J. Phys. Chem. A **2000,** *104,* 1621−1626

ARTICLES

Reduction of the Aqueous Mercuric Ion by Sulfite: UV Spectrum of $HgSO_3$ and Its Intramolecular Redox Reaction

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

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

Received: December 6, 1999

Aqueous hydrogen sulfite reacts with Hg^{2+} to form, in the absence of excess HSO_3^-, the $HgSO_3$ complex, observed here for the first time. Its UV spectrum is described by $\epsilon(234\ \text{nm}) = (1.57 \pm 0.05) \times 10^4\ M^{-1}\ cm^{-1}$. $HgSO_3$ decomposes in an intramolecular redox reaction which is kinetically first-order. The rate constant is independent of $[Hg^{2+}]$, $[HSO_3^-]$, $[O_{2(aq)}]$, and ionic strength. An acid-assisted pathway becomes significant at pH ≤ 1, attributed to the contribution of $HgSO_3H^+$. The rate of the intramolecular reaction of $HgSO_3$ was measured by trapping the Hg^0 product as Hg_2^{2+}; the value of the rate constant is $k_0 = (0.0106 \pm 0.0009)\ s^{-1}$ at 25.0 °C, pH 3. The activation parameters for pH 3, $\Delta H^\ddagger$ and $\Delta S^\ddagger$, are (105 ± 2) kJ/mol and (68 ± 6) J/mol·K, respectively, consistent with a unimolecular bond cleavage mechanism. A pathway involving H_2O-induced concerted $2e^-$ transfer is proposed.

Introduction

Both mercury and sulfur dioxide are ubiquitous trace contaminants of air. The global average concentration of air-borne mercury is 1.5 ng/m^3, for a total tropospheric burden of ca. 6000 tonnes.[1] Most of this is in the form of gas-phase Hg^0. Because of its long atmospheric lifetime, ca. one year,[1] ambient mercury levels vary little from region to region, although in recent years a disturbing increase in concentration has been noted and attributed to rising anthropogenic emissions.[2] In contrast, sulfur dioxide has a much shorter lifetime in air, on the order of days, and its concentrations range from less than 0.2 ppb in remote areas to as much as 200 ppb in urban, polluted areas.[3] Its high water solubility leads to appreciable quantities of HSO_3^- in clouds.[4]

The mercury found in cloud droplets, and therefore susceptible to wet deposition, is not $Hg^0_{(aq)}$ but the more soluble mercuric ion. Redox processes in clouds are believed to be important determinants of its speciation, and hence its temporal and geographical deposition patterns.[5,6] The high affinity of the mercuric ion for sulfur-containing ligands suggests that mercuric−sulfite complexes are important species in clouds, even in relatively nonpolluted air.[7] Such complexes have been suggested to be noninnocent in the global mercury cycle[8,9] because sulfite may reduce the mercuric ion to elemental mercury, which, being much less water-soluble, partitions back into the gas phase where it is again subject to long-range transport.[5]

The rate of reduction of mercuric ions by excess HSO_3^- was the subject of a previous report, in which the observed rate law was deemed valid only under conditions where the predominant species is thought to be $Hg(SO_3)_2^{2-}$.[10] $HgSO_3$ was reported to be unstable and has not been directly observed. The rate of its decomposition was estimated from a composite rate constant, assuming $HgSO_3$ to be a steady-state intermediate. We have reinvestigated the reduction of the aqueous mercuric ion by sulfite in acidic solution. We have observed the $HgSO_3$ complex under conditions where it is formed quantitatively and directly measured the rate constant for its decomposition. Our results suggest that the rate and mechanism of mercuric ion reduction by sulfite are quite different from those currently used in global mercury modeling.

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 0.1 M Hg^{2+} in 0.77 M $HClO_4$. These solutions were standardized by titration with KSCN (Baker ACS Reagent) to the ferric alum endpoint.[11] The stock solution was diluted to the desired concentration for use in stoichiometry and kinetics experiments.

The solution of Hg_2^{2+} was prepared by stirring the Hg^{2+} solution described above with $Hg^0_{(l)}$ overnight, followed by decantation of the aqueous phase. The concentration of Hg_2^{2+} was calculated from its absorbance at 236 nm ($\epsilon = 2.8 \times 10^4\ M^{-1}\ cm^{-1}$).[12,13]

Sulfite solutions were prepared by dissolving Na_2SO_3 (99.99% Aldrich Reagent Plus, anhydrous) in water. Since aqueous sulfite is susceptible to trace-metal-catalyzed autoxidation, the stock solution was standardized immediately before use by iodometric titration.[14]

Perchloric acid solutions were prepared by diluting the concentrated acid to the desired concentration. Solutions of $NaClO_4$ (99%, Aldrich ACS Reagent) were prepared by

---

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

10.1021/jp994268s CCC: $19.00

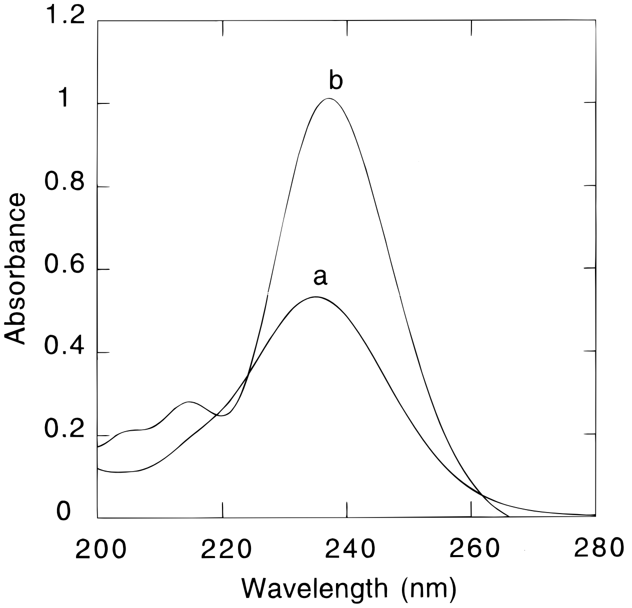


Figure 1. UV spectra of (a) 0.40 mM $HgSO_3$, and (b) 0.40 mM Hg_2^{2+}, at pH 3 ($HClO_4$).

dissolving the salt in water. 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. 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 the last reagent, and absorbance changes with time were recorded. Rate constants were obtained as nonlinear least-squares fits to the first-order integrated rate equation, $A_t = A_0 + (A_\infty - A_0)(1 - e^{-kt})$.[15]

Results

Formation and UV Spectrum of $HgSO_3$. The complex formed by reaction of the aqueous mercuric ion with sulfite, in the absence of excess sulfite, is believed to be $HgSO_3$. However, this species is reported to be unstable,[10,16] and its UV spectrum is not known. Solutions containing equimolar amounts of Hg^{2+} and sulfite at room temperature decompose to Hg^0 and sulfate within minutes at room temperature.

We discovered that $HgSO_3$ can readily be observed by UV−visible spectroscopy provided the reactant solutions are chilled to at least 15 °C prior to mixing. A spectrum was recorded immediately following addition of 40 μM sulfite to an air-saturated solution of 400 μM Hg^{2+} in 1 mM $HClO_4$ at 15 °C. A peak was observed with $\lambda_{max} = 234$ nm, Figure 1a. Its intensity varies linearly with the concentration of added sulfite in the range 8−67 μM, Figure 2, yielding the extinction coefficient $\epsilon(234 \text{ nm}) = (1.57 \pm 0.05) \times 10^4$ M^{-1} cm^{-1}. The spectrum is virtually invariant with pH; in 0.1 M $HClO_4$, $\epsilon(234 \text{ nm}) = (1.63 \pm 0.07) \times 10^4$ M^{-1} cm^{-1}. We propose that the absorbing species is $HgSO_3$, formed as in eq 1.

$$Hg^{2+}_{(aq)} + HSO_3^{-}{}_{(aq)} = HgSO_{3(aq)} + H^{+}_{(aq)} \qquad (1)$$

Stoichiometry of $HgSO_3$ Decomposition. The initial spectrum of the $HgSO_3$ solution changes with time. This process is shown in Figure 3 for a solution containing 40 μM $HgSO_3$ and 400 mM Hg^{2+} at pH 3 and 15.0 °C. There are two clean isosbestic points at 219 and 224 nm. The final spectrum is identical to that of independently prepared Hg_2^{2+}, with peaks at 236, 215, and 204 nm, Figure 1b. The yield of Hg_2^{2+} depends linearly upon the initial concentration of $HgSO_3$. The apparent extinction coefficient of the peak at 236 nm is $\epsilon = (2.74 \pm 0.09) \times 10^4$ M^{-1} cm^{-1} based on the initial concentration of $HgSO_3$, Figure 4. For comparison, the reported spectrum of $Hg_2^{2+}{}_{(aq)}$ has $\epsilon(236 \text{ nm}) = 2.8 \times 10^4$ M^{-1} cm^{-1}.[12,13] The reaction stoichiometry established by this result is shown in eq 2.

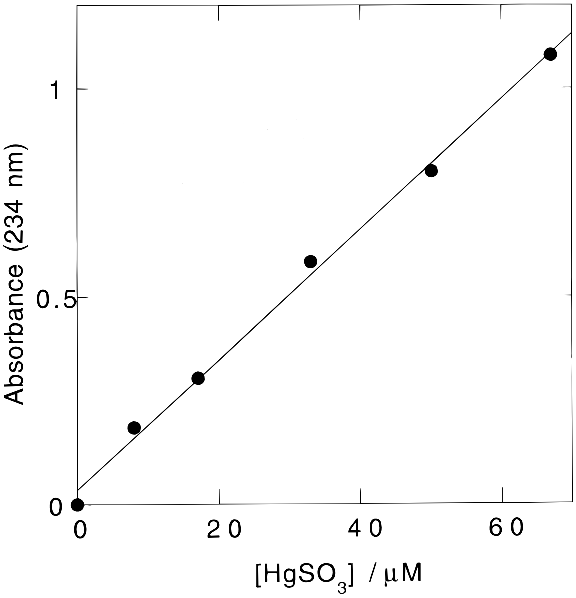


Figure 2. Extinction coefficient of $HgSO_3$ at pH 3 ($HClO_4$).

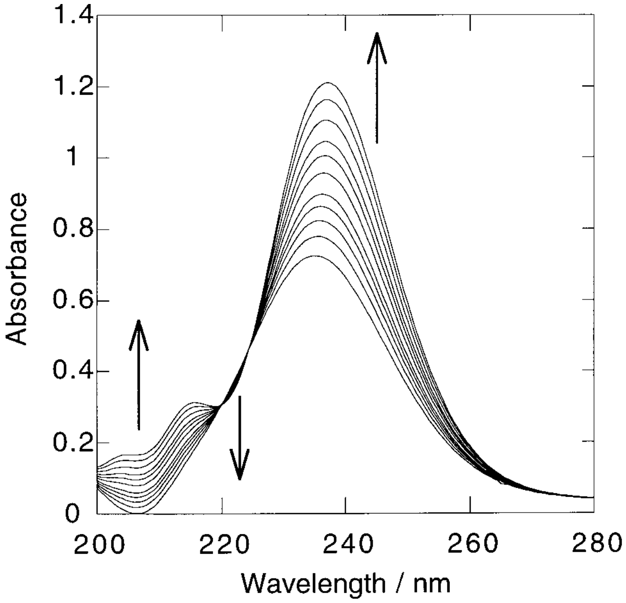


Figure 3. Evolution of the spectrum of 40 μM $HgSO_3$ in the presence of 400 μM Hg^{2+}, over the course of 15 min at 15.0 °C and at pH 3 ($HClO_4$).

$$HgSO_3 + Hg^{2+} + H_2O \rightarrow Hg_2^{2+} + HSO_4^{-} + H^{+} \qquad (2)$$

The yield of Hg_2^{2+} was identical in a reaction performed in the absence of dissolved oxygen.

Rate Law. The kinetics of the reaction were followed by monitoring the increase in absorbance at 236 nm, where $\Delta\epsilon =$

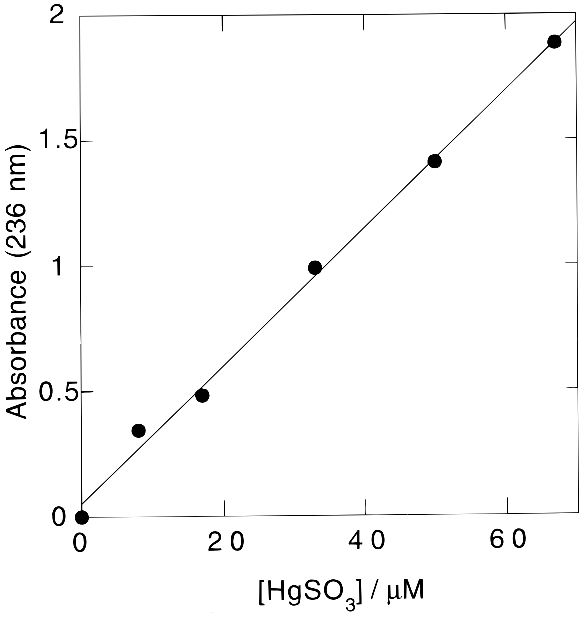


Figure 4. Extinction coefficient of the product of decomposition of $HgSO_3$.

1.2×10^4 M^{-1} cm^{-1}, Figure 5a. The time-evolution of the absorbance change is accurately described by a single-exponential function, characteristic of a first-order reaction. The first-order rate constant is independent of [$HgSO_3$] and free [Hg^{2+}] (required to be present in excess) and insensitive to the presence or absence of [$O_{2(aq)}$], Figure 5b. The rate constant is invariant with ionic strength in the range 0.001 to 1.0 M ($HClO_4$/$NaClO_4$), Figure 6a. Thus the rate law is authentically first-order and not pseudo-first-order (except for the kinetically undetectable participation of water). The measured rate constants are collected in Table 1.

These results are consistent with rate-determining intramolecular reduction of the mercuric ion in the $HgSO_3$ complex, eq 3, followed by rapid comproportionation of $Hg^0_{(aq)}$ with free Hg^{2+}, eq 4.

$$HgSO_{3(aq)} \rightarrow Hg^0_{(aq)} + S(VI) \quad (3)$$

$$Hg^{2+}_{(aq)} + Hg^0_{(aq)} = Hg_2{}^{2+}_{(aq)} \quad (4)$$

The rate constant for comproportionation is 5.9×10^8 M^{-1} s^{-1}, and the equilibrium constant is 1.8×10^8 M^{-1} at 25 °C;[17] therefore, the formation of $Hg_2{}^{2+}$ is fast and quantitative (as demonstrated by Figure 4). The lack of a significant ionic strength effect on the rate reflects the absence of charge separation in the rate-determining step. The indifference of the rate to the presence of dissolved oxygen requires that radical intermediates such as $SO_3{}^{\bullet-}$ are not involved.[18] The rate law at pH 3 is therefore

$$-d[HgSO_3]/dt = d[Hg_2{}^{2+}]/dt = k_0\,[HgSO_3] \quad (5)$$

The rate constant at (25.0 ± 0.2) °C, pH 3, and ionic strength $\mu = 0.0026$ M is $k_0 = (0.0106 \pm 0.0009)$ s^{-1}.

Acid Dependence. Although the UV spectrum of $HgSO_3$ is unaffected by lowering the pH from 3 to 1 (vide supra), the rate constant for its decomposition is slightly higher at the lower pH. The effect is linear at constant ionic strength $\mu = 1.08$ M, Figure 6b, with slope (0.0084 ± 0.0006) M^{-1} s^{-1}. The complete expression for the first-order rate constant in this pH range is

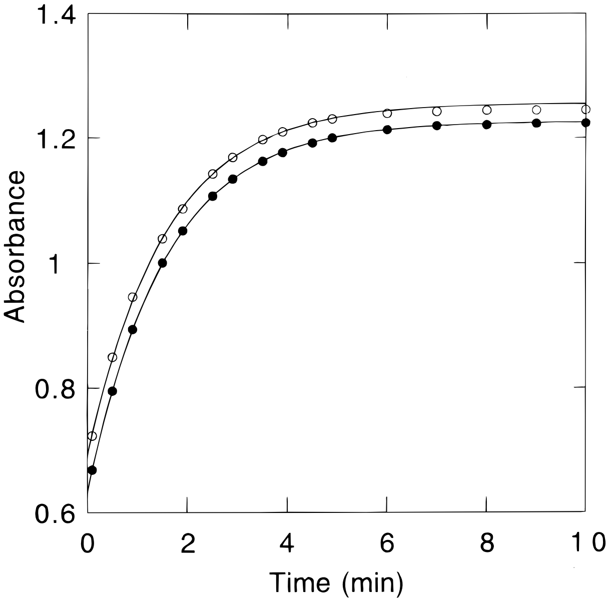


Figure 5. Kinetic profiles for decomposition of $HgSO_3$ in the presence of excess Hg^{2+} at 25.0 °C and pH 3 ($HClO_4$); open circles: air-saturated, and closed circles: argon-saturated solutions. The latter were slightly offset to better display the data.

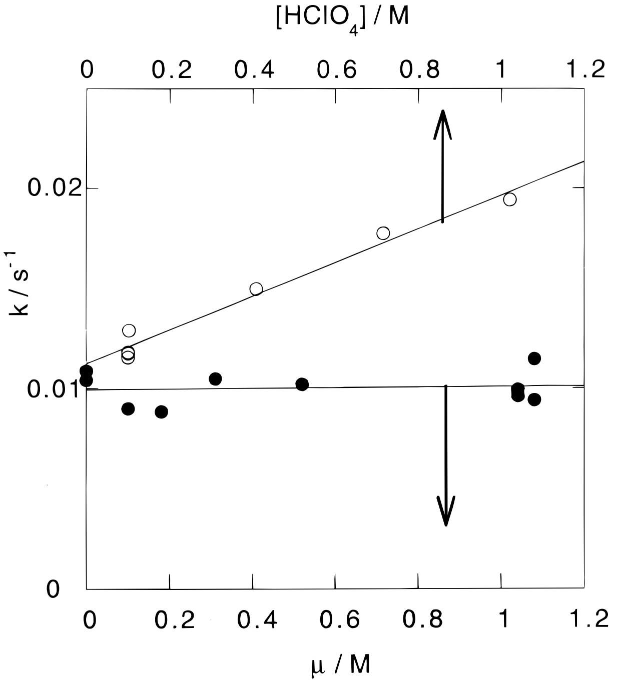


Figure 6. Dependence of the first-order rate constants for $HgSO_3$ decomposition on ionic strength ($HClO_4$/$NaClO_4$) at pH 3 (closed circles), and acid ($HClO_4$) at ionic strength $\mu = 1.0-1.1$ M ($HClO_4$/$NaClO_4$) (open circles).

$$k = k_0 + k_1[H^+] \quad (6)$$

where $k_0 = (0.0113 \pm 0.0003)$ s^{-1} and $k_1 = (0.0084 \pm 0.0006)$ M^{-1} s^{-1}. At pH 3, the acid-catalyzed path contributes less than 0.1% to the overall rate of decomposition such that $k \approx k_0$. The stoichiometry at pH 0 is the same as that shown in eq 2, i.e., one $Hg_2{}^{2+}$ is formed per $HgSO_3$.

Temperature Effect. The rate of decomposition of $HgSO_3$ is strongly temperature dependent. Rate constants at tempera-

TABLE 1: Rate Constants for Reduction of Mercuric Ion by Sulfite at 25.0 °C

$[Hg^{2+}]$ mM	[S(IV)][a] mM	$[HClO_4]$ M	$[NaClO_4]$ M	10^3k^b s^{-1}	$[Hg^{2+}]$ mM	[S(IV)][a] mM	$[HClO_4]$ M	$[NaClO_4]$ M	10^3k^b s^{-1}
0.400	0.040	0.001		10.75 ± 0.07	0.333	0.029	0.100		12.60 ± 0.05
0.400	0.040	0.001		10.770 ± 0.001[c]	0.333	0.009	0.100		12.7 ± 0.3 (3)
0.333	0.010	0.003		10.9 ± 0.1	0.333	0.018	0.100		13.2 ± 0.2 (3)
0.333	0.010	0.003		10.4 ± 0.1	0.333	0.042	0.100		12.7 ± 0.5 (2)
0.333	0.029	0.003		11.18 ± 0.03	0.830	0.042	0.100		13.3 ± 0.5 (3)
0.333	0.030	0.003		9.138 ± 0.007	0.650	0.011	0.100		12.40 ± 0.02
0.333	0.009	0.003		11.7 ± 0.5 (3)	0.333	0.010	0.100		13.2 ± 0.7 (2)[c]
0.400	0.040	0.004		12.468 ± 0.003	0.333	0.010	0.100		12.8 ± 0.5[d]
0.400	0.040	0.006		12.680 ± 0.005	0.333	0.055	0.100		12.48 ± 0.02
0.400	0.040	0.008		12.83 ± 0.01	0.333	0.092	0.100		12.3 ± 0.2
0.333	0.030	0.003	0.100	9.082 ± 0.005	0.333	0.009	0.100	0.050	13.0 ± 0.5 (2)
0.333	0.009	0.003	0.100	10.8 ± 0.3 (4)	0.333	0.030	0.100	0.0910	11.8 ± 0.1
0.333	0.010	0.003	0.100	9.0 ± 0.2	0.333	0.032	0.100	0.310	12.5 ± 0.1
0.333	0.010	0.003	0.180	8.8 ± 0.3	0.333	0.032	0.100	0.520	11.95 ± 0.02
0.333	0.030	0.003	0.191	10.40 ± 0.07	0.333	0.034	0.100	1.000	11.57 ± 0.07 (2)
0.333	0.032	0.003	0.310	10.48 ± 0.02	0.333	0.027	0.100	1.000	11.7 ± 0.1
0.333	0.032	0.003	0.520	10.22 ± 0.03	0.400	0.039	0.102	0.972	12.927 ± 0.007
0.333	0.034	0.003	1.040	9.8 ± 0.1 (3)	0.400	0.039	0.400	0.648	14.97 ± 0.01
0.400	0.039	0.001	1.080	9.42 ± 0.03	0.400	0.039	0.710	0.324	17.75 ± 0.02
0.400	0.040	0.004	1.080	11.467 ± 0.008	0.400	0.039	1.02		19.42 ± 0.01

[a] Total added sulfite, sum of $[SO_3^{2-}]$, $[HSO_3^-]$, and $[SO_{2(aq)}]$. [b] Number of experiments is shown in parentheses, where greater than one. Errors are standard deviations of the average rate constant, except for single experiments, where the error in the nonlinear least-squares fit is shown. [c] Argon-saturated. In all other experiments, the solutions were air-saturated. [d] Hg^{2+} was the last reagent added. In all other experiments, sulfite was the last reagent added.

TABLE 2: Temperature Dependence of Rate Constants for Reduction of Mercuric Ion by Sulfite, at Ionic Strengths 0.003−0.10 M

pH	temperature °C	k s^{-1}	number of expts
3	6.5	0.00055 ± 0.00005	2
3	15.5	0.0027 ± 0.0001	2
3	25.0	0.0106 ± 0.0009	15
3	35.0	0.040 ± 0.002	2
1	6.6	0.000675 ± 0.000015	3
1	16.0	0.00303 ± 0.00005	4
1	25.0	0.0129 ± 0.0003	17
1	34.4	0.048 ± 0.012	5

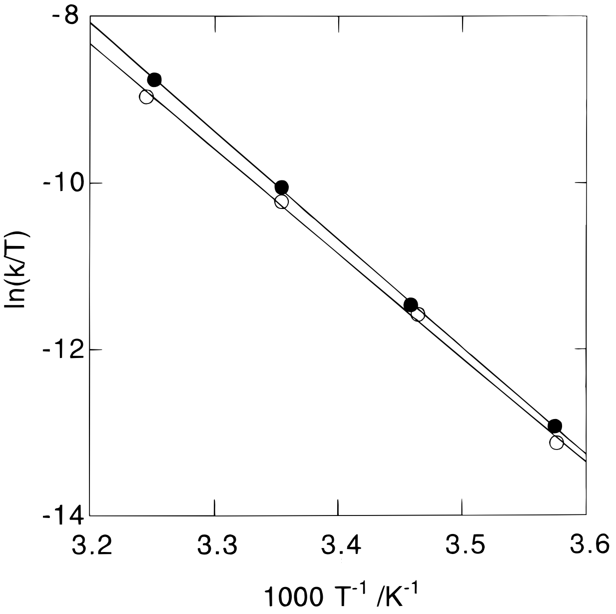


Figure 7. Eyring plot of the temperature-dependent rate constants for $HgSO_3$ decomposition. Open circles: pH 1; closed circles: pH 3.

tures ranging from 5 to 35 °C are shown in Table 2. Each 10° increase in temperature results in roughly a quadrupling of the rate constant. At pH 3, the Eyring plot, Figure 7, is linear with slope −12595 K and intercept 31.971. The values derived for $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ are (105 ± 2) kJ/mol and (68 ± 6) J/mol·K, respectively.[15,19] The comparable Eyring plot at pH 1 is almost parallel, with $\Delta H^{\ddagger} = (108 \pm 1)$ kJ/mol and $\Delta S^{\ddagger} = (81 \pm 5)$ J/mol·K.

Discussion

Although aqueous sulfite exists almost exclusively as HSO_3^-/SO_3H^- at pH 3, its complex with the mercuric ion, $HgSO_3$, is not protonated at this pH. Its UV spectrum is acid-independent, and its rate of decomposition at pH 3 is almost independent of ionic strength, as expected for a neutral complex whose reaction involves little or no charge formation in the transition state. The intense band at 234 nm in the UV spectrum of $HgSO_3$ is consistent with ligand-to-metal charge transfer in a sulfur-bonded sulfito complex.[20] For comparison, the spectrum of $Pt(NH_3)_3(SO_3)$ consists of a peak at 234 nm with $\epsilon = 5650$ M^{-1} cm^{-1}.[21] The IR spectrum of the more stable $Hg(SO_3)_2^{2-}$ complex confirms metal−sulfur coordination.[22,23]

Although $HgSO_3H^+$ is spectroscopically undetectable in our experiments, it makes a significant contribution to the rate of decomposition in strongly acidic solution. The first-order $[H^+]$-dependence in eq 6 requires that a proton be present in the transition state for the acid-catalyzed path. Since protonation equilibria for oxyanions are usually established very quickly and are therefore unlikely to be rate-determining in this reaction, the most probable origin of the second term in eq 6 is a protonation equilibrium involving the $HgSO_3$ complex, eq 7.

$$HgSO_3H^+ = HgSO_3 + H^+ \qquad (7)$$

A substantial decrease in pK_a occurs for Bronsted acid ligands upon coordination to a Lewis acidic metal cation. For example, the pK_a of $HgCO_3H^+$ is 4.1,[24] compared to 10.3 for HCO_3^-. Since HSO_3^- (pK_a 7.2) is a considerably stronger acid than HCO_3^-, the pK_a of $HgSO_3H^+$ is predicted to be ≤1. The relative contribution of $HgSO_3H^+$ to the overall rate of decomposition is 7% at pH 1 and 43% at pH 0. $HgSO_3H^+$ can be kinetically significant although spectroscopically unobservable provided its rate constant is much higher than the rate constant k_0 for decomposition of the major species $HgSO_3$.

The redox decomposition of $HgSO_3$/$HgSO_3H^+$ amounts to the reduction of the mercuric ion to Hg^0 by coordinated sulfite. When free $Hg^{2+}{}_{(aq)}$ is present, its trapping of the Hg^0 product to give the strongly absorbing $Hg_2{}^{2+}$ ion serves as a convenient kinetic probe for the reaction. The observation of two isosbestic points in the evolution of the spectrum of $HgSO_3$ to that of $Hg_2{}^{2+}$ is consistent with a reaction that has no observable intermediates. The decomposition of $HgSO_3$ is an authentic first-order reaction, confirming that the redox reaction is intramolecular, as previously suggested.[10] However, our rate constant for decomposition of $HgSO_3$ is about 50 times slower than previously reported.[10] In that study, a composite rate constant was measured in the presence of excess sulfite, and the value of the equilibrium constant for sulfite dissociation from $Hg(SO_3)_2{}^{2-}$ was estimated in order to obtain an approximate value for k_0. By choosing conditions under which the rate law is particularly simple, as in eq 5, we have instead measured the value of k directly.

Our kinetic results require a reevaluation of the previously proposed mechanism.[10] The intramolecular redox reaction generates neither Hg^+ nor sulfite radical anions. The latter are rapidly trapped by dissolved oxygen, which initiates a chain autoxidation of sulfite,[18] eq 8−10.

$$SO_3{}^{-\bullet} + O_2 \rightarrow SO_5{}^{-\bullet} \qquad (8)$$

$$SO_5{}^{-\bullet} + SO_3{}^{2-} \rightarrow SO_4{}^{-\bullet} + SO_4{}^{2-} \qquad (9)$$

$$SO_4{}^{-\bullet} + SO_3{}^{2-} \rightarrow SO_4{}^{2-} + SO_3{}^{-\bullet} \qquad (10)$$

Since we found that the stoichiometry of the reduction of mercuric ion by sulfite, as well as its rate constant, are independent of the concentration of dissolved oxygen, we can rule out one-electron transfer mechanisms with radical intermediates. The observed $Hg_2{}^{2+}$ product must therefore be formed by comproportionation of Hg^0 with Hg^{2+} rather than by dimerization of Hg^+.

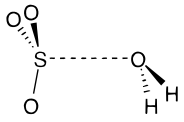
Our direct measurement of k_0 also permits a straightforward evaluation of its temperature dependence. Global mercury models assume that this reaction is temperature-independent,[7] based on a published remark that temperature effects in this system are small.[10] We find that the rate constant k_0 roughly quadruples with each 10 °C increase in temperature. The activation parameters are very large and positive. Both their signs and magnitudes are consistent with a unimolecular reaction involving significant bond-breaking in the transition state.

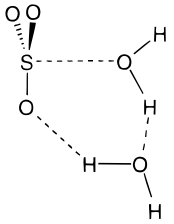
Sulfite is known to reduce metal ions by one-electron transfer[25,26] (for example, $MnO_4{}^-$),[27] by oxygen atom abstraction (for example, ferrate),[28] and by halogen abstraction (for example, $AuCl_4{}^-$).[29] The redox decomposition of $HgSO_3$ does not appear to belong to any of these categories. It most resembles the intramolecular acid-catalyzed reduction of Pt(IV) in *cis*-$Pt(NH_3)_4(SO_3)_2$ to $Pt(NH_3)_3(SO_3)$.[21] Concerted two-electron transfer can be accomplished by heterolytic cleavage of the metal−sulfur bond. $HgSO_3$, although formed as a mercuric−sulfite complex, is formally equivalent to a donor−acceptor adduct of mercury(0) with sulfur trioxide. In other words, while the sulfite anion brought both electrons of the Hg−S bond into its union, it leaves them behind when it departs, eq 11.

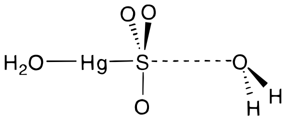
$$Hg^{2+}{}_{(aq)} + SO_3{}^{2-}{}_{(aq)} = Hg^{II}S^{IV}O_3 \rightarrow Hg^0S^{VI}O_3 \rightarrow Hg^0{}_{(aq)} + S(VI) \qquad (11)$$

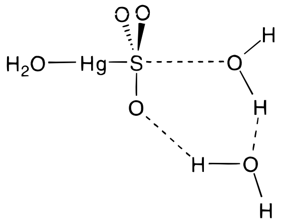
Both SO_3 and SO_2 are capable of forming strong donor−acceptor complexes with Lewis bases such as NH_3[30,31] and transition metals such as Ni(0).[32]

The hydration of SO_3 by H_2O has been studied kinetically in the gas phase,[33] and a donor−acceptor complex, I, has been characterized by microwave spectroscopy.[34] Its conversion to H_2SO_4 requires a second water molecule, II, to form a structure in which S−O bond formation and proton migration are concerted within the six-membered ring.[35,36] We propose that a similar water-assisted departure of the sulfite ligand as either $SO_3{\cdot}H_2O$ or $H_2SO_4{\cdot}H_2O$ may induce the redox decomposition of $HgSO_3$. The mercury coordination number in $HgSO_3$ is not known, but there is likely at least one water molecule in its primary coordination sphere, and it is probably subject to strong trans-labilization by the sulfite ligand.[20] The transition state for the redox reaction must incorporate an additional one or two water molecules in the second coordination sphere, III and IV.


I


II


III


IV

Protonation of the sulfite ligand, as in $HgSO_3H^+$, will make the donor−acceptor interaction with H_2O stronger and obviate the need for proton transfer from the second water molecule, thus accelerating the reaction.

This mechanism for sulfite reduction of Hg^{2+} can, when coupled with the rapid reoxidation of $Hg^0{}_{(aq)}$ by dissolved O_3,[37] also be viewed as a mercury-catalyzed path for the oxidation of S(IV) to S(VI).

Our direct evaluation of the behavior of $HgSO_3$ now permits kinetic measurements of previously estimated mercuric ion-sulfite sequential binding constants and thus allows us to predict mercuric ion speciation in clouds. These results, and their impact on global mercury deposition patterns will be reported shortly.

Conclusion

The accuracy of the rate constants for atmospheric redox transformations of mercury is critical to the successful application of global mercury models. We have determined the rate constant and activation parameters for sulfite reduction of the aqueous mercuric ion. Their values are significantly different from the previous best estimates. In particular, the strong temperature dependence of the reaction must influence the fate of mercuric ions in the variable temperature aqueous environment of clouds.

Acknowledgment. E. M. thanks the University of Ottawa for a Research Scholarship. S.L.S. thanks NSERC for a Research

Grant and a Women's Faculty Award and TSRI (Health Canada) for partial support of this work.

References and Notes

(1) Slemr, F.; Schuster, G.; Seiler, W. *J. Atmos. Chem.* **1985**, *3*, 407−434.

(2) Slemr, F.; Langer, E. *Nature* **1992**, *355*, 434−437.

(3) Martin, L. R. *SO_2, NO and NO_2 Oxidation Mechanisms: Atmospheric Considerations*; Calvert, J. G., Ed.; Butterworth: Markham, Ontario, 1984; pp 63−99.

(4) Fried, A.; Tyndall, G. *Atmospheric Chemistry and Global Change*; Brasseur, G. P., Orlando, J. J., Tyndall, G. S., Eds.; Oxford University Press: New York, 1999; pp 349−370.

(5) Schroeder, W. H.; Yarwood, G.; Niki, H. *Water, Air, Soil Pollut.* **1991**, *56*, 653−666.

(6) Lindberg, S. E.; Stratton, W. J. *Environ. Sci. Technol.* **1998**, *32*, 49−57.

(7) Pai, P.; Karamchandani, P.; Seigneur, C. *Atmos. Environ.* **1997**, *31*, 2717−2732.

(8) Brosset, C. *Water, Soil, and Air Pollut.* **1987**, *34*, 145−166.

(9) Iverfeldt, A.; Lindqvist, O. *Atmos. Environ.* **1986**, *20*, 1567−1573.

(10) Munthe, J.; Xiao, Z. F.; Lindqvist, O. *Water, Air, Soil Pollut.* **1991**, *56*, 621−630.

(11) Kolthoff, M.; Sandell, E. B. *Textbook of Quantitative Inorganic Analysis*; Macmillan: New York, 1952.

(12) Fujita, S.; Horii, H.; Taniguchi, S. *J. Phys. Chem.* **1973**, *77*, 2868−2871.

(13) Higginson, W. C. E. *J. Chem. Soc.* **1951**, 1438.

(14) Davies, R.; Kipling, B.; Sykes, A. G. *J. Am. Chem. Soc.* **1973**, *95*, 7250−7256.

(15) Espenson, J. H. *Chemical Kinetics and Reaction Mechanisms*; McGraw-Hill: New York, 1981.

(16) Marsicano, F.; Hancock, R. D. *J. Coord. Chem.* **1976**, *6*, 21−29.

(17) Clever, H. L.; Johnson, S. A.; Derrick, M. E. *J. Phys. Chem.* **1985**, *14*, 631−680. Note that this value of the equilibrium constant is valid for dissolved $Hg^0_{(aq)}$, not $Hg_{(l)}$. Since comproportionation is rapid, Hg^0 never accumulates and therefore its concentration does not exceed its solubility in water.

(18) Hayon, E.; Treinin, A.; Wilf, J. *J. Am. Chem. Soc.* **1972**, *94*, 47−57.

(19) The errors were derived from the appropriate error propagation formulae. Morse, P. M.; Spencer, M. D.; Wilson, S. R.; Girolami, G. S. *Organometallics* **1994**, *13*, 1646−1655.

(20) Spitzer, U.; van Eldik, R. *Inorg. Chem.* **1982**, *21*, 4008−4014.

(21) Koshy, K. C.; Harris, G. M. *Inorg. Chem.* **1983**, *22*, 2947−2953.

(22) Hall, J. P.; Griffith, W. P. *Inorg. Chim. Acta* **1981**, *48*, 65−71.

(23) Newman, G.; Powell, D. P. *Spectrochim. Acta* **1963**, *19*, 213−224.

(24) Bilinski, H.; Markovic, M.; Gessner, M. *Inorg. Chem.* **1980**, *19*, 3440−3443.

(25) Wilmarth, W. K.; Stanbury, D. M.; Byrd, J. E.; Po, H. N.; Chua, C.-P. *Coord. Chem. Rev.* **1983**, *51*, 155−179.

(26) Brandt, C.; van Eldik, R. *Chem. Rev.* **1995**, *95*, 119−190.

(27) Simándi, L. I.; Jáky, M.; Schelly, Z. A. *J. Am. Chem. Soc.* **1984**, *106*, 6866−6867.

(28) Johnson, M. D.; Bernard, J. *Inorg. Chem.* **1992**, *31*, 5140−5142.

(29) Berglund, J.; Elding, L. *Inorg. Chem.* **1995**, *34*, 513−519.

(30) Douglas, J. E.; Kollman, P. A. *J. Am. Chem. Soc.* **1978**, *100*, 5226−5227.

(31) Douglas, J. E.; Kenyon, G. L.; Kollman, P. A. *Chem. Phys. Lett.* **1978**, *57*, 553−556.

(32) Sakaki, S.; Sato, H.; Imai, Y.; Morokuma, K.; Ohkubo, K. *Inorg. Chem.* **1985**, *24*, 4538−4544.

(33) Kolb, C. E.; Jayne, J. T.; Worsnop, D. R.; Molina, M. J.; Meads, R. F.; Viggiano, A. A. *J. Am. Chem. Soc.* **1994**, *116*, 10314−10315.

(34) Phillips, J. A.; Canagaratna, M.; Goodfriend, H.; Leopold, K. R. *J. Phys. Chem.* **1995**, *99*, 501−504.

(35) Hoffmann, M.; Schleyer, P. v. R. *J. Am. Chem. Soc.* **1994**, *116*, 4947−4952.

(36) Morokuma, K.; Muguruma, C. *J. Am. Chem. Soc.* **1994**, *116*, 10316−10317.

(37) Munthe, J. *Atmos. Environ.* **1992**, *26A*, 1461−1468.