A Kinetics Study of the Reaction of HO_2 with SO_2 and NO[1a]

W. A. Payne,[1b,2] L. J. Stief,[2a] and D. D. Davis*[2b,3]

Contribution from the Astrochemistry Branch,
Laboratory for Extraterrestrial Physics, NASA/Goddard Space Flight Center,
Greenbelt, Maryland 20771, and the Chemistry Department,
University of Maryland, College Park, Maryland 20742.
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Abstract: Using the photochemical $^{18}O_2$ competitive isotope labeling technique, rate constants have been determined for reaction of the hydroperoxyl radical with the atmospheric gas SO_2. All measurements were made relative to the disproportionation reaction $HO_2 + HO_2 \rightarrow H_2O_2 + O_2$. At 300°K the rate constant for reaction of SO_2 with HO_2 was found to be $(8.7 \pm 1.8) \times 10^{-16}$ cm^3 molecule^{-1} sec^{-1}. The quoted uncertainty reflects the uncertainty in the measurement of the rate constant ratio $k_2/(k_7)^{1/2}$. Because of existing uncertainties in the value of k_7, however, the possible range of values in k_2 is 8.2×10^{-16} to 1.5×10^{-15} cm^3 molecule^{-1} sec^{-1}. Also using the photochemical $^{18}O_2$ competitive isotope labeling technique, it has been possible to estimate the value of the rate constant for reaction of HO_2 with NO. The rate constant for this system, k_3, was found to be 3×10^{-13} cm^3 molecule^{-1} sec^{-1} with the uncertainty in its value being a factor of ±3. The possible importance of secondary reactions in the determination of k_2 and k_3 is discussed.

We have previously used the photochemical $^{18}O_2$ competitive isotope labeling technique[4] to study the important reaction

$$HO_2 + CO \longrightarrow CO_2 + OH \qquad (1)$$

In that study, we found reaction 1 to be quite slow with the data yielding an upper limit for the rate constant for this process of $k_1 = 1.5 \times 10^{-20}$ cm^3 molecule^{-1} sec^{-1}.[4] These results clearly showed that reaction 1 cannot be considered as an important process for the conversion of CO to CO_2 in either the stratosphere or the troposphere of the earth. It also is now apparent that this reaction will be of negligible importance as a means of maintaining the stability of the CO_2 atmosphere on Mars.[5]

In this study, we have further explored the possible important reactions of the hydroperoxyl radical with two additional atmospheric trace gases, SO_2 and NO. The most likely reaction in both cases would consist of the abstraction of an O atom from the HO_2 species with the production of the more reactive OH radical, *i.e.*

$$HO_2 + SO_2 \longrightarrow SO_3 + OH \qquad \Delta H_{rx} = -19 \text{ kcal/mol} \qquad (2)$$

$$HO_2 + NO \longrightarrow NO_2 + OH \qquad \Delta H_{rx} = -10 \text{ kcal/mol} \qquad (3)$$

An examination of the literature has revealed that for only one of these reactions, (3), has an experimental measurement been made, and this measurement was of an indirect nature.[6]

The possible importance of reactions 2 and 3, when combined with the atmospheric processes 4 and 5, is

$$OH + CO \longrightarrow CO_2 + H \qquad (4)$$

$$H + O_2 + N_2 \longrightarrow HO_2 + N_2 \qquad (5)$$

seen to be the chain conversion of SO_2 to SO_3 and NO to NO_2. The SO_3 formed in reaction 2 would than be expected to react with H_2O (probably in a heterogeneous process) to form the familiar sulfuric acid aerosol. On the other hand, the formation of NO_2 from reaction 3 would give rise to the photochemical production of atomic oxygen which, in turn, could result in the production of O_3 and the further oxidation of a wide assortment of hydrocarbons.

Since the mechanisms for conversion of NO to NO_2 and SO_2 to SO_3 are now considered to be of major importance both in the natural and perturbed atmosphere, we have undertaken a kinetic investigation of reactions 2 and 3. The technique employed in this study has been the photochemical $^{18}O_2$ competitive isotope labeling method. All measurements were carried out at 298°K.

Experimental Section

A schematic drawing of the photolysis system is shown in Figure 1. The gas handling system utilized in these experiments consisted of a conventional high-vacuum line equipped with high-vacuum Teflon-seated valves. The system was maintained Hg free. Low pressures (1 mTorr to 1 Torr) were measured with a 1-Torr Granville–Phillips capacitance manometer head; high pressures were measured with either a 200-Torr Granville–Phillips or a 0–760-Torr Wallace and Tiernan gauge. The reaction cell in all experiments was a 500-cm^3 spherical Pyrex vessel equipped with a suprasil window which transmitted radiation at wavelengths >1650 Å. The window was attached to the cell with Varian "Torr Seal."

The light source used throughout this study was a microwave powered mercury resonance lamp. The output of the lamp was examined on a McPherson 1/2 meter vacuum monochromator and found to emit 98% of its radiation at 1849 and 2537 Å with the intensity of the two lines being approximately equal. All other emission lines from the lamp (2% of total) were at wavelengths >2537 Å. Calculations based on known extinction coefficients[7]

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(1) (a) The results from this research were first reported at the Symposium on "Sources, Sinks, and Concentrations of CO and CH_4 in the Earth's Environment," a joint meeting of the AGU and AMS, St. Petersburg, Florida, Aug 1972. (b) The research reported on here is part of a thesis to be submitted to the Graduate School of the University of Maryland in partial fulfillment of the requirements for the Masters degree in Chemistry.

(2) (a) NASA/Goddard Space Flight Center; (b) University of Maryland.

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(4) D. D. Davis, W. A. Payne, and L. J. Stief, *Science*, **179**, 280 (1973).

(5) M. B. McElroy and T. M. Donahue, *Science*, **177**, 986 (1972).

(6) H. S. Johnston and Zafonte, work cited in National Bureau of Standards Report No. 10447.

(7) (a) K. Watanabe, M. Zelikoff, and E. C. Y. Inn, Air Force Cambridge Research Center Technical Report No. 53-23 (1953); (b) N. Washida, Y. Mori, and I. Tanaka, *J. Chem. Phys.*, **54**, 1119 (1971); (c) D. Golomb, K. W. Watanabe, and F. F. Marmo, *ibid.*, **36**, 958 (1962); (d) B. A. Thompson, P. Harteck, and R. R. Reeves, Jr., *J. Geol. Res.*, **68**, 6431 (1963).

for the gases H_2O, CO, O_2, N_2, and NO showed that none of these gases or any of the possible products from this system (*e.g.*, CO_2 and H_2O_2) absorbed 2537-Å radiation significantly at the pressures used. Although SO_2 does absorb significantly at 2537 Å ($k = 5$ cm^{-1} atm^{-1}),[7d] control experiments discussed in the next section showed that this does not lead to formation of the products $C^{16}O_2$ or $C^{16,18}O_2$. In these experiments, therefore, no attempt was made to block the 2537-Å line. Actinometry at 1849 Å was carried out using two methods. In the first approach, measurements were made on the amount of CO_2 produced when 20 Torr of H_2O was irradiated in the presence of 1 to 3 Torr of CO. This method assumes the quantum yield for dissociation of H_2O into H and OH is unity at 1849 Å and that there are no loss mechanisms for OH other than reaction with CO to produce CO_2. The second method involved the photolysis of N_2O at 1849 Å where the quantum yield for N_2 production is 1.44.[8] The results of both methods agreed to within 10% and a value of 3.5×10^{15} photons/cm^2/sec was obtained for the intensity of the lamp.

The $^{18}O_2$ (99%) used in this study was obtained from Miles Laboratories, Inc., in 100-cm^3 break-seal bulbs. A mass spectrum analysis showed that the major impurities in the gas were $C^{18}O_2$ and $C^{16,18}O_2$. These impurities were removed by passing the O_2 through a liquid N_2 trap filled with glass beads. Subsequent analysis showed this to be an efficient method of removing the CO_2 impurity. Carbon monoxide and N_2 were obtained from the Matheson Co., Inc. The nitrogen (99.999% purity) was used without further purification; traces of iron carbonyl were removed from the CO with a liquid N_2 trap filled with glass beads. The SO_2 was obtained from Baker Chemical Co. After degassing at −196°, mass spectrum analysis showed the impurity level to be <0.05%. The gas NO was Matheson Co. chemical grade; it was purified by first degassing at −196° followed by distillation from a trap at −183°. A mass spectrum analysis of the purified gas indicated that the NO_2 level was <0.1%.

In a typical experimental run, the procedure was to prepare the reaction mixture (H_2O, CO, O_2, N_2, and SO_2), allow 10–15 min mixing time, and then commence irradiation of the mixture with the resonance lamp for a period of 1 to 3 min. After the desired irradiation time, the condensable products and reactants were trapped at −196° and noncondensable products and reactants pumped away. The products and reactants remaining were then allowed to warm to room temperature and subsequently the cold finger on the photolysis vessel was reduced to −130° using an *n*-pentane slush. At this temperature CO_2, which was the major product of interest in this study, has a vapor pressure of 2 Torr, SO_2 has a vapor pressure of 5 mTorr, and all of the remaining products and reactants have vapor pressures of <1 mTorr. Thus, the CO_2 produced in the reaction was measured without significant interference from other gases. The CO_2 product was then transferred to a removable collecting vessel and attached directly to the inlet of the CEC 21-620 mass spectrometer for isotopic analysis.

In all experiments reported on in this study, the source of H atoms was the photolysis of 20 Torr of H_2O. Based on the extinction coefficient[7a] of 1.5 cm^{-1} atm^{-1} at 1849 Å, it was calculated that 30% of the incident radiation at this wavelength would have been absorbed.

Results and Discussion

As was described in an earlier publication from our laboratories[4] the photochemical $^{18}O_2$ isotope labeling technique involves a measurement of the relative rates of reaction of HO_2 with a known reactant (in this case either SO_2 or NO) *vs.* HO_2 itself. In this system, therefore, the extent of each reaction is given by the rate of formation of $C^{16,18}O_2$ *vs.* $C^{16}O_2$ (see reaction schemes 6, 4, 5, 2, 4′, 7, and 8).

The results from the SO_2 experiments are shown in Table I. Not included in Table I are the results from several control experiments. These included: experiments in which H_2O was left out of the photolysis mixture and the SO_2 pressure varied from 0.2 to 0.5 Torr; experiments in which the Hg resonance lamp was left off and the mixture allowed to stand for a period of 20 min; experiments with CO left out of the photolysis mixture; and finally, experiments in which a Corning 7-54 filter was used between the Hg lamp and the reaction cell to eliminate the 1849-Å line while transmitting approximately 40% at 2537 Å. In all these control experiments less than 1 mTorr of CO_2 was detected. This is to be compared with a yield of 40 mTorr of CO_2, the smallest amount of CO_2 formed in the experiments reported in Table I.

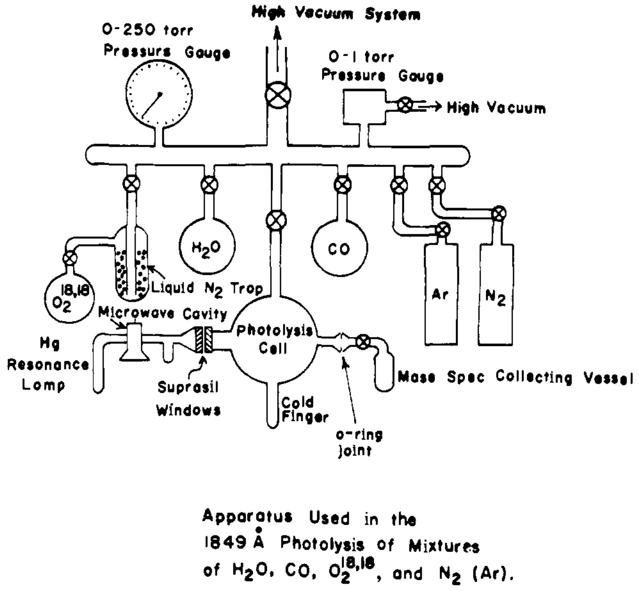

Figure 1. Photolysis apparatus used in the $^{18}O_2$ competitive isotope labeling technique involving kinetic studies on the reaction of HO_2.

Table I. Reaction of HO_2 with SO_2[a]

			Carbon dioxide yield, molecules cm^{-3} sec^{-1} $\times 10^{-12}$	
SO_2, mTorr	CO, Torr	N_2, Torr	$C^{16}O_2$	$C^{16,18}O_2$
82.5	1.0	18.0	12.1	3.7
82.5	1.0	18.0	13.1	5.3
82.5	1.0	18.0	12.8	2.2
109.0	1.0	18.0	13.1	5.8
175.0	10.0	9.0	11.5	7.0
175.0	10.0	9.0	15.7	9.9
250.0	10.0	9.0	11.8	12.8
325.0	10.0	9.0	10.2	15.4
400.0	10.0	9.0	11.8	20.2

[a] Pressure of reactants: H_2O = 20 Torr, $^{18}O_2$ = 1 Torr. Photolysis time: 1–3 min. Intensity at 1849 Å: 3.5×10^{15} photons/cm^2/sec.

The most noticeable features of the data presented in Table I are the steady increase in $R_{C^{16,18}O_2}$ with increasing amounts of SO_2 and the reasonably constant $R_{C^{16}O_2}$. Over the range of 82.5 to 400 mTorr of SO_2, the ratio of $R_{C^{16,18}O_2}/R_{C^{16}O_2}$ changes from approximately 0.3 to 1.7. This qualitative observation would indicate that HO_2 is being formed under our experimental conditions and that its reaction with SO_2 does occur at a measureable rate. The relatively constant $R_{C^{16}O_2}$ indicates that, under the conditions of the experiments in Table I, addition of increasing amounts of SO_2 did not lead to loss of OH and that all available OH radicals were quantitatively converted to CO_2. Experiments at 0.3 Torr of SO_2 (H_2O = 20 Torr, $^{18}O_2$ = 1 Torr) further showed that while $R_{C^{16}O_2}$ increased with an increase in

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(8) M. Zelikoff and L. M. Aschenbrand, *J. Chem. Phys.*, 22, 1680 (1954).

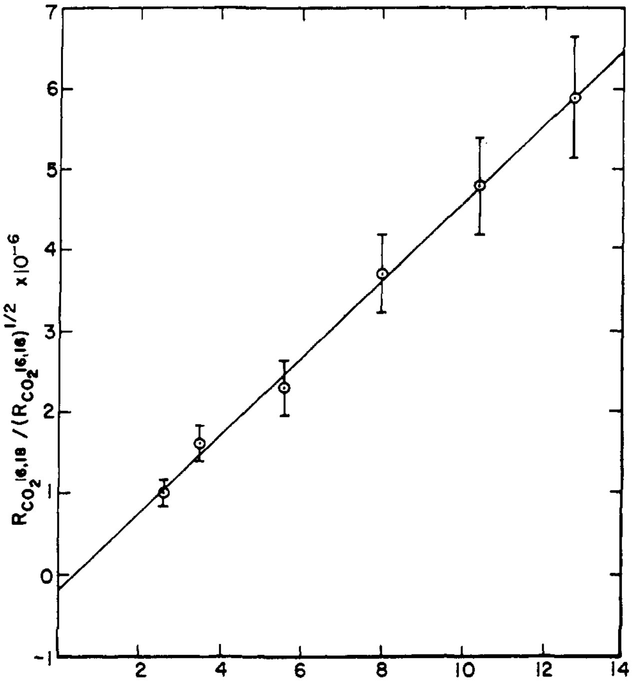

Figure 2. A plot of the ratio, $R_{C^{16,18}O_2}/(R_{C^{16}O_2})^{1/2}$, as a function of the SO_2 concentration where $R_{C^{16,18}O_2}$ and $R_{C^{16}O_2}$ are the rates of formation of the photolysis products $C^{16,18}O_2$ and $C^{16}O_2$ in units of molecules cm^{-3} sec^{-1}.

CO pressure from 1 to 10 Torr, there was no change in $R_{C^{16}O_2}$ in the presence of 19 Torr of CO. This further indicates complete scavenging of OH at the pressure of CO employed.

To treat the data presented in Table I quantitatively, a similar approach was used as reported earlier for the $HO_2 + CO$ system.[4] In this case, the following reaction scheme was employed.

$$H_2O + h\nu \xrightarrow{k_6} H + {}^{16}OH \tag{6}$$

$$^{16}OH + C^{16}O \xrightarrow{k_4} C^{18}O_2 + H \tag{4}$$

$$H + {}^{18}O_2 + M \xrightarrow{k_5} H^{18}O_2 + M \qquad (M = N_2, H_2O) \tag{5}$$

$$H^{18}O_2 + S^{16}O_2 \xrightarrow{k_2} S^{16,16,18}O_3 + {}^{18}OH \tag{2}$$

$$^{18}OH + C^{16}O \xrightarrow{k_{4'}} C^{16,18}O_2 + H \tag{4'}$$

$$H^{18}O_2 + H^{18}O_2 \xrightarrow{k_7} H_2{}^{18}O_2 + {}^{18}O_2 \tag{7}$$

$$S^{16,16,18}O_3 + H_2O \xrightarrow{k_8} H_2SO_4 \tag{8}$$

The photochemical decomposition of H_2O_2 has been neglected in the above reaction scheme since its contribution to the formation of $C^{16,18}O_2$ is very small. Also the reaction $HO_2 + CO \rightarrow CO_2 + OH$ has been omitted from the above scheme due to its extremely small rate constant $<10^{-20}$ cm^3 molecule^{-1} sec^{-1}. As discussed above, the labeled CO_2 produced in reaction 4′ is a direct measure of the extent of reaction 2. From a steady-state treatment of reactions 6, 4, 5, 2, 4′, and 7, the following relationship may be derived

$$\frac{R_{C^{16,18}O_2}}{(R_{C^{16}O_2})^{1/2}} = \frac{k_2}{(k_7)^{1/2}}[SO_2]$$

where $R_{C^{16,18}O_2}$ and $R_{C^{16}O_2}$ are the rates of formation of labeled and unlabeled CO_2 in units of molecules cm^{-3} sec^{-1}.

Table II. Variation of Light Intensity and $^{18}O_2$ Pressure[a]

$I^a \times 10^{-15}$, photons/cm^2/sec	$^{18}O_2$, Torr	Range of SO_2 pressure, mTorr	$k_2 \times 10^{16}$, cm^3 molecule^{-1} sec^{-1}
3.5	1.0	82.5–400	8.7 ± 1.8[b]
3.5	2.0	140–400	8 ± 2
14.0	1.0	250–400	12 ± 4

[a] Pressure of reactants: H_2O = 20 Torr, CO = 1 Torr, N_2 = 18 Torr. Photolysis time: 1 to 4 min. [b] See Table I and Figure 2.

From the mathematical expression above, a plot of the ratio $R(C^{16,18}O_2)/(R(C^{16}O_2))^{1/2}$ against $[SO_2]$ should yield a straight line with the slope equal to the rate constant ratio $k_2/(k_7)^{1/2}$. Figure 2 shows the results of such a plot. For those pressures where there were two or three separate experiments, the point shown represents the average value of $R(C^{16,18}O_2)/(R(C^{16}O_2))^{1/2}$. The line drawn through the points is based on a weighted least-squares treatment of the data. From the slope and using the preferred value[9] of $k_7 = 3.3 \times 10^{-12}$ cm^3 molecule^{-1} sec^{-1}, we obtain the result $k_2 = (8.7 \pm 1.3) \times 10^{-16}$ cm^3 molecule^{-1} sec^{-1}. The quoted error limit was obtained by assigning an experimentally determined uncertainty (±15%) to each value of $R(C^{16,18}O)/(R(C^{16}O_2))^{1/2} \times 10^{-6}$ in Figure 2 (based on uncertainties in measurements of the heights of the mass 46 to 44 peaks and the time of photolysis) and by drawing lines of maximum and minimum slope through the indicated error bars. Although a slight negative intercept is observed in Figure 2, within the experimental uncertainty of these measurements this intercept could also be given a small positive value. The latter case is what would be expected since a very small amount of $C^{16,18}O_2$ would have been formed *via* the photolysis of the product $H_2{}^{18}O_2$.

In addition to the experiments reported in Table I and Figure 2, a study was made of the effect of increasing the pressure of $^{18}O_2$ and the effect of increasing the light intensity. These experiments were each done at three different SO_2 pressures and the data treated quantitatively as described above to derive values for k_2. Good linear plots of $R(C^{16,18}O_2)/(R(C^{16}O_2))^{1/2}$ *vs.* $[SO_2]$ were obtained. The results of these experiments are summarized in Table II. It may be seen that within the experimental error, increasing the $^{18}O_2$ pressure from 1 to 2 Torr or increasing the light intensity from 3.5 × 10^{15} to 1.4 × 10^{16} photons cm^{-2} sec^{-1} has no effect on the value derived for the rate constant, k_2.

In addition to the reaction scheme 6, 4, 5, 2, 4′, 7, and 8, several other processes must also be considered for their possible influence on the observed ratios of $R_{C^{16,18}O_2}/R_{C^{16}O_2}$. Many of these reactions have already been discussed in an earlier publication[4] and, thus, will not be treated here in any detail, *i.e.*

$$^{18}O_2 + h\nu\ (1849\ \text{Å}) \longrightarrow 2{}^{18}O \tag{9}$$

$$^{18}O + C^{16}O + M \longrightarrow C^{16,18}O_2 + M \tag{10}$$

$$^{18}O + H^{18}O_2 \longrightarrow {}^{18}OH + {}^{18}O_2 \tag{11}$$

$$H + H^{18}O_2 \longrightarrow {}^{18}OH + {}^{18}OH \tag{12}$$

$$H + {}^{18}O_3 \longrightarrow {}^{18}OH + {}^{18}O_2 \tag{13}$$

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(9) (a) A. C. Lloyd, National Bureau of Standards Report No. 10447, 1971; (b) D. L. Baulch, D. D. Drysdale, and A. C. Lloyd, "Evaluated Kinetic Data for High Temperature Reactions," Vol. 1, Butterworths, London, 1972.

Suffice it to say that in all cases in which SO_2 was absent from the reaction mixture, processes 9–13 could account for at most 6% of the $C^{16,18}O_2$ formed, and this number is more likely to be <2%.

With SO_2 added to the system, a large number of new reactions become possible, *e.g.*

$$OH + SO_2 + M \longrightarrow HSO_3 + M \tag{14}$$

$$S^{16}O_2 + h\nu\,(1849) \longrightarrow S^{16}O + {}^{16}O \tag{15}$$

$${}^{16}O + S^{16}O_2 + M \longrightarrow S^{16}O_3 + M \tag{16}$$

$${}^{16}O + {}^{18}O_2 + M \longrightarrow {}^{16,18,18}O_3 \tag{17}$$

$$H + {}^{16,18,18}O_3 \longrightarrow {}^{18}OH + {}^{16,18}O_2 \tag{18}$$

$$H + SO_2 + M \longrightarrow HSO_2 + M \tag{19}$$

$$H + CO + M \longrightarrow HCO + M \tag{20}$$

$$SO_2 + h\nu\,(2537) \longrightarrow SO_2{}^{*1} \longrightarrow h\nu + SO_2 \tag{21}$$

$$SO_2{}^{*1} \longrightarrow SO_2{}^{*3} \tag{22}$$

$$SO_2{}^{*3} + {}^{18}O_2 \longrightarrow S^{16,16,18,18}O_4 \tag{23}$$

$$H + S^{16,16,18,18}O_4 \longrightarrow S^{16,16,18}O_3 + {}^{18}OH \tag{24}$$

$$S^{16,16,18}O_3 + C^{16}O \longrightarrow C^{16,18}O_2 + S^{16}O_2 \tag{25}$$

$$S^{16,16,18}O_3 + H \longrightarrow {}^{18}OH + S^{16}O_2 \tag{26}$$

Qualitative evidence for the possible importance of reaction 14 was the observation that, at low CO pressures (1 Torr), addition of higher pressures of SO_2 (>0.2 Torr) led to a decrease in $R_{C^{16}O_2}$. These data are summarized in Table III. From a steady-state treatment of reactions 6, 4, and 14, the following relationship may be derived

$$\frac{R^0{}_{CO_2} - R_{CO_2}}{R^0{}_{CO_2}} = \frac{k_{14}(SO_2)(M)}{k_4(CO)}$$

where $R^0{}_{CO_2}$ is the rate of formation of $C^{16}O_2$ in the absence of SO_2, and R_{CO_2} is the rate in the presence of SO_2. Thus, a plot of $(R^0 - R)/R^0$ *vs.* SO_2/CO should give a straight line with zero intercept and a slope equal to $k_{14}(M)/k_4$. The data in Table III were used to prepare such a plot. From the slope of 1.4 and a value of $k_4 = 1.3 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1},[10] we obtain the result $k_{14}(M) = 1.9 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1}. For our system, this implies $k_{14} = 1.5 \times 10^{-31}$ cm^6 molecule^{-2} sec^{-1} for $M = N_2 + H_2O$ (18 and 20 Torr, respectively). The only value for k_{14} that we are aware of in the literature is that calculated by Wheeler[11] from measurements by McAndrew and Wheeler[11] on the effect of SO_2 on recombination rates in propane-air flames. Wheeler estimates $k_{14+19} = 1.1 \times 10^{-31}$ cm^6 molecule^{-2} sec^{-1} at 2080°K. Fair and Thrush[12] have determined that $k_{19} < 1.5 \times 10^{-33}$ cm^6 molecule^{-2} sec^{-1} at 298°K and that reaction 14 is the major contributor to the value for k_{14+19} deduced by Wheeler. Thus, values for k_{14} at 2080°K obtained from flame studies and at 298° from the present work are both of the order of 10^{-31} cm^6 molecule^{-2} sec^{-1}. More recently Davis and Schiff[13] have made preliminary measurements of $OH + SO_2 + He \rightarrow HSO_2$ which gave $k_{14} = 2 \times 10^{-32}$ (± factor 2) cm^6 molecule^{-2} sec^{-1}. It is expected that H_2O would be at least 10 times more efficient as a third body than He.

Table III. Reaction of OH with $SO_2{}^a$

SO_2, mTorr	$R^{16}{}_{CO_2}$, molecule cm^{-3} sec^{-1} $\times 10^{-13}$
0	5.2
250	3.7
325	3.0
400	2.6

^{a} Pressure of reactants: H_2O = 20 Torr, CO = 1 Torr, $^{18}O_2$ = 1 Torr, N_2 = 18 Torr. Photolysis time: 1 min. Intensity at 1849 Å: 1.4×10^{16} photons cm^{-2} sec^{-1}.

Both processes 16 and 17 involve the initial formation of ^{16}O from the photodecomposition of $S^{16}O_2$ at 1849 Å, reaction 15. The rate of production of ^{16}O will be significant since the SO_2 absorption coefficient at 1849 Å is 100 cm^{-1} atm^{-1}.[7c] However, using available rate constants for reaction 16 and 17,[14,15] it is seen that the dominant reaction is 16 (*e.g.*, $k_{16}/k_{17} \cong 50$). From the above arguments is also follows that reaction 18 can be discarded as unimportant.

Because significant amounts of $S^{16,16,18}O_3$ could be formed *via* reaction 2 and 16, it is of some importance that reactions 25 and 26 be shown to be negligible compared with reaction 8. In this case, even though rate constants are not available for these three processes, arguments can be given which show reaction 8 to be the dominant reaction path. Evidence supporting this conclusion is found in the observation that aerosol was produced in the photolysis vessel for photolysis times of approximately 3 min (note: no quantitative data were taken at times longer than 3 min). This presumably would follow from reaction 8 and the subsequent condensation reaction between H_2SO_4 and H_2O molecules. A final observation, which would tend to rule out reaction 26 as significant, is the results from those experiments carried out at increased light intensity (Table II). The argument here is that since reaction 26 involves two reactants, both directly dependent on the light intensity, the rate of reaction 26 should depend on the square power of I_0. However, in experiments in which I_0 was increased by a factor of 4, no change (within the experimental uncertainty) was observed in the value of the rate constant k_2.

The sequence of reactions 21–24 represents still another mechanism which could have produced $H^{18}O$ and hence $C^{16,18}O_2$ in this study. The important intermediate in this scheme is the yet unidentified species $S^{16,16,18,18}O_4$. The SO_4 species has previously been suggested as a possible important intermediate in the photooxidation of SO_2 in the atmosphere.[16] In our system, if this reaction had been important, it would again be expected that the measured rate constant, k_2, would have shown a significant dependence on the light intensity. As indicated in the previous discussion of reaction 26, no such dependence was observed even with a fourfold change in I_0.

The final set of secondary reactions which needs to be considered in the SO_2–HO_2 system are processes 19 and 20. If important, they would have tended to make the observed rate constant too low. In this case, a com-

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(11) R. Wheeler, *J. Phys. Chem.*, **66**, 229 (1962).

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(15) R. E. Huie, J. T. Herron, and D. D. Davis, *J. Phys. Chem.*, **76**, 2653 (1972).

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parison of the rate constants for reaction 5 with those of reactions 19 or 20 (*e.g.*, $k_5 = 5.4 \times 10^{-32}$ cm^6 molecule^{-2} sec^{-1},[17] $k_{19} = 1.5 \times 10^{-33}$ cm^6 molecule^{-2} sec^{-1},[12] and $k_{20} = 0.8 \times 10^{-34}$ cm^6 molecule^{-2} sec^{-1},[18] clearly shows that even with the maximum pressures of 0.5 Torr of SO_2 and 10 Torr of CO present, the rate of reaction 5 at 1 Torr of O_2 would be some 60 times greater than that for reaction 19 or 20. In addition, the fact that the observed rate constant k_2 did not change when the pressure of $^{18}O_2$ was increased from 1 to 2 Torr (Table II) shows that reactions 19 and 20 were not important compared with reaction 5.

As indicated in the introduction, no previous measurements of the rate constant for reaction 2 have been reported in the literature. However, since a direct comparison with other values cannot be made, it is perhaps important that upper and lower limits to k_2 be discussed in terms of the reference reaction 7. An examination of the literature,[9] for example, shows that although the preferred value for k_7 is 3.3×10^{-12} cm^3 molecule^{-1} sec^{-1}, values for this rate constant range from a low of 2.9×10^{-12} to a high of 9.5×10^{-12} cm^3 molecule^{-1} sec^{-1}. If one takes this range of values to represent the upper and lower limits for the rate constant of reaction 7, then it follows that the reported rate constant for reaction 2 could have maximum and minimum values of 1.5×10^{-15} and 8.2×10^{-16} cm^3 molecule^{-1} sec^{-1}, respectively.

The results from experiments involving the reactant NO, reaction 3, were somewhat more difficult to interpret than those from the HO_2–SO_2 system. These results, therefore, should be considered as only semiquantitative in value.

In the investigation of reaction 3, initial experiments were carried out in which 50 to 100 μ of NO was added to gas mixtures consisting of 20 Torr of H_2O, 1 Torr of CO, 1 Torr of $^{18}O_2$, and 20 Torr of N_2. However, in contrast to the results from the SO_2–HO_2 system, the NO–HO_2 system was found to be very sensitive to addition of even small amounts of NO. Thus, in one experiment 50 mTorr of NO was added to the above gas mixture with the result that the rate of production of CO_2 increased by about a factor of 5 and the ratio of labeled to unlabeled CO_2 was ~3:1. Also, the absolute yield of labeled CO_2 was nearly eight times greater than the amount of added NO, indicating that not only was NO reacting very rapidly with HO_2 to form the product NO_2, but that the NO_2 was being converted back to NO. The most likely reaction to explain the latter observation would be process 27, *i.e.*

$$\begin{aligned} H + N^{16,18}O_2 &\longrightarrow N^{18}O + {}^{16}OH \qquad (27) \\ &\longrightarrow N^{16}O + {}^{18}OH \end{aligned}$$

In subsequent experiments to minimize the possible reaction of H with NO_2, the pressure of NO was reduced to 1 mTorr and the light intensity was reduced by a factor of 20 (photolysis time = 1 min). In this case the maximum amount of NO_2 that could have been present was 1 mTorr. Thus, the rate of H atom removal *via* reaction 5 would have been ~5 times faster than by reaction 27 ($k_{27} = 4.8 \times 10^{-11}$ cm^3 molecule^{-1} sec^{-1}; $k_5 = 4.3 \times 10^{-31}$ cm^6 molecule^{-1} sec^{-1} for M = H_2O).[19,20]

Since the kinetic expression for the ratio of $R_{C^{16,18}O_2}/[R_{C^{16}O_2}]^{1/2}$ with NO as the reactant would be of the same form as the equation for the reactant SO_2, it follows that when

$$\left(\frac{R_{C^{16,18}O_2}}{[R_{C^{16}O_2}]^{1/2}}\right)_{NO} = \left(\frac{R_{C^{16,18}O_2}}{[R_{C^{16}O_2}]^{1/2}}\right)_{SO_2}$$

then $k_2(SO_2) = k_3(NO)$. Under the conditions outlined above (1 mTorr of NO and photolysis time = 1 min), it was found that

$$\left(\frac{R_{C^{16,18}O_2}}{[R_{C^{16}O_2}]^{1/2}}\right)_{NO} = 5.3 \times 10^6 \text{ cm}^{-3/2} \text{ molecule}^{1/2} \text{ sec}^{-1/2}$$

and the ratio of labeled to unlabeled CO_2 was 1.4. An examination of the SO_2 data shows that at an SO_2 concentration of 11.7×10^{15} molecules cm^{-3} a similar value for $R_{C^{16,18}O_2}/[R_{C^{16}O_2}]^{1/2}$ was measured. Using the expression $k_2(SO_2) = k_3(NO)$, a value of k_3 is thus calculated of ~3×10^{-13} cm^3 molecule^{-1} sec^{-1}, the uncertainty being at least a factor of ±3.

A comparison of the rate constant reported in this work with the only other number published in the literature[6] ($k_3 \simeq 10^{-15}$ cm^3 molecule^{-1} sec^{-1}) shows a discrepancy of nearly two orders of magnitude. Other values for k_3, which are at this writing unpublished, are those reported by Niki[21] and Simonaitis and Heicklen.[22] Niki[21] has an indirect measurement which suggests a value of ~4×10^{-13} for k_3; whereas, Simonaitis and Heicklen in a photochemical study have given a value of $k_3 \geq 1.5 \times 10^{-13}$ cm^3 molecule^{-1} sec^{-1}. It would appear, therefore, that all recent measurements of k_3 are in reasonably good agreement.

Summary and Conclusions

Using the photochemical $^{18}O_2$ competitive isotope labeling technique, rate constants have been determined for reaction of HO_2 with SO_2 and NO. At 300°K the rate constants for these two processes were found to be 8.7×10^{-16} and 3×10^{-13} cm^3 molecule^{-1} sec^{-1}, respectively. The reasonably fast rate constant found for the HO_2–NO system would clearly indicate this process as being of major importance in the net conversion of NO to NO_2 in the lower atmosphere and the dominant reaction of the HO_2 species. On the other hand, the rate constant found for reaction 2 would initially indicate that this process is probably only of minor importance in the conversion of SO_2 to SO_3 in the unperturbed as well as urban atmosphere. However, until more realistic estimates can be made of the HO_2 concentration, under widely differing meteorological conditions, the actual importance of this process must remain somewhat uncertain. In the lower stratosphere the rate of reaction of SO_2 with HO_2 would

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(21) H. Niki, private communication.

(22) R. Simonaitis and J. Heicklen, report presented at the CIAP Workshop, National Bureau of Standards, Oct 1972.

now appear to be more significant than the SO_2 + $O(^3P)$ + M reaction in leading to the conversion of SO_2 to SO_3 and sulfuric acid aerosol. The point should also be made that based on these results the OH + SO_2 + M reaction would appear to be of major importance in both the troposphere and stratosphere.

Temperature Jump Relaxation Kinetics of the Chelation of Nickel(II) and Cobalt(II) with Some Aromatic Ligands[1]

Joseph C. Williams and Sergio Petrucci*

Contribution from the Polytechnic Institute of Brooklyn,
Brooklyn, New York 11201.
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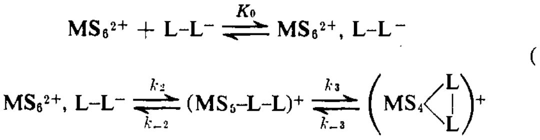
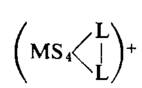
Abstract: The temperature jump relaxation kinetics of Ni^{2+} with anthranilate ion at 25° and salicylate and 5-sulfosalicylate ions at temperatures between 15 and 35° and Co^{2+} with salicylate and 5-sulfosalicylate ions at 20° have been studied and the results reported here. In all cases the forward rate constant k_f appears to be significantly smaller than that required by the "normal" Eigen chelation mechanism in terms of the product $(1/S)K_0k_{ex}$ (with $1/S$ a statistical factor, generally equal to 0.2, K_0 the Fuoss outer-sphere preequilibration constant, and k_{ex} the solvent exchange rate constant determined from nmr measurements). For nickel(II) sulfosalicylate, k_f is the same, within experimental error, as for nickel(II) salicylate. However, because of the extra charge of the sulfonate group and consequently larger K_0, one would expect a much larger rate constant k_f for this ion with respect to the salicylate ion. That this is not the case is suggested by the activation parameters $\Delta H_f^{\ddagger}$ and $\Delta S_f^{\ddagger}$ being comparable for both ligands. The preceding is reflected in measurements of complexation rates of Co^{2+} with salicylate and sulfosalicylate ions, the rate constants being within a factor of 2 of each other. A discussion of the statistical reason for this similarity in the rate constants for the salicylate and sulfosalicylate ions is given in terms of charge delocalization with respect to the point of attack at the reaction site. For nickel(II) salicylate comparison between $\Delta H_{ex}^{\ddagger}$ and $\Delta S_{ex}^{\ddagger}$ with the quantities $(\Delta H_f^{\ddagger} - \Delta H_0)$ and $(\Delta S_f^{\ddagger} - \Delta S_0)$ (with ΔH_0 and ΔS_0 the outer-sphere activation parameters) suggests that the source of the deviation from the normal chelation mechanism is entropic.

The kinetics of chelation of ionic complexation reactions has been the subject of many discussions and investigations in the past.[2] One may discuss the equilibrium between a divalent metal cation MS_6^{2+} (with S a solvent molecule) and a monovalent bidentate ligand $(L–L)^-$ in terms of the Eigen multistep mechanism



$$\begin{gathered} MS_6^{2+} + L{-}L^- \overset{K_0}{\rightleftharpoons} MS_6^{2+}, L{-}L^- \\ MS_6^{2+}, L{-}L^- \underset{k_{-2}}{\overset{k_2}{\rightleftharpoons}} (MS_5{-}L{-}L)^+ \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \left(MS_4\langle \begin{smallmatrix} L \\ | \\ L \end{smallmatrix}\right)^+ \end{gathered} \qquad (1)$$

where MS_6^{2+}, $L–L^-$ is an outer-sphere ion pair, $(MS_5–L–L)^+$ the metal ligand monodentate complex, and



$$\left(MS_4\langle \begin{smallmatrix} L \\ | \\ L \end{smallmatrix}\right)^+$$

the chelate complex. By applying the rate equations to scheme 1 and imposing a steady state condition on the intermediate, $d(MS_5–LL)^+/dt = 0$, with the additional requirement of the preequilibration of the first step, one obtains the relations[3,4] in terms of the overall rate constants k_f and k_r.

$$k_f = K_0k_2k_3/(k_3 + k_{-2}) \qquad (2)$$

$$k_r = k_{-2}k_{-3}/(k_3 + k_{-2}) \qquad (3)$$

For an interchange dissociative process (I_d), the second step in the above scheme will have a rate constant k_2 equal to k_{ex} (the one for solvent exchange) within a statistical factor[5,6] $1/S \simeq 0.2$.[5,6] K_0 may be calculated through the Fuoss relation[7]

$$K_0 = (4\pi Na^3/3000)e^be^{-b\kappa a/(1+\kappa a)} \qquad (4)$$

where the symbols $b = |z_1z_2|e^2/aDkT$ and $\gamma_{\pm}^2 = e^{-b\kappa a/(1+\kappa a)}$ are[7] the Bjerrum parameter and the activity coefficient according to Debye and Hückel. k_{ex} is the experimental pseudo-first-order constant for solvent exchange as determined by nmr ^{17}O line broadening.[8]

It is apparent that in the majority of the cases, if $(k_3/k_{-2}) \gg 1$

$$\begin{gathered} k_f = K_0k_2 = (1/S)K_0k_{ex} \\ k_r = k_{-2}(k_{-3}/k_3) \end{gathered} \qquad (5)$$

and the closing of the chelate ring is faster than the breaking of the first metal–ligand bond ("normal chelation").

Evidence of the converse condition $(k_3/k_{-2}) \ll 1$ has

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