

SO₂ OXIDATION VIA THE HYDROXYL RADICAL: ATMOSPHERIC FATE OF HSO_x RADICALS

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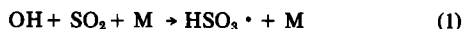
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Abstract. Reported in this study are the results from a gas kinetics — aerosol laboratory study involving the OH induced oxidation of SO₂. At tropospheric and lower stratospheric pressures, reaction (1) is neither a third order process nor is it a simple bimolecular reaction. The effective bimolecular *k* value at one atmosphere (N₂) pressure has been estimated by these authors to be $9 \times 10^{-13} \text{ cm}^3/\text{molec}/\text{s}$. Based on estimated *k* values and concentrations for several trace gases, it is suggested here that the resulting HSO₃ radical from reaction (1) under atmospheric conditions would react predominantly with O₂ in both the lower stratosphere and the troposphere. It is further suggested that the product HSO₃ radical would undergo hydration in both atmospheric regions.

Introduction

Presently, one of the major unanswered scientific questions related to atmospheric chemistry is that involving the mechanism(s) by which the trace gas (sometimes pollutant) SO₂ is converted into H₂SO₄ and/or sulfate aerosol. It is generally agreed that qualitative data now exists which would support the idea that both homogeneous as well as heterogeneous processes are of importance. However, the necessary quantitative data which would enable one to assess the relative importance of each mechanism type under different atmospheric conditions has been lacking.

Davis, et al. (1973, 1974a, 1974b, 1975a) have examined several possible homogeneous oxidation paths for SO₂ involving the reactive species O³P, O₃, NO₂, N₂O₅, and HO₂. Only in the case of the reaction HO₂ + SO₂ → OH + SO₃ did it appear that the rate of conversion of SO₂ would be of any atmospheric significance. Even for this reaction, however, it would seem that exceptionally high levels of HO₂ would be required to explain 1/e conversion times for SO₂ of 3-4 days. More recently, Davis and Klauber (1975a), Castleman and Tang (1977), Harris and Wayne (1975), Cox (1974), Atkinson, et al. (1976), and Gordon and Mulac (1975) have presented data which would indicate that the reaction of the hydroxyl radical with SO₂ could be of major importance, i.e.,



Adding significantly to the hypothesis that reaction (1) might be of major importance has been the first set of direct measurements of the atmospheric concentration of OH, Davis, et al. (1976), Davis, et al. (1979), Wang, et al. (1975), and Perner, et al. (1976).

The purpose of this paper is that of (1) presenting more detailed information on the kinetics of the OH-SO₂ reaction; and (2) presenting calculations which would suggest the possible atmospheric fate of HSO_x radicals.

Experimental

The technique employed in the study of the OH-SO₂ system was that of flash photolysis-resonance fluorescence. This technique has been described numerous times in the literature (Davis, et al., 1974c, 1975b); and thus, only those details relevant to this particular study will be presented here.

In a typical experiment, a gas mixture consisting of 50 m Torr of H₂O, 2-20 m Torr of SO₂ and either 5-20 Torr N₂, 20-500 Torr He, or 20-500 Torr Ar would be flash photolyzed with vacuum UV radiation, producing $\sim 10^{11}$ OH radicals/cc. The kinetic decay of the OH radical was then followed by monitoring OH resonance fluorescence. Since

the SO₂ concentration was in large excess relative to the OH level, the observed kinetic decays were pseudo-first order. To produce a smooth well-averaged kinetic decay curve, the results from several flashes were added together using a multi-channel analyzer operated in the multi scaling mode (counts versus time). In all cases, the number of flashes per gas filling was restricted so as to limit the % conversion of SO₂ to products to less than 1%.

In a second series of experiments, significant changes were made in both the intensity of the photoflash (350 J versus 80) and in the H₂O concentration (300-500 m Torr versus 50). The purpose of the latter experiments was that of determining the possible effects of water vapor and the OH concentration level on aerosol formation.

Results and Discussion

Kinetics Studies Involving Low OH Concentrations. The results from the pressure dependent kinetic study of reaction (1) have been summarized in the form of Table 1. For each diluent gas pressure listed, five to seven individual experiments were performed to define the effective bimolecular rate constants reported.

From an examination of Table 1, four significant conclusions can be drawn about the OH-SO₂ system: (a) It is readily apparent that the measured values for the bimolecular rate constant do depend on the total pressure, thus indicating that one of the major products from reaction (1) is the HSO₃• radical species. (b) Since the effective bimolecular rate constant does not scale linearly with an increase in the pressure of He, Ar, or N₂ (see Table 1), the reaction can not be labeled as either a simple third order or second order process but must be classified as being in the "high pressure fall off" region. At tropospheric pressures, therefore, *k* values must be measured over the entire pressure range of 20-760 Torr. Based on the reported N₂ and Ar data, however, it is likely that at one atmosphere N₂ pressure the value of *k*₁ is very close to its high pressure limit where it would have the appearance of being a simple bimolecular reaction. (c) From Table 1 it can be seen that at low pressures (i.e. ≤ 50 Torr), the relative efficiencies of the diluent gases He, Ar, and N₂ are 1, 1.5, 4.2, respectively. And (d), due to the fact that the OH-SO₂ reaction is an addition process, it is very likely that the reaction will have a negative temperature dependence. Based on related reactions, a best guess would put this number to be between 400-1500 cal/mole.

A comparison of our data with that of other investigators under comparable pressures shows moderately good agreement (within a factor of 1½). Cox (1974) and Castleman, et al. (1977) measured the rate constant relative to the reaction of OH + CO. Both groups reported *k* values for one atmosphere (N₂, O₂) pressure of $4.2 \times 10^{-13} \text{ cm}^3/\text{molec}/\text{s}$. However, since the *k* value used for the reference reaction, OH + CO, was taken to be 1.5×10^{-13} instead of the newly reported O₂ high pressure value of $\sim 3 \times 10^{-13} \text{ cm}^3/\text{molec}/\text{s}$, one should adjust the earlier numbers measured by Cox (1974) and Castleman (1977) to give one atmosphere values of $\sim 8.4 \times 10^{-13} \text{ cm}^3/\text{molec}/\text{s}$. Atkinson, et al. (1976) measured *k*₁ as a function of Ar pressure; their results for comparable Ar pressures were a factor of 1½ higher than that reported here. Based on the kinetic data presented here, in conjunction with the results from other investigators, we have estimated using 1/*k* vs. 1/*p* plot the one atmosphere (N₂) *k* value for reaction (1) to be $9 \times 10^{-13} \text{ cm}^3/\text{molec}/\text{s}$. We place the uncertainty in this estimate to be a factor of -1.5, +2.5. Obviously, new (direct) high pressure N₂ kinetic experiments are needed.

Aerosol Kinetic Studies. Of considerable interest in the OH-SO₂ experiments was the question of whether or not aerosol formation

Table 1. Effective Bimolecular Rate Constants as a Function of Diluent Gas Pressure for the Reaction $\text{OH} + \text{SO}_2 \xrightarrow{\text{M}} \text{HSO}_3^*$

Diluent Gas Pressure (Torr)	SO ₂ Conc. Range (m Torr)	H ₂ O Conc. (m Torr)	Eff. Bimol. Rate Constant $\times 10^{13}$ (cm ³ /molec/s)***
50 He	5 – 15	50	0.92 \pm .07
150 He	3 – 15	50	1.66 \pm .08
500 He	3 – 10	50	2.67 \pm .12
20 Ar	5 – 20	50	0.78 \pm .10
50 Ar	5 – 15	50	1.44 \pm .07
150 Ar	3 – 12	50	2.51 \pm .11
500 Ar	2 – 6	50	3.71 \pm .15
5 N ₂	5 – 15	50	0.75 \pm .07
10 N ₂	3 – 10	50	1.41 \pm .08
20 N ₂ **	2 – 6	50	2.16 \pm .20

* The photo flash energy in nearly all experiments was $\sim 80\text{J}$. With 50m Torr of H₂O this would result in 1.2×10^{11} OH/cc produced each flash.

** The limited pressure range employed in the case of N₂ was the result of reduced sensitivity for the detection of OH in the presence of N₂. N₂ is a much stronger quencher of OH fluorescence than He or Ar.

*** The errors quoted are those calculated from a least squares treatment of all data and represent 2σ .

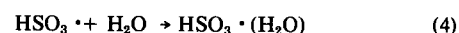
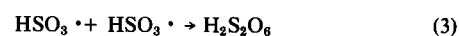
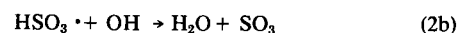
would occur. This question was of importance for two reasons: (1) In the case of the gas kinetic rate constant studies, it was essential that significant aerosol formation not occur since the increase in the background noise level resulting from increased scattering of the OH resonance lamp radiation would have rendered the experiments impractical to perform. And (2), in contrast to the above statement, it was of considerable importance to be able to show that under certain conditions the product HSO₃ radical could undergo further reaction to form light scattering aerosol species.

With regard to the first concern, no measureable increase in the background scatter light level was ever observed when flashing H₂O, SO₂, Ar, or N₂ gas mixtures under conditions like those reported in Table 1. This, of course, does not prove that aerosol species were totally absent from the flash reactor, but it would imply that either the number of aerosol species was low or that the average size (for large numbers present) was very small therefore resulting in unmeasurable scatter. A second observation which further confirmed the lack of importance of aerosol species in the gas kinetic experiments was the absence of curvature in the OH decay curves even for two and three 1/e decay times. If an OH-aerosol reaction had affected this kinetic system, the apparent OH decay rates would have been seen increasing at long observation times. As noted above, no such deviations were recorded.

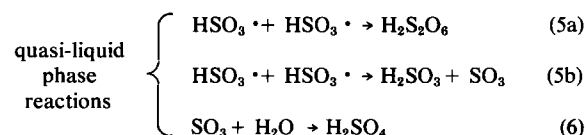
Although no evidence of aerosol formation could be detected under the conditions outlined in Table 1, increases in the flash lamp intensity and the H₂O concentration did result in significant aerosol formation. (The latter change enhanced the possibility of aerosol formation due both to the increased levels of OH and to the higher relative humidity.) The two operational configurations under which aerosol data were collected are: (1) flash intensities of 176J and H₂O concentrations of 200 mTorr; and (2) flash intensities of $\sim 350\text{J}$ and H₂O levels of 500 mTorr. The OH Levels in each configuration corresponded to $\sim 1.5 \times 10^{12}$ and $\sim 7 \times 10^{12}/\text{cm}^3$, respectively. In all cases, the amount of light absorbed by H₂O was estimated to be 8 times greater than that by SO₂. Under the first set of conditions, aerosol formation was observed only after multiple flashes (10-15) had been delivered to a given gas mixture. In these experiments there appeared to be an induction period for aerosol formation since the actual detection of aerosol would usually occur within one or two flashes. Under these conditions, one could see both the decay in the OH signal on a very short time scale and the onset of increased scattering from aerosol species at long times. The second configuration was unique in that aerosol formation was observed after just a single flash. Although the exact time for measurable aerosol to appear

varied from experiment to experiment, an average time of 300-500 ms was typical. Continued monitoring of the aerosol light scattering signal showed steady increases up to times of 10 seconds. At this point we can not be sure whether these further increases in signal were due to an increase in the aerosol number density or to a systematic growth in the average radii of existing aerosol particles or both.

The mechanism by which aerosol formation occurred under the previously described laboratory setting is probably atypical of that which might operate under normal atmospheric conditions. This would be a result of both the high concentrations of free radicals available ($5\text{--}7 \times 10^{12}$) and the absence of O₂ in the system. In the laboratory system, the four possible reaction channels for the product HSO₃ radical would be:



On the basis of estimated rate constants (see Table 2) and the calculated concentrations of OH, HSO₃ · and H₂O, as present in the laboratory quartz reactor, reaction (4) would appear to be the dominant reaction channel. Further growth of the hydrated HSO₃ radical could be expected to occur both via the addition of H₂O molecules (see later discussion) and the coagulation of stable HSO₃ · (H₂O)_x clusters. In the laboratory system, the HSO₃ radical would probably lose its radical identity in the hydrated cluster as a result of the reactions:



At this point, there is still much that is not understood about the reported laboratory aerosol experiments and far more detailed investigations will undoubtedly want to be carried out in the future. What now seems to be highly probable is that (1) HSO₃ radicals under laboratory conditions involving very low relative humidities do form light scattering aerosol species; and (2) the time required (300-500 ms) to produce light scattering species from HSO₃ would suggest that these species may have excellent nucleating properties.

Fate of HSO_x Radicals Under Atmospheric Conditions

Whereas the previous discussion was centered on the fate of HSO₃ radicals in a laboratory environment, of even greater importance is the question of the atmospheric fate of HSO₃ under natural atmospheric conditions. In contrast to the laboratory configuration, the natural system would have very high concentrations of O₂, higher as well as lower amounts of H₂O, and higher levels of the trace gases NO, NO₂, and HO₂. In an effort to provide further insight into this question, these authors have carried out order-of-magnitude calculations involving estimated concentrations and rate constants for the several possible reaction channels of HSO₃ as well as other HSO_x species (see Tables 2 & 3¹). The concentration data used in these calculations is based on both recent field measurements (Davis, 1978) as well as one and two-D modelling calculations by Crutzen and Fishman (1977), Levy (1973), Chameides (1978), and Chang, et al. (1978). The reliability of the specified concentration ranges is expected to be reasonably high. The major difficulty encountered in assessing the importance of each of the reactions listed in Tables 2 and

¹ Table 3 is available on microfiche. Order from American Geophysical Union, 1909 K Street, N.W., Washington, D.C. 20006. Document L79-001; \$1.00. Payment must accompany order.

Table 2. Atmospheric Fate of HSO₃• Species in the Tropospheric Boundary Layer*

HSO ₃ • Species	Second Reactant	Estimated Conc. Range for Species A molec/cc	Estimated Effective** Bimolecular k Value Range for Each Process-cc/molec/s	Estimated Relative Rate for Each Process (kxA)s ⁻¹
HSO ₃ •	O ₂	6 × 10 ¹⁸	1 × 10 ⁻¹³ –1 × 10 ⁻¹¹	6 × 10 ⁵ –6 × 10 ⁷
	NO ₂	2.5–16 × 10 ⁸	10 ⁻¹⁴ –10 ⁻¹¹	2.5 × 10 ⁻⁶ –1.6 × 10 ⁻³
	•HO ₂	5–30 × 10 ⁸	10 ⁻¹⁴ –1 × 10 ⁻¹¹	5 × 10 ⁻⁵ –3 × 10 ⁻²
	•OH	5–15 × 10 ⁸	1 × 10 ⁻¹³ –1 × 10 ⁻¹¹	5 × 10 ⁻⁷ –1.5 × 10 ⁻⁴
	•HSO ₃	10 ⁻¹ –10 ¹	1 × 10 ⁻¹⁴ –5 × 10 ⁻¹²	1 × 10 ⁻¹⁵ –5 × 10 ⁻¹¹
	H ₂ O	3–6 × 10 ¹⁷	1st hydration 10 ⁻¹⁴ –5 × 10 ⁻¹² †	3 × 10 ³ –3 × 10 ⁶
	CN Part.	10 ¹ –10 ³	10 ⁻⁷ –10 ⁻¹⁰	10 ⁻⁹ –10 ⁻⁴
HSO ₅ •	O ₂	6 × 10 ¹⁸	<<10 ⁻²¹	<<6 × 10 ⁻³
	NO ₂	2.5–16 × 10 ⁸	10 ⁻¹⁴ –10 ⁻¹²	2.5 × 10 ⁻⁶ –1.6 × 10 ⁻³
	NO	2.5–16 × 10 ⁸	10 ⁻¹³ –10 ⁻¹¹	2.5 × 10 ⁻⁵ –1.6 × 10 ⁻²
	•HO ₂	5–30 × 10 ⁸	10 ⁻¹³ –1 × 10 ⁻¹¹	5 × 10 ⁻⁵ –1.5 × 10 ⁻²
	•OH	5–15 × 10 ⁸	10 ⁻¹⁴ –1 × 10 ⁻¹¹	5 × 10 ⁻⁸ –1.5 × 10 ⁻⁴
	•HSO ₃	10 ⁻¹ –10 ¹	10 ⁻¹⁴ –5 × 10 ⁻¹²	1 × 10 ⁻¹⁵ –5 × 10 ⁻¹¹
	H ₂ O	3–6 × 10 ¹⁷	1st hydration 10 ⁻¹⁴ –5 × 10 ⁻¹² †	3 × 10 ³ –3 × 10 ⁶
	CN Part.	10 ¹ –10 ³	10 ⁻⁷ –10 ⁻¹⁰	10 ⁻⁹ –10 ⁻⁴

† Results have only been presented for HSO₃ and HSO₅; however, the calculations for HSO₄ gave similar results as for HSO₅. The dominant reaction path again would be hydration. Benson (1978), has also recently suggested the importance of the HSO₄ (H₂O) complex in the atmosphere.

* For those processes that are third order, the third order k values have been multiplied by the concentration M.

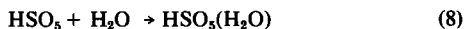
† The model reaction used for this system was SO₃ + H₂O → SO₃(H₂O); k ≈ 10⁻¹² Castleman, et al. (1975).

3 was that of estimating an appropriate range of k values for each process. In this case, the authors' approach was that of reviewing the gas kinetics literature with the purpose of identifying related model systems. The k values from these model systems were then bracketed by one or two orders of magnitude. Thus, it is unlikely, we believe, that the actual value of the rate constant lies more than one order of magnitude outside of the range quoted. In calculating the relative rate for each reaction, the range quoted represents the maximum and minimum possible given the range of values for [A] and k.

From an examination of Tables 2 & 3, it can be seen that even though a very wide range of k and [A] values have been used, the dominant reaction path for HSO₃ in the stratosphere, as well as the very moist tropical tropospheric boundary layer, is clearly defined to be that of reaction with molecular oxygen,



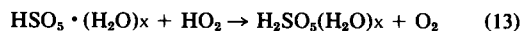
Benson (1978), from thermodynamic considerations, has also concluded that the HSO₅ species should be relatively stable under atmospheric conditions. The dominant reaction path for HSO₅ radicals both in the lower stratosphere and troposphere should be hydration, see Tables 2 & 3.



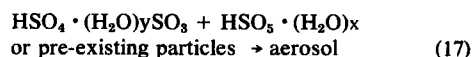
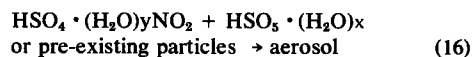
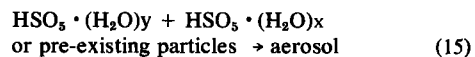
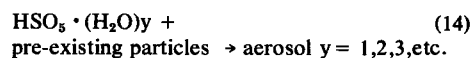
Since reactions (7) and (8) are suggested to be the dominant processes in the tropical tropospheric boundary layer as well as the dry lower stratosphere, it stands to reason that these conclusions are probably equally valid for the entire troposphere. Although no detailed information now exists on the kinetics of reaction (8), two pieces of related data seem quite relevant. (1) In the laboratory experiments reported on in this study, evidence exists suggesting that the HSO₃ radical undergoes a hydration process to form HSO₃•(H₂O)_x and subsequently aerosol; and (2) Castleman, et al. (1975) have shown that SO₃ undergoes rapid hydration (k ≈ 10⁻¹²) to form SO₃•(H₂O). We would expect HSO₃ to hydrate at least as fast as HSO₃ or SO₃, probably faster.

The fate of the hydrated HSO₅(H₂O) species can not be predicted with certainty; but in view of the HSO₃ laboratory results which showed aerosol formation, we would suggest that HSO₅(H₂O) should undergo further hydration, each step possibly occurring with some-

what lower efficiency than the first hydration step. This could continue up to the point where a critical cluster radius would be reached. During the growth process it is very likely that the hydrated HSO₅•(H₂O)_x clusters would also undergo further chemistry with a wide variety of other atmospheric trace gases. These possibilities have been summarized here in the form of the reaction scheme (9) – (13).

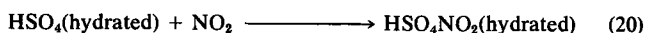
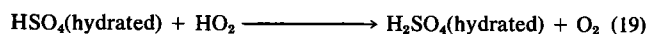


Reactions (11) – (13) should not necessarily be considered as simple gas kinetic or heterogeneous processes. We would label them as quasi-heterogeneous reactions. H₂SO₄/sulfate aerosol could be a product of both condensation and/or coagulation mechanisms, i.e.



It is likely that the above aerosol species would continue to undergo extensive chemistry. The NO₂ in HSO₄•(H₂O)_xNO₂ could convert into NO₃ (Middleton, et al., 1978). The SO₃ in HSO₄•(H₂O)_xSO₃ would undergo further reaction to form H₂SO₄. H₂SO₄, known as "Caro's acid," could hydrolyze to give H₂SO₄ and H₂O₂. H₂O₂, in turn, could result in the oxidation of newly arrived (via diffusion) SO₂ to H₂SO₄. The hydrated HSO₄• radical should also be considered to

be a highly reactive species which could undergo several possible reactions.



Understanding that many of the above processes are still speculative due to an absence of kinetic data, these authors' purpose in presenting the latter discussion is that of illustrating the interesting new complexities that are introduced into the field of gas-to-particle conversion when the concept of the hydrated free radical is considered. The reaction processes listed will undoubtedly be difficult ones to study and will most definitely require new kinetic tools. At this point, we believe that one of the important implications of the hydrated free radical chemistry being suggested is the possibility that a single OH radical may result in the oxidation of more than one SO₂ molecule. Chemical multiplication factors, resulting from processes 11-20, of two or greater may occur. A second consideration to be given to the hydrated free radical is the possibility that the nucleating properties of this species could be significantly different from that of H₂SO₄ molecules (Kiang, et al., 1974). Friend (1979), during the review of this paper has presented new data which also suggests the importance of hydrated HSO_x radicals in nucleation processes.

Conclusions

- (1) The reaction of OH with SO₂ is a pressure dependent process; however, it is not a simple third order reaction at those pressures which exist in the troposphere or lower stratosphere. Our kinetic data plus that of other investigators would suggest a one atmosphere k value for reaction (1) of $9 \times 10^{-13} \text{cm}^3/\text{molec}/\text{s}$.
- (2) There is now strong evidence which indicates that the principal product from the OH-SO₂ reaction is the HSO₃ radical. Laboratory observations also suggest that the HSO₃ species, even at very low relative humidities, lead to the production of light scattering sulfur aerosols.
- (3) Order of magnitude calculations, using estimated rate constants and model as well as field measurement values for concentration data, suggest that the HSO₃ species first reacts with O₂ to form HSO₅ (both in the troposphere and lower stratosphere). The latter species could undergo rapid hydration, forming highly reactive free radical water clusters. One must then consider the chemical reactions of these hydrated radical clusters with trace species such as NO, SO₂ or HO₂.
- (4) Aerosol species could be produced by both condensation and coagulation of the hydrated radical clusters.

Acknowledgements. The author, D. D. Davis, would like to express his appreciation to Sidney Benson and C. S. Kiang for their helpful discussions. He would also like to acknowledge the assistance provided by R. Schiff, W. Bollinger and G. Machado in carrying out some of the laboratory experiments.

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(Received September 11, 1978;
accepted November 30, 1978.)