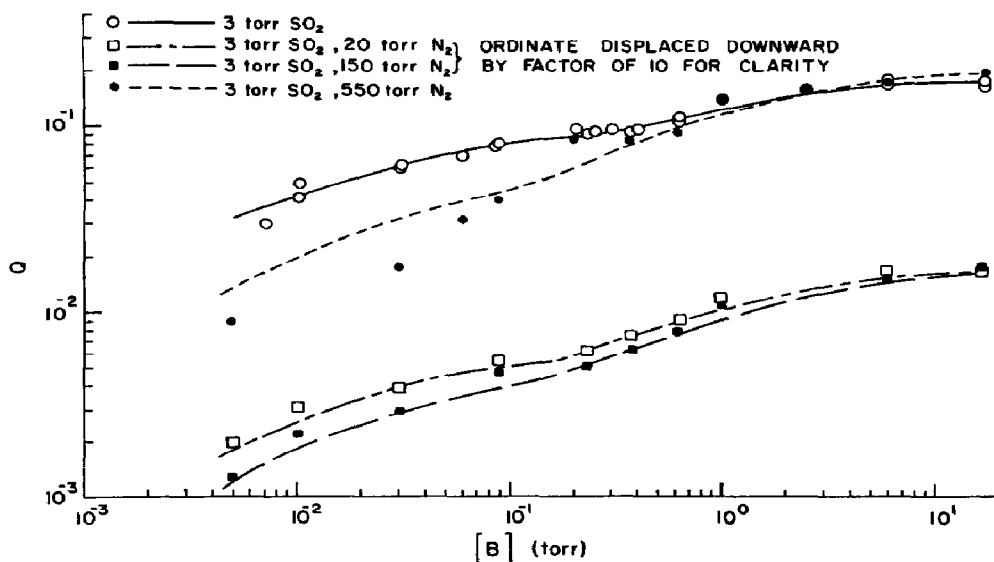


Fig. 2. Log-log plots of the relative biacetyl phosphorescence yield vs. biacetyl pressure both in the absence and presence of 20, 150, or 550 Torr of N<sub>2</sub> when sensitized by 3 Torr of SO<sub>2</sub> excited with 3020 Å radiation at 25°C. The lower two curves have been displaced downward by a factor of 10 for clarity. The lines represent theoretically computed values using the rate constant ratios listed in Table 1.

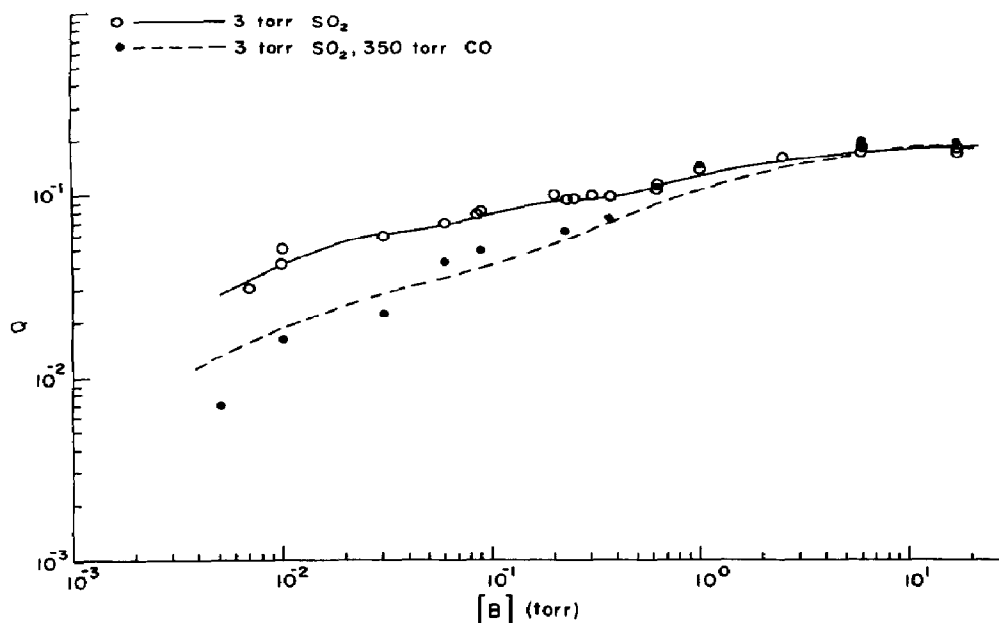


Fig. 3. Log-log plots of the relative biacetyl phosphorescence yield vs. biacetyl pressure both in the absence and presence of 350 Torr of CO when sensitized by 3 Torr of  $\text{SO}_2$  excited with 3020 Å radiation at 25°C. The lines represent theoretically computed values using the rate constant ratios listed in Table I.

emission by about 5%. Further additions of  $\text{N}_2$  up to 700 Torr or CO up to 350 Torr caused no further change. However, if trace amounts of  $\text{O}_2$  were present, then the emission was markedly quenched. Because of the difficulty in purifying the CO, we never used more than 350 Torr. The small enhancement in the emission yield when a second gas is added results from the elimination of the wall quenching of triplet biacetyl which has been shown to occur at pressures below 1 Torr<sup>29</sup>. To check this point, another set of experiments was carried out with 0.1 Torr of biacetyl. Now the addition of 3 Torr of  $\text{SO}_2$  enhanced the emission by 80%. Further additions of  $\text{SO}_2$  up to 20 Torr had no further effect. Consequently, in our studies, which were all done with 3 or 15 Torr of  $\text{SO}_2$  present, the wall reaction is unimportant, and the addition of the other gases used does not quench the biacetyl emission. It is also well known that biacetyl itself does not quench its own phosphorescence when excitation is at 4358 Å.

A further complication with 3020 Å radiation results from the direct absorption of biacetyl itself to produce its phosphorescence. Therefore, for all of the  $\text{SO}_2$ -sensitized experiments, blanks were run in which the  $\text{SO}_2$  was omitted (but the quenching gas was present). The residual emission yield was completely negligible for biacetyl pressures < 5 Torr. However, above this pressure, the yield was measurable and could account for up to 10% of the total yield at 17 Torr of biacetyl. The yields reported here are all corrected for this residual contribution.

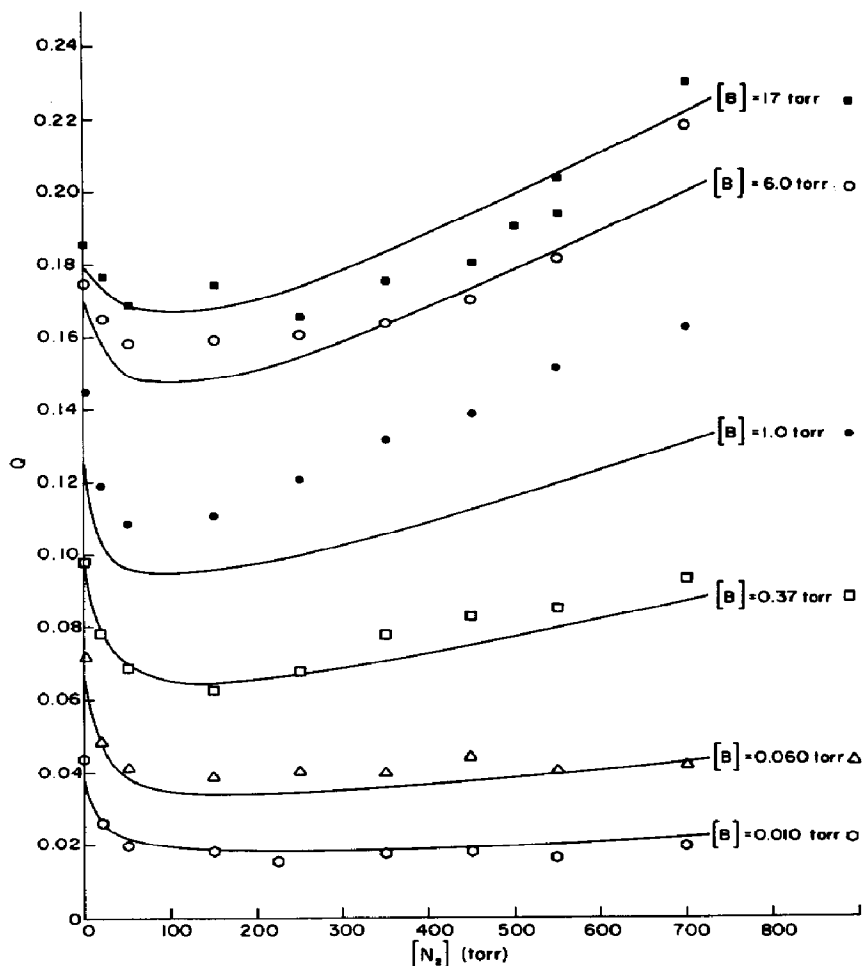


Fig. 4. Plots of the relative biacetyl phosphorescence yield vs. N<sub>2</sub> pressure at various biacetyl pressures when sensitized by 3 Torr of SO<sub>2</sub> excited with 3020 Å radiation at 25°C. The lines represent theoretically computed values using the rate constant values listed in Table 1.

Our results give only relative emission yields,  $Q$ . The proportionality factor was different at 3 and 15 Torr of SO<sub>2</sub>, because of the different fraction of radiation absorbed at the two wavelengths. Since at 15 Torr of SO<sub>2</sub>, a significant proportion of the radiation is absorbed, the effective fluorescence volume in the cell moves forward and the geometry is altered. The emission yields reported,  $Q$ , with 15 Torr of SO<sub>2</sub> are adjusted arbitrarily by a scale factor to be concordant with those at 3 Torr of SO<sub>2</sub>.

With 3 Torr of SO<sub>2</sub>, a series of runs was made with biacetyl pressures from 0.007 to 17 Torr. The biacetyl phosphorescence yields,  $Q$ , are shown in Fig. 2. The yield rises with biacetyl pressure, pauses slightly at 0.2–0.4 Torr, then continues to rise until it levels off above 6 Torr. The same trend is observed if 20, 150, or

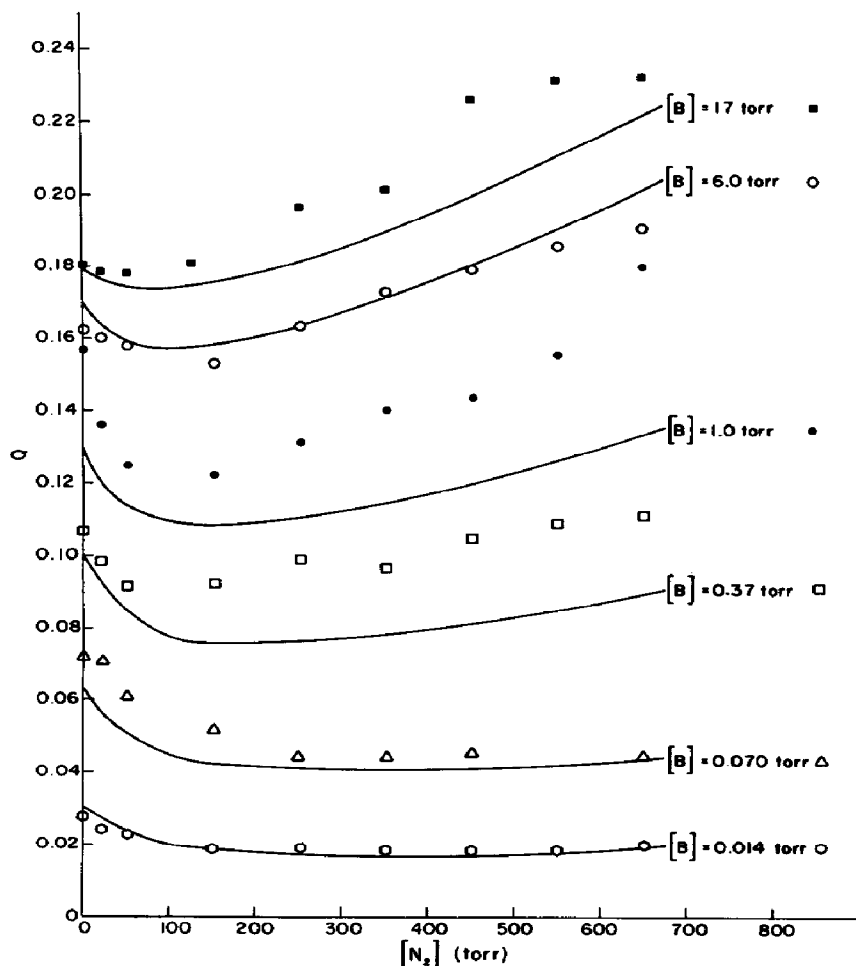


Fig. 5. Plots of the relative biacetyl phosphorescence yield vs.  $N_2$  pressure at various biacetyl pressures when sensitized by 15 Torr of  $SO_2$  excited with 3020 Å radiation at 25°C. The lines represent theoretically computed values using the rate constant ratios listed in Table 1.

550 Torr of  $N_2$  are also present. Similar results are obtained with 350 Torr of CO added as shown in Fig. 3.

To further study the effect of added gases, series of runs were done at constant biacetyl and  $SO_2$  pressures, in which a quenching gas was added in increments to the same mixture. In this way any error in the  $SO_2$  or biacetyl pressures or in the instrument readings will be the same in any series, and relative effects can be seen in detail. The results are shown in Figs. 4–10.

Figure 4 shows the effect of added  $N_2$ . The addition of  $N_2$  to mixtures of 3 Torr of  $SO_2$  and 0.010 Torr biacetyl reduces the yield to about 36% of its initial value. It is absolutely clear that the emission is not quenched to zero. (The ratio of signal to background reading was about 100.) Furthermore the half-quenching



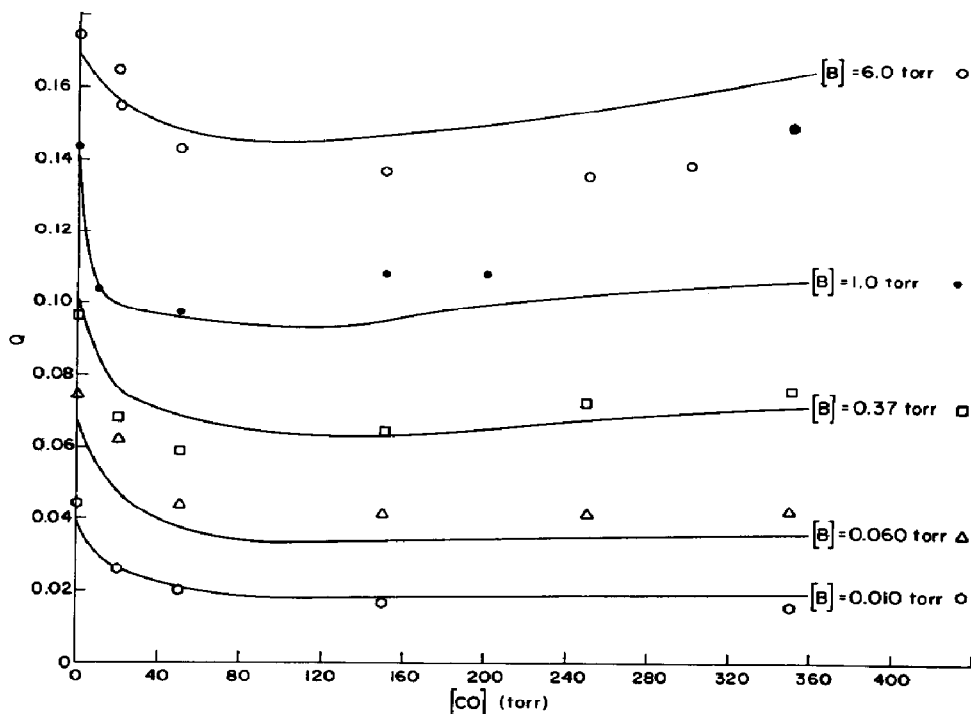


Fig. 6. Plots of the relative biacetyl phosphorescence yield vs. CO pressure at various biacetyl pressures when sensitized by 3 Torr of SO<sub>2</sub> excited with 3020 Å radiation at 25°C. The lines represent theoretically computed values using the rate constant ratios listed in Table 1.

pressure is about 20 Torr of N<sub>2</sub>. At higher biacetyl pressures, the quenching by N<sub>2</sub> is less pronounced, but the N<sub>2</sub> quenching half-pressure is about the same; and at high N<sub>2</sub> pressures, Q tends to rise.

Similar results are obtained with 15 Torr of SO<sub>2</sub> (Fig. 5), or with CO, CO<sub>2</sub>, and N<sub>2</sub>O as quenching gases at 3 Torr of SO<sub>2</sub> (Figs. 6–8). With H<sub>2</sub>O or thiophene as quenching gases, only about 1 Torr is needed to half-quench (Figs. 9 and 10). The emission then remains constant for any biacetyl pressure as the quenching gas is raised to its vapor pressure.

## DISCUSSION

Let us first consider the possibility that the sensitization of biacetyl can be explained by <sup>3</sup>SO<sub>2</sub>. Then the most general mechanism consists of:



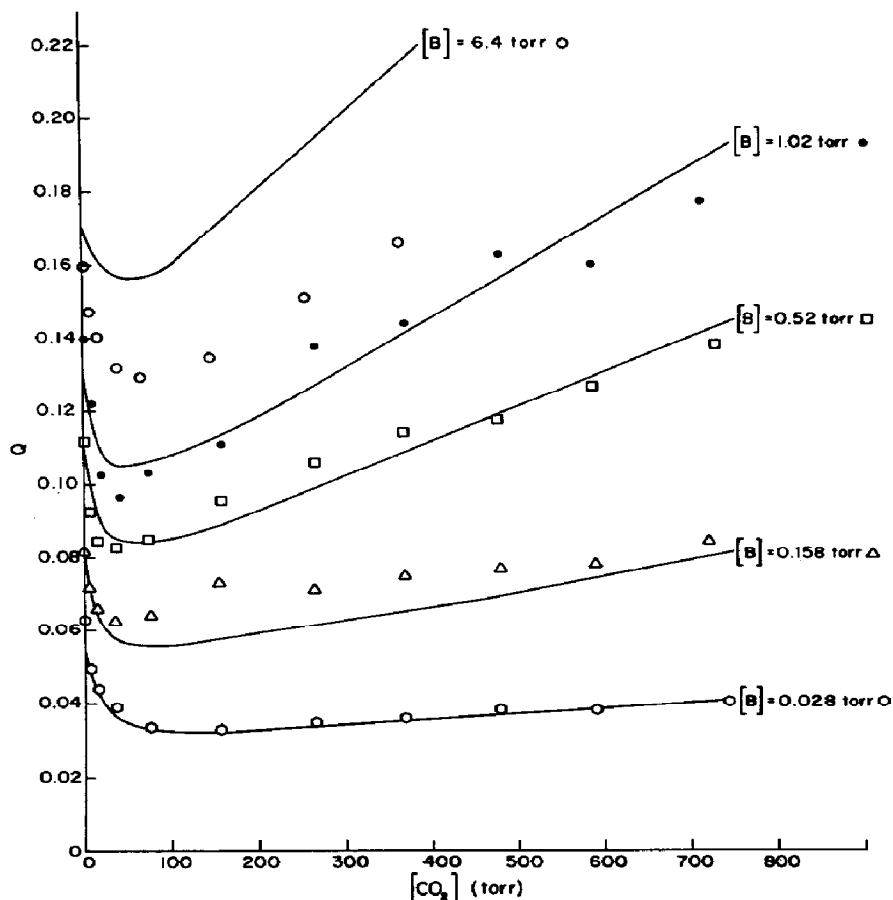
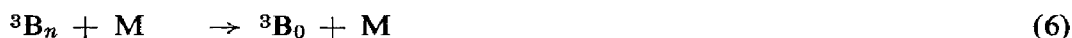


Fig. 7. Plots of the relative biacetyl phosphorescence yield vs.  $\text{CO}_2$  pressure at various biacetyl pressures when sensitized by 3 Torr of  $\text{SO}_2$  excited with  $3020 \text{ \AA}$  radiation at  $25^\circ\text{C}$ . The lines represent theoretically computed values using the rate constant ratios listed in Table 1.



where B stands for biacetyl, and  ${}^3\text{B}_n$  represents high vibrational levels of triplet biacetyl ( $> 80 \text{ kcal/mol}$ ) which are capable of decomposition, whereas  ${}^3\text{B}_0$  represents low vibrational levels which are incapable of dissociation<sup>30</sup>. For pressures of  $\text{SO}_2$  of 3 Torr or greater, reaction (1) is negligible<sup>3,4</sup>, so the expression for biacetyl emission due to  ${}^3\text{SO}_2$  sensitization,  ${}^3\text{Q}$ , is:

$${}^3\text{Q} = \frac{[\text{B}] \alpha}{(k_2[\text{SO}_2] + k_3[\text{M}] + k_4[\text{B}])} \left( k_{4b} + \frac{k_{4a} k_6[\text{M}]}{k_5 + k_6[\text{M}]} \right) \quad (II)$$

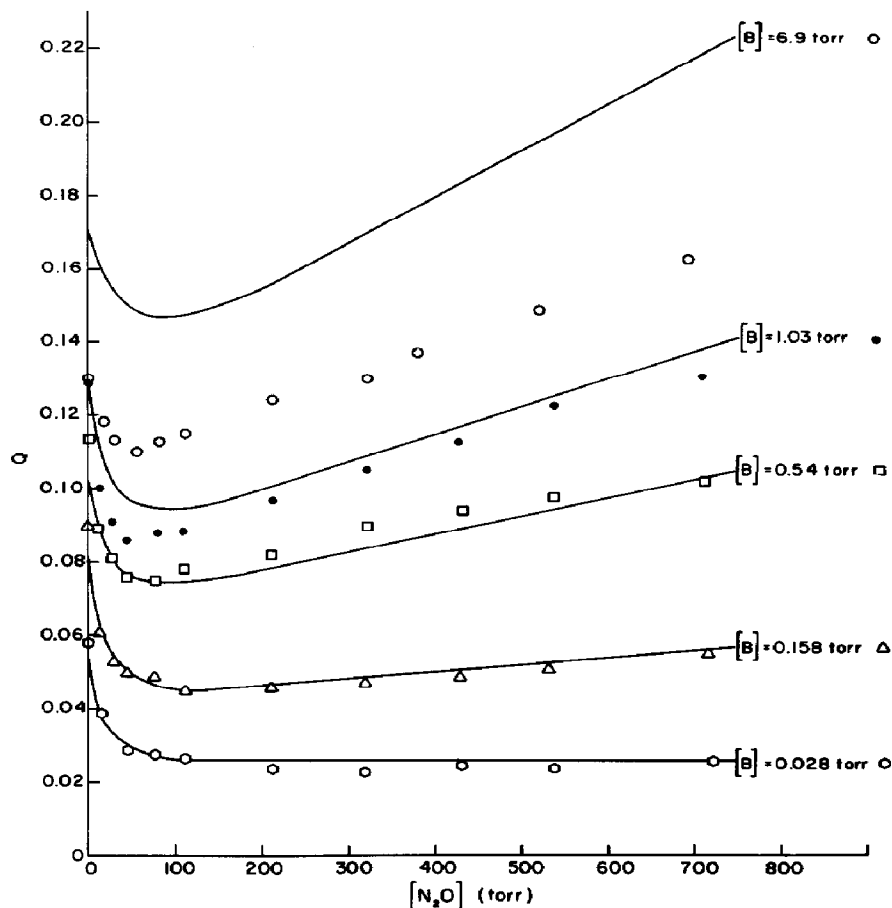


Fig. 8. Plots of the relative biacetyl phosphorescence yield vs. N<sub>2</sub>O pressure at various biacetyl pressures when sensitized by 3 Torr of SO<sub>2</sub> excited with 3020 Å radiation at 25°C. The lines represent theoretically computed values using the rate constant ratios listed in Table 1.

In the analysis from Calvert's laboratory, reaction (6) has been ignored, but we include it for generality. If it occurs at all, it can only be important at high pressures of M. The rate constant ratio  $k_3/k_2$  has been measured in three laboratories for several quenchers and the results are all in good agreement<sup>13</sup>. The only direct measurement of  $k_4/k_2$  (i.e. not by biacetyl sensitization) was made by Sidebottom *et al.*<sup>31</sup> and they found a value of 360. Again let us assume that the observation of Wampler *et al.*<sup>12</sup> with 2662 Å incident radiation is applicable here and that  $\alpha$  is a function of  $[M]/[SO_2]$ . Then at a high constant value of  $[M]$ , for  $[SO_2] = 3$  Torr, and for biacetyl pressures between 0.010 and 0.37 Torr, both  $\alpha$  and the last term in parentheses in eqn. (II) are constant. The increase in  ${}^3Q$  as  $[B]$  rises from 0.010 to 0.37 Torr can be computed from the known values of  $k_3/k_2$  and  $k_4/k_2$ . For both N<sub>2</sub> and CO,  $k_3/k_2 = 0.25$ <sup>13</sup>. The computed increases for 150 Torr N<sub>2</sub>, 550 Torr N<sub>2</sub>, and 350 Torr of CO are factors of 9.4, 19.5 and 15.6, respectively, whereas the

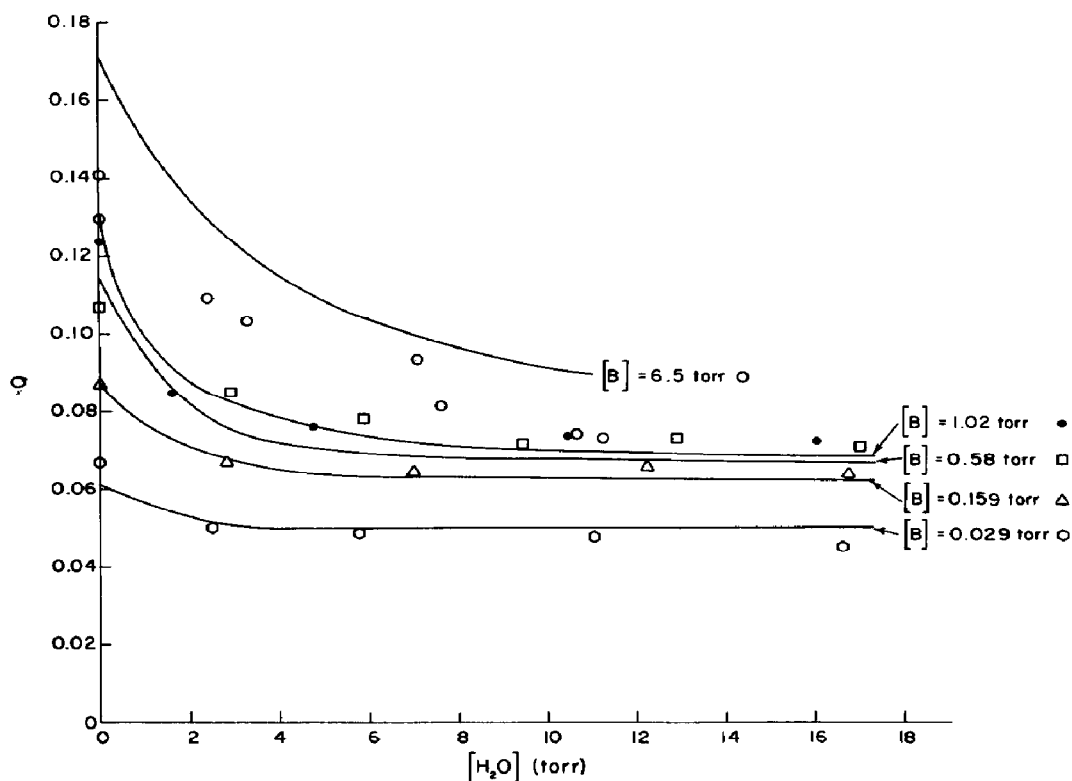


Fig. 9. Plots of the relative biacetyl phosphorescence yield vs.  $\text{H}_2\text{O}$  pressure at various biacetyl pressures when sensitized by 3 Torr of  $\text{SO}_2$  excited with  $3020 \text{ \AA}$  radiation at  $25^\circ\text{C}$ . The lines represent theoretically computed values using the rate constant ratios listed in Table 1.

observed values (from Figs. 2 and 3) are 2.7, 7.1 and 4.7, respectively. In order to fit the data it is necessary that  $k_3$  be zero, a conclusion clearly incompatible with previous investigations.

Of course  $\alpha$  may be independent of  $[\text{M}]$  as found with incident radiation at  $3130 \text{ \AA}$  by Stockburger *et al.*<sup>13</sup>. Then consider the situation in which  $[\text{B}]$  is held constant, but in which  $[\text{M}]$  varies from 0 to some value sufficiently small so that reaction (6) is unimportant (*i.e.*  $< 100$  Torr). Then the half-quenching pressure for Q must increase with  $[\text{B}]$ , *e.g.* the half-quenching pressure of  $\text{N}_2$  must be greater at 0.37 Torr of biacetyl than at 0.010 Torr of biacetyl. Just a cursory examination of Figs. 4–10 shows that this is not so for any M. Again the impossible conclusion is reached that  $k_3$  must be zero.

The inescapable conclusion from the above arguments is that  $^3\text{SO}_2$  is not the principal state sensitizing biacetyl emission. As further proof, consider the results with  $\text{H}_2\text{O}$  as a quenching gas (Fig. 9).  $\text{H}_2\text{O}$  has been found to be a good quencher of  $^3\text{SO}_2$ , being more efficient than  $\text{SO}_2$  itself<sup>13</sup>. Yet even the addition of 16.6 Torr of  $\text{H}_2\text{O}$  only reduces the emission yield 15% with as little as 0.030 Torr of biacetyl present. Under these conditions over 70% of the  $^3\text{SO}_2$  is removed

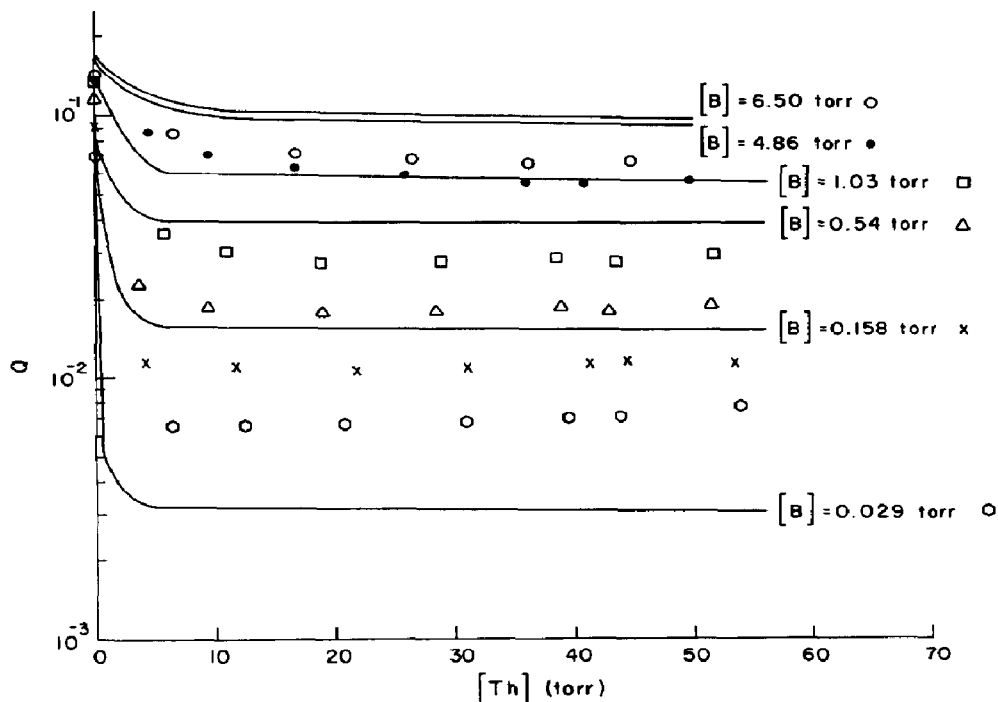


Fig. 10. Semilog plots of the relative biacetyl phosphorescence yield vs. thiophene pressure at various biacetyl pressures when sensitized by 3 Torr of SO<sub>2</sub> excited with 3020 Å radiation at 25°C. The lines represent theoretically computed values using the rate constant ratios listed in Table 1.

by H<sub>2</sub>O<sup>13</sup>. Consequently, at low biacetyl pressures no more than 15% of the emission can come from <sup>3</sup>SO<sub>2</sub>. Since this value is within the experimental uncertainty of our data, we discard further consideration of <sup>3</sup>SO<sub>2</sub>, even though it undoubtedly makes a minor contribution to the sensitization of biacetyl.

From the above arguments it is clear that the SO<sub>2</sub> triplet which sensitizes biacetyl emission is not quenched by N<sub>2</sub> or CO (or by extension, CO<sub>2</sub> or N<sub>2</sub>O). Such a state is the one proposed by Cehelnik *et al.*<sup>17,23</sup> to explain the photochemical production of CO<sub>2</sub> in the presence of CO, *i.e.* SO<sub>2</sub>\*\* . The most general mechanism for this state consistent with the photochemical results in the presence of CO and N<sub>2</sub> is:



Then the sensitized emission from this state, Q\*\*, is:

$$Q^{**} = \frac{\beta[B]}{(k_8 + k_9[B])} \left( k_{9b} + \frac{k_{9a} k_6 [M]}{k_5 + k_6 [M]} \right) \quad (III)$$

For this expression to fit the data at low [B] and at 3 Torr of SO<sub>2</sub>, it is necessary that  $k_9/k_8 = 120 \text{ Torr}^{-1}$  and that  $\beta$  be a function of [M]. In order to fit the photochemical results, Cehelnik *et al.*<sup>17,23</sup> found  $k_9/k_8 = 1 \text{ Torr}^{-1}$  and  $\beta$  to be independent of [M]. Consequently SO<sub>2</sub>\*\* is not the important sensitizing state at low biacetyl pressures (though as we shall show it is important at higher biacetyl pressures). Attempts to fit the data at low biacetyl pressure by a combination of <sup>3</sup>SO<sub>2</sub> and SO<sub>2</sub>\*\* also fail for the same reasons as those already outlined.

In order to fit the data at low biacetyl pressure, a triplet state of SO<sub>2</sub> is needed which gives rise to the same general expression as eqn. (III), but with  $\beta$  dependent on [M], and  $k_9/k_8 \sim 120 \text{ Torr}^{-1}$ . It is necessary to postulate a third triplet state of SO<sub>2</sub>, which we call SO<sub>2</sub><sup>‡</sup>. There appears to be no way to escape this conclusion and still fit the data. The processes involving this state would be:



This mechanism leads to the following expression for the intensity, Q<sup>‡</sup>, of biacetyl emission sensitized by SO<sub>2</sub><sup>‡</sup>:

$$Q^{\ddagger} = \frac{\gamma [\text{B}]}{(k_{10} + k_{11}[\text{SO}_2] + k_{12}[\text{B}]) \left( k_{12b} + \frac{k_{12a}k_6[\text{M}]}{k_5 + k_6[\text{M}]} \right)} \quad (IV)$$

$\gamma$  is the fraction of  $I_a$  which produces SO<sub>2</sub><sup>‡</sup>. It is a function of the various gas pressures. If SO<sub>2</sub><sup>‡</sup> is produced only from the state initially absorbing the radiation, then the general form for  $\gamma$  is:

$$\gamma = \frac{C_1 C_4 + C_5 [\text{SO}_2] + C_2 C_6 [\text{B}] + C_3 C_7 [\text{M}]}{C_1 + [\text{SO}_2] + C_2 [\text{B}] + C_3 [\text{M}]} \quad (V)$$

where  $C_1$ ,  $C_2$ , and  $C_3$  give the relative importance of removal of the precursor absorbing state by first-order processes, by quenching by biacetyl, and by quenching by M, respectively, compared to quenching by SO<sub>2</sub>. The constants  $C_4$ ,  $C_5$ ,  $C_6$ , and  $C_7$  give the fraction of the time that SO<sub>2</sub><sup>‡</sup> is produced from first-order processes and from quenching by SO<sub>2</sub>, biacetyl, and M, respectively. Of course SO<sub>2</sub><sup>‡</sup> may be produced from more than one precursor state, and then  $\gamma$  would be much more complex. The coefficients,  $C_1$ – $C_7$ , would represent more or less average values. For simplicity we consider  $\gamma$  to have the form given by eqn. (V).

The question now remains if the total emission from biacetyl, Q, can be explained by sensitization of biacetyl solely by SO<sub>2</sub><sup>‡</sup>. For high values of M (*e.g.* 550 Torr of N<sub>2</sub>), Q<sup>‡</sup> should rise with the biacetyl pressure to a constant value and then level off. Further increases in biacetyl pressure should have no further effect.

However, the data in Fig. 2 clearly show a second plateau which is half reached at about 1 Torr of biacetyl. Possibly at biacetyl pressures  $> 1$  Torr,  $\gamma$  is somewhat influenced by [B], and this accounts for the increase at high biacetyl pressures. If so, then the formation of the second plateau should occur at lower biacetyl pressures when [M] is lower. The four curves in Fig. 2, as well as the two curves in Fig. 3, show that this is not so. The second plateau, which also occurs with CO<sub>2</sub> and N<sub>2</sub>O as the quenching gas, can be explained by sensitization of biacetyl by SO<sub>2</sub>\*\*.

Further evidence that the second plateau at high biacetyl pressure is due to a second triplet state comes from the results with added H<sub>2</sub>O. The addition of H<sub>2</sub>O rapidly decreases Q at first, but additions beyond 10 Torr have no effect. Q at H<sub>2</sub>O pressures  $> 10$  Torr,  $Q_{\infty}$ , is plotted against [B] in Fig. 11. It is clear that the second plateau has vanished, but the results below  $\sim 0.3$  Torr of biacetyl are hardly affected. H<sub>2</sub>O is known to quench <sup>3</sup>SO<sub>2</sub><sup>13</sup>, and presumably it also quenches SO<sub>2</sub>\*\* (or whatever state is responsible for the second plateau).



Additional evidence for the importance of states other than <sup>3</sup>SO<sub>2</sub> or SO<sub>2</sub><sup>≠</sup> sensitizing biacetyl emission is given with added thiophene. The addition of thiophene (Th) rapidly reduces Q to a constant value for pressures of thiophene in

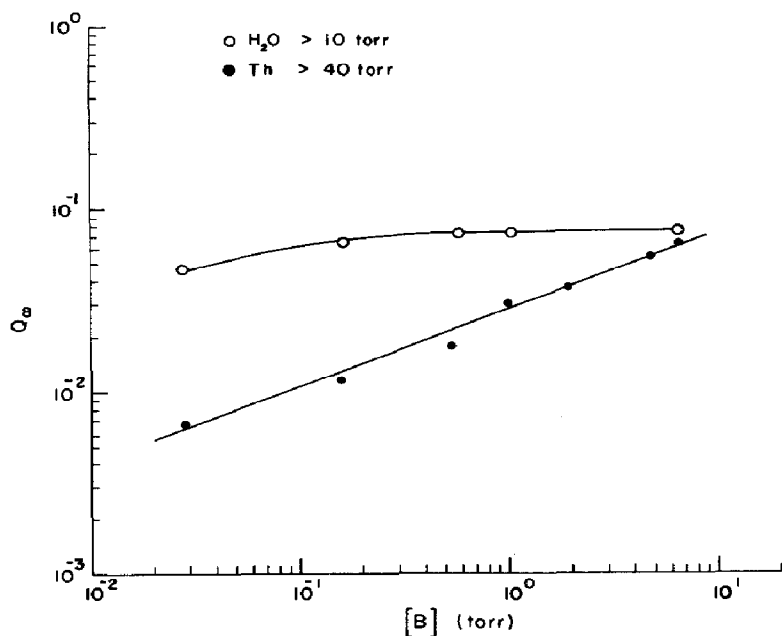


Fig. 11. Log-log plots of the relative biacetyl phosphorescence yield vs. biacetyl pressure in the presence of  $> 10$  Torr of H<sub>2</sub>O or  $> 40$  Torr of thiophene when sensitized by 3 Torr of SO<sub>2</sub> excited with 3020 Å radiation at 25°C.

excess of 10 Torr. At low biacetyl pressures, 90% of Q is removed by adding > 10 Torr of thiophene. Clearly both  ${}^3\text{SO}_2$  and  $\text{SO}_2^\ddagger$  are quenched.

The values of Q at high thiophene pressures,  $Q_\infty$ , are plotted against [B] in Fig. 11. Q continues to rise as [B] increases. The fact that the plot does not level off indicates at least two states are sensitizing biacetyl emission. One is undoubtedly  $\text{SO}_2^{**}$ , and the other (or others) is excited thiophene produced from quenching excited  $\text{SO}_2^\ddagger$ .<sup>24</sup> Presumably a reaction of importance is:



Now let us summarize our interpretations. There are three triplet states of  $\text{SO}_2$ , which we have designated  ${}^3\text{SO}_2$ ,  $\text{SO}_2^{**}$ , and  $\text{SO}_2^\ddagger$ . The first state is the emitting triplet. It contributes no more than 15% of Q. Since our experimental data are not more accurate than  $\sim 15\%$ , we ignore  ${}^3\text{SO}_2$  for simplicity. The state  $\text{SO}_2^\ddagger$  is primarily responsible for Q at low [B], but  $\text{SO}_2^{**}$  makes a contribution at high [B].

So far these arguments have been rigorous, but semi-quantitative or qualitative. It is now desirable to see if the data for  $Q = Q^\ddagger + Q^{**}$  can be fitted quantitatively. To do this a number of simplifications are introduced into eqns. (III), (IV), and (V), since the data can be fitted with fewer rate constant ratios than contained in those equations.

The data can be fitted with  $k_5 \gg k_6[M]$  for all M. Then for  $Q^{**}$ :

$$Q^{**} = \frac{(\beta k_{9b}/k_8)[B]}{(1 + k_9[B]/k_8 + k_{13}[\text{H}_2\text{O}]/k_8)} \left( 1 + k_{9a}k_6[M]/k_{9b}k_5 \right) \quad (VI)$$

There are four rate constant parameters for  $Q^{**}$ . The first is the scale factor  $\beta k_{9b}/k_8$ . The ratio  $k_9/k_8$  is known<sup>23</sup> to be 1.0 Torr<sup>-1</sup>, and this value is used. The ratio  $k_{13}/k_8$  is the relative quenching constant for  $\text{SO}_2^{**}$ , and is applicable only with  $\text{H}_2\text{O}$  as the quenching gas. The fourth parameter is  $k_{9a}k_6/k_{9b}k_5$  and it can be different for each quenching gas. It is needed to explain the enhancement in Q at high pressures of quenching gas.

For  $Q^\ddagger$  the expression is: (VII)

$$Q^\ddagger = \frac{\gamma(k_{12b}/k_{12})[B]}{(k_{10}/k_{12} + k_{11}[\text{SO}_2]/k_{12} + [B] + k_{14}[\text{Th}]/k_{12})} \left( 1 + k_6k_{12a}[M]/k_5k_{12b} \right)$$

This expression contains five rate constant parameters which play similar functions to those for  $Q^{**}$ . One of these is specific for thiophene, and plays no role with the other quenching gases. Of course,  $\gamma$  as given by eqn. (V) also contains seven parameters which need to be fitted. Actually much fewer are needed. For simplicity we have assumed that  $C_1$  and  $C_4$  are zero,  $C_2 = 1$ , and  $C_5 = C_6$ . Then the scale parameter for  $Q^\ddagger$  becomes  $C_5k_{12b}/k_{12}$ . The two parameters  $C_7/C_5$  and  $C_3$  are used to fit the extent of the decrease in Q as M is first added, and the half-pressure for the decrease, respectively.



The data have been computer fitted, and the values of the parameters are listed in Table 1. Theoretical curves were computed with these parameters and these theoretical curves have been drawn in Figs. 2–10. The data in Figs. 2 and 3 are reasonably fitted by the curves. In Fig. 4, five of the six sets of runs are well fitted. The set with 1.0 Torr of biacetyl gives the theoretical curve about 20% below the data points, though the curve shape is well reproduced. The discrepancy may reflect experimental error, as mixtures of 1 Torr of biacetyl and 3 Torr of SO<sub>2</sub> were the most difficult to prepare accurately. In Fig. 5, four of the sets of runs are well fitted, but the two intermediate sets show some deviation. Again at 1.0 Torr biacetyl, the theoretical curve is about 20% below the data points, though the curve shape is well reproduced.

Figure 6 is satisfactory, but Fig. 7–9 show deviations at ~ 7 Torr of biacetyl. This is undoubtedly experimental error rather than an inadequacy in the mechanism, since the experimental values at ~ 7 Torr of biacetyl in the absence of M are lower than for the identical points in Figs. 4 and 6.

In Fig. 10, the fit is not good. It is clear that the theoretical lines are too low at low biacetyl pressures and too high at high biacetyl pressures. With thiophene the mechanism must be more complex than outlined here. Excited states of thiophene are produced, and these may also sensitize biacetyl emission.

Further tests of the reasonableness of the mechanism come from an examination of the quenching constants in Table 1.  $C_3$  is about the same for N<sub>2</sub> and CO. It is somewhat larger and the same for CO<sub>2</sub> and N<sub>2</sub>O. In all four cases it is < 1 indicating that these gases are less efficient quenchers than SO<sub>2</sub>. On the other hand  $C_3 = 4.0$  for H<sub>2</sub>O showing its large quenching efficiency. The trend for these molecules is as expected. Thiophene is such an efficient quencher of SO<sub>2</sub><sup>\*</sup> that neither  $C_3$  nor  $C_7$  could be measured in this case. The same trend is shown for  $k_6k_{9a}/k_5k_{9b}$ , though in this case sufficient pressures of H<sub>2</sub>O and thiophene could not be used to measure their efficiencies.

TABLE 1

RATE CONSTANT RATIOS USED TO FIT DATA WITH VARIOUS QUENCHING GASES

Ratio	Units	N <sub>2</sub>	CO	CO <sub>2</sub>	N <sub>2</sub> O	H <sub>2</sub> O	Thiophene
$\beta k_{9b}/k_8$	Torr <sup>-1</sup>	0.11	0.11	0.11	0.11	0.11	0.11
$k_9/k_8^a$	Torr <sup>-1</sup>	1.0	1.0	1.0	1.0	1.0	1.0
$k_{13}/k_8$	Torr <sup>-1</sup>	—	—	—	—	1.8	—
$k_6k_{9a}/k_5k_{9b}$	Torr <sup>-1</sup>	0.0010	0.0010	0.0023	0.0014	—	—
$C_5k_{12b}/k_{12}$	None	0.075	0.075	0.075	0.075	0.075	0.075
$k_{10}/k_{12}$	Torr	0.0049	0.0049	0.0049	0.0049	0.0049	0.0049
$k_{11}/k_{12}$	None	0.00116	0.00116	0.00116	0.00116	0.00116	0.00116
$k_{14}/k_{12}$	None	—	—	—	—	—	2.8
$k_6k_{12a}/k_5k_{12b}$	None	0.0008	0.0008	0.0003	0	—	—
$C_3$	None	0.20	0.20	0.30	0.30	4.0	—
$C_7$	None	0.30	0.30	0.45	0.35	0.85	—

<sup>a</sup> From Cehelnik *et al.*<sup>23</sup>.

It would be expected that  $k_6k_{12a}/k_5k_{12b}$  should show the same trend with different quenching gases as the other quenching constants. For H<sub>2</sub>O and thiophene sufficient pressures were not reached to measure this ratio. In fact, with CO the same is true. We just used 0.0008 because it was the same as for N<sub>2</sub>. For N<sub>2</sub>O the value is 0, and the data for CO<sub>2</sub> are fitted about equally well with 0 as with 0.003. Only with N<sub>2</sub> is a non-zero value needed to get the best fit. However, if 0 is used for  $k_6k_{12a}/k_5k_{12b}$ , a reasonably good fit is still achieved. Probably  $k_{12a}$  is essentially zero.

The data require three excited triplet states of SO<sub>2</sub> when absorption is into the band centered at 2900 Å. The lowest lying is the emitting state, <sup>3</sup>SO<sub>2</sub>, and it has been definitely identified as <sup>3</sup>B<sub>1</sub> symmetry<sup>32</sup>. The other two states must be <sup>3</sup>A<sub>2</sub> and <sup>3</sup>B<sub>2</sub>. Probably <sup>3</sup>B<sub>2</sub> lies at higher energy than <sup>3</sup>A<sub>2</sub>, since the corresponding singlets are in that order. Of the two states which sensitize biacetyl emission SO<sub>2</sub>\*\* probably lies higher than SO<sub>2</sub><sup>z</sup> since  $k_{9a}/k_{9b} > k_{12a}/k_{12b}$ . If this supposition is correct, then SO<sub>2</sub>\*\* is probably the <sup>3</sup>B<sub>2</sub> state and SO<sub>2</sub><sup>z</sup> the <sup>3</sup>A<sub>2</sub> state.

The possibility that biacetyl emission was sensitized by the excited singlet states of SO<sub>2</sub> was omitted in the above analysis. The justification for this is that Cehelnik *et al.*<sup>23</sup> found that biacetyl did not quench the chemically active singlet states with 3130 Å incident radiation. Furthermore, the addition of excess quenching gases completely removes the emitting singlet state of SO<sub>2</sub><sup>13</sup>.

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