# The Quenching Reactions of the First Excited Singlet and Triplet States of Sulfur Dioxide with Oxygen and Carbon Dioxide[1]

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**Abstract:** A determination has been made of the quantum yields of fluorescence ($\phi_f$) and phosphorescence ($\phi_p$) of sulfur dioxide excited at 2875 Å and 25° in mixtures with added oxygen or carbon dioxide. From the variation of $\phi_f$ and $\phi_p/\phi_f$ with [$SO_2$], [$O_2$], and [$CO_2$], and the published lifetime data for excited sulfur dioxide,[2,6] estimates of the rate constants (l.-mole-sec units) for the quenching reactions of both the first excited singlet ($^1SO_2$) and triplet ($^3SO_2$) sulfur dioxide molecules with $SO_2$, $O_2$, and $CO_2$ were derived: $^1SO_2 + SO_2 \rightarrow (2SO_2)$ (1a), $^1SO_2 + SO_2 \rightarrow {}^3SO_2 + SO_2$ (2a), $k_{1a} + k_{2a} = (1.5 \pm 0.7) \times 10^{10}$; $^1SO_2 + O_2 \rightarrow (SO_2\text{-}O_2)$ (1b), $^1SO_2 + O_2 \rightarrow {}^3SO_2 + O_2$ (2b), $k_{1b} + k_{2b} = (0.47 \pm 0.22) \times 10^{10}$; $^1SO_2 + CO_2 \rightarrow (SO_2\text{-}CO_2)$ (1c), $^1SO_2 + CO_2 \rightarrow {}^3SO_2 + CO_2$ (2c), $k_{1c} + k_{2c} = (1.1 \pm 0.5) \times 10^{10}$; $^3SO_2 + SO_2 \rightarrow (2SO_2)$ (8a), $k_{8a} = (1.4 \pm 0.7) \times 10^7$; $^3SO_2 + O_2 \rightarrow (SO_2\text{-}O_2)$ (8b), $(1.1 \pm 0.6) \times 10^7 \leq k_{8b} \leq (5.9 \pm 0.6) \times 10^7$; $^3SO_2 + CO_2 \rightarrow (SO_2\text{-}CO_2)$ (8c), $k_{8c} = (0.87 \pm 0.50) \times 10^7$. The smallness of the rate constant for reaction 8b is unexpected and represents the lowest reported value for a triplet molecule quenching reaction by oxygen.

Previous studies of sulfur dioxide photochemistry suggest that some striking differences exist between the reactivities of the first excited singlet ($^1SO_2$) and triplet ($^3SO_2$) states in sulfur dioxide. Fluorescence from the $^1SO_2$ state is quenched on virtually every collision with ground-state sulfur dioxide molecules,[2-5] and, in the order of decreasing efficiency, $CO_2$, $H_2$, $O_2$, and He quench $^1SO_2$ somewhat less rapidly than $SO_2$.[2] On the other hand, apparently the phosphorescence from the $^3SO_2$ state is quenched very inefficiently by ground-state sulfur dioxide. About one in $10^3$ or $10^4$ collisions are effective in deactivating this molecule,[3,5,6] and Caton and Duncan[6] observed no preferential quenching of the $^3SO_2$ state in experiments with added oxygen. The apparent very low reactivity of the $^3SO_2$ species with oxygen appears to be unique among the known photochemical systems, and this observation should be verified and further defined in quantitative studies.

Accurate rate data on the reactions of the $^1SO_2$ and the $^3SO_2$ states with oxygen and other gases would be most valuable in the evaluation of the role of each state in the photochemistry of sulfur dioxide and in its mixtures with oxygen. These data would be of great practical value as well in the delineation of the paths of sulfur dioxide removal in the polluted atmosphere. In this work we describe the quantitative determinations of the rate constants for the quenching of both the $^1SO_2$ and the $^3SO_2$ states by oxygen and carbon dioxide. These have been made through a study of the effect of oxygen and carbon dioxide on the quantum yields of fluorescence and phosphorescence of sulfur dioxide excited at 2875 Å and 25°. The data allow some interesting conclusions concerning several aspects of the photochemistry of sulfur dioxide.

## Experimental Section

All emission data were determined on an absolute spectrofluorimeter (Turner Model 210) using the procedures which have been described previously.[5] The exciting light was at 2875 Å with a 150-Å band width. The second of the two methods outlined previously[5] was employed in the determination of quantum yields of fluorescence ($\phi_f$) and phosphorescence ($\phi_p$) of sulfur dioxide. Quantum yield data determined from $SO_2$–$O_2$ and $SO_2$–$CO_2$ mixtures are summarized in Tables I and II, respectively.

## Discussion of the Results

The quenching rate constants for both $^1SO_2$ and $^3SO_2$ states of sulfur dioxide with $SO_2$, $O_2$, and $CO_2$ can be estimated from the emission data determined in this work. The quantum yields of fluorescence and phosphorescence from sulfur dioxide excited at 2875 Å and 25° in $SO_2$–$O_2$ and $SO_2$–$CO_2$ mixtures can be described well in terms of an extension of the mechanism suggested previously for pure sulfur dioxide.[5]

$$SO_2 + h\nu \rightarrow {}^1SO_2 \tag{I}$$

$$^1SO_2 + SO_2 \rightarrow (2SO_2) \tag{1a}$$

$$\rightarrow {}^3SO_2 + SO_2 \tag{2a}$$

$$^1SO_2 + O_2 \rightarrow (SO_2\text{-}O_2) \tag{1b}$$

$$\rightarrow {}^3SO_2 + O_2\ (^3\Sigma,\ ^1\Delta,\text{ or }^1\Sigma) \tag{2b}$$

$$^1SO_2 + CO_2 \rightarrow (SO_2\text{-}CO_2) \tag{1c}$$

$$\rightarrow {}^3SO_2 + CO_2 \tag{2c}$$

$$^1SO_2 \rightarrow SO_2 + h\nu_f \tag{3}$$

$$\rightarrow SO_2 \tag{4}$$

$$\rightarrow {}^3SO_2 \tag{5}$$

$$^3SO_2 \rightarrow SO_2 + h\nu_p \tag{6}$$

$$\rightarrow SO_2 \tag{7}$$

$$^3SO_2 + SO_2 \rightarrow (2SO_2) \tag{8a}$$

$$^3SO_2 + O_2 \rightarrow (SO_2\text{-}O_2) \tag{8b}$$

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[1] Presented in part at the 156th National American Chemical Society Meeting, Atlantic City, N. J., Sept 1968. The authors acknowledge gratefully the support of this work through a research grant from the National Air Pollution Control Administration, U. S. Department of Health, Education, and Welfare, Public Health Service, Arlington, Va.

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**Table I.** Quantum Yields of Fluorescence ($\phi_f$) and the Ratio of $\phi_f$ to the Quantum Yield of Phosphorescence ($\phi_p$) for Sulfur Dioxide Excited at 2875 Å and 25° in Mixtures with Oxygen

| Concentration, $M \times 10^5$ SO$_2$ | O$_2$ | $\phi_f \times 10^3$ | $\phi_f/\phi_p$ |
|---|---|---|---|
| 1.52 | 0.00 | 8.55 | ... |
| 1.52 | 2.57 | 5.24 | ... |
| 1.52 | 4.60 | 5.00 | ... |
| 1.52 | 9.60 | 3.26 | ... |
| 1.65 | 0.00 | 7.94 | 7.14 |
| 1.65 | 1.79 | 6.10 | 7.65 |
| 1.65 | 5.03 | 6.21 | 9.35 |
| 1.65 | 6.75 | 4.52 | 10.37 |
| 1.65 | 8.69 | 4.69 | ... |
| 1.65 | 14.72 | 2.26 | ... |
| 3.45 | 0.00 | 3.92 | 7.14 |
| 3.45 | 0.066 | ... | 7.28 |
| 3.45 | 0.131 | ... | 7.35 |
| 3.45 | 0.20 | 3.94 | ... |
| 3.45 | 0.39 | 3.57 | ... |
| 3.45 | 4.57 | 2.72 | 10.3 |
| 3.45 | 15.3 | 1.75 | 10.9 |
| 5.18 | 0.00 | 2.63 | 7.14 |
| 5.18 | 0.13 | 2.54 | ... |
| 5.18 | 0.39 | 2.45 | ... |
| 5.18 | 1.08 | 2.35 | 7.57 |
| 5.18 | 3.45 | 2.04 | 8.28 |
| 5.18 | 4.31 | 2.09 | ... |
| 5.18 | 8.62 | 1.77 | 8.78 |
| 5.18 | 14.3 | 1.34 | 10.01 |
| 7.76 | 0.00 | ... | 7.14 |
| 7.76 | 1.94 | ... | 8.07 |
| 7.76 | 3.45 | ... | 8.35 |
| 7.76 | 4.31 | ... | 8.64 |
| 10.34 | 0.00 | 1.33 | 7.14 |
| 10.34 | 1.08 | 1.25 | 7.35 |
| 10.34 | 1.94 | ... | 7.50 |
| 10.34 | 3.45 | 1.20 | 8.00 |

**Table II.** Quantum Yields of Fluorescence ($\phi_f$) and the Ratio of $\phi_f$ to the Quantum Yield of Phosphorescence ($\phi_p$) for Sulfur Dioxide Excited at 2875 Å and 25° in Mixtures with Carbon Dioxide

| Concentration, $M \times 10^5$ SO$_2$ | CO$_2$ | $\phi_f \times 10^3$ | $\phi_f/\phi_p$ |
|---|---|---|---|
| 1.65 | 0.00 | 7.92 | 7.14 |
| 1.65 | 2.10 | 3.74 | 5.33 |
| 1.65 | 4.38 | 2.85 | 5.36 |
| 1.65 | 5.26 | 2.40 | ... |
| 1.65 | 7.40 | 1.87 | 4.25 |
| 3.45 | 0.00 | 3.91 | 7.14 |
| 3.45 | 1.72 | ... | 7.41 |
| 3.45 | 1.94 | ... | 7.30 |
| 3.45 | 4.10 | 1.93 | 6.22 |
| 3.45 | 5.26 | 1.73 | ... |
| 3.45 | 7.11 | 1.40 | 5.91 |
| 3.45 | 10.56 | 1.15 | ... |
| 3.45 | 13.27 | 0.988 | ... |
| 4.31 | 0.00 | 3.15 | ... |
| 4.31 | 3.10 | 2.09 | ... |
| 4.31 | 4.31 | 1.81 | ... |
| 4.31 | 7.10 | 1.47 | ... |
| 4.31 | 8.62 | 1.29 | ... |
| 5.17 | 0.00 | ... | 7.14 |
| 5.17 | 1.72 | ... | 7.06 |
| 5.17 | 2.59 | ... | 6.99 |
| 5.17 | 3.45 | ... | 6.02 |
| 5.17 | 4.31 | ... | 6.28 |
| 7.76 | 0.00 | ... | 7.14 |
| 7.76 | 1.72 | ... | 7.89 |
| 7.76 | 3.45 | ... | 6.70 |
| 7.76 | 4.31 | ... | 7.30 |
| 9.48 | 0.00 | 1.45 | ... |
| 9.48 | 3.23 | 1.07 | ... |
| 9.48 | 6.25 | 0.961 | ... |
| 9.48 | 8.84 | 0.879 | ... |
| 9.48 | 11.51 | 0.781 | ... |
| 9.48 | 13.28 | 0.698 | ... |
| 9.48 | 16.17 | 0.623 | ... |
| 10.34 | 0.00 | ... | 7.14 |
| 10.34 | 0.86 | ... | 7.31 |
| 10.34 | 1.72 | ... | 6.84 |
| 10.34 | 2.59 | ... | 6.75 |
| 10.34 | 3.45 | ... | 6.88 |

$$^3SO_2 + CO_2 \rightarrow (SO_2\text{-}CO_2) \qquad (8c)$$

At this early stage of the research on sulfur dioxide photochemistry, it is not possible to separate the extent of chemical change and that of relaxation to ground-state molecules which occur in reactions 1a–c and 8a–c. The designation of the products of these reactions in parentheses implies that either one or both of these reactions paths occur and that there are no excited states of sulfur dioxide generated in these reactions.

**The Quenching Reactions of the First Excited Singlet State of Sulfur Dioxide with Oxygen and Carbon Dioxide.** According to the mechanism outlined the quantum yield of fluorescence of sulfur dioxide in SO$_2$–O$_2$ mixtures should be related to the concentrations of sulfur dioxide and oxygen by relation 9. We have tested the functional

$$\frac{1}{\phi_f} = [O_2]\frac{k_{1b} + k_{2b}}{k_3} + \frac{[SO_2](k_{1a} + k_{2a}) + k_3 + k_4 + k_5}{k_3} \qquad (9)$$

form of (9) using the data of Table I for a series of runs at different sulfur dioxide and oxygen concentrations. In a given series of runs made at a fixed [SO$_2$], we would expect a linear relation between $1/\phi_f$ and [O$_2$]. In theory the intercepts of a series of such plots at different fixed [SO$_2$] values are expected to be a function of [SO$_2$], but the slopes of the series of lines should all be equal. Indeed within the experimental error of the data this is the observed result in Figure 1; the slopes ($M^{-1} \times 10^{-6}$) of the least-squares lines are[7] 2.0 ± 0.8, 1.9 ± 0.5, 2.1 ± 0.2, 2.4 ± 0.3, and 2.2 ± 1.5 at [SO$_2$] ($M \times 10^5$) = 1.65, 1.52, 3.45, 5.19, and 10.34, respectively.

Expression 10 should describe $\phi_f$ for sulfur dioxide in experiments with added carbon dioxide. The functional

$$\frac{1}{\phi_f} = [CO_2]\frac{k_{1c} + k_{2c}}{k_3} + \frac{[SO_2](k_{1a} + k_{2a}) + k_3 + k_4 + k_5}{k_3} \qquad (10)$$

form of (10) is tested in Figure 2 using the data of Table II. Again within the experimental error the slopes are equal for the different series at fixed [SO$_2$] as theoretically expected; the slopes ($M^{-1} \times 10^{-6}$) of the least-squares lines are 5.2 ± 0.7, 5.6 ± 0.4, 5.2 ± 0.2, and 5.4 ± 0.6, at [SO$_2$] ($M \times 10^5$) = 1.65, 3.45, 4.31, and 9.48, respectively.

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(7) In every case in this work the error limits shown represent the 95% confidence limits (twice the standard deviation) as determined by the method of least squares.

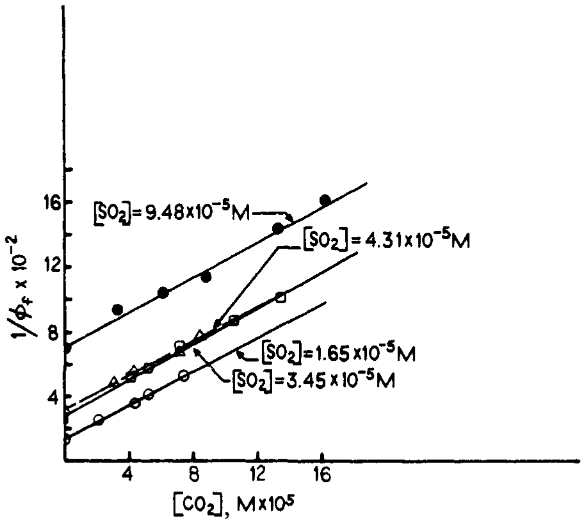

Figure 1. Plots of the reciprocal of the quantum yield of fluorescence from sulfur dioxide, excited at 2875 Å and 25° in mixtures with oxygen, *vs.* the oxygen concentration for several values of $[SO_2]$, $M \times 10^5$: ○, 1.52; △, 1.65; □, 3.45; ●, 5.18; ■, 10.3.

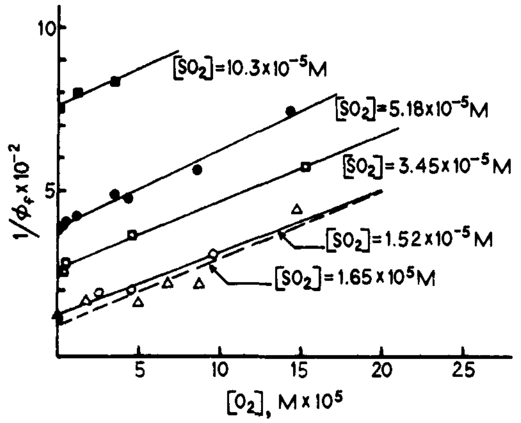

Figure 2. Plots of the reciprocal of the quantum yield of fluorescence from sulfur dioxide, excited at 2875 Å and 25° in mixtures with carbon dioxide, *vs.* the carbon dioxide concentration for several values of $[SO_2]$, $M \times 10^5$: ○, 1.65; □, 3.45; △, 4.31; ●, 9.48.

From the intercept to slope ratios of the plots in Figures 1 and 2 it is possible to derive the estimates of the desired quenching rate constant for the $^1SO_2$ species reacting with oxygen and carbon dioxide. In theory the intercept to slope ratios for the $SO_2$–$O_2$ mixtures are given by relation 11 and those for the $SO_2$–$CO_2$ mixtures by the analogous relation 12.

$$\left[\frac{\text{intercept}}{\text{slope}}\right]_{\text{Fig 1}} = [SO_2]\frac{k_{1a} + k_{2a}}{k_{1b} + k_{2b}} + \frac{k_3 + k_4 + k_5}{k_{1b} + k_{2b}} \qquad (11)$$

$$\left[\frac{\text{intercept}}{\text{slope}}\right]_{\text{Fig 2}} = [SO_2]\frac{k_{1a} + k_{2a}}{k_{1c} + k_{2c}} + \frac{k_3 + k_4 + k_5}{k_{1c} + k_{2c}} \qquad (12)$$

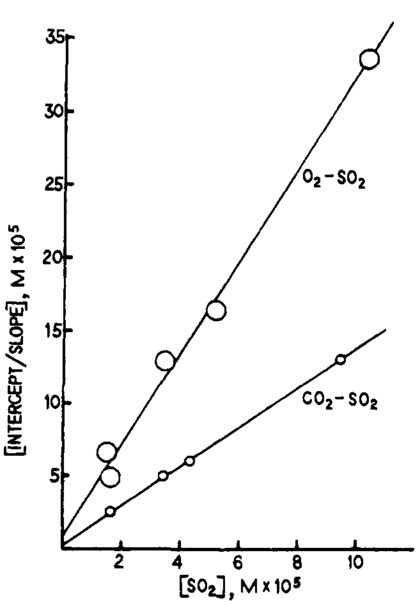

Figure 3. Plots of the intercept to slope ratios from the least-squares lines of Figure 2 for $SO_2$–$O_2$ mixtures and Figure 3 for $SO_2$–$CO_2$ mixtures; the slopes and intercepts of these plots are used to derive estimates of rate constants for $^1SO_2$ quenching by $SO_2$, $O_2$, and $CO_2$.

The plot of the appropriate intercept to slope ratios (taken from Figure 1 for $O_2$ and Figure 2 for $CO_2$) *vs.* $[SO_2]$ should be a linear function. The test of this dependency is shown in Figure 3. Within the experimental error the theoretically expected linear relation between the variables is seen to hold well for both the oxygen and the carbon dioxide data. The slope and intercept for the least-squares lines in Figure 3 yield the following rate constant estimates.

$$(\text{slope } SO_2\text{–}O_2)_{\text{Fig 3}} = \frac{k_{1a} + k_{2a}}{k_{1b} + k_{2b}} = 3.18 \pm 0.33$$

$$(\text{slope } SO_2\text{–}CO_2)_{\text{Fig 3}} = \frac{k_{1a} + k_{2a}}{k_{1c} + k_{2c}} = 1.36 \pm 0.01$$

$$(\text{intercept } SO_2\text{–}O_2)_{\text{Fig 3}} = \frac{k_3 + k_4 + k_5}{k_{1b} + k_{2b}} = (0.85 \pm 1.8) \times 10^{-5}\ \text{l./mole}$$

$$(\text{intercept } SO_2\text{–}CO_2)_{\text{Fig 3}} = \frac{k_3 + k_4 + k_5}{k_{1c} + k_{2c}} = (0.23 \pm 0.07) \times 10^{-5}\ \text{l./mole}$$

Taking the inverse of the lifetime estimate of Greenough and Duncan[2] for $k_3 + k_4 + k_5 = (2.38 \pm 0.13) \times 10^4$ sec$^{-1}$, we find $k_{1a} + k_{2a} = (0.90 \pm 1.9) \times 10^{10}$ l./(mole sec) ($O_2$–$SO_2$ data); $k_{1a} + k_{2a} = (1.4 \pm 0.4) \times 10^{10}$ ($CO_2$–$SO_2$ data); $k_{1b} + k_{2b} = (0.28 \pm 0.60) \times 10^{10}$; $k_{1c} + k_{2c} = (1.03 \pm 0.30) \times 10^{10}$ l./(mole sec). Within the experimental error the two independent estimates of $k_{1a} + k_{2a}$ derived here agree with one another and with the independent estimate of this rate constant sum derived recently from fluorescence studies of pure $SO_2$: $k_{1a} + k_{2a} = (2.2 \pm 1.0) \times 10^{10}$ l./(mole sec).[5] Probably the best estimates of the quenching constants which we can derive from the present data are from an average of the estimates of $k_{1a} + k_{2a}$ and the fairly accurate rate constant ratios derived from the slopes of Figure 3. With this procedure we estimate

$$k_{1a} + k_{2a} = (1.5 \pm 0.7) \times 10^{10} \text{ l./(mole sec)}$$
$$k_{1b} + k_{2b} = (0.47 \pm 0.22) \times 10^{10} \text{ l./(mole sec)}$$
$$k_{1c} + k_{2c} = (1.1 \pm 0.5) \times 10^{10} \text{ l./(mole sec)}$$

**The Quenching of the First Excited Triplet of Sulfur Dioxide with Oxygen and Carbon Dioxide.** A consideration of the variation of the ratio of the quantum yield of fluorescence to that of phosphorescence of sulfur dioxide with added gas allows the determination of the rate constants for $^3SO_2$ quenching by the added gas. From the mechanism outlined, the variation of $\phi_f/\phi_p$ for sulfur dioxide in mixtures with oxygen should follow relation 13. In our previous study we have derived the

$$(\phi_f/\phi_p)([SO_2]k_{2a} + [O_2]k_{2b} + k_5) = (k_3/k_6)([SO_2]k_{8a} + [O_2]k_{8b} + k_6 + k_7) \quad (13)$$

estimates $k_{2a} = (0.18 \pm 0.08) \times 10^{10}$ l./(mole sec), and $k_5 = (1.5 \pm 0.8) \times 10^3 \text{ sec}^{-1}$. From these values it can be seen that the following inequality holds for our conditions: $([SO_2]k_{2a} + [O_2]k_{2b}) \gg k_5$. Simplification of 13 can be made neglecting $k_5$.[8]

$$(\phi_f/\phi_p)\left([SO_2] + \frac{[O_2]}{k_{2a}/k_{2b}}\right) = \frac{k_3}{k_6k_{2a}}([SO_2]k_{8a} + [O_2]k_{8b} + k_6 + k_7) \quad (14)$$

Similarly the function 15 can be shown to apply for the $CO_2$–$SO_2$ mixtures for the conditions employed here.

$$(\phi_f/\phi_p)\left([SO_2] + \frac{[CO_2]}{k_{2a}/k_{2c}}\right) = \frac{k_3}{k_6k_{2a}}([SO_2]k_{8a} + [CO_2]k_{8c} + k_6 + k_7) \quad (15)$$

From the present study all of the quantities to the left of the equality sign in (14) and (15), other than $k_{2a}/k_{2b}$ and $k_{2a}/k_{2c}$, have been determined. The needed rate constant ratios cannot be evaluated directly. However, it is probably a reasonable assumption that the fraction of the quenching collisions which result in spin inversion in $^1SO_2$ is independent of the nature of the colliding gas; that is, $k_{2a}/(k_{1a} + k_{2a}) = k_{2b}/(k_{1b} + k_{2b}) = k_{2c}/(k_{1c} + k_{2c})$. For this condition $k_{2a}/k_{2b} = (k_{1a} + k_{2a})/(k_{1b} + k_{2b}) = 3.18$ and $k_{2a}/k_{2c} = (k_{1a} + k_{2a})/(k_{1c} + k_{2c}) = 1.36$. For the case of $^1SO_2$–$O_2$ collisions there must be some question as to whether there is an apparent enhancement of the spin inversion of the $^1SO_2$ with $k_{2a}/k_{2b} < (k_{1a} + k_{2a})/(k_{1b} + k_{2b})$. At this point we will accept the first hypothesis, and a test of the alternate hypothesis will be made later. For runs at constant $[SO_2]$, one expects a linear relationship between the function on the left of eq 14 and the $[O_2]$, or eq 15 and the $[CO_2]$. As with fluorescence quenching studies we expect in theory that different series of runs, each at a fixed $[SO_2]$, would have identical slopes, $(k_{8b}k_3/k_6k_{2a})$ for $O_2$–$SO_2$ runs, and $(k_{8c}k_3/k_6k_{2a})$ for $CO_2$–$SO_2$ runs, but the intercepts would be a function of the $[SO_2]$. Functions 14 and 15 have been derived from the data at several concentrations of sulfur dioxide (Tables I and II) and are plotted for the $O_2$–$SO_2$ data in Figure 4 and for the $SO_2$–$CO_2$ mixtures in Figure 5. Indeed, the theoretically expected equality of the slopes is observed within the somewhat larger experimental error in these series:[9] for the $O_2$–$SO_2$ runs the least-squares slopes are $4.0 \pm 0.5$, $4.2 \pm 0.4$, $4.1 \pm 0.3$, $5.3 \pm 0.6$, and $5.1 \pm 0.7$ for $[SO_2](M \times 10^5) = 1.65, 3.45, 5.18, 7.76,$ and $10.34$, respectively; or the $CO_2$–$SO_2$ runs the least-square slopes are $2.6 \pm 0.8$, $3.5 \pm 0.8$, $3.2 \pm 1.6$, $4.6 \pm 3.3$, and $3.7 \pm 1.5$ at $[SO_2]$ $(M \times 10^5) = 1.65, 3.45, 5.17, 7.76,$ and $10.34$, respectively. The intercept to slope ratios taken from the data of Figure 4 should in theory be a linear function of $[SO_2]$.

$$\left(\frac{\text{intercept}}{\text{slope}}\right)_{\text{Fig 4}} = [SO_2]k_{8a}/k_{8b} + (k_6 + k_7)/k_{8b} \quad (16)$$

Similarly the function 17 is expected to describe the intercept to slope ratio for the $CO_2$–$SO_2$ data in Figure 5.

$$\left(\frac{\text{intercept}}{\text{slope}}\right)_{\text{Fig 5}} = [SO_2]k_{8a}/k_{8c} + (k_6 + k_7)/k_{8c} \quad (17)$$

The intercept to slope ratios from Figures 4 and 5 are plotted as a function of $[SO_2]$ in Figure 6. Within the experimental error the data for $O_2$–$SO_2$ and $CO_2$–$SO_2$ mixtures follow the theoretically expected linear relationships. From the slopes and the intercepts derived by a least-squares treatment of these data, we estimate the following rate constant ratios.

$$(\text{slope } SO_2\text{–}O_2)_{\text{Fig 6}} = k_{8a}/k_{8b} = 1.27 \pm 0.26$$
$$(\text{slope } SO_2\text{–}CO_2)_{\text{Fig 6}} = k_{8a}/k_{8c} = 1.62 \pm 0.48$$
$$(\text{intercept } SO_2\text{–}O_2)_{\text{Fig 6}} = (k_6 + k_7)/k_{8b} = (1.38 \pm 1.72) \times 10^{-5}\ M$$
$$(\text{intercept } SO_2\text{–}CO_2)_{\text{Fig 6}} = (k_6 + k_7)/k_{8c} = (2.21 \pm 3.0) \times 10^{-5}\ M$$

Using the inverse of the lifetime of $^3SO_2$ from Caton and Duncan,[6] $k_6 + k_7 = (1.43 \pm 0.16) \times 10^2 \text{ sec}^{-1}$, the above rate ratios can be used to calculate two independent estimates of $k_{8a}$.[10]

$$k_{8a} = (1.3 \pm 1.7) \times 10^7 \text{ l./(mole sec)} \quad (SO_2\text{–}O_2 \text{ data})$$
$$= (1.1 \pm 1.5) \times 10^7 \text{ l./(mole sec)} \quad (SO_2\text{–}CO_2 \text{ data})$$

These values are equal to one another within the error limits, and they compare well to recent estimates of $k_{8a}$ derived from very different experiments; $k_{8a} \cong 2.5 \times 10^7$ from the Strickler and Howell[3,5] study of the dependence

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[8] The neglect of $k_5$ introduces a maximum error of 4% in the runs at $[SO_2] = 1.65 \times 10^{-5}\ M$ and $[O_2] = [CO_2] = 0$. In all other runs the error is much less.

[9] The method used to determine the values of $\phi_p$ involves the difference between the total intensity of emission, fluorescence plus phosphorescence, at several wavelengths, and the fluorescence intensities at these wavelengths. Thus there is considerably more error present in the values of $\phi_f/\phi_p$ than those of $\phi_f$ reported in this work.

[10] The $^3SO_2$ lifetime estimate of Caton and Duncan[6] must be accepted with some reservation since their results showed no detectable dependence on the pressure of sulfur dioxide up to 300 μ. However, the rate constant data of Strickler and Howell,[3] Rao, Collier, and Calvert,[5] and the present data suggest that a significant decrease in $\tau$ (from 55 to 280%) should have been observed over this pressure range. It seems probable that their estimate of $\tau$ for $P_{SO_2} = 0$ is nearly correct, but the large scatter in the data may have masked the expected pressure effect on the lifetime.

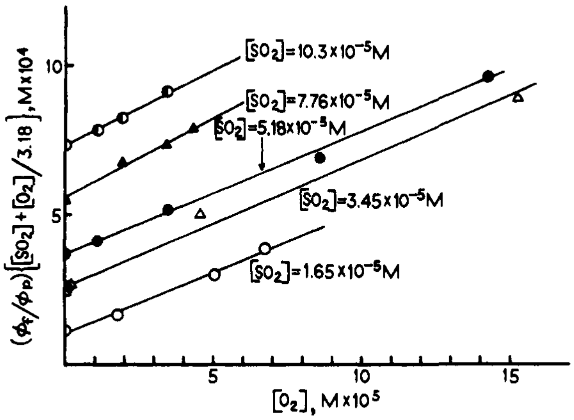

Figure 4. Plot of a function of $\phi_f/\phi_p$ (relation 14 of the text) *vs.* oxygen concentration; data from experiments with $SO_2$ excitation at 2875 Å and 25° in $SO_2$ mixtures with oxygen and at fixed $[SO_2]$, $M \times 10^5$: ○, 1.65; △, 3.45; ●, 5.18; ▲, 7.76; ◐, 10.3.

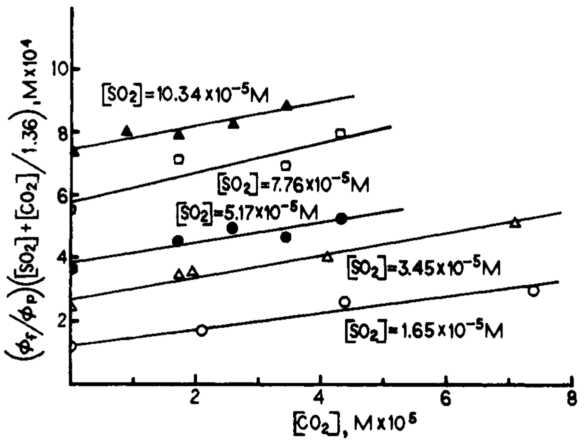

Figure 5. Plot of a function of $\phi_f/\phi_p$ (relation 15 of the text) *vs.* carbon dioxide concentration; data from experiments with $SO_2$ excitation at 2875 Å and 25° in $SO_2$ mixtures with carbon dioxide and at fixed $[SO_2]$, $M \times 10^5$: ○, 1.65; △, 3.45; ●, 5.17; □, 7.76; ▲, 10.34.

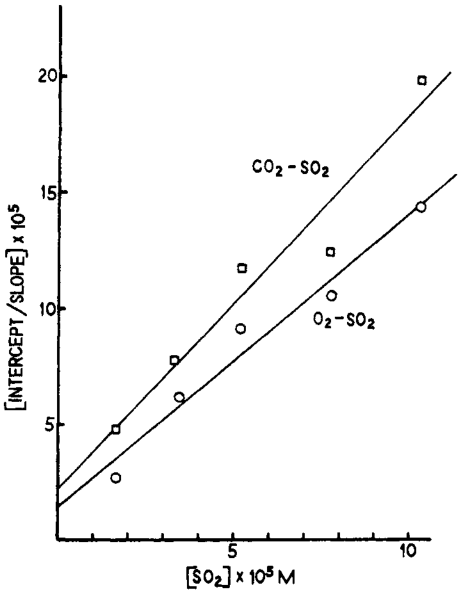

Figure 6. Plots of the intercept to slope ratios from the least-squares lines of Figure 4 for $SO_2$–$O_2$ mixtures and Figure 5 for $SO_2$–$CO_2$ mixtures; the slopes and intercepts of these plots are used to derive estimates of rate constants for $^3SO_2$ quenching by $SO_2$, $O_2$, and $CO_2$.

of $\phi_p$ on $[SO_2]$ at low $[SO_2]$, and $k_{8a} = (0.49 \pm 1.4) \times 10^7$ l./(mole sec) from the Rao, Collier, and Calvert[5] study of the quantum yields of $^3SO_2$-sensitized biacetyl phosphorescence. The rate constant ratios derived here and the best estimate of $k_{8a}$ (from the average of all the available estimates of this constant) yield the following rate constant estimates.

$$k_{8a} = (1.4 \pm 0.7) \times 10^7 \text{ l./(mole sec)}$$
$$k_{8b} = (1.1 \pm 0.6) \times 10^7 \text{ l./(mole sec)}$$
$$k_{8c} = (0.87 \pm 0.50) \times 10^7 \text{ l./(mole sec)}$$

In view of the surprisingly small magnitude of $k_{8b}$, one must check carefully the one assumption made in its estimation from the quenching data; namely, is the approximation, $k_{2a}/k_{2b} = (k_{1a} + k_{2a})/(k_{1b} + k_{2b})$, justified? It is theoretically possible that oxygen enhances the spin inversion of $^1SO_2$ through the reaction

$$^1SO_2{}^v + O_2(^3\Sigma) \rightarrow {}^3SO_2 + O_2(^1\Delta, {}^1\Sigma) \qquad (2b')$$

Reaction 2b′ is energetically possible for the vibrationally nonequilibrated, excited singlet molecules ($^1SO_2{}^v$) formed at 2875 Å.[11] However, we did not observe a special high efficiency of quenching of $^1SO_2$ species by oxygen. It quenches $^1SO_2$ at only four-tenths of the rate of $CO_2$, at about the same relative efficiency as one would expect if both $CO_2$ and $O_2$ quenching of $^1SO_2$ involved vibrational relaxation processes only. Although $k_{1a}$ dominates over $k_{2a}$,[5] it is possible that $k_{2b}$ is much greater than $k_{1b}$, so that the rate constant sums observed experimentally, $k_{1a} + k_{2a}$ and $k_{1b} + k_{2b}$, may tend to mask the true effect of oxygen in (1b) and (2b) in these experiments. It is important to test the effect of the possible inequality, $k_{2a}/k_{2b} < (k_{1a} + k_{2a})/(k_{1b} + k_{2b})$, on the $^1SO_2$–$O_2$ quenching rate constant estimates derived in this work. The maximum value which $k_{2b}$ can have is $k_{2b} = k_{1b} + k_{2b} = 0.47 \times 10^{10}$ l./(mole sec), estimated in this study. The value $k_{2a} = 0.12 \times 10^{10}$ l./(mole sec) can be estimated from the average value, $k_{1a} + k_{2a} = 1.5 \times 10^{10}$ l./(mole sec), derived above, and $k_{2a}/(k_{1a} + k_{2a}) = 0.080$, found in our previous study.[5] Now taking the ratio $k_{2a}/k_{2b} = 0.26$ instead of 3.18 used previously, the data of Table I can be used to calculate function 14, and plots similar to those in Figures 4 and 6 can be made as before. This treatment gives a slope, $k_{8a}/k_{8b} = 0.24 \pm 0.05$, and an intercept, $(k_6 + k_7)/k_{8b} = -(0.39 \pm 0.29) \times 10^{-5}\ M$. Taking $k_{8a} = 1.4 \times 10^7$ l./(mole sec), the average value of the previous estimates, and neglecting the impossible negative number of the less accurate intercept, we find $k_{8b} \leqslant (5.9 \pm 0.6) \times 10^7$ l./(mole sec). Thus we can conclude that the true value of $k_{8b}$ lies in the range $(1.1 \pm 0.6) \times 10^7 \leqslant k_{8b} \leqslant (5.9 \pm 0.6) \times 10^7$ l./(mole sec). It seems highly probable to the authors that the lower limit of $k_{8b}$ is the best estimate of the quantity; in the same calculation in which this estimate was made, $CO_2$–$SO_2$ and $O_2$–$SO_2$

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[11] The singlet–triplet energy separation in $SO_2$, $E_{S_1^0} - E_{T_1^0} \cong 13$ kcal/mole; $\Delta E = 22.6$ kcal/mole for $O_2(^3\Sigma) \rightarrow O_2(^1\Delta)$ and 37.7 kcal/mole for $O_2(^3\Sigma) \rightarrow O_2(^1\Sigma)$.

data gave near equal estimates of $k_{8a}$, and these estimates were also equal within the experimental error to the other estimates of this constant from entirely independent and different kinds of experiments.[3,5] However, the same plot whose slope was used to derive the high estimate of $k_{8b}$ gives the impossible result of a negative value for the intercept, presumably equal to $(k_6 + k_7)/k_{8b}$.

**Comparison of the Rates of $^1SO_2$ and $^3SO_2$ Quenching Reactions.** The results of this study confirm the unusual reactivity difference between the singlet and triplet excited states of sulfur dioxide. It is interesting to compare the ratio of quenching rates observed in this study for $SO_2$, $CO_2$, and $O_2$ molecules.

$$\frac{\text{rate of } ^1SO_2 \text{ with } SO_2}{\text{rate of } ^1SO_2 \text{ with } O_2} = 3.18 \pm 0.33$$

$$\frac{\text{rate of } ^1SO_2 \text{ with } SO_2}{\text{rate of } ^1SO_2 \text{ with } CO_2} = 1.36 \pm 0.01$$

$$\frac{\text{rate of } ^1SO_2 \text{ with } O_2}{\text{rate of } ^1SO_2 \text{ with } CO_2} = 0.43 \pm 0.04$$

$$\frac{\text{rate of } ^3SO_2 \text{ with } SO_2}{\text{rate of } ^3SO_2 \text{ with } O_2} = 1.27 \pm 0.26$$

$$\frac{\text{rate of } ^3SO_2 \text{ with } SO_2}{\text{rate of } ^3SO_2 \text{ with } CO_2} = 1.62 \pm 0.48$$

$$\frac{\text{rate of } ^3SO_2 \text{ with } O_2}{\text{rate of } ^3SO_2 \text{ with } CO_2} = 1.28 \pm 0.54$$

The comparisons show that there is a surprising similarity in the quenching rates of $^1SO_2$ with $SO_2$, $O_2$, and $CO_2$. It has been shown that the rate constants for these reactions are all near the collision number. The above results confirm the order of the rates of quenching reported by Greenough and Duncan[2] several years ago: $k_{1a} > k_{1c} > k_{1b}$. One can rationalize these results through the picture proposed by Douglas[12] and Strickler and Howell.[3] They have considered the $^1SO_2$ state as a composite of excited singlet, triplet, and ground vibronic states. Presumably collisional relaxation is fast since the $^1SO_2$ molecule behaves like a highly vibrationally excited ground-state molecule. One expects from this hypothesis that the efficiency of various gases for $^1SO_2$ quenching or vibrational relaxation would be related to the number of degrees of internal freedom of the colliding molecule. The observed near equality of the quenching rates for $SO_2$ and $CO_2$, which possess near equivalent number of internal degrees of freedom, and the somewhat lower rate for $O_2$ with the smaller number of internal degrees of freedom are trends consistent with this hypothesis.

Perhaps the most surprising result from this work is the demonstrated unselective quenching of the $^3SO_2$ species. Oxygen is a less efficient quencher of $^3SO_2$ than sulfur dioxide, and it is only slightly more effective than carbon dioxide. However, the very low absolute value of the rate constant for the quenching reaction with oxygen is very unexpected: $(1.1 \pm 0.6) \times 10^7 \leqslant k_{8b} \leqslant (5.9 \pm 0.6) \times 10^7$ l./(mole sec). However, we believe that this result is correct; it is also consistent with the qualitative observations of Caton and Duncan[6] who reported that the presence of a small amount of oxygen in sulfur dioxide gave no observable effect on the lifetime of $^3SO_2$, and there was no preferential quenching of $^3SO_2$ by oxygen over that by sulfur dioxide. One might have expected that energy transfer from $^3SO_2$ to $O_2$ would occur efficiently by reaction 8b′, forming singlet oxygen, as well as by (8b), forming vibrationally excited ground-state oxygen molecules ($^3\Sigma$).

$$^3SO_2 + O_2(^3\Sigma) \rightarrow SO_2 + O_2(^1\Delta, {}^1\Sigma) \qquad (8b')$$

Reactions analogous to (8b′), involving triplets of polynuclear aromatics, dye molecules, etc., are very fast (near the collision number in the gas phase or diffusion controlled in the liquid phase) and are believed to be important steps in the photooxidations of these compounds.[13] Since oxygen quenches $^3SO_2$ at about the same rate as does carbon dioxide where electronic energy transfer is impossible, reaction 8b′ does not occur efficiently, if at all, for our conditions. Kawaoka, Khan, and Kearns[13b] have considered the theory of the quenching of organic triplet states by oxygen and found that the most important contribution to the oxygen quenching of triplet-state molecules is by transfer of electronic energy to oxygen rather than by enhanced intersystem crossing. They further showed that the rapidity of the electronic energy transfer was in large part due to the participation of charge-transfer states in the quenching process.[13b] It may be significant that oxygen has little or no effect on the enhancement of the $^3SO_2 \leftarrow SO_2$ absorption, and charge-transfer states, often invoked to explain $O_2$ enhancement of the singlet–triplet band,[14] seem to be of little importance in the $SO_2$–$O_2$ system.[15] We may propose the hypothesis that the relative slowness of energy transfer to oxygen from $^3SO_2$ in reaction 8b′ is related to the relative unimportance of charge-transfer states in the $O_2$–$^3SO_2$ collision complex.

In our continuing research on the photochemistry of sulfur dioxide, we are attempting to correlate the photophysical primary processes, delineated in this and our previous work,[5] with the photochemical changes which have been observed in sulfur dioxide containing systems.[16] Under study are the rate constants for sulfur trioxide formation from the reactions of $^1SO_2$ and $^3SO_2$ species with sulfur dioxide and oxygen, and those for sulfinic acid and other products from the reactions of the $^1SO_2$ and the $^3SO_2$ species with the paraffinic and olefinic hydrocarbons.

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(12) A. E. Douglas, *J. Chem. Phys.*, **45**, 1007 (1966).

(13) For references to the extensive original literature, see (a) C. S. Foote, S. Wexler, W. Ando, and R. Higgins, *J. Am. Chem. Soc.*, **90**, 975 (1968); (b) K. Kawaoka, A. U. Khan, and D. R. Kearns, *J. Chem. Phys.*, **46**, 1842 (1967).

(14) H. Tsubomura and R. S. Mulliken, *J. Am. Chem. Soc.*, **82**, 5966 (1960).

(15) S. S. Collier, unpublished observations on direct singlet–triplet absorption in sulfur dioxide–oxygen mixtures.

(16) For a recent comprehensive review of the present literature concerned with the photochemical studies of sulfur dioxide in a variety of mixtures, see P. Urone and W. H. Schroeder, *J. Environ. Sci. Technol.*, in press.