Sulfite Stabilization and Reduction of the Aqueous Mercuric Ion: Kinetic Determination of Sequential Formation Constants

Lisa L. Van Loon, Elizabeth A. Mader, and Susannah L. Scott*

Department of Chemistry, University of Ottawa, Ottawa, Ontario, Canada K1N 6N5

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The aqueous sulfite ion reacts with $Hg^{2+}_{(aq)}$ to form 1:1 and 2:1 coordination complexes. The $Hg(SO_3)_2^{2-}$ complex is redox stable. However, dissociation of a sulfite ligand forms redox-unstable $HgSO_3$. Under conditions where $Hg(SO_3)_2^{2-}$ predominates, the rate of reduction of the mercuric ion to Hg^0 by coordinated sulfite depends inversely on the concentration of uncoordinated sulfite, while it is unaffected by the amount of sulfite liberated by dissociation. Analysis of the kinetics yields the sequential sulfite binding constants $K_1 = 2.1 \times 10^{13}$ and $K_2 = 1.0 \times 10^{10}$ at $\mu = 0.10$ M. These values lead to the prediction that $HgSO_3$ is more abundant in clouds than is $Hg(SO_3)_2^{2-}$ under virtually all atmospheric conditions. The product of the redox reaction appears to be a strongly bound $Hg^0 \cdot SO_2$ complex, which is at least 3 orders of magnitude more soluble than uncomplexed $Hg^0_{(aq)}$. This finding may have important implications for the partitioning of atmospheric mercury from the gas phase into atmospheric water droplets prior to its wet deposition.

Introduction

Knowledge of the atmospheric speciation of mercury is crucial to the construction of accurate models for its global cycling, because the stability and solubility of various forms strongly influence the rate of mercury removal from the atmosphere by wet deposition. Most (ca. 98%) of atmospheric mercury exists in the gas phase in the elemental form.[1] However, the concentration of mercury found in cloud droplets, and therefore susceptible to being rained out, may exceed the solubility of $Hg^0_{(aq)}$ by as much as 3 orders of magnitude.[2,3] This finding is the basis for the proposal that, unlike in the gas phase, the mercury in atmospheric water exists mostly as the more soluble mercuric ion.[4] The high affinity of Hg(II) for sulfur-donor ligands further suggests that mercuric-sulfite complexes are important species in clouds, even in relatively nonpolluted air.[5] The atmospheric chemistry of mercury is complicated by the ability of sulfite to reduce the mercuric ion to elemental mercury, which, due to its lower water solubility, is thought to partition back into the gas phase where it is subject to long-range transport.[3]

Recently, we reported conditions under which the unstable coordination complex $HgSO_3$ can be observed directly and measured the rate of its intramolecular reaction to give $Hg^0_{(aq)}$.[6] However, $HgSO_3$ is not generally assumed to be the dominant mercuric species when the ambient S(IV) concentration greatly exceeds $[Hg]_{total}$, as is the case even in clean air. Under natural conditions, it has been suggested that $Hg(SO_3)_2^{2-}$ is a major mercury species present in atmospheric water droplets.[7]

$$Hg^{2+}{}_{(aq)} + SO_3{}^{2-}{}_{(aq)} \leftrightarrows HgSO_{3(aq)} \qquad K_1 \qquad (1)$$

$$HgSO_{3(aq)} + SO_3{}^{2-}{}_{(aq)} \leftrightarrows Hg(SO_3)_2{}^{2-}{}_{(aq)} \qquad K_2 \qquad (2)$$

Unfortunately, the sequential formation constants for mercuric-sulfite complexes, eqs 1 and 2, are not measurable by conventional methods because of the short lifetime of $HgSO_{3(aq)}$.[8] The overall formation constant, eq 3, is known because $Hg(SO_3)_2^{2-}$ is considerably more stable than $HgSO_3$, particularly in neutral or alkaline solutions.

$$Hg^{2+}{}_{(aq)} + 2SO_3{}^{2-}{}_{(aq)} \leftrightarrows Hg(SO_3)_2{}^{2-}{}_{(aq)} \qquad \beta_2 \qquad (3)$$

Because reduction of the mercuric ion appears to proceed uniquely via the $HgSO_3$ complex, the magnitudes of the sequential formation constants are important parameters for models of the global mercury cycle.

In this contribution, we report a kinetic study of the reduction of the mercuric ion in aqueous solution in the presence of excess S(IV). In combination with results from our previous study of this system,[6] we have extracted the formation constants for mercuric-sulfite complexes from kinetic measurements. We also present evidence that the product of the redox reaction may not be, as previously supposed, $Hg^0_{(aq)}$, but a soluble complex of Hg^0 with SO_2.

Experimental Section

All solutions were prepared with distilled deionized (Milli-q Plus) water in glass bottles and handled with all-glass syringes. Solutions of mercuric ion were prepared by dissolving red HgO (99.999%, Aldrich) in concentrated $HClO_4$ (Analar, 70%) followed by dilution with water to produce stock solutions containing approximately 0.06 M Hg^{2+} in 0.2 M $HClO_4$. These solutions were standardized by titration with KSCN (Baker ACS Reagent) to the ferric alum endpoint.[9] Stock solutions were diluted daily to the desired concentration for use in titration and kinetics experiments.

Sulfite solutions were prepared by dissolving Na_2SO_3 (99.99% Aldrich Reagent Plus, anhydrous) in either Ar- or air-saturated water. Because aqueous sulfite is susceptible to trace-metal-catalyzed autoxidation, the stock solution was prepared daily and standardized immediately before use by iodometric titration. Sodium dithionate was prepared according to the literature procedure.[10]

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* To whom correspondence should be addressed. E-mail: sscott@science.uottawa.ca. Fax: 613-562-5170.

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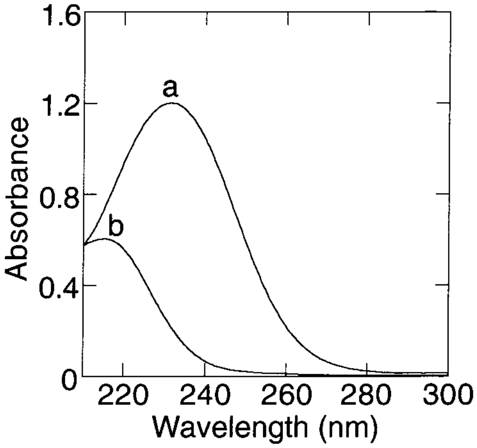

Figure 1. UV spectrum of 40 μM $Hg(SO_3)_2^{2-}$ in the presence of 0.10 mM free HSO_3^-/SO_3^{2-} at (a) pH 3; and (b) pH 12, in a 1 cm path length cell. In each case, the UV spectrum of free HSO_3^-/SO_3^{2-} has been subtracted.

Perchloric acid solutions were prepared by diluting the concentrated acid to the desired concentration. Argon-saturated solutions for air-free experiments were prepared by bubbling Cr-scrubbed Ar via Teflon microtubing and white rubber septa (Aldrich) through the solutions for at least 15 min. UV spectra were recorded on a Cary 1E UV−visible spectrophotometer at 1 nm resolution and a scan speed of 300 nm/min.

Procedure for Kinetics Experiments. Solutions were mixed in 1 cm square quartz cuvettes using syringe-septa techniques and deaerated by bubbling with Ar. Prior to addition of the last reagent, the samples were thermally equilibrated (15 min) in the thermostated cell block of the spectrophotometer. Reactions were initiated by addition of sulfite, and absorbance changes over time were recorded. Rate constants were obtained from nonlinear least-squares fits to the first-order integrated rate equation

$$A_t = A_0 + (A_\infty - A_0)(1 - e^{-kt}) \qquad (4)$$

If left standing for several hours in air, the sulfite solutions undergo autoxidation,[11] which renders their rate of reduction of the mercuric ion irreproducible. Therefore, most kinetics experiments were performed in the absence of dissolved oxygen by bubbling the solutions with argon prior to mixing.

Procedure for Spectrophotometric Titration. A mercuric ion solution was deaerated with Ar in a three-necked flask, then cooled to approximately 5 °C. Sulfite was added, followed by enough $NaOH_{(s)}$ to raise the pH to 13. Following addition of each aliquot of $HClO_4$, the pH was measured using a Corning 430 pH meter and a 3 mL sample was removed by syringe in order to record its UV spectrum.

Results

UV Spectrum of $Hg(SO_3)_2^{2-}$. The complex formed by binding two sulfite anions to the aqueous mercuric cation, $Hg(SO_3)_2^{2-}{}_{(aq)}$, has been reported in neutral and acidic mercuric ion solutions containing excess uncoordinated SO_3^{2-}/HSO_3^-. The UV−visible spectrum in acidic solution (pH 3, $HClO_4$) is reported to consist of a peak at 230 nm with $\epsilon = 27\,000$ M^{-1} cm^{-1}.[7] We recorded the UV spectrum of the complex formed following addition of 0.180 mM sulfite to an air-saturated solution of 40 μM Hg^{2+} in 1.0 mM $HClO_4$. The spectrum of complex **I** consists of a peak at $\lambda_{max} = 230$ nm, Figure 1a. Its intensity varies linearly with the concentration of mercuric ion, with $\epsilon(230\ nm) = (2.98 \pm 0.01) \times 10^4$ M^{-1} cm^{-1} after subtraction of the spectral contribution of free HSO_3^-, Figure 2a. Upon adjusting the pH of the solution to 12 with NaOH, and after spectral subtraction of the contribution due to the free SO_3^{2-}, a peak was observed with $\lambda_{max} = 215$ nm, Figure 1b. Its intensity also varies linearly with the concentration of mercuric ion, Figure 2b, yielding $\epsilon(215\ nm) = (1.68 \pm 0.02) \times 10^4$ M^{-1} cm^{-1} for complex **II**.

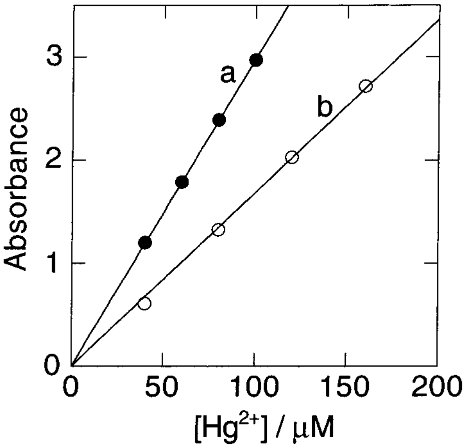

Figure 2. Determination of the extinction coefficient of $Hg(SO_3)_2^{2-}$ at (a) pH 3, $\lambda_{max} = 230$ nm; and (b) pH 12, $\lambda_{max} = 215$ nm.

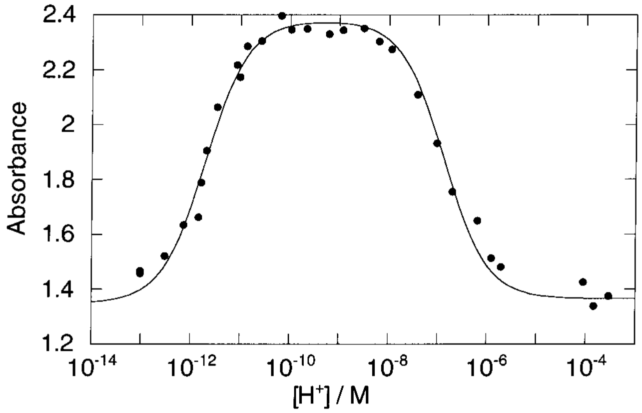

Figure 3. Spectrophotometric titration of 40 μM $Hg(SO_3)_2^{2-}$ in the presence of 1.50 mM free HSO_3^-/SO_3^{2-}, from pH 13 to pH 4, with $HClO_4$. The solid line is the three-parameter nonlinear least-squares fit to eq 5.

Spectrophotometric Titration. The pH-dependence of the UV spectrum was further investigated by titration. The pH of a solution containing 40 μM $Hg(SO_3)_2^{2-}$ and 1.5 mM free SO_3^{2-} initially at pH 13 was gradually lowered to pH 3 by addition of aliquots of $HClO_4$. The absorbance at 230 nm after each addition is shown as a function of pH in Figure 3. Two K_a values are required to account for the behavior of the UV spectrum over this pH range. The extinction coefficients of complexes **I** and **II** were fixed at their measured values, $\epsilon_I = 2.98 \times 10^4$ and $\epsilon_{II} = 7.3 \times 10^3$ M^{-1} cm^{-1}, at 230 nm. The curve in Figure 3 was accurately reproduced with a three-parameter fit to eq 5:

$$\mathrm{Abs} = [Hg^{2+}]_{total}\,(\epsilon_I\,[H^+] + \epsilon_{II}\,K'')/([H^+] + K'') + [S(IV)]_{free}\,(\epsilon'\,K')/([H^+] + K') \qquad (5)$$

in which the first term represents the pH-dependent contribution of mercury-sulfite complexes to the total absorbance and the second term the pH-dependent contribution of HSO_3^-/SO_3^{2-}. The parameters of the nonlinear curve fit are $K' = (1.3 \pm 0.2)$

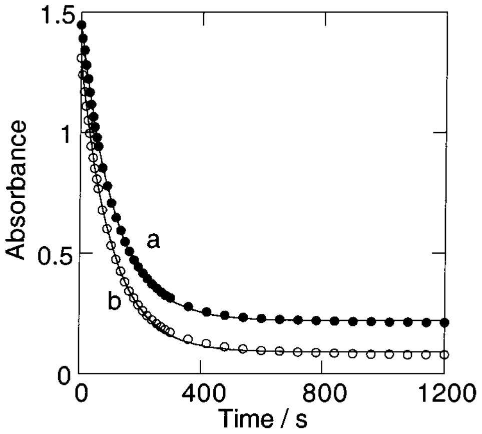

Figure 4. Kinetic profiles for the decomposition of 40 μM $Hg(SO_3)_2^{2-}$ at pH 3 and 45 °C, in the presence of 0.15 mM free HSO_3^-, in (a) air-saturated; and (b) air-free solutions. One curve is slightly offset to better display the data. Solid lines are nonlinear least-squares fits to the integrated first-order rate equation.

$\times 10^{-7}$, $K'' = (2.0 \pm 0.2) \times 10^{-12}$, and $\epsilon' = (676 \pm 11)$ M^{-1} cm^{-1}. K' agrees with the known acid dissociation constant for HSO_3^-, $K_{a2} = 1.6 \times 10^{-7}$ at $\mu = 0.1$ M,[12] while ϵ' is reasonably close to our independently measured value for SO_3^{2-} at 230 nm, 525 ± 19 M^{-1} cm^{-1} (the value of ϵ for HSO_3^- at this wavelength is negligible). We therefore assign K'' to the equilibrium between complexes **I** and **II**. The protonated form, complex **I**, is the predominant mercury species in acidic solution, and thus in all the kinetic work that follows. On the basis of the results described below, we believe complex **I** corresponds to $Hg(SO_3)_2^{2-}$. Its deprotonation in alkaline solution must therefore involve a coordinated water molecule, eq 6:

$$\underset{\textbf{I}}{Hg(SO_3)_2(H_2O)_n^{2-}} \rightleftarrows \underset{\textbf{II}}{Hg(SO_3)_2(H_2O)_{n-1}(OH)^{3-}} + H^+ \qquad K'' = 2.0 \times 10^{-12} \qquad (6)$$

Rate Law for Reduction of the Mercuric Ion. The complex $Hg(SO_3)_2^{2-}$ is not stable indefinitely, although it decomposes more slowly than does $HgSO_3$.[6] Addition of 40 μM Hg^{2+} to a freshly prepared air-saturated solution containing 150 μM HSO_3^- in 1.0 mM $HClO_4$ at 45 °C causes a first-order decay of intensity at 230 nm, Figure 4a. An identical curve was obtained when the experiment was repeated with argon-saturated solutions, Figure 4b. The rate is thus independent of the presence of dissolved oxygen. It is also independent of the concentration of $Hg(SO_3)_2^{2-}$: experiments in the presence of 81 μM uncoordinated HSO_3^- gave the same pseudo-first-order rate constants for the decay of both 40 μM and 80 μM $Hg(SO_3)_2^{2-}$.

The pseudo-first-order rate constants vary linearly with the concentration of $[H^+]$ at constant $[HSO_3^-] = 0.20$ mM, and inversely with the concentration of uncoordinated HSO_3^- at constant pH = 3.0 and $\mu = 0.10$ M ($NaClO_4$). Taken together, these observations imply that the reaction is inhibited by free SO_3^{2-}. Its concentration was calculated from the acid dissociation constants for $SO_{2(aq)}$ and HSO_3^-, $K_{a1} = 0.024$ and $K_{a2} = 1.6 \times 10^{-7}$.[12] Most rate constants were measured at 45 °C, Table 1, a temperature at which the decomposition of $Hg(SO_3)_2^{2-}$ is conveniently fast. The plot of k_{obs}^{-1} vs free $[SO_3^{2-}]$, Figure 5, contains both variable $[H^+]$ and variable $[HSO_3^-]$ data. The pseudo-first-order rate constant k_{obs} is therefore described by

$$k_{obs}^{-1} = a + b\,[SO_3^{2-}] \qquad (7)$$

TABLE 1: Pseudo-First-Order Rate Constants for the Redox Decomposition of $Hg(SO_3)_2^{2-}{}_{(aq)}$ at $\mu = 0.10$ M ($NaClO_4$)

T/°C	[S(IV)]/mM[a]	$[H^+]$/mM[b]	$10^4\ k_{obs}$/s^{-1}[c]
25.2	0.077	1.0	1.233 ± 0.007
	0.140	1.0	0.7134 ± 0.003
	0.200	1.0	0.400 ± 0.001
35.5	0.10	1.0	8.0 ± 0.7
	0.20	1.0	4.2 ± 0.3
	0.32	1.0	1.8 ± 0.3
	0.50	1.0	1.25 ± 0.3
45.2	0.020	1.0	77 ± 1
	0.079	1.0	45 ± 1
	0.14	1.0	28.7 ± 0.6
	0.20	1.0	22.6 ± 0.6
	0.30	1.0	15.2 ± 0.9
	0.20	2.0	25.3 ± 0.6
	0.20	5.0	42.5 ± 0.3
	0.20	7.0	102.0 ± 0.3
	0.20	10.0	136.9 ± 0.3
55.0	0.098	1.0	122 ± 3
	0.21	1.0	90.1 ± 0.7
	0.43	1.0	56 ± 1

[a] Sum of contributions of $SO_{2(aq)}$ and HSO_3^-, not coordinated to mercury. [b] In excess of the amount required to protonate the sulfite not coordinated to mercury. [c] Errors are from nonlinear least-squares fit to the integrated first-order rate equation.

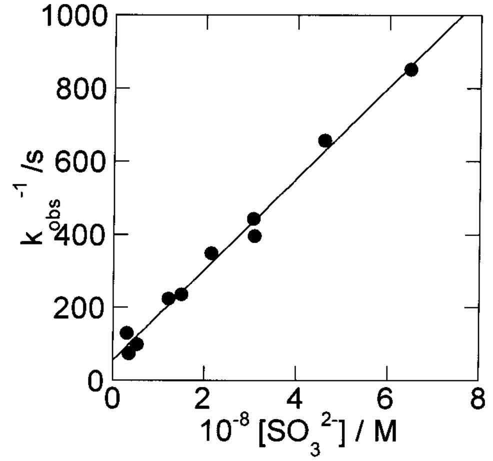

Figure 5. Dependence of the inverse of the pseudo-first-order rate constants for decomposition of 40 μM $Hg(SO_3)_2^{2-}$ on the concentration of uncoordinated SO_3^{2-}, at 45 °C and $\mu = 0.10$ M ($NaClO_4$).

TABLE 2: Temperature Dependence of Kinetic Parameters for the Reduction of Mercuric Ion in the Presence of Excess Aqueous Sulfite

T/°C	k_d^{-1}/s	$10^{11}\ K_2/k_r$	k_r/s^{-1} [6]
25.2	–[a]	9 ± 2	0.0106
35.5	–[a]	1.2 ± 0.1	0.040
45.2	55 ± 14	0.125 ± 0.005	0.134
55.0	51 ± 3	0.0194 ± 0.0008	0.462

[a] Insignificantly different from zero, based on the data obtained in Table 1.

with a = (55 ± 14) s and b = $(1.25 \pm 0.05) \times 10^{10}$ s M^{-1} at 45 °C and $\mu = 0.10$ M ($NaClO_4$).

Temperature Dependence. Similar kinetic behavior was observed at temperatures between 26 and 55 °C, Table 2. However, at temperatures below 45 °C, the value of a is insignificantly different from zero. The Eyring plot constructed for the kinetic parameter $b^{-1} = k_r/K_2$, Figure 6, is linear with slope $-(2.00 \pm 0.05) \times 10^4$ K^{-1} and intercept (34 ± 1). From these values, we obtain the apparent activation parameters $\Delta H_{obs}^{\ddagger} = (166 \pm 4)$ kJ/mol and $\Delta S_{obs}^{\ddagger} = (85 \pm 11)$ J/K·mol.

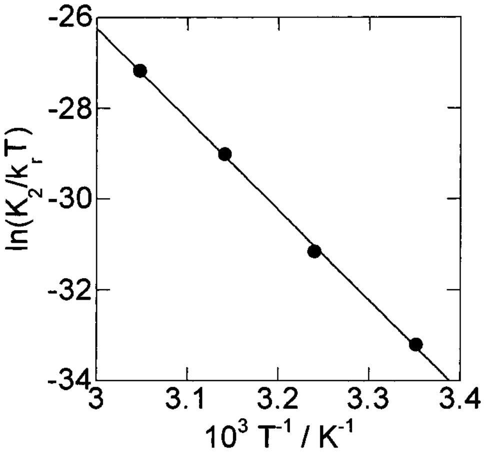

Figure 6. Eyring plot for the redox decomposition of $Hg(SO_3)_2^{2-}$.

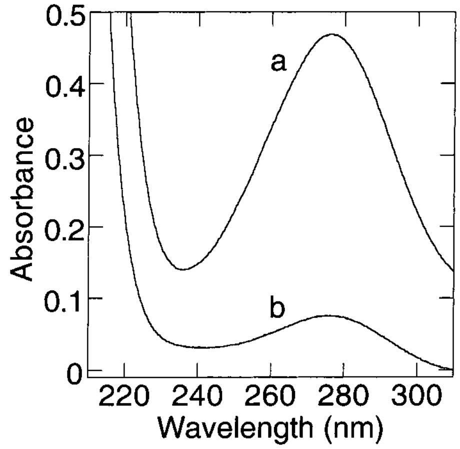

Figure 7. (a) UV spectrum recorded after the decomposition of 1.0 mM $Hg(SO_3)_2^{2-}$ at pH 3 and 45 °C, in the presence of 20 μM free HSO_3^-; (b) spectrum of 1.0 mM HSO_3^- at pH 3. Both spectra were recorded in a 5 cm path length cell.

Products. Because non-UV-absorbing products, in particular $S_2O_6^{2-}$, are often generated in sulfite oxidations by metal ions,[14] we determined the quantity of unreacted S(IV) after completion of its reaction with Hg(II). Iodometric titration of a solution originally containing 14.5 μmol $Hg(SO_3)_2^{2-}$ and 28.7 μmol uncoordinated HSO_3^-, following decomposition of $Hg(SO_3)_2^{2-}$, resulted in an endpoint at 43.2 μmol HSO_3^-. Thus the spent solution contains all of the S(IV) present initially as free $HSO_3^-{}_{(aq)}$ as well as one equiv of S(IV) released from $Hg(SO_3)_2^{2-}$ as it decomposes to Hg^0.[15]

The final spectrum of the solution after reduction of the mercuric ion by excess sulfite consists of a broad peak centered at 276 nm, Figure 7a. Its apparent ϵ, based on $[Hg]_{total}$, is 94 M^{-1} cm^{-1}. The UV spectrum of $SO_{2(aq)}$ also consists of a peak at 276 nm, but with $\epsilon = 430$ M^{-1} cm^{-1}.[13] However, $SO_{2(aq)}$ constitutes only a small fraction of the total S(IV) content of the solution at pH 3 and contributes little to the spectrum, Figure 7b. The nature of the species responsible for the peak in the product spectrum is discussed below.

Discussion

The reduction of mercuric ion by excess aqueous sulfite in mildly acidic solutions was the subject of a previous report.[7] The values of the kinetic parameters *a* and *b* were measured at 25 °C, and the unknown value of K_2 was estimated in order to extract individual rate constants. We find, in agreement with that study, that the rate of the reaction is inversely dependent on the concentration of uncoordinated S(IV), which exists mostly in the form HSO_3^- under the reaction conditions. Our measured value for *b* at 25 °C, $(9 \pm 2) \times 10^{11}$ s M^{-1}, compares to $b = 4.3 \times 10^{11}$ s M^{-1} reported previously.[7]

From the inverse $[H^+]$ dependence of k_{obs}, the form of S(IV) which retards the reduction of the mercuric ion in acidic solution is SO_3^{2-} rather than HSO_3^-, although the concentration of the latter exceeds that of SO_3^{2-} by a factor of 10^4 at pH 3. We attribute the apparent lack of affinity of the mercuric ion for monoprotonated HSO_3^- to the structure of its major tautomer, in which the proton resides on S rather than on O.[16] Most HSO_3^- is thus not inclined to react with the mercuric ion, which is known to coordinate to sulfite through the lone pair on S.[17]

Although the spectrum of the complex formed between the mercuric ion and excess sulfite in acidic solution is pH-dependent, the complex is most likely $Hg(SO_3)_2(H_2O)_n^{2-}$, rather than $Hg(SO_3)(SO_3H)^-$. The pK_a for SO_3H^- (protonated at O) has been estimated as 5.4.[16] Coordination of a proton-containing ligand to a metal complex generally lowers the pK_a, so that $Hg(SO_3)(SO_3H)^-$ is probably not formed in appreciable quantities even at the lowest pH (2) attained in this study. The pK_a of 11.7 found in the spectrophotometric titration of $Hg(SO_3)_2^{2-}$ must therefore be attributed to another proton-containing ligand, most likely a coordinated water molecule such as that shown in eq 6. Furthermore, the ligand dissociation required by the observed kinetic behavior of complex **I** is of SO_3^{2-}, rather than HSO_3^-, which is inconsistent with the expected aquation behavior of $Hg(SO_3)(SO_3H)^-$.

A mechanism that agrees with the experimental rate law for reduction of Hg(II) in the presence of excess hydrogen sulfite involves dissociation of sulfite from $Hg(SO_3)_2^{2-}$, followed by decomposition of $HgSO_3$, eqs 8 and 9:

$$Hg(SO_3)_2{}^{2-}{}_{(aq)} \rightleftarrows HgSO_{3(aq)} + SO_3{}^{2-}{}_{(aq)} \qquad k_d, k_b \quad (8)$$

$$HgSO_{3(aq)} + nH_2O \rightarrow Hg^0{}_{(aq)} + HSO_4{}^-{}_{(aq)} + H^+ \qquad k_r \quad (9)$$

where k_d and k_b are rate constants for the dissociation of sulfite from $Hg(SO_3)_2^{2-}$ and the binding of sulfite to $HgSO_{3(aq)}$, respectively, and k_r is the rate constant for the water-assisted reduction of the mercuric ion by its coordinated sulfite ligand. Application of the steady-state approximation for the intermediate $HgSO_3$ yields the rate law

$$-d[Hg(SO_3)_2{}^{2-}]/dt = k_dk_r\,[Hg(SO_3)_2{}^{2-}]/(k_b\,[SO_3{}^{2-}]_{free} + k_r) \quad (10)$$

which reproduces the experimental rate law (including pseudo-first-order behavior) with $a = k_d^{-1}$ and $b = k_b/k_dk_r$, provided the formation of sulfite according to eq 8 does not cause the value of $[SO_3^{2-}]_{free}$ to change significantly. Because k_r (45 °C) $= 0.134$ s^{-1} is known from our previous work,[6] we calculate $K_2 = k_b/k_d = (1.68 \pm 0.07) \times 10^9$. Furthermore, $k_d = a^{-1} = 0.018 \pm 0.005$ s^{-1}, which allows us to evaluate $k_b = (3.0 \pm 0.8) \times 10^7$ M^{-1} s^{-1}.

Even kinetic experiments conducted under conditions where the sulfite released from $Hg(SO_3)_2^{2-}$ far exceeded the initial value of $[HSO_3^-]_{free}$ showed no appreciable deviation from pseudo-first-order behavior. This feature of the kinetics was not addressed in a previous study.[7] Ligand dissociation from $Hg(SO_3)_2^{2-}$ in the first step of the mechanism (eq 8, 9) ought to slow the decomposition reaction in most of our experiments,

TABLE 3: Summary of Thermodynamic Parameters for the Aqueous Mercuric Ion−Sulfite System

reaction	K	$\Delta G°$ kJ/mol	$\Delta H°$ kJ/mol	$\Delta S°$ J/K·mol
$Hg^{2+} + SO_3^{2-} \rightleftarrows HgSO_3$	$2.1 \times 10^{13\,a}$	−77	−30	158
$HgSO_3 + SO_3^{2-} \rightleftarrows Hg(SO_3)_2^{2-}$	$1.0 \times 10^{10\,b}$	−56	−61	−17
$Hg^{2+} + 2\,SO_3^{2-} \rightleftarrows Hg(SO_3)_2^{2-}$	$2.1 \times 10^{23\,c}$	−133	−91	141

[a] Data in this row derived using values from ref 8. [b] Data in this row calculated from kinetic measurements in this work. [c] Data in this row previously reported at 298 K, $\mu = 0.5$ M.[8]

because this sulfite should increase the concentration of uncoordinated S(IV) as the reaction proceeds. However, no deviations from pseudo-first-order behavior were observed. For example, decomposition of 0.93 mM $Hg(SO_3)_2^{2-}$ in a solution containing 0.11 mM uncoordinated HSO_3^- in 1.0 mM $HClO_4$ at 45 °C generated a pseudo-first-order decay of absorbance at 230 nm, with $k_{obs} = (0.0058 \pm 0.00035)\ s^{-1}$. Furthermore, values of k_{obs}^{-1} correlate with the initial concentration of uncoordinated [S(IV)], rather than the sum of this concentration and the sulfite released according to eq 8. Nonetheless, at the end of the reaction, the total titratable S(IV) is the sum of both contributions.

The simplest explanation for this phenomenon is that the sulfite product liberated in eq 8 is unavailable for binding to the mercuric ion. The reaction shown in eq 11 accounts for the observed behavior, kinetically masking the presence of one equiv of sulfite while still permitting it to be titrated.

$$Hg^0_{(aq)} + HSO_3^-{}_{(aq)} + H^+ \rightleftarrows Hg\cdot SO_{2(aq)} + H_2O \quad (11)$$

Although very little coordination chemistry of Hg^0 has been reported, SO_2 is well-known as a ligand to low-valent transition metal complexes and binds strongly on metallic surfaces. The formation of an SO_2 complex with Hg^0 is further consistent with the peak we observe in the product spectrum at 276 nm. The solubility of the putative $Hg\cdot SO_{2(aq)}$ must be at least 3 orders of magnitude greater than the solubility of Hg^0 in distilled water, $(3.03 \pm 0.12) \times 10^{-7}$ M at 25 °C.[18] This statement is based on the observation of pseudo-first-order kinetic behavior, even when $[Hg(SO_3)_2^{2-}] = 1.0$ mM, since the final concentration of the proposed $Hg\cdot SO_2$ in this case is also 1.0 mM.

At temperatures below 45 °C, the dissociation of sulfite from $Hg(SO_3)_2^{2-}$ is best described as a rapid preequilibrium preceding the rate-determining internal redox reaction of $HgSO_3$, because the *y*-intercepts of the plots of k_{obs}^{-1} vs $[SO_3^{2-}]$ are not significant. However, at higher temperatures, a steady-state treatment of the intermediate $HgSO_3$ is appropriate and the value of k_d can be estimated. The large derived value of k_b is consistent with rapid capture of the sulfite ligand by $HgSO_3$.

The form of the Eyring equation for the kinetic parameter b^{-1} is given in eq 12:

$$\ln(1/bT) = \ln(k_r/K_2T) = \ln(R/Nh) + (\Delta S_r^{\ddagger} - \Delta S_2°)/R - (\Delta H_r^{\ddagger} - \Delta H_2°)/RT \quad (12)$$

where $\Delta S_r^{\ddagger}$ and $\Delta H_r^{\ddagger}$ are the entropy and enthalpy of activation for the redox reaction of $HgSO_3$, eq 9, and $\Delta S_2°$ and $\Delta H_2°$ are the entropy and enthalpy of binding of the second sulfite anion to $HgSO_3$. Because $\Delta H_r^{\ddagger}$ and $\Delta S_r^{\ddagger}$ have been measured independently as (105 ± 2) kJ/mol and (68 ± 6) J/mol·K, respectively,[6] the thermodynamic parameters for sulfite binding are $\Delta H_2° = -(61 \pm 2)$ kJ/mol and $\Delta S_2° = -(17 \pm 3)$ J/K·mol, such that $\Delta G_2° = -(56 \pm 10)$ kJ/mol at 25 °C. This calculation permits an independent evaluation of K_2 from the temperature-dependence of k_{obs}, yielding $K_2 = 7 \times 10^9$ at 25 °C, compared to 1.0×10^{10} obtained from the measured value of *b* at the same temperature (see above).

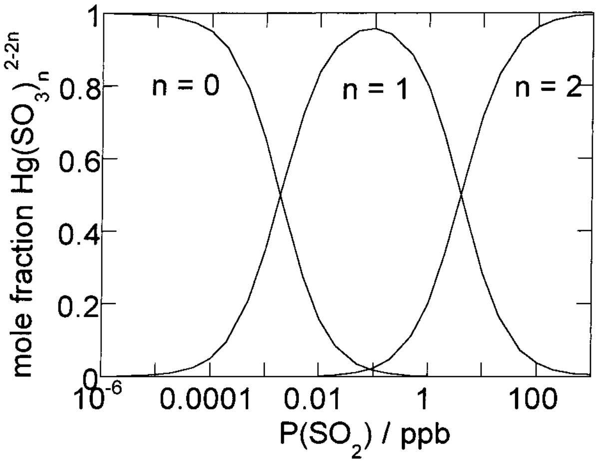

Figure 8. Speciation diagram for aqueous mercuric complexes Hg^{2+}, $HgSO_3$, and $Hg(SO_3)_2^{2-}$ at pH 4.0, in equilibrium with $SO_{2(g)}$.

The sequential formation constants for mercuric ion−sulfite complexes have not previously been measured; however, modelers often use values estimated from the known value of β_2 and a K_1-K_2 correlation established for complexes of the mercuric ion with halides and other univalent anions.[19] From this relationship and $\beta_2 = 1.2 \times 10^{24}$ (18 °C, $\mu = 0$),[12] $K_1 = 5.0 \times 10^{12}$ and $K_2 = 2.5 \times 10^{11}$ were estimated, for a ratio $K_1/K_2 = 20$.[7] However, linear free energy relationships for univalent anions are not necessarily appropriate for divalent anions. For example, the first two sequential binding constants for carbonate anions to Hg^{2+} are 1.0×10^{11} and 3.1×10^3.[20] Using the reported value for β_2 at 298 K and $\mu = 0.50$ M of $(2.1 \pm 0.1) \times 10^{23}$[8] we can now derive $K_1 = (2.1 \pm 0.4) \times 10^{13}$. The values of $\Delta G_1°$, $\Delta H_1°$, and $\Delta S_1°$ can also be calculated from the reported values[8] for the overall formation of $Hg(SO_3)_2^{2-}$ and our derived values for the second binding of sulfite. All of the rate and equilibrium constants established for the mercuric ion-sulfite system are summarized in Table 3.

Our values for the sequential sulfite binding constants lead to significantly different predictions for the speciation of mercuric ions in pH 4.0 clouds, Figure 8, compared to a previous estimate.[7] The major mercuric ion species in water droplets in equilibrium with 0.1 ppb $SO_{2(g)}$ (i.e., clean air) is unstable $HgSO_3$, which undergoes reduction to Hg^0 with a half-life of approximately one minute at 25 °C. The major mercuric complex is not predicted to be the $Hg(SO_3)_2^{2-}$ ion, even when $P(SO_2)$ approaches 1 ppb (as in highly polluted air).

On the basis of these results, it is possible that the formation of a complex such as $Hg\cdot SO_{2(aq)}$, either by direct reaction of Hg^0 with gaseous SO_2 or aqueous hydrogen sulfite, or by reduction of aqueous Hg(II) in the presence of excess sulfite, has an important effect on the deposition rate for atmospheric Hg. As a result of the apparently high solubility of this complex, it may not be necessary to suppose that the major form of mercury in rain is Hg(II).

Conclusion

Previously estimated kinetic and thermodynamic parameters have now been measured or derived for the aqueous mercuric ion−sulfite system. The mercuric ion has a high affinity for sulfite, which is expected to be its major ligand in atmospheric cloud droplets, but binds only the deprotonated form. Kinetic behavior is accurately predicted for conditions in which either the mercuric ion or the sulfite ion is present in excess, across a wide range of pH values and temperatures. The role of atmospheric SO_2 in the wet deposition of mercury is complex, increasing the solubility of Hg^0 (as $Hg{\cdot}SO_2$), stabilizing Hg^{II} (as $Hg(SO_3)_2{}^{2-}$) and reducing Hg^{II} (in $HgSO_3$).

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