Rates and Mechanism of Carbonyl Sulfide Oxidation by Peroxides in Concentrated Sulfuric Acid

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We measured the rates of carbonyl sulfide (OCS) oxidation by hydrogen peroxide H_2O_2 (HP) and peroxymonosulfuric acid $HOOSO_2OH$ (PSA) in 13.5–18.0 M (76–96 wt %) sulfuric acid (SA) between 290 and 306 K. The reaction is first order in both [OCS] and [peroxide], having nearly identical second-order rate constants k_1 for HP or PSA as oxidants. k_1 increases exponentially with Hammett acidity H_o in the range investigated: $\log(k_1/\text{M}^{-1}\ \text{s}^{-1}) = -(9.57 \pm 0.41) - (0.80 \pm 0.05)\ H_o$, ($H_o < 0$), at 306 K. OCS is, however, inert toward HP in concentrated perchloric acid at equivalent H_o values. We infer that OCS oxidation by HP in SA proceeds by an acid-catalyzed process involving the intermediacy of PSA rather than $H_3O_2^+$. k_1 depends on temperature according to $\log(k_1/\text{M}^{-1}\ \text{s}^{-1}) = (6.64 \pm 1.58) - (2606 \pm 472)/T$, in 18 M SA. The observed kinetic behavior and parameters are typical of sulfide oxidations by PSA in very acidic media. Present data, in conjunction with data on ambient HP and sulfate aerosol levels in the lower stratosphere, lead to reaction lifetimes that are many orders of magnitude longer than the currently estimated OCS atmospheric residence time of about 4 years.

Introduction

Carbonyl sulfide, the most abundant sulfur compound in the atmosphere, has been long considered a potential source of stratospheric sulfate aerosol.[1,2] However, OCS is relatively inert in the troposphere, where it is homogeneously distributed at a constant tropospheric mixing ratio of 470 ± 30 pptv (parts per 10^{12} by volume). The photochemical decomposition of OCS has its onset in the lower stratosphere under $300 < \lambda/\text{nm} < 388$ radiation, but peaks above the ozone layer at about 25 km, i.e., 5–10 km higher than the densest aerosol.[3] Since stratospheric aerosol plays crucial roles in both ozone depletion and in the global radiative balance,[4,5] it is important to explore for chemical pathways converting OCS into background sulfur aerosol in the lower stratosphere.

One-dimensional photochemical models based on gas-phase oxidations driven by $O(^3P)$ and OH radicals predict a stratospheric lifetime of about 10 years for OCS.[1] This is considerably longer than the global atmospheric lifetime of 4.0 years derived from current estimates of OCS global fluxes and nonvolcanic, background aerosol levels.[6] Although there are several possible causes for this discrepancy, such as an overestimation of background levels, the existence of yet unidentified atmospheric OCS sinks remains an open issue. In this paper, we consider the oxidation of OCS by H_2O_2, a normal component of the lower stratosphere, in highly acidic aerosol droplets as a possible mechanism for the conversion of OCS into sulfate. We report the results of experiments on OCS oxidation by H_2O_2 in concentrated sulfuric acid solutions relevant to atmospheric aerosol conditions. We find that H_2O_2, once activated by conversion into peroxymonosulfuric acid $HOOSO_2OH$ (PSA), is indeed able to oxidize OCS at appreciable rates.

Experimental Section

The oxidation of OCS was studied in 50 mL round-bottom Pyrex bulbs equipped with rubber septa and PTFE vacuum valves. In a typical experiment, 5 mL of sulfuric acid–water mixtures were introduced into thoroughly cleaned bulbs, and degassed in three freeze–pump–thaw cycles. The bulb reactors were then filled with a gas mixture slightly above 1 atm total pressure, with a typical mixing ratio of OCS:Ar:He = 40:60:700 Torr, and later immersed in a controlled-temperature water bath. The reaction was initiated by injection of a given amount of H_2O_2 solution of known concentration through the septum. We verified that OCS was indefinitely stable in the dark or under room fluorescent lighting in the absence of H_2O_2, in accord with previous results on OCS hydrolysis,[7,8] and with negligible photochemical effects. Gas aliquots (20 μL) were sampled at regular intervals and analyzed for OCS and CO_2 as described below. Oxidations with OXONE ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$) were carried out by equilibrating OXONE with the sulfuric acid–water mixture at the reaction temperature prior to the introduction of the gas mixture into the reactor by means of a 100 mL gas syringe.

Headspace gas analysis was performed with a Hewlett-Packard 5890 series II gas chromatograph equipped with a 60 m, 0.32 mm fused silica column coated with a 5 μm, 100% dimethyl polysiloxane film (Rtx-1 Crossbond, Restek), and a Hewlett-Packard 5972 MSD mass spectrometer detector tuned to $m/z = 44$ (CO_2^+) and 60 (OCS^+) ions. The injector, column, and detector interface were held constant at 110 °C. Gas samples (20 μL) were split in the ratio 30:1 with a 2 mL/min He carrier flow through the column. Argon was used as an internal standard.

Sulfuric acid 96% (GFS Chemicals; supplied in PTFE bottles and certified as containing <0.00001% heavy metals and <0.000002% iron levels) was used as received. The use of high-purity sulfuric acid is intended to prevent possible catalysis by trace metal contaminants. Sulfuric acid solutions in water (Milli-Q, 18 MΩ cm^{-1}) were prepared gravimetrically and their density confirmed by pycnometry. Carbonyl sulfide (Aldrich, >97.5%) was frozen at 77 K and degassed, prior to mixing it with argon

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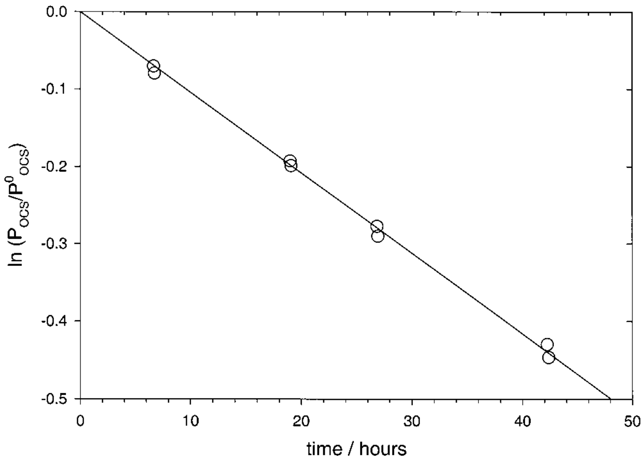

Figure 1. Pseudo-first-order decay plot for OCS oxidation, reaction 1, of 51.7 mL of a OCS + Ar + He = 40 + 60 + 700 Torr gas mixture in 5.0 mL 80 wt % SA + 0.20 mL 7.5M H_2O_2 liquid phase at 306 K. P^0_{OCS} is OCS initial partial pressure.

and helium (both Matheson, UHP grade). Hydrogen peroxide (EM Science, 30%) was used as received. Its concentration was verified by titration periodically. OXONE, $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, (Aldrich) was used as received.

Results and Discussion

OCS is found to react with excess H_2O_2 in sulfuric acid media greater than 78 wt % to produce CO_2 in stoichiometric amounts. We did not detect any gas-phase sulfur-containing products by the analytical procedure described above. However, we found traces of SO_2 in the gases evolved halfway through the course of a reaction run in the absence of He or Ar, and condensed in a coldfinger. Hence, we propose the following reaction stoichiometry:

$$OCS + 4H_2O_2 + 2H^+ \xrightarrow{H_2SO_4} CO_2 + H_2SO_4 + 4H_2O \quad (1)$$

Reaction 1 leads to the first-order decay of OCS (Figure 1), with pseudo-first-order rate constants k_1' that are proportional to $[H_2O_2]$. Second-order rate constants for reaction 1 were calculated from k_1' values by assuming that dissolved OCS(s) is in equilibrium with OCS(g), i.e., $[OCS(s)] = K_H \times P_{OCS}$, where K_H is Henry's constant for OCS dissolution in the $H_2SO_4-H_2O$ media, and P_{OCS} is the partial pressure of OCS in the reactor headspace. The overall rate of OCS(g) disappearance is given by

$$\frac{dP_{OCS}}{dt} = -k_1'P_{OCS} = -k_1\left(\frac{V_L K_H RT}{V_G + V_L K_H RT}\right)[\mathrm{OXIDANT}]P_{OCS} \quad (2)$$

where typical values of $V_L$and V_G, the volumes of the gas and liquid phases within the reactor, were 5 and 50 cm^3, respectively. Values for K_H were taken from De Bruyn et al.[9] who found that $RT\ \ln(K_H/55.5) = 4195 - 29.6T$ for OCS in water and sulfuric acid solutions up to 1 M. We made no attempt to adjust K_H for possible (and unknown) salting-out or salting-in effects in more concentrated sulfuric acid solutions. Using the expression from De Bruyn, we adopted 0.0186, 0.024, and 0.0272 M atm^{-1} as the value for K_H at 306, 298, and 290 K, respectively. k_1 can be obtained from reaction 2 once the actual identity of the oxidant is established.

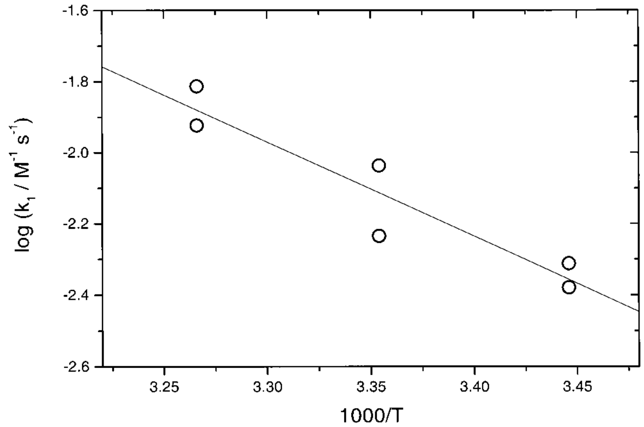

Figure 2. Arrhenius plot for k_1 in 96 wt % SA.

To probe whether sulfuric acid catalysis proceeds by protonation of either OCS or H_2O_2 (but not of both) we investigated the reaction in perchloric acid media of comparable acidity. In these cases, OCS oxidation by H_2O_2 takes place at measurable rates in 78 wt % sulfuric acid, which has a Hammett acidity $H_o = -7.03$, while there is no reaction in 70 wt % $HClO_4$ ($H_o = -7.72$) after 72 h. This experiment clearly demonstrates that the apparent acid catalysis is specific to sulfuric acid. In other words, although $H_3O_2^+$, with $pK_a = -4.7$ is certainly formed at $H_o < -5$,[10,11] we find evidence for the generation of a far more reactive intermediate in HP/SA media.

It is well-known that acids generally catalyze hydrogen peroxide oxidations via the formation of peracid intermediates.[12-14] In this case, hydrogen peroxide seems to undergo metathesis with sulfuric acid to produce peroxymonosulfuric acid:

$$H_2O_2 + HOSO_2OH \rightleftharpoons HOOSO_2OH + H_2O \quad (3)$$

We actually confirmed that PSA is the reactive intermediate by carrying out the oxidation of OCS using OXONE, a mixed potassium peroxymonobisulfate/bisulfate of known stoichiometry (see Experimental Section) in sulfuric acid. Second-order rate constants, k_1, based on the calculated [PSA] are identical within experimental error to those measured for HP as oxidant. The comparison between the rates measured for the two oxidants must take into account the kinetics and equilibrium of reaction 3. We estimate that equilibrium between HP and PSA in SA >13 M is established in less than a second[15] and, therefore, that step 3 can be treated as a rapid preequilibrium kinetic process. However, only a fraction of the initial HP concentration, $[H_2O_2]_o$, is converted into reactive PSA. In other words, it is necessary to multiply the second-order rate constants calculated from eq 2 with [OXIDANT] = $[H_2O_2]_o$ by the factor $f = [H_2O_2]_o/[PSA]$. This correction factor, evaluated from literature data on K_2 as a function of acidity,[15] amounts to $f \sim 1.2$ at [SA] = 13 M and monotonically approaches $f = 1.02$ at [SA] = 18 M.

The temperature dependence of k_1 in 18 M SA is shown in Figure 2. The Arrhenius parameters:

$$\log(k_1/M^{-1}\ s^{-1}) = (6.64 \pm 1.58) - (2606 \pm 472)/T \quad (4)$$

are very similar to those measured for the oxidations of alkyl aryl sulfides into the corresponding sulfoxides by PSA in sulfuric acid media.[16] These oxidations typically have low *A*-factors and activation energies. The value of E_2 = 11.9 kcal mol^{-1} is

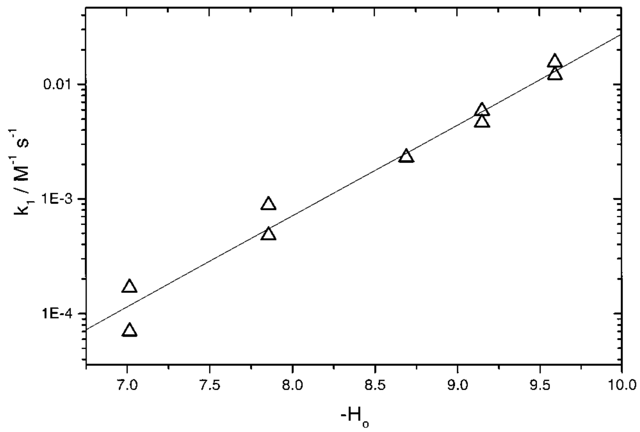

Figure 3. The second-order rate constant k_1 vs the sulfuric acid Hammett acidity function $-H_o$ at 306 K.

comparable to the activation energy determined for $MeSC_6H_4$-NO_2 oxidation by PSA in 9.9 wt % SA.[13]

We also found, in accord with previous work on PSA oxidations, that k_1 is a strongly increasing function of overall acidity. For example, plots of log k_1 vs $-H_o$ are linear, with specific slopes that are substrate dependent. For weak bases, such as OCS, the observed slopes are generally smaller than one. In fact, the dependence of k_1 on $-H_o$ at 306 K follows the expected behavior, as shown in Figure 3, which corresponds to the following parameters:

$$\log(k_1/\mathrm{M}^{-1}\ \mathrm{s}^{-1}) = -(9.57 \pm 0.41) - (0.80 \pm 0.05)\, H_o \quad (5)$$

The marked solvent effect on oxidations by HSO_5^- is consistent with the development of positive charge on both sulfur and the transferred oxygen atoms.[17,18] We did not attempt to separate protonation from solvent effects. Equation 5 provides an empirical indication of the expected dependence of k_1 on sulfuric acid concentrations at all temperatures.

To assess the potential role of reaction 1 in the atmospheric oxidation of OCS we proceeded to estimate an upper limit to its lifetime under typical conditions. In the stratosphere at noon, 40° N, 20 km altitude, $[H_2O_2] \sim 10^9$ molecules cm^{-3}, $T \sim 225$ K. Local aerosol typically consists of 0.1 μm diameter droplets with an average density of 10 cm^{-3},[19] which amounts to a reactive ratio of $V_{\mathrm{aerosol}}/V_{\mathrm{air}} \sim 5 \times 10^{-16}$. The latter is consistent with independent reports of about 10^7 SA molecules cm^{-3}. Assuming a Henry's law constant for H_2O_2 in concentrated SA: $K_H \sim 3 \times 10^{10}$ M/atm,[9,20,21] we obtain $[H_2O_2] \sim 1$ M within the aerosol droplets. If we further assume that all of the HP is quantitatively converted into PSA, i.e., that [PSA] $\sim$ 1M, and that [SA] $\sim$ 18 M at the aerosol interface,[22] we can calculate the OCS reaction lifetime as

$$\tau^{-1} = k_1[\mathrm{PSA}]V_{\mathrm{aerosol}}/V_{\mathrm{air}} \quad (6)$$

With $k_1 = 1 \times 10^{-5}$ M^{-1} s^{-1} in SA 18 M at 225 K (from eq 4), we get $\tau \sim 6 \times 10^{12}$ years! Therefore, reaction 1 is utterly irrelevant regarding the atmospheric fate of OCS.

Given the slowness of reaction 1, there appears to be no viable oxidation pathway for OCS by known stratospheric oxidants that are fast enough to meet the kinetic constraints imposed by current considerations on "missing sinks". In retrospect, we observe that when the "missing sink" hypothesis was first put forward, estimated global OCS production flows exceeded destruction rates by about a factor of 2. Since then, however, new findings lead to a budget that is nearly balanced within the limits of uncertainty.[23] Further, Hamill et al. recently concluded that the life cycle of the sulfate aerosol particles is well understood. Aerosol droplets are largely formed during the ascent of air masses across the tropical tropopause, suggesting that the stratospheric H_2SO_4 has a tropospheric origin.[5] Assessing the OCS budget and its contribution to stratospheric sulfate involves assumptions about the level of the background aerosol. In this regard, it should be emphasized that the last five years were the longest volcanically quiescent period for which measurements of stratospheric sulfate aerosol are available. A new, lower limit to the background aerosol levels would be consistent with slower OCS oxidation rates.[24] Further investigation and more accurate budgets and lifetimes of the Junge aerosol layer will ultimately settle the question of whether a "substantial, yet unidentified, systematic error" remains in the chemical kinetic database for OCS.

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