

## THE PHOTOSENSITIZED PRODUCTION AND PHYSICAL QUENCHING OF $O_2(^1\Sigma_g^+)$ \*

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### SUMMARY

Sensitizer formation of  $O_2(^1\Sigma_g^+)$  by various molecules has been studied *via* a flash photolysis technique by monitoring the luminescence of  $O_2(^1\Sigma_g^+)$  at 7620 Å. Sensitizers studied included  $SO_2$ , benzene, naphthalene, octafluoronaphthalene, phenanthrene and benzaldehyde. The results indicate, in the case of  $SO_2$ , that it is the  $^3B_1$  state which sensitizes the formation of  $O_2(^1\Sigma_g^+)$ . Studies on the physical quenching of the  $O_2(^1\Sigma_g^+)$  state by various substituted hydrocarbon molecules were also carried out. These indicate that the efficiency of a molecule as a quencher of  $O_2(^1\Sigma_g^+)$  decreases as halogens of increasing atomic weight are substituted for hydrogen in hydrocarbon molecules. The quenching effect explains in part the higher yield of  $O_2(^1\Sigma_g^+)$  when sensitized by the fluorinated hydrocarbons.

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### INTRODUCTION

The photosensitized production of the low energy excited states of  $O_2$ — $O_2(^1\Delta_g)$  and  $O_2(^1\Sigma_g^+)$ —has recently attracted considerable interest because of the possible involvement of these species in the complex processes of photochemical air pollution. Investigations in other laboratories<sup>1-8</sup> have primarily been directed toward the photosensitized production of the lower energy (1270 nm) species,  $O_2(^1\Delta_g)$ . These studies demonstrated that  $O_2(^1\Delta_g)$  may be produced *via* energy transfer when sensitizer- $O_2$  mixtures are irradiated with ultra-violet light. The production of  $O_2(^1\Delta_g)$  in these systems most probably proceeds *via* process (1) followed by process (2) although reactions (3) and (4) are also energetically possible but probably occur to a much lesser extent<sup>11</sup>.

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Herron and Huie<sup>9,10</sup> found that the rate of reaction of  $\text{O}_2({}^1\Delta_g)$  with olefins is, in most cases, much too slow to play any appreciable role in atmospheric photochemical processes. This, of course, does not discount the possibility of rapid reactions between  $\text{O}_2({}^1\Delta_g)$  and other atmospheric pollutants.

Although it has been theoretically predicted<sup>11</sup> that  $\text{O}_2({}^1\Sigma_g^+)$  should be formed predominately in the initial energy transfer process (1) with about 10 times the efficiency of  $\text{O}_2({}^1\Delta_g)$  the first experimental investigation of process (1) was carried out in our laboratory<sup>12</sup> using 1-fluoronaphthalene as a sensitizer. Subsequently, Duncan and Kearns<sup>13</sup> have found that quinoxaline also may act as a sensitizing species. More recently we<sup>14</sup> have shown that  $\text{SO}_2$ , benzene, naphthalene, octafluoronaphthalene, phenanthrene and benzaldehyde effect the production of  $\text{O}_2({}^1\Sigma_g^+)$  when gaseous mixtures of these compounds and  $\text{O}_2$  are flash irradiated in the ultra-violet region.

The results of that preliminary investigation are described in more detail here together with the results of our more recent studies of the physical quenching of  $\text{O}_2({}^1\Sigma_g^+)$ . In the course of these studies it has been found that  $\text{O}_2({}^1\Sigma_g^+)$  may be formed *via* process (1) when  $\text{SO}_2$ - $\text{O}_2$  mixtures are irradiated only with wavelengths found in the solar spectrum ( $\lambda > 3000 \text{ \AA}$ ) and that this transfer of electronic excitation energy appears to be not nearly as efficient relative to the physical quenching of  $\text{SO}_2({}^3\text{B}_1)$  by  $\text{O}_2$  as would be predicted by the calculations of Kawoaka and Kearns<sup>11</sup>.

## EXPERIMENTAL

In order to obtain a sufficiently high concentration of  $\text{O}_2({}^1\Sigma_g^+)$  that its emission at 762 nm could be detected and studied kinetically the technique of flash photolytic excitation was employed. Since, at the moderate pressures employed in this study only one in  $10^4$  to  $10^5$  of the  $\text{O}_2({}^1\Sigma_g^+)$  molecules initially formed relaxes to the ground state by the emission of a photon, it was necessary to detect a relatively weak short-lived signal. For this reason, it was essential that the photomultiplier (EMI 9558 Q) be carefully shielded from the electrical and magnetic fields produced during the flash discharge as well as from the photolytic flash itself. The details of this filter and shielding system are presented schematically in Fig. 1. Even with these precautions a background signal was still observed when the flash lamp was discharged with the sample cell evacuated. This background signal was highly reproducible showing no significant variation in five successive discharges even at 10 times the sensitivity normally employed in taking data. Thus,

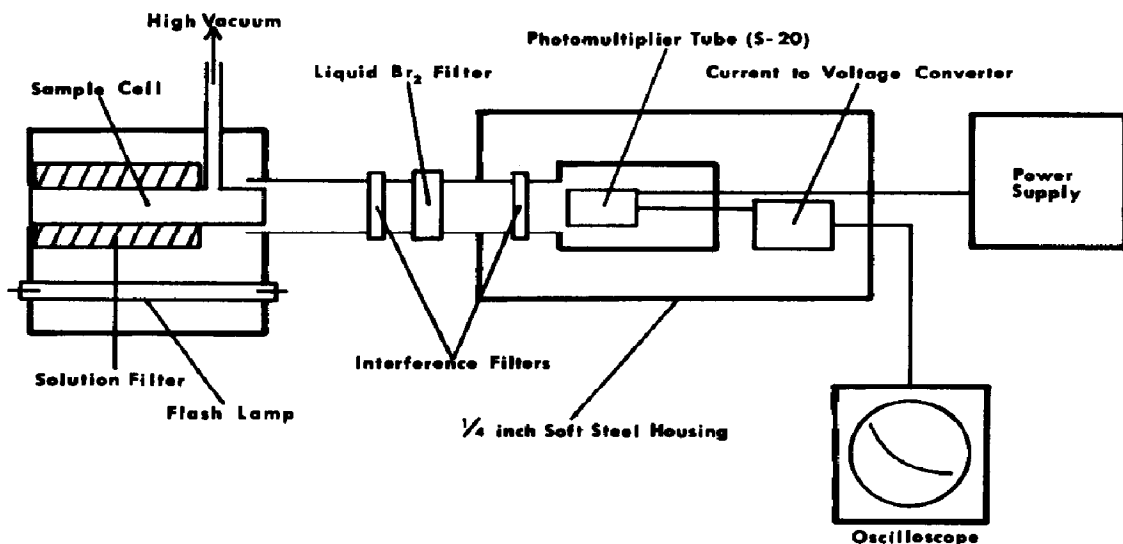


Fig. 1. Filtering, shielding and detection system.

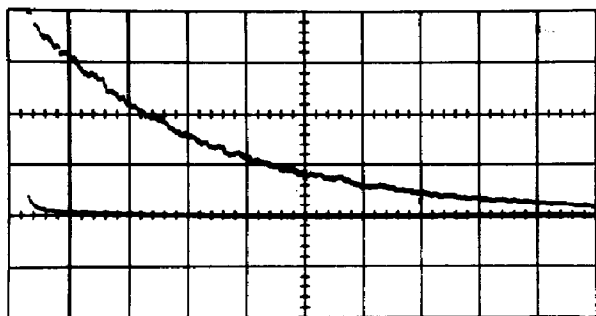


Fig. 2.  $O_2(^1\Sigma_g^+)$  emission at 762 nm after flash irradiation. Lower trace is with cell evacuated. Upper trace is with 71.9 Torr of  $O_2$  and 18.0 Torr of  $SO_2$ . The time scale is 0.5 msec/division.

each piece of data consisted of a photograph of two oscilloscope traces, the lower corresponding to the background signal with the sample cell evacuated and the upper due to emission at 762 nm when the sensitizer  $O_2$  mixture was flash irradiated (Fig. 2). The difference between these traces is a measure of the concentration of  $O_2(^1\Sigma_g^+)$  with time.

In the purification of compounds, particular attention was paid to the removal of water since it is known to be such an efficient quencher of  $O_2(^1\Sigma_g^+)^{15-20}$ . For this reason prior to use all the quenching species as well as  $O_2$  and  $SO_2$  were passed through a  $P_2O_5$  filled trap cooled with appropriate slush baths. The solid materials were first zone refined under  $N_2$  (80 zones) and thoroughly degassed. Liquids were dried over Linde molecular sieves, type 5A, and degassed in several freeze-pump-thaw cycles.

## RESULTS AND DISCUSSION

*The SO<sub>2</sub> sensitized production of O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>)*

In a preliminary investigation of the photosensitized production of O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) it was found that SO<sub>2</sub>, benzene, naphthalene, octafluoronaphthalene, phenanthrene and benzaldehyde can function more or less efficiently as photosensitizers of O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>). In these studies mixtures of the sensitizing species and O<sub>2</sub> were flash irradiated through a 4M NiSO<sub>4</sub>-quartz filter and the emission of O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) at 762 nm was detected by means of an S-20 response multiplier phototube. It is quite likely, on the basis of energetic considerations and spin conservation, that in all cases the energy transfer proceeds as in process (1). SO<sub>2</sub> was chosen for more extensive study because of the relatively high concentration of this species in some polluted atmospheres and because the simplicity of its structure might lend itself to theoretical investigations of the nature of the interaction leading to the transfer of electronic excitation energy.

As a means of verification that SO<sub>2</sub> could effect the formation of O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) with wavelengths found in the solar spectrum, SO<sub>2</sub>-O<sub>2</sub> mixtures were flash irradiated through a 4M NiSO<sub>4</sub>-Pyrex filter and a 2M CuSO<sub>4</sub>-quartz filter (see Fig. 3). In both cases O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) emission was observed although at an intensity less than that obtained by irradiation through the 4M NiSO<sub>4</sub>-quartz filter used in all subsequent investigations.

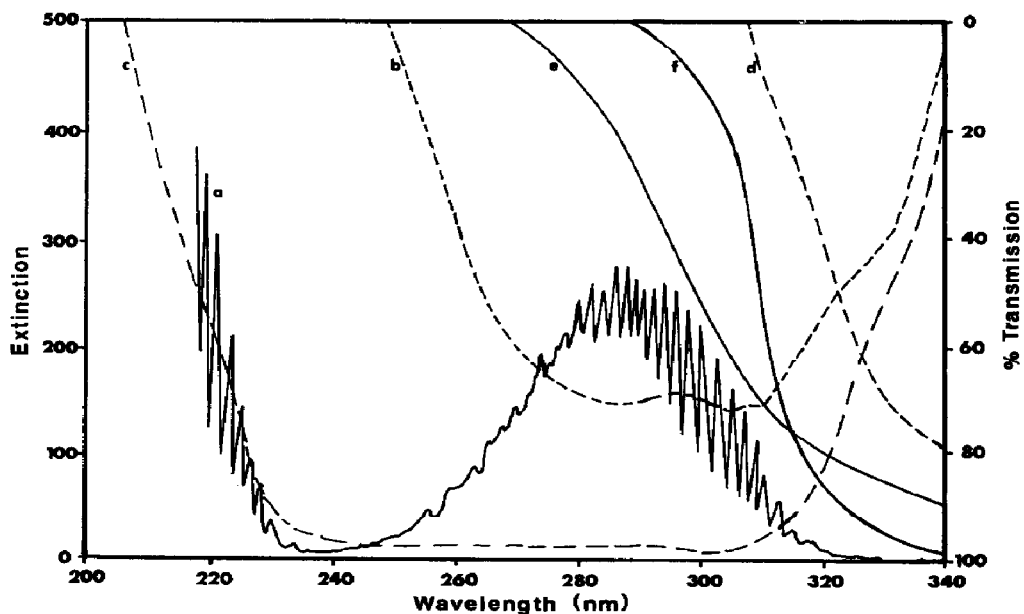
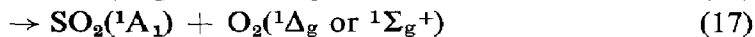
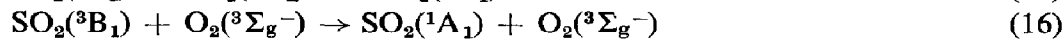
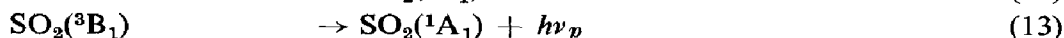
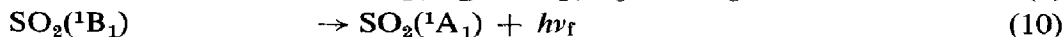
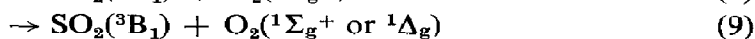
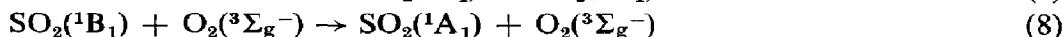


Fig. 3. The absorption spectrum of SO<sub>2</sub> and the transmission of the atmosphere and filter systems. (a) Absorption spectrum of SO<sub>2</sub><sup>25</sup>; (b) transmission of NiCl<sub>2</sub> filter solution; (c) transmission of NiSO<sub>4</sub> filter solution; (d) transmission of CuSO<sub>4</sub> filter solution; (e) transmission of the atmosphere (calculated from data in Leighton<sup>25</sup>); (f) transmission of Pyrex filter.

In order to obtain an upper limit for the efficiency of the energy transfer process a kinetic analysis of the SO<sub>2</sub>-O<sub>2</sub> system was undertaken. The reaction scheme assumed was:



Over the pressure range employed:

$$(1.3 \text{ Torr} \leq \text{SO}_2 \leq 17.3 \text{ Torr}, 3.2 \text{ Torr} \leq \text{O}_2 \leq 109.6 \text{ Torr})$$

the decay of O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) was first order. Extrapolating log intensity vs. time plots to zero time gave the relative initial luminescence intensities of O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) as a function of O<sub>2</sub> and SO<sub>2</sub> pressures presented in Table 1.

TABLE 1

INITIAL INTENSITY OF EMISSION AT 7620 Å AS A FUNCTION OF [SO<sub>2</sub>] AND [O<sub>2</sub>]

[O <sub>2</sub> ] (Torr)	[SO <sub>2</sub> ] (Torr)														
	1.3	1.5	1.9	2.3	2.8	3.4	4.2	5.2	6.3	7.7	9.5	11.6	14.2	17.3	
3.2	2.7			5.6				5.5	5.6			6.4			
5.3		4.7			6.7				7.2	7.2			7.7		
6.5			5.7			7.9			8.4		9.3			9.9	
8.0				6.8			9.3			10.4		11.2			
9.7					9.1			11.5			13.4		14.5		
11.9						11.1			14.2			17.5		18.5	
14.5	6.1						12.8			17.8			22.2		
17.8		7.5						15.3			21.1			26.1	
21.7			9.9						21.8			26.3			
26.6		8.7		12.1						26.1			31.5		
32.6	7.7		11.1		14.9						31.8			38.1	
39.9		9.0		13.5		18.0						38.9			
48.8			12.0		18.2		23.1						45.7		
59.7				15.3		23.6		28.2						55.7	
71.3	10.3				18.3		32.3		34.5						
89.5		12.8				24.0		31.7		40.5					
109.6			15.8				28.9		38.1		49.4				

Assuming that the ratio of the rate constants for collision induced internal conversion of  $\text{SO}_2(^1\text{B}_1)$  to the collision induced intersystem crossing of  $\text{SO}_2(^1\text{B}_1)$  is independent of the species colliding with  $\text{SO}_2(^1\text{B}_1)$  a straightforward kinetic analysis yields:

$$1/I_0 = C \frac{k_{13} + k_{14} + k_{15} [\text{SO}_2] + (k_{16} + k_{17}) [\text{O}_2]}{k_{17} [\text{O}_2] k_4 \{1 - 10^{-E_b(\text{SO}_2)}\}} \quad (19)$$

where  $I_0$  is the initial intensity of  $\text{O}_2(^1\Sigma_g^+)$  emission, and  $C$  is a proportionality constant.

Table 2 shows the slope, intercept and slope to intercept ratio of the series of lines obtained by plotting  $1/I_0$  vs.  $1/[\text{O}_2]$  at a given  $[\text{SO}_2]$ . If the slope to intercept ratio (eqn. 20) is plotted against  $[\text{SO}_2]$  the slope of this line yields  $k_{15}/(k_{16} + k_{17})$  while the intercept is  $(k_{13} + k_{14})/(k_{16} + k_{17})$ .

$$\frac{\text{Slope}}{\text{Intercept}} = \frac{k_{13} + k_{14} + k_{15} [\text{SO}_2]}{k_{16} + k_{17}} \quad (20)$$

Such a plot is shown in Fig. 4. The fact that the intercept is zero within experimental error indicates that the rate constants for the unimolecular decay of  $\text{SO}_2(^3\text{B}_1)$  are much less than the rate constants for the bimolecular quenching of  $\text{SO}_2(^3\text{B}_1)$ . The slope of  $5.6 \pm 1.1$  shows that  $\text{SO}_2(^1\text{A}_1)$  is approximately 5 times as efficient a quencher of  $\text{SO}_2(^3\text{B}_1)$  as is  $\text{O}_2(^3\Sigma_g^-)$ . These results are in agreement with data from Calvert's laboratory<sup>21,22</sup> for the quenching of  $\text{SO}_2(^3\text{B}_1)$  phosphorescence which was made available to us subsequent to our own study. In their studies the  $\text{SO}_2(^3\text{B}_1)$  was excited directly by a laser pulse and its decay monitored by its time resolved emission. The rate constants obtained by this more direct method for

TABLE 2

LEAST SQUARES DATA OF  $1/[\text{O}_2]$  vs.  $1/I_0$  PLOTS AT CONSTANT  $[\text{SO}_2]$ 

$[\text{SO}_2]$ (Torr)	Intercept	Slope	Slope/intercept
17.3	$6.30 \times 10^{-3}$	$6.03 \times 10^{-1}$	95.7
14.2	$7.48 \times 10^{-3}$	$6.29 \times 10^{-1}$	84.1
11.6	$9.57 \times 10^{-3}$	$6.23 \times 10^{-1}$	65.1
9.5	$1.39 \times 10^{-2}$	$6.06 \times 10^{-1}$	43.6
7.7	$1.19 \times 10^{-2}$	$6.67 \times 10^{-1}$	56.1
6.3	$1.80 \times 10^{-2}$	$6.73 \times 10^{-1}$	37.4
5.2	$2.23 \times 10^{-2}$	$6.81 \times 10^{-1}$	30.5
4.2	$3.02 \times 10^{-2}$	$6.46 \times 10^{-1}$	21.4
3.4	$3.34 \times 10^{-2}$	$6.65 \times 10^{-1}$	19.9
2.8	$4.26 \times 10^{-2}$	$6.46 \times 10^{-1}$	15.2
2.3	$5.21 \times 10^{-2}$	$6.65 \times 10^{-1}$	12.8
1.9	$6.71 \times 10^{-2}$	$6.37 \times 10^{-1}$	9.5
1.5	$8.79 \times 10^{-2}$	$6.23 \times 10^{-1}$	7.1
1.2	$1.12 \times 10^{-1}$	$5.88 \times 10^{-1}$	5.3

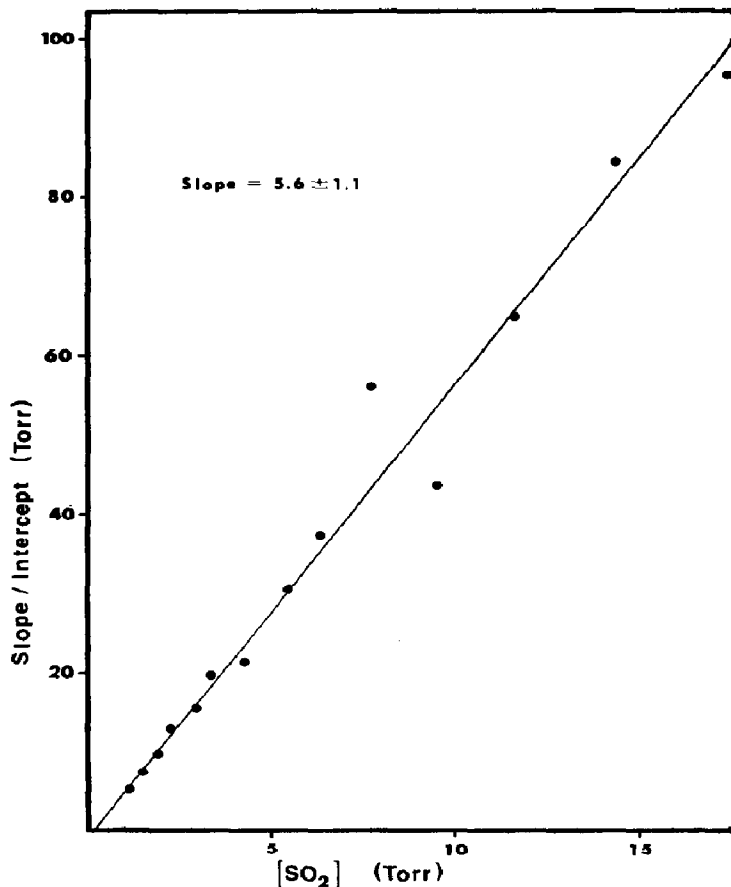


Fig. 4. Slope to intercept ratio of  $1/I_0$  vs.  $1/[O_2]$  plots vs.  $[SO_2]$ , a determination of the ratio of the efficiency of quenching of  $SO_2(^3B_1)$  by  $SO_2(^1A_1)$  and  $O_2(^3\Sigma_g^-)$ .

processes (16) and (17) are  $3.9 \times 10^8 M^{-1} \text{sec}^{-1}$  and  $9.6 \times 10^7 M^{-1} \text{sec}^{-1}$  respectively. The agreement between these results and our own, support our contention that  $SO_2(^3B_1)$  is the predominant sensitizing species and lend some validity to the assumptions made in our kinetic analysis. In the laser excitation studies it was also found that  $SO_2(^3B_1)$  is quenched only slightly more efficiently by  $O_2$  than by  $N_2$ <sup>21</sup>. If the rate constants for physical quenching by these species are approximately the same this would suggest that the transfer of electronic excitation energy accounts for only a small fraction of the total quenching of  $SO_2(^3B_1)$  by  $O_2$ . In other words  $k_{17}$  is not greater than  $k_{16}$  as has been predicted by Kawoaka and Kearns<sup>11</sup>. In any event since the quantum yield of  $SO_2(^3B_1)$  formation is  $\sim 0.1$ <sup>23, 24</sup> when the initial excitation is into the  $SO_2(^1B_1)$  state, the quantum yield of  $O_2(^1\Sigma_g^+)$  formation under atmospheric conditions as a result of energy transfer from  $SO_2$  would certainly be less than, and probably much less than, 0.02.

*The physical quenching of  $O_2(^1\Sigma_g^+)$* 

In the second phase of this study the rate constants for the quenching of  $O_2(^1\Sigma_g^+)$  emission by various added gases were determined. In all cases the  $O_2(^1\Sigma_g^+)$  was formed by energy transfer from  $SO_2$  when  $SO_2$ - $O_2$  mixtures were flash irradiated through a  $NiSO_4$ -quartz filter.

The quenching rate constants obtained are presented in Table 3. These rate constants were determined as the slope of the line obtained by plotting the rate of decay of  $O_2(^1\Sigma_g^+)$ ,  $k_{exp}$ , vs. the quencher pressure (Fig. 5) for at least 5 different quencher pressures at the same  $SO_2$  and  $O_2$  pressures. This procedure was repeated for at least 4 different  $SO_2$  and  $O_2$  pressures and the rate constant was taken as the average of these independent determinations. The error limits given in Table 3 are the standard deviations of the individual determinations from the average. Where data are available the values obtained by our method compare favorably with those obtained in other laboratories where  $O_2(^1\Sigma_g^+)$  was formed either by vacuum ultra-violet flash photolysis of  $O_2^{18-20,25}$  or by the energy pooling of two  $O_2(^1\Delta_g)$  molecules in a microwave discharge system<sup>15-17</sup>. Note particularly that the quenching efficiency within the hydrocarbon series studied decreases in the order  $C_nH_{2n+2} > C_nD_{2n+2} > C_nF_{2n+2} > C_nCl_{2n+2}$ . This point will be discussed in more detail in a subsequent paper, but it is worth emphasizing that this effect can be employed in choosing the sensitizing species. By employing sensitizers with no hydrogen present the lifetime (or the steady state concentration) of  $O_2(^1\Sigma_g^+)$  can be dramatically increased. We have in fact observed that the lifetime of  $O_2(^1\Sigma_g^+)$  was several orders of magnitude larger in the presence of octafluoronaphthalene at its vapor pressure than in the presence of naphthalene at its vapor pressure at 298 K.

TABLE 3

RATE CONSTANTS FOR THE QUENCHING OF  $O_2(^1\Sigma_g^+)$  GENERATED BY ELECTRONIC ENERGY TRANSFER FROM  $SO_2$  ( $M^{-1} \text{ sec}^{-1}$ )

$H_2$	$6.6 \pm 0.1 \times 10^8$
$D_2$	$1.0 \pm 0.2 \times 10^9$
$CO_2$	$2.5 \pm 0.2 \times 10^8$
$SO_2$	$4.0 \pm 0.5 \times 10^5$
$CS_2$	$1.7 \pm 0.3 \times 10^{6*}$
$H_2S$	$3.8 \pm 0.3 \times 10^8$
$CH_4$	$5.0 \pm 0.2 \times 10^7$
$CF_4$	$1.6 \pm 0.2 \times 10^6$
$CCl_4$	$2.7 \pm 0.4 \times 10^5$
$C_2H_6$	$2.7 \pm 0.1 \times 10^8$
$C_2D_6$	$1.0 \pm 0.1 \times 10^8$
$C_2F_6$	$1.9 \pm 0.1 \times 10^6$

\* This rate constant may be slightly in error because at wavelengths shorter than 2600 Å  $CS_2$  may dissociate into CS and S, while the excitation was in the region 3200 Å to 2200 Å.



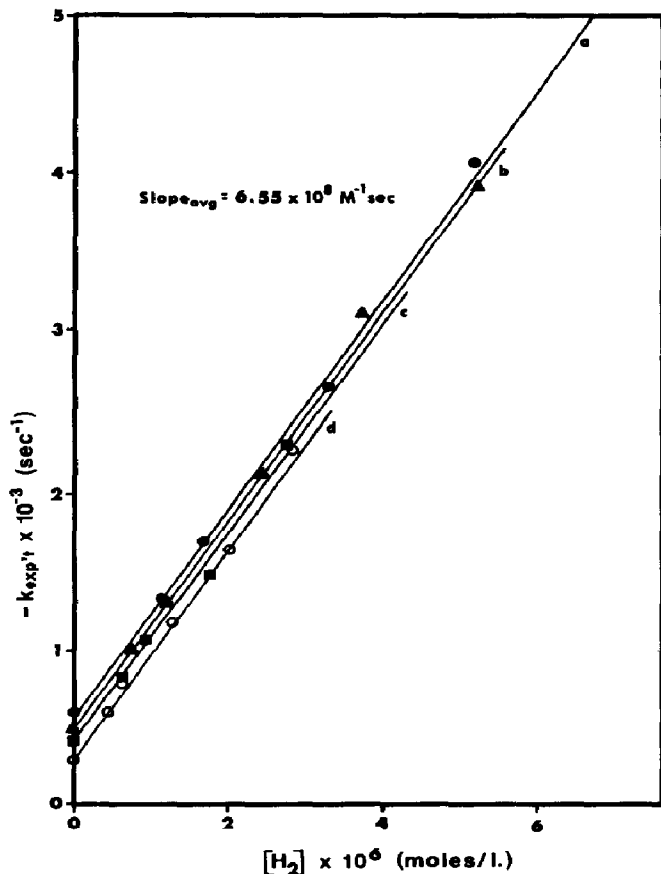


Fig. 5. Determination of the rate constant for the quenching of O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) by H<sub>2</sub>. (a) ●: [SO<sub>2</sub>] = 8.61 × 10<sup>-4</sup> M/l, [O<sub>2</sub>] = 4.18 × 10<sup>-3</sup> M/l, 0.00 ≤ [H<sub>2</sub>] ≤ 7.30 × 10<sup>-6</sup> M/l, slope = 6.47 × 10<sup>8</sup> l/M sec; (b) ▲: [SO<sub>2</sub>] = 6.28 × 10<sup>-4</sup> M/l, [O<sub>2</sub>] = 2.06 × 10<sup>-3</sup> M/l, 0.00 ≤ [H<sub>2</sub>] ≤ 5.34 × 10<sup>-6</sup> M/l, slope = 6.52 × 10<sup>8</sup> l/M sec; (c) ■: [SO<sub>2</sub>] = 4.59 × 10<sup>-4</sup> M/l, [O<sub>2</sub>] = 2.23 × 10<sup>-3</sup> M/l, 0.00 ≤ [H<sub>2</sub>] ≤ 2.77 × 10<sup>-6</sup> M/l, slope = 6.49 × 10<sup>8</sup> l/M sec; (d) ○: [SO<sub>2</sub>] = 3.36 × 10<sup>-4</sup> M/l, [O<sub>2</sub>] = 1.63 × 10<sup>-3</sup> M/l, 0.00 ≤ [H<sub>2</sub>] ≤ 2.85 × 10<sup>-6</sup> M/l, slope = 6.63 × 10<sup>8</sup> l/M sec.

## CONCLUSIONS

The following points deserve particular emphasis.

(1) O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) has been found to be formed when mixtures of O<sub>2</sub>(<sup>3</sup>Σ<sub>g</sub><sup>-</sup>) and a number of compounds absorbing in the ultra-violet region are flash irradiated.

(2) The SO<sub>2</sub> photosensitized production of O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) occurs with wavelengths found in the solar spectrum.

(3) On the basis of the relative efficiencies of the quenching of SO<sub>2</sub>(<sup>3</sup>B<sub>1</sub>) by O<sub>2</sub> and N<sub>2</sub> the prediction that the quenching of triplet states by O<sub>2</sub> will proceed predominantly by the formation of O<sub>2</sub>(<sup>1</sup>Σ<sub>g</sub><sup>+</sup>) is almost certainly erroneous in this case.

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