*J. Phys. Chem.* **1990,** *94,* 4535–4540

a single isomer, $BrONO_2$, which would have a 6–7 kcal $mole^{-1}$ *stronger* bond than $ClONO_2$! This would fix the heat of formation of $BrONO_2$ to be the same as $ClONO_2$, an unlikely possibility." A similar situation exists when comparing the measured low-pressure limit rate coefficient for $IO + NO_2$ with that for $ClO + NO_2$. Clearly, the thermochemistry of $XONO_2$ (X = Br, I) requires further investigation, as does the possible formation of isomers such as $OXNO_2$, XOONO, or OXONO.

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# Kinetics of the Reaction OH + $SO_2$ in He, $N_2$, and $O_2$ at Low Pressure

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The rate constants of the gas-phase reaction of OH with $SO_2$ for M = He, $N_2$, and $SO_2$ have been determined by using the discharge flow/resonance fluorescence technique. The termolecular rate constants (all in units of $cm^6$ $molecule^{-2}$ $s^{-1}$) and the corresponding experimental conditions are as follows: $k(M{=}He) = (1.1 \pm 0.3) \times 10^{-32} \exp[(640 \pm 200)/T]$ (280–413 K, 1–6 Torr); $k(M{=}SO_2) = (3.3 \pm 1.5) \times 10^{-31} \exp[(1055 \pm 500)/T]$ (280–363 K, $P < 0.23$ Torr); $k(M{=}N_2) = (2.4 \pm 0.7) \times 10^{-31}$ (298 K, 0.6–4.5 Torr); the uncertainties represent 95% confidence limits. The rate constants are in reasonable agreement with Leu's results. The rate constant for M = $O_2$ was also estimated to be (1.0–1.8) × $10^{-31}$ $cm^6$ $molecule^{-2}$ $s^{-1}$ at 298 K, smaller than previous measurements.

## Introduction

The reaction

$$OH + SO_2 + M \rightarrow HOSO_2 + M \tag{1}$$

is the first step in the gas-phase oxidation of atmospheric $SO_2$ to $H_2SO_4$.[1-5] This reaction has been extensively studied at higher pressures by following the loss of OH in the presence of excess $SO_2$ and several buffer gases by using various techniques.[6-16] The rate constants reported by Wine et al.[6] using the laser flash photolysis/resonance fluorescence technique covered the most extensive experimental conditions ($260 \le T/K \le 420$, $13 \le P/Torr \le 696$, and M = He, Ar, $N_2$, $SF_6$), and the reaction was found to be in the falloff region between third and second order over the entire range of experimental conditions investigated. The falloff parameters have been derived by using the method proposed by Troe.[17-19]

However, there are only a few studies of reaction 1 at low pressure. Harris and Wayne studied the reaction in Ar and in $N_2$ (1–4 Torr) at 295 K using the discharge flow/resonance fluorescence technique.[20] Later, Leu investigated the reaction over more extensive experimental conditions ($261 \le T/K \le 414$, $0.9 \le P/Torr \le 10$, and M = He, Ar, $N_2$, $O_2$, $CO_2$, $SO_2$) using a similar technique.[21] The rate constants reported by these two laboratories differed by as much as a factor of 4. Recently, while our study was in progress, Martin et al.[22] used the discharge flow/EPR technique to study reaction 1 at room temperature and reported rate constants for the reaction in He, which are in agreement with those reported by Leu. However, the work by Leu remains to be the only study of the temperature dependence at low pressure.

The reaction

$$HOSO_2 + O_2 \rightarrow SO_3 + HO_2 \tag{2}$$

has recently been studied by Gleason et al.[23,24] The relatively high reaction rate constant determined in their study confirmed the earlier estimates by Margitan[3] and Martin et al.[22] These findings showed that odd-hydrogen radicals are catalysts in the gas-phase oxidation of $SO_2$, as proposed by Stockwell and Calvert.[1] In the earlier discharge-flow studies, the reactant OH was generated by the reaction of H atoms with $NO_2$. Thus, it is suspected that in the study of reaction 1 for M = $O_2$, the regeneration of OH in the system from reactions 2 and 3 may affect the measurements of the rate constant. In Leu's experiments with M = $O_2$, it was reported that the decay rate of [OH] decreased with reaction time, consistent with the proposed reaction scheme.

$$HO_2 + NO \rightarrow NO_2 + OH \tag{3}$$

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The difficulties in the laboratory investigation of reaction 1 at low pressure using the discharge-flow technique are mainly due to the presence of heterogeneous reactions at the wall of the flow tube and, if fluorescence detection of OH was employed, to the interference from $SO_2$ fluorescence in the same spectral region. In view of the current understanding about reaction 1 at low pressure, we felt the need to obtain more accurate rate constants at various temperatures by minimizing the above-mentioned interferences in order to compare with the only study of the temperature dependence previously reported. The reinvestigation of reaction 1 in $O_2$ with a different OH source that could avoid the interference by reactions 2 and 3 was also desirable.

## Experimental Section

The experimental technique for the discharge flow/resonance fluorescence system is similar to that described earlier;[25,26] hence only a brief description is given here.

For the studies of reaction 1 in He and $N_2$, OH was produced by reacting excess $NO_2$ with H atoms generated by a microwave discharge of a mixture of $H_2$ and He gas. For the study of reaction 1 in $O_2$, OH was produced by reacting excess $O_3$ with atomic hydrogen. A few data points for reaction 1 in He were determined with this OH source, and no apparent discrepancy in the rate constant from the previous OH source has been observed. To avoid heterogeneous reactions, the flow tube (25-mm i.d.) and the injector (9-mm o.d.) were coated with halocarbon wax for experiments at temperatures lower than 310 K. For experiments at higher temperatures, a Teflon tube (22-mm i.d.) was inserted inside the flow tube and the injector was coated with fluoropolymers. The $k'_w$ for the injector was measured by observing the OH decay with no $SO_2$ in the system as the injector was pulled out. The value of $k'_w$ was typically $-(1-2)\ s^{-1}$. The value of $k_w$ for the flow tube, determined by passing $NO_2$ through the injector to react with H atoms in the flow tube (with no $SO_2$ in the system) and observing the OH decay as the injector was pulled out, was typically less than 3 $s^{-1}$. It was found that at temperatures below 310 K, the surface of the Teflon tube (without coating) deteriorated gradually as $SO_2$ was added to the flow tube. When this deterioration occurred, the OH fluorescence counts did not reach the original value after the injector was pulled out and then pushed back to the same position. However, this problem disappeared at high temperatures. Such a problem was not observed even at low temperatures when the flow tube was carefully coated with halocarbon wax.

$SO_2$ is a strongly fluorescing molecule. It was found that by placing a filter that cuts off at about 250 nm in front of the OH resonance lamp, as performed by Leu, the $SO_2$ fluorescence was not completely eliminated. An explanation is that the OH resonance lamp also emits at 306–318 nm while $SO_2$ absorbs in the 240–320-nm region.[27] In our experiments, the scattering light was therefore measured at the beginning and at the end of each pseudo-first-order decay measurement for each $[SO_2]$ with identical flow conditions except that the microwave discharge of $H_2$ was turned off. The photon counts due to $SO_2$ fluorescence was determined to be 4–30% of the total fluorescence, depending on the temperature and $[SO_2]$ employed. Failure to exclude $SO_2$ fluorescence from the OH counts resulted in lower rate constants, to be discussed in the following section.

Typical experimental conditions were as follows: flow velocity $\bar{v} = 600\text{–}1200\ cm\ s^{-1}$; total pressure $P = 0.6\text{–}6.5$ Torr; $[OH]_0 = (0.8\text{–}6) \times 10^{11}$ molecules $cm^{-3}$; $[SO_2] = (0.4\text{–}5.6) \times 10^{15}$ molecules $cm^{-3}$; total flow rate $F_t = 4\text{–}21$ STP $cm^3\ s^{-1}$; temperature $T = 280\text{–}413$ K.

The $SO_2$ has a stated purity of 99.7%. High-resolution (0.01 $cm^{-1}$) FTIR absorption spectrometry with a 20-m multipass cell revealed no measurable absorption due to possible contaminants such as OCS, $CS_2$, $CO_2$, and $H_2SO_4$. In a few experiments in which vacuum-distilled $SO_2$ was used, the measured rate constants were similar to those from unpurified samples. The $NO_2$ was prepared by slowly reacting pure NO with an excess of $O_2$ and stored under oxygen for at least 24 h before use. The $O_3$ was produced with a commercial ozonizer from the discharge of $O_2$ and stored in a silica gel trap kept at 195 K. Sometimes the $O_3$ was generated and used during the experiments. The He (99.9995%) and $H_2$ (99.999%) were passed through a 77 K trap before being discharged. $O_2$ (99.97%) and $N_2$ (99.99%) were used without further purification.

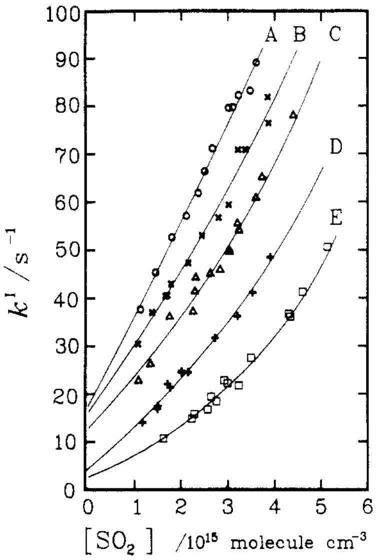

**Figure 1.** Plot of $k^I$ vs $[SO_2]$ at 298 K for M = He: A, 5 Torr; B, 4 Torr; C, 3 Torr; D, 2 Torr; E, 1 Torr. The origins have been displaced vertically by 20, 15, 10, and 5 $s^{-1}$, respectively, for lines A, B, C, and D.

## Results and Discussion

The reaction was studied under pseudo-first-order conditions with $[SO_2]$ at least $5 \times 10^3$ times larger than the initial concentration of OH. The decay of the OH resonance fluorescence as a function of the reaction distance was measured to give the pseudo-first-order rate constant. The rate constant was then corrected for the removal of OH by the injector wall ($k'_w$) and the axial diffusion (eq 4 in ref 25).

The corrected pseudo-first-order rate constant, $k^I$, can be expressed as

$$k^I = k^{II}_{int}[SO_2] + \sum_M k^{III}_M[M][SO_2] + k^{III}_{SO_2}[SO_2]^2 \quad (4)$$

in which $k^{II}_{int}$ is the intercept in the $k^{II}_M$ vs $[SO_2]$ plot, $k^{III}_M$ is the termolecular rate constant for the third-body M (M = He, $O_2$, or $N_2$), and $k^{III}_{SO_2}$ the termolecular rate constant due to $SO_2$ as a third body. The apparent bimolecular rate constant $k^{II}_M$ is defined as the slope of the plot of $k^I_M$ vs $[SO_2]$, in which

$$k^I_M = k^I - k^{III}_{SO_2}[SO_2]^2 \quad (5)$$

is the apparent first-order reaction rate constant after correction for the contribution from the termolecular reaction due to $SO_2$ as a third body.

For the reaction in He at 1–5 Torr at 298 K, the plot of $k^I$ vs $[SO_2]$ is shown in Figure 1. The pronounced upward curvature at lower pressures was due to the greater contribution from $k^{III}_{SO_2}[SO_2]^2$ at greater concentrations of $SO_2$. From eq 4, $k^{III}_{SO_2}$ was evaluated from the slope of the line in the plot of $k^I/[SO_2]$ vs $[SO_2]$, illustrated in Figure 2. The results fitted by least-squares analysis are listed in Table I, with uncertainties representing 1 standard error. At each temprature the average $k^{III}_{SO_2}$ obtained at various pressures, also listed in Table I was used in eq 5 to derive $k^I_M$. At 298 K, $k^{III}_{SO_2} = 1.0 \times 10^{-30}\ cm^6\ molecule^{-2}\ s^{-1}$.

Figure 3 shows the plots of $k^I_M$ vs $[SO_2]$ for $P_{He}$ = 1–5 Torr at 298 K. The curvature shown in Figure 1 has been eliminated,

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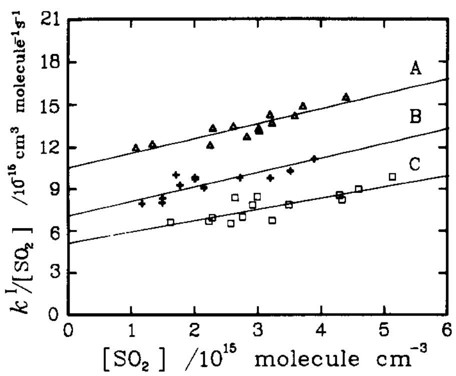

**Figure 2.** Plot of $k^I/[SO_2]$ vs $[SO_2]$ at 298 K for M = He: A, 3 Torr; B, 2 Torr; C, 1 Torr.

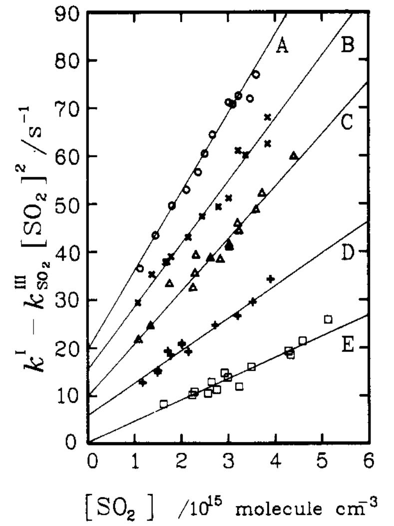

**Figure 3.** Plot of $(k^I - k^{III}_{SO_2}[SO_2]^2)$ vs $[SO_2]$ at 298 K for M = He: A, 5 Torr; B, 4 Torr; C, 3 Torr; D, 2 Torr; E, 1 Torr. The origins have been displaced vertically by 20, 15, 10, and 5 $s^{-1}$ respectively, for lines A, B, C, and D.

and the data are fitted well to straight lines. The slope of such a plot yields the apparent bimolecular rate constant $k^{II}_M$, in which

$$k^{II}_M = k^{II}_{int} + \sum_M k^{III}_M[M], \quad M = \text{He}, N_2, \text{ or } O_2 \qquad (6)$$

according to eqs 4 and 5.

In the case of M = He, a plot of $k^{II}_{He}$ vs [He] should produce a straight line with a slope $k^{III}_{He}$. The values of $k^{II}_{He}$ are also listed in Table I. Five of the eight different runs at temperatures 280–413 K are shown in Figure 4. The data points are fitted reasonably well to straight lines. From the least-squares fits, the values of $k^{II}_{int}$ and $k^{III}_{He}$ at each temperature are also listed in Table I. At 298 K, $k^{III}_{He} = 9.0 \times 10^{-32}$ cm$^6$ molecule$^{-2}$ s$^{-1}$. The $k^{III}_{He}$ was insensitive to $k^{III}_{SO_2}$ because of the relatively small correction involved in eq 5. A change in $k^{III}_{SO_2}$ by a factor of 2 altered $k^{III}_{He}$ less than 15%.

Although previous work by Wine et al.[6] showed that the data reported by Leu[21] at low pressures could be fitted satisfactorily to a falloff curve derived from Troe's theory,[17-19] Leu's data were also fitted well to a straight line with a small interecept. The intercept, $k^{II}_{int}$, may result from either heterogeneous reactions at the reactor wall or the falloff of $k^{III}_{He}$ at high pressures. The observed dependence of $k^{II}_{int}$ on surface conditions suggested that heterogeneous wall reactions played an important role. However, with present experimental accuracy, it is difficult to judge if the pressure range studied in this work is in the falloff region.

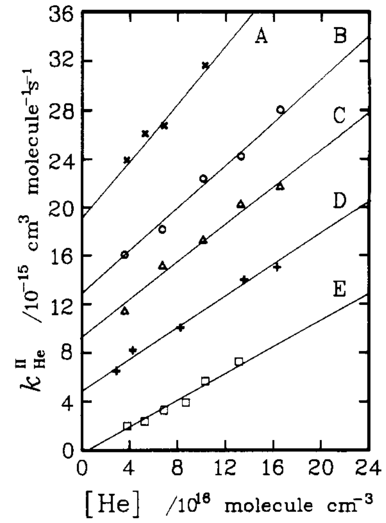

**Figure 4.** Plot of $k^{II}_{He}$ vs [He] over the temperature range 280–413 K: A, 280 K; B, 298 K; C, 333 K; D, 363 K; E, 413 K. The origins have been displaced vertically by 16, 12, 8, and 4 × $10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$, respectively, for lines A, B, C, and D.

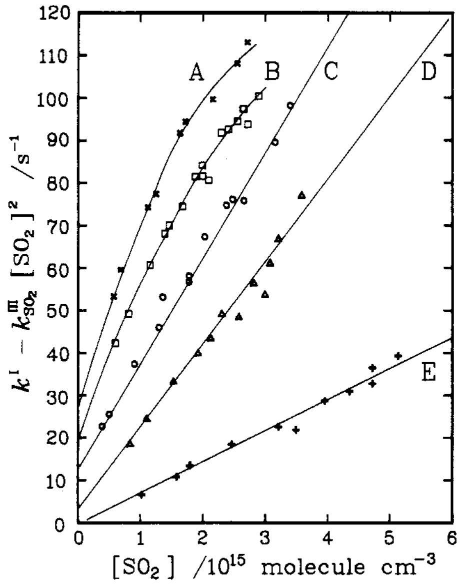

**Figure 5.** Plot of $(k^I - k^{III}_{SO_2}[SO_2]^2)$ vs $[SO_2]$ at 298 K for M = $N_2$: A, 4.5 Torr; B, 4 Torr; C, 3 Torr; D, 2 Torr; E, 0.6 Torr. The origins have been displaced vertically by 30, 20, and 10 $s^{-1}$, respectively, for lines A, B, and C.

In the determination of $k^{III}_M$ for M = $N_2$ and $O_2$, because a small stream of helium was used to carry $H_2$ through the microwave discharge, values of $k^{III}_{He}$ listed in Table I were used in eq 6 to derive $k^{III}_{N_2}$ and $k^{III}_{O_2}$. The amount of $O_2$ in the flow system was further limited by the decrease in the detectivity of OH due to the high efficiency in the quenching of OH fluorescence by $O_2$. In the case of M = $N_2$ with a fixed small concentration of He, the $k^I - k^{III}_{SO_2}[SO_2]^2$ vs $[SO_2]$ plot leveled off with higher $[SO_2]$ at higher pressures, as depicted in Figure 5. This phenomenon was not observed for M = He even at $[SO_2]$ as high as 6 × $10^{15}$ molecule cm$^{-3}$. At present time, we do not have a good explanation for this observation. For the derivation of $k^{III}_{N_2}$ at higher pressures, only data at smaller $[SO_2]$ were used in the linear least-squares fitting. The data and the fitted $k^{III}_M$ are tabulated in Table II, with $k^{III}_{N_2} = 2.38 \times 10^{-31}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ and $k^{III}_{O_2} = 1.2 \times 10^{-31}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ at 298 K.

The initial concentration of OH in the flow tube was kept in the range (0.8–2.0) × $10^{11}$ molecules cm$^{-3}$. Care has been taken to minimize the effect from the interfering reaction

$$OH + OH \rightarrow \text{products} \qquad (7)$$

with $k_7 = 1.9 \times 10^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$.[28] The smallest $k^{II}_{He}$ under our experimental conditions was 2.0 × $10^{-15}$ cm$^3$ molecule$^{-1}$ s$^{-1}$ at 1.63 Torr and 413 K (Table I). A ratio $[SO_2]_0/[OH]_0$ larger than 1.9 × $10^4$ is needed to keep the error due to reaction 7 less than 5%. At higher pressures or lower temperatures, the minimum

**TABLE I: Summary of Experimental Results for M = He**

| $T$/K | [He][a] | $[SO_2]$[a] | no. of expts | $k^{III}_{SO_2}$[b] | av $k^{III}_{SO_2}$[b] | $k^{II}_{He}$[c] | $k^{II}_{int}$[c] | $k^{III}_{He}$[b] |
|---|---|---|---|---|---|---|---|---|
| 280 | 371 | 5-38 | 9 | 161 ± 17 | | 790 ± 35 | 357 ± 61 | 11.5 ± 0.9 |
| | 531 | 7-37 | 8 | 159 ± 20 | | 1011 ± 37 | | |
| | 683 | 8-40 | 12 | 118 ± 11 | | 1075 ± 22 | | |
| | 1025 | 4-22 | 7 | 130 ± 52 | 142 ± 19 | 1563 ± 62 | | |
| 295 | 351 | 8-44 | 8 | 168 ± 6 | | 671 ± 81 | 265 ± 75 | 10.3 ± 0.8 |
| | 678 | 9-45 | 10 | 115 ± 14 | | 942 ± 21 | | |
| | 991 | 8-28 | 7 | 106 ± 19 | | 1203 ± 32 | | |
| | 1313 | 6-23 | 9 | 133 ± 36 | 131 ± 24 | 1682 ± 46 | | |
| 298 | 357 | 16-51 | 14 | 96 ± 3 | | 405 ± 11 | 87 ± 27 | 9.0 ± 0.2 |
| | 672 | 11-39 | 11 | 86 ± 6 | | 693 ± 14 | | |
| | 1011 | 10-44 | 15 | 108 ± 4 | | 1036 ± 16 | | |
| | 1325 | 10-30 | 12 | 107 ± 7 | | 1223 ± 18 | | |
| | 1653 | 11-36 | 12 | 109 ± 8 | 101 ± 9 | 1602 ± 18 | | |
| 330 | 357 | 19-46 | 9 | 47 ± 4 | | 344 ± 14 | 122 ± 42 | 7.9 ± 0.4 |
| | 672 | 11-37 | 10 | 63 ± 8 | | 711 ± 16 | | |
| | 1011 | 13-37 | 10 | 55 ± 9 | | 926 ± 22 | | |
| | 1325 | 9-35 | 9 | 88 ± 7 | | 1227 ± 19 | | |
| | 1653 | 8-39 | 9 | 66 ± 5 | 64 ± 14 | 1371 ± 12 | | |
| 333 | 317 | 13-56 | 10 | 97 ± 3 | | 357 ± 18 | 20 ± 44 | 8.9 ± 0.4 |
| | 605 | 10-52 | 9 | 89 ± 5 | | 586 ± 15 | | |
| | 1471 | 7-42 | 13 | 123 ± 8 | | 1297 ± 17 | | |
| | 1763 | 12-39 | 9 | 162 ± 8 | 103 ± 15 | 1687 ± 20 | | |
| 358 | 375 | 15-40 | 15 | 58 ± 6 | | 357 ± 16 | 143 ± 27 | 5.8 ± 0.2 |
| | 690 | 13-40 | 10 | 63 ± 6 | | 581 ± 17 | | |
| | 1037 | 10-39 | 9 | 54 ± 7 | | 679 ± 19 | | |
| | 1356 | 9-46 | 9 | 40 ± 5 | | 935 ± 13 | | |
| | 1710 | 7-40 | 11 | 50 ± 5 | 53 ± 8 | 1143 ± 13 | | |
| 363 | 290 | 14-55 | 7 | 47 ± 5 | | 251 ± 11 | 106 ± 24 | 6.5 ± 0.2 |
| | 425 | 11-53 | 10 | 71 ± 3 | | 419 ± 8 | | |
| | 823 | 11-50 | 11 | 53 ± 2 | | 605 ± 7 | | |
| | 1353 | 8-44 | 8 | 87 ± 5 | | 999 ± 12 | | |
| | 1630 | 11-36 | 8 | 83 ± 8 | 68 ± 16 | 1102 ± 18 | | |
| 413 | 380 | 16-37 | 7 | 24 ± 5 | | 199 ± 14 | 60 ± 22 | 5.8 ± 0.3 |
| | 527 | 18-45 | 11 | 24 ± 3 | | 237 ± 8 | | |
| | 688 | 20-50 | 11 | 27 ± 2 | | 329 ± 7 | | |
| | 870 | 11-38 | 9 | 20 ± 7 | | 391 ± 13 | | |
| | 1031 | 10-43 | 11 | 17 ± 6 | | 566 ± 14 | | |
| | 1313 | 15-44 | 11 | 24 ± 2 | 23 ± 3 | 726 ± 4 | | |

[a] In units of $10^{14}$ molecules $cm^{-3}$. [b] In units of $10^{-32}$ $cm^6$ $molecule^{-2}$ $s^{-1}$. The errors represent 1 standard deviation. [c] In units of $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. The errors represent 1 standard deviation.

**TABLE II: Summary of Experimental Results for M = $N_2$ and M = $O_2$ at 298 K**

| [He][a] | [M][a] | $[SO_2]_0$[a] | no. of expts | $k^{II}_M$[b] | $k'^{II}_M$[b,c] | $k^{II}_{int}$[b] | $k^{III}_M$[d] |
|---|---|---|---|---|---|---|---|
| | | | | M = $N_2$ | | | |
| 38 | 150 | 9-51 | 11 | 684 ± 10 | 650 | 401 ± 51 | 23.8 ± 0.7 |
| 63 | 258 | 11-41 | 7 | 1060 ± 35 | 1004 | | |
| 133 | 514 | 8-37 | 12 | 1868 ± 28 | 1748 | | |
| 128 | 516 | 8-36 | 10 | 1972 ± 36 | 1857 | | |
| 160 | 647 | 7-33 | 8 | 1899 ± 53 | 1755 | | |
| 195 | 775 | 9-34 | 11 | 2427 ± 28 | 2251 | | |
| 259 | 1030 | 6-23 | 10 | 2899 ± 28 | 2666 | | |
| 290 | 1161 | 5-17 | 6 | 3535 ± 46 | 3274 | | |
| | | | | M = $O_2$ | | | |
| 228 | 99 | 10-33 | 6 | 694 ± 34 | 489 | 368 ± 31 | 11.8 ± 1.2 |
| 342 | 147 | 8-28 | 6 | 818 ± 22 | 510 | | |
| 682 | 262 | 5-23 | 6 | 1365 ± 33 | 751 | | |
| 908 | 389 | 5-23 | 8 | 1619 ± 34 | 801 | | |

[a] In units of $10^{14}$ molecules $cm^{-3}$. [b] In units of $10^{-17}$ $cm^3$ $molecule^{-1}$ $s^{-1}$. The errors represent 1 standard deviation. [c] $k'^{II}_M = k^{II}_M - k^{III}_{He}[He]$. [d] In units of $10^{-32}$ $cm^6$ $molecule^{-2}$ $s^{-1}$. The errors represent 1 standard deviation.

$[SO_2]_0/[OH]_0$ required to keep reaction 7 below 5% decreased. This criterion was fulfilled in most experiments except for a few with a slightly low concentration of $SO_2$.

The reaction

$$OH + HOSO_2 \rightarrow H_2O + SO_3 \tag{8}$$

could be important if the rate coefficient $k_8$ is large. Computer simulation of the reactions in the flow tube was carried out using the GEAR integration program. If reaction 8 with an upper limit of $k_8 = 5 \times 10^{-11}$ $cm^3$ $molecule^{-1}$ $s^{-1}$ was included in the simulation at 298 K, about 18–27% and 10% increase in $k^I$ and $k^{II}$, respectively, were predicted for $[OH]_0 = 6 \times 10^{11}$ molecules $cm^{-3}$, $[SO_2] = (1–6) \times 10^{15}$ molecules $cm^{-3}$, and $P = 1$ Torr. Similarly, 15–25% and 12% increase in $k^I$ and $k^{II}$, respectively, were found for $[OH]_0 = 6 \times 10^{11}$ molecules $cm^{-3}$, $[SO_2] = (1–6) \times 10^{15}$ molecules $cm^{-3}$, and $P = 6$ Torr. The increase in $k^{III}_{He}$ due to reaction 8 was found to be less than 3%.

Rate constants for the reactions of OH with OCS or $CS_2$, the possible trace impurities in $SO_2$, are smaller than the apparent bimolecular rate constants observed in this study.[28] Therefore, the error of $k^{III}_M$ due to these impurities can be neglected. Careful

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**TABLE III: Summary of the Termolecular Rate Constants for the Reaction OH + $SO_2$ + M at Low Pressure (M = He, $N_2$, $O_2$, and $SO_2$)**

| M | P, Torr | $k^{\mathrm{III}}_{\mathrm{M}}$[a] | T range, K | $k(T) = A\exp(-E/RT)$ | | $k(T) = k_{300}(T/300)^{-n}$ | | method[b] | ref |
|---|---|---|---|---|---|---|---|---|---|
| | | | | A[a] | $-E/R$, $K^{-1}$ | $k_{300}$[a] | n | | |
| He | 1–6 | 9.0 ± 2.7 | 280–413 | 1.1 ± 0.3 | 640 ± 200 | 9.6 ± 3.0 | 1.9 ± 0.6 | DF-RF | this work |
| | 1–10 | 8.45 ± 0.31 | 261–414 | $0.36^{+0.10}_{-0.08}$ | 913 ± 74 | 7.91 ± 0.24 | 2.85 ± 0.21 | DF-RF | Leu[21] |
| | 1–6.4 | 8.1 ± 0.2 | | | | | | DF-EPR | Martin et al.[22] |
| $N_2$ | 0.6–4.5 | 24 ± 7 | | | | | | DF-RF | this work |
| | 1–4 | 25.4 ± 3.3 | | | | | | DF-RF | Leu[21] |
| $O_2$ | 0.4–1.5 | (10–18)[c] | | | | | | DF–RF | this work |
| | 1.7–2.3 | 24.6 ± 3.2 | | | | | | DF-RF | Leu[21] |
| $SO_2$ | 0.012–0.23 | 100 ± 50 | 280–363 | 3.3 ± 1.5 | 1055 ± 500 | 110 ± 50 | 3.3 ± 1.5 | DF-RF | this work |
| | 0.02–0.20 | 124 ± 33 | 261–414 | $5.31^{+2.70}_{-1.78}$ | 908 ± 129 | 115 ± 9 | 2.78 ± 0.39 | DF-RF | Leu[21] |
| | 0.01–0.18 | 133 ± 40 | | | | | | DF-EPR | Martin et al.[22] |

[a] In units of $10^{-32}$ $cm^6$ $molecule^{-2}$ $s^{-1}$. [b] DF, discharge flow; RF, resonance fluorescence; EPR, electron paramagnetic resonance. [c] Estimate.

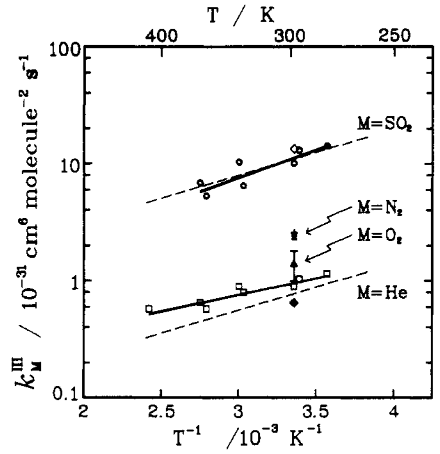

**Figure 6**. Dependence of rate constant $k^{\mathrm{III}}_{\mathrm{M}}$ upon $1/T$: ○, M = $SO_2$; □, M = He; ×, M = $N_2$; △, M = $O_2$ (this work); ◇, M = $SO_2$ (Martin et al.); ◆, M = He (Martin et al.); +, M = $N_2$, $O_2$ (Leu). The lines represent the least-squares fitting of the data for M = $SO_2$ and He. Solid lines, this work; dashed lines, Leu.

tests have also been performed to study the dependence of the rate constants on the ratio $[NO_2]_0/[OH]_0$. A variation of $[NO_2]_0/[OH]_0$ from 10 to 100 did not change the measured rate constant $k^{\mathrm{I}}$. In the studies of M = $SO_2$ and $O_2$, because the gas mixture contained less than 15% and 30% of $SO_2$ and $O_2$, respectively, the uncertainties in the $k^{\mathrm{III}}_{\mathrm{M}}$ measurements are much larger than those for $k^{\mathrm{III}}_{\mathrm{He}}$ or $k^{\mathrm{III}}_{\mathrm{N_2}}$. The instrumental errors have been estimated to be approximately 9%.[25,26] Considering all these possible errors, we estimated that the 95% confidence limits in our measurements for $k^{\mathrm{III}}_{\mathrm{M}}$ are ±30% for M = He and $N_2$ and ±50% for M = $SO_2$. For M = $O_2$, because of the difficulties associated with the experiments, our data could not provide accurate measurements of the rate constant. A range (1.0–1.8) × $10^{-31}$ $cm^6$ $molecule^{-2}$ $s^{-1}$ was estimated for $k^{\mathrm{III}}_{\mathrm{O_2}}$ on the basis of the experimental results.

The values $k^{\mathrm{III}}_{\mathrm{SO_2}}$ and $k^{\mathrm{III}}_{\mathrm{He}}$ at various temperatures in the range 280–413 K are shown in Figure 6, along with previous measurements at low pressure for comparison. The observed termolecular rate constants were fitted to yield the Arrhenius expressions

$$k^{\mathrm{III}}_{\mathrm{He}} = (1.1 \pm 0.3) \times 10^{-32} \exp[(640 \pm 200)/T] \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \tag{9}$$

$$k^{\mathrm{III}}_{\mathrm{SO_2}} = (3.3 \pm 1.5) \times 10^{-32} \exp[(1055 \pm 500)/T] \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \tag{10}$$

in which the uncertainties represent 95% confidence limits. The expression reporduced the measured rate constants to within 9 and 14%, respectively, for M = He and M = $SO_2$. The data for M = $SO_2$ at 413 K were excluded in the fitting because of the relatively small contribution from $SO_2$ to the total termolecular reaction studied. Alternatively, the rate constants could be fitted to the expressions

$$k^{\mathrm{III}}_{\mathrm{He}} = (9.6 \pm 3.0) \times 10^{-32}(T/300)^{-(1.9\pm0.6)} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \tag{11}$$

$$k^{\mathrm{III}}_{\mathrm{SO_2}} = (1.1 \pm 0.5) \times 10^{-30}(T/300)^{-(3.3\pm1.5)} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \tag{12}$$

which reproduced the measured rate constants to within 9 and 14%, respectively, over the temperature range studied.

A summary of the reported rate constants for the reaction OH + $SO_2$ + M at low pressure is given in Table III. Our value $k^{\mathrm{III}}_{\mathrm{He}}$ = (9.0 ± 2.7) × $10^{-32}$ $cm^6$ $molecule^{-2}$ $s^{-1}$ (with errors representing 95% confidence limits) is in excellent agreement with the values (8.45 ± 0.31) × $10^{-32}$ and (8.1 ± 0.2) × $10^{-32}$ $cm^6$ $molecule^{-2}$ $s^{-1}$ reported by Leu[21] and Martin et al.,[22] respectively, at room temperature. Our results showed slightly smaller temperature dependence than those reported by Leu:

$$k^{\mathrm{III}}_{\mathrm{He}}(\mathrm{Leu}) = (3.61^{+0.98}_{-0.78}) \times 10^{-33} \exp[(913 \pm 74)/T] \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \tag{13}$$

or

$$k^{\mathrm{III}}_{\mathrm{He}}(\mathrm{Leu}) = (7.91 \pm 0.24) \times 10^{-32}(T/298)^{-(2.85\pm0.21)} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \tag{14}$$

For M = $N_2$, our value $k^{\mathrm{III}}_{\mathrm{N_2}}$ = (2.4 ± 0.7) × $10^{-31}$ $cm^6$ $molecule^{-2}$ $s^{-1}$ is also very close to that reported by Leu, (2.54 ± 0.33) × $10^{-31}$ $cm^6$ $molecule^{-2}$ $s^{-1}$. For M = $SO_2$, $k^{\mathrm{III}}_{\mathrm{SO_2}}$ = (1.0 ± 0.5) × $10^{-30}$ $cm^6$ $molecule^{-2}$ $s^{-1}$ at 298 K is slightly smaller than the values (1.24 ± 0.33) × $10^{-30}$ and (1.33 ± 0.40) × $10^{-30}$ $cm^6$ $molecule^{-2}$ $s^{-1}$ reported by Leu and Martin et al., respectively. However, owing to the larger uncertainties involved in these measurements, the error bars for all three studies overlap. The temperature dependence of $k^{\mathrm{III}}_{\mathrm{SO_2}}$ is similar to that reported by Leu:

$$k^{\mathrm{III}}_{\mathrm{SO_2}}(\mathrm{Leu}) = (5.31^{+2.70}_{-1.78}) \times 10^{-32} \exp[(908 \pm 129)/T] \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \tag{15}$$

or

$$k^{\mathrm{III}}_{\mathrm{SO_2}}(\mathrm{Leu}) = (1.15 \pm 0.09) \times 10^{-30}(T/298)^{-(2.78\pm0.39)} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1} \tag{16}$$

Although our results yielded a slightly larger negative activation energy, the discrepancy from that reported by Leu is well within experimental uncertainties, as illustrated in Figure 6.

In the study for M = $O_2$, the problem of OH regeneration has been eliminated in this work through the use of H + $O_3$ as a source of OH. The OH source from H + $O_3$ reaction has been known to generate vibrationally excited OH.[29] In our experiments the

OH source was placed about 20 cm upstream from the OH + $SO_2$ reaction zone in order to allow ample time for the vibrationally excited OH to relax. The $k^{III}{}_{He}$ determined at 298 K by using this source is within experimental uncertainties of those obtained by using the H + $NO_2 \rightarrow$ OH + NO reaction. However, the effect on $k^{III}{}_{O_2}$ due to excited OH radicals cannot be positively ruled out. Although $HO_2$ reacts with $O_3$ to form OH

$$HO_2 + O_3 \rightarrow OH + 2O_2 \qquad (17)$$

the slow rate constant $k_{17} = 1.1 \times 10^{-14} \exp[(500^{+500}_{-100})/T]$ cm$^3$ molecule$^{-1}$ s$^{-1}$ suggests that OH regeneration from reaction 17 is unimportant.[28] The relative rates of the reactions

$$OH + SO_2 + M \rightarrow HOSO_2 + M \quad (slow) \qquad (1)$$

$$HOSO_2 + O_2 \rightarrow SO_3 + HO_2 \quad (rapid) \qquad (2)$$

suggest that the rate constant observed under our experimental conditions was mostly due to $k_1$ because $k_2 = 1.34 \times 10^{-12} \exp(-330/T)$ cm$^3$ molecule$^{-1}$ s$^{-1}$ is much larger than $k_1$[M],[24] making reaction 1 rate-determining. Our estimate $(1.0–1.8) \times 10^{-31}$ cm$^6$ molecule$^{-2}$ s$^{-1}$ is smaller than that reported by Leu, $(2.46 \pm 0.32) \times 10^{-31}$ cm$^6$ molecule$^{-2}$ s$^{-1}$, using H + $NO_2$ as an OH source. Although the efficiencies for M = $N_2$ and $O_2$ in many termolecular reactions have been reported to be approximately equal, there are cases in which the efficiency for M = $O_2$ is as low as 70% of that for M = $N_2$.[30] Considering the large uncertainties in these measurements, the observed rate coefficient for M = $O_2$ is not beyond this limit. The low estimated value suggests that further study on this reaction in $O_2$ is called for.

In conclusion, the temperature dependence of $k^{III}{}_{He}$ and $k^{III}{}_{SO_2}$ for the title reaction at low pressure has been accurately determined, and the results are in reasonable agreements with the only previous study by Leu. Our experiments also provided the study of $k^{III}{}_{N_2}$ and $k^{III}{}_{O_2}$ at 298 K. The latter was determined without the complication from OH regeneration due to secondary reactions.

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# Picosecond and Nanosecond Studies of the Photoreduction of Benzophenone by 1,4-Diazabicyclo[2.2.2]octane: Characterization of the Transient

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The transient that is produced in the quenching of triplet benzophenone by 1,4-diazabicyclo[2.2.2]octane (DABCO) has been examined by use of nano- and picosecond laser photolysis. The initial step in all solvents, both polar and nonpolar, is electron transfer to form a triplet contact ion pair. In nonpolar solvents, the ion pair remains in this form until it decays. For polar solvents, the spectra change somewhat over the first 100 ps showing that the solvation changes and the ion pair becomes solvent separated. The lifetime of the ion pair varies greatly with the solvent. In saturated hydrocarbons it is about 80 ps. Nonpolar solvents with either π electrons or a lone pair of electrons stabilize the ion pair on the nanosecond to microsecond time scale. A small amount of alcohol in benzene also stabilizes the ion pair by hydrogen bonding. A shift in the peak position with time toward the blue accompanies the formation of hydrogen bonds in this case. Quenching of the ion pair by oxygen and the dependence of the ion-pair lifetime on temperature show different behavior for the two types of solvent and correlate with the form of the ion pair. The lifetime of the triplet ion pair is controlled alternatively by the rates of intersystem crossing, intrapair proton transfer, or the energetics of back electron transfer.

## I. Introduction

For a full understanding of a chemical reaction it is essential to understand the properties of any transient reaction intermediates. This statement is particularly true for a photochemical reaction like the quenching of benzophenone triplet by amines which involves electron transfer and an intermediate ion pair. A thorough knowledge of the transient will not only help elucidate the reaction mechanism but will also indicate the means to control the energy-wasting step of back electron transfer to regenerate the starting materials. For the past 20 years the photoreduction of aromatic ketones by amines[1-27] has been an active area of research. In addition to optical absorption spectroscopy, techniques like CIDNP[28,29] and CIDEP[30,31] have been employed to study the

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