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Kinetics of Oxygen Exchange between the Two Isomers of Bisulfite Ion, Disulfite Ion ($S_2O_5^{2-}$), and Water As Studied by Oxygen-17 Nuclear Magnetic Resonance Spectroscopy

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The nuclear magnetic transverse relaxation time of oxygen-17 in aqueous sodium bisulfite solutions in the pH range from 2.5 to 5 was measured over a range of temperatures, pH, and S(IV) concentrations at an ionic strength of 1.0 m. From these data the rate law for oxygen exchange between bisulfite ion and water was determined and found to be consistent with oxygen exchange occurring via the reactions $SHO_3^- + H^+ \underset{k_1}{\overset{k_{-1}}{\rightleftarrows}} SO_2 + H_2O$, $SO_3H^- + SHO_3^- \overset{k_{16a}}{\rightleftarrows} SO_3^{2-} + SO_2 + H_2O$, and $SO_3H^- + SHO_3^- \overset{k_{16b}}{\rightleftarrows} S_2O_5^{2-} + H_2O$, where the symbol SHO_3^- refers to both isomeric forms of bisulfite ion, one in which the hydrogen is bonded to the sulfur (denoted HSO_3^-) and another in which the hydrogen is bonded to an oxygen atom (denoted SO_3H^-). The SO_3H^- isomer exchanges oxygen atoms with water much more rapidly than does the HSO_3^- isomer. The value of k_{-1} was determined and is in essential agreement with the results of a previous determination by relaxation measurements. The value of $k_{16a} + k_{16b}$ was also found, and k_{16b} is at least as large as k_{16a}. The rate and mechanism of oxygen exchange between the two bisulfite ion environments were studied by analyzing the broadening of the HSO_3^- resonance. Oxygen exchange occurs through isomerization caused by proton transfers.

Introduction

When sulfur dioxide dissolves in water, it retains its structure as SO_2 rather than forming sulfurous acid.[1] Consequently, its first and second ionizations are represented as

$$SO_2 + H_2O \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} SHO_3^- + H^+ \tag{1}$$

and

$$SHO_3^- \underset{k_{-2}}{\overset{k_2}{\rightleftarrows}} SO_3^{2-} + H^+ \tag{2}$$

where SHO_3^- represents bisulfite ion in both the HSO_3^- and SO_3H^- isomeric forms. (The hydrogen atoms in HSO_3^- and SO_3H^- are bonded to the sulfur atom and an oxygen atom, respectively.) Thus the rate of reaction 2, for example, is the sum of the dissociation rates of the HSO_3^- and SO_3H^- isomers. The rate constant, k_2, and the equilibrium quotient, Q_2, for this overall reaction can be expressed in terms of the total bisulfite ion concentration, which we denote as $[SHO_3^-]$.

The rate of reaction 1 has been measured previously. Eigen, Kustin, and Maass[2] studied the frequency dependence of the attenuation of sound waves in sulfur dioxide solutions of pH < 2 and 0.1 m ionic strength. The sound absorption

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was presumed to shift the equilibrium of reaction 1. Betts and Voss[3] studied the kinetics of oxygen exchange between sulfite ion and water as a function of sulfite concentration and pH in alkaline solutions (pH > 8) of ionic strength 0.9 M by using oxygen-18 as a tracer. They reported a value of k_{-1} and also a value of k_3, the rate constant for the dimerization of bisulfite ion:

$$2SHO_3^- \overset{k_3}{\rightleftharpoons} S_2O_5^{2-} + H_2O \qquad (3)$$

More recently k_{-1} has been measured by polarographic and voltammetric methods. Reynolds and Yuan[4] as well as Tolmachev and Scherson[5] measured the limiting current during the reduction of bisulfite solutions. In both studies the rate of SO_2 reduction was assumed to be limited by the rate of its formation from bisulfite ion. Values of k_{-1} reported by these four groups are in poor agreement, differing by more than a factor of 30. We undertook the present work to redetermine the rate of reaction 1, gain information about the kinetics of reaction 3, and explore the individual kinetic roles of the two bisulfite isomers.

We have studied the kinetics of reactions 1−3 using oxygen-17 NMR methods.[6] Line-broadening analysis was employed in the region between pH 3 and 5, in which the S(IV) and water resonances are distinct but exchange-broadened. In the $SO_2-SHO_3^--SO_3^{2-}$ system the analysis is complicated by exchange between the two isomers of bisulfite ion.[7] We investigated the rate and mechanism of the isomerization reaction

$$HSO_3^- \underset{k_{-4}}{\overset{k_4}{\rightleftharpoons}} SO_3H^- \qquad (4)$$

by studying the broadening of the ^{17}O resonance of HSO_3^-.

Experimental Section

NMR Measurements. Details of the NMR spectrometer, sample temperature control, and the preparation of oxygen-free sodium bisulfite solutions have been reported elsewhere.[7] The ^{17}O and ^1H resonance frequencies were 27.4 and 200 MHz, respectively. A broad-band, multinuclear, 10 mm probe was used in the ^{17}O experiments, while ^1H NMR spectra were acquired using a 5 mm proton probe.

The transverse relaxation time of ^{17}O in the water of each bisulfite solution was found by fitting a Lorentz line shape to the water peak in a spectrum obtained by Fourier transformation of the sum of between 200 and 6000 free induction decays produced by single pulses. Preacquisition delay times were selected according to the method of Canet et al.[8] The measured transverse relaxation time was corrected for an extra broadening of $2.9 \pm 0.8\ s^{-1}$ arising from magnetic field inhomogeneity, the magnitude of which was estimated from the difference between the measured line width (half-width at half-height) and the $1/T_1$ of ^{17}O in the water of a 1.0 m NaCl solution. For one solution ([S(IV)] = 0.45 m, pH = 4.98) the free induction decays were acquired at a frequency of 67.8 MHz using a Bruker NMR spectrometer fitted with a broad-band, multinuclear, 10 mm probe, and the transverse relaxation time of ^{17}O in the water site was found by the Carr−Purcell−Meiboom−Gill method.[9] The length of the 180° pulse was approximately 45 μs. Widths of the bisulfite peaks were obtained by fitting Lorentz line shapes to spectra in which the solvent signal had been suppressed by a two-pulse excitation sequence.[7]

Each data point represents a single Lorentz line shape fitting of a single solution. Uncertainties assigned to the line widths were those obtained from the least-squares fitting of the peaks with Lorentz line shapes and reflect goodness of fit rather than reproducibility of the data. Uncertainties are reported as plus or minus one standard deviation. Some possible errors not accounted for by the error bars are errors in solution pH, concentration of bisulfite ion, and magnetic field inhomogeneity correction. Such errors would appear as systematic errors in data obtained from a single solution.

Longitudinal relaxation times of ^{17}O were measured using the inversion recovery method[10] and the pulse phase-shifting technique of Cutnell et al.[11] The value of T_1 of the water site was determined by fitting the amplitude of the water peak at 10 different values of τ to the expression

$A(\tau) = A(\infty)\{1 - (1 + W)\exp(-\tau/T_1)\}$, where τ is the time between 180° and sampling pulses, $A(\tau)$ is the amplitude of the water peak at time τ, and W is a parameter that compensates for incomplete inversion of the magnetization by the 180° pulse.[12]

On our chemical shift scale the water peak was always assigned a shift of zero and downfield shifts were positive.

Solution Composition. Total concentrations of S(IV) are reported in units of molality, which is defined in this work as moles of S(IV)/55.5 mol of water. Concentrations of the various species in the bisulfite solutions were calculated from the equilibrium quotients of reactions 1−4 and the water dissociation reaction using values at 298 K of $Q_1 = 10^{-1.37}$ m,[13,14] $Q_2 = 10^{-6.34}$ m,[13,14] pQ_w = 13.79,[13] $Q_3 = 0.082\ M^{-1}$,[15] and $Q_4 = 4.9$.[7] Q_3 was determined at an ionic strength of 1.0 M, while Q_1, Q_2, and Q_4 were measured at 1.0 m ionic strength. In calculating solute molalities, we ignored the small difference between molarity and molality in our solutions. At 298 K and 1.0 m ionic strength the equilibrium quotients for the acid dissociation of SO_3H^- and HSO_3^- are 5.5×10^{-7} and 2.7×10^{-6} m, respectively.

Using a pH meter calibrated against standard buffers, hydrogen ion molalities were calculated from the pH meter readings, assumed to be equal to $-\log(a_{H^+})$, and an activity coefficient of 0.754. Here the mean activity coefficient of 0.01 M HCl in 1 m NaCl[16] was substituted for the unknown activity coefficient of H^+ in the bisulfite solutions. The pH meter reading will be referred to by the term "pH".

Concentrations at temperatures other than 298 K were calculated after first correcting the equilibrium quotients for changes in

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temperature using the van't Hoff equation. Q_1 and Q_2 were corrected for changes in temperature using 298 K values of ΔH at 1.0 m ionic strength, $\Delta C_p°$, and $d\Delta C_p°/dT$,[17] while Q_w was calculated using 298 K values of ΔH at 1.0 m ionic strength and $\Delta C_p°$.[18] Values of ΔH_1, ΔH_2, and ΔH_w at ionic strength 1.0 m employed in this calculation were -3.99, -0.12, and 13.71 kcal/mol, respectively. They were calculated[19] from the reaction enthalpies at ionic strength 0 [17] or 0.5 m [13] and relative partial molal enthalpies of solutes at ionic strength 0.5 and 1.0 m,[20] with the relative partial molal enthalpy of $NaHCO_3(aq)$ substituting for the unknown relative partial molal enthalpy of $NaHSO_3(aq)$. Q_4 was calculated at temperatures other than 298 K using $\Delta H_4 = -2.9$ kcal/mol, which was determined at 298 K and ionic strength 1.0 m.[7] Q_3 was calculated using the 298 K, ionic strength 2.1 m reaction enthalpy $\Delta H_3 = -1.1$ kcal/mol,[15] because the relative apparent molal enthalpies needed to correct ΔH_3 to ionic strength 1.0 m were not available.

Results

Introduction. The ^{17}O NMR spectra of sodium bisulfite solutions having S(IV) concentrations in the range from 0.1 to 0.5 m and with pH between 2.5 and 5 exhibit resonances at ca. 195, ca. 175, and 0 ppm arising from SO_3H^-, HSO_3^-, and H_2O, respectively.[7,21] Spectral changes resulting from variation of the pH of the solution are illustrated in Figure 1 of ref 7. The SO_3H^- peak at 195 ppm broadened with increasing temperature and decreasing pH and below pH 3.6 was too broad to observe. The water peak also broadened as the pH decreased from 5 to 3.5 and then narrowed as the pH was decreased below 3.5. The HSO_3^- peak at 175 ppm broadened with increases in temperature, pH, and S(IV) concentration. At and above pH 5 we did not observe separate 195 or 175 ppm resonances; the pH 5 spectra contained a single solute resonance at approximately 192 ppm that broadened with increasing temperature and whose area corresponded to the total concentration of bisulfite ion.

The difference between $1/T_2$ and $1/T_1$ of ^{17}O in the water site, shown in Figure 1, along with the pH and temperature dependence of their difference, provides evidence for an oxygen exchange process involving water. The ratio of the additional broadening ($1/T_2 - 1/T_1$) of the water peak to that of the SO_3H^- peak is about equal to the inverse of the ratio of peak areas, as would be expected if chemical exchange occurs between these two species.[22]

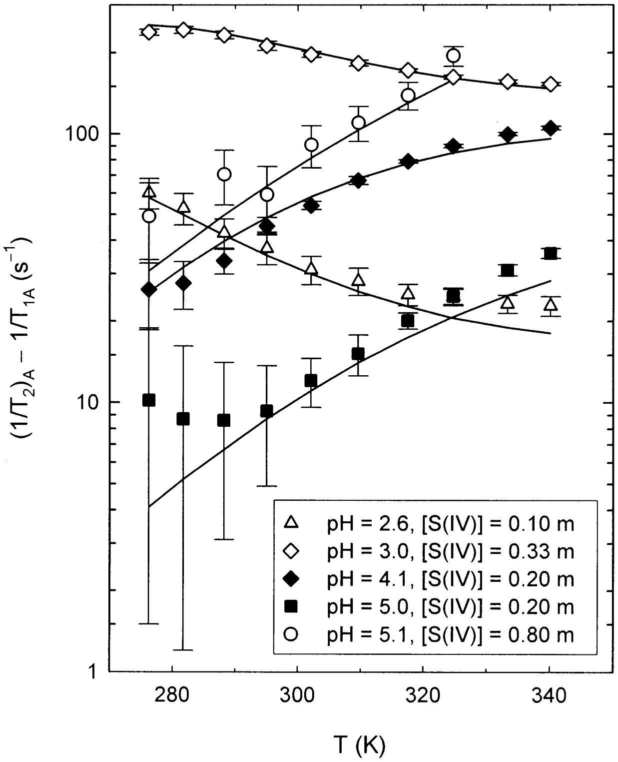

Figure 1. Temperature dependence of the difference between the measured $1/T_2$ and $1/T_1$ of the ^{17}O in the water (site A) of sodium bisulfite solutions of $[S(IV)] = 0.1-0.8$ m and various concentrations of H^+. $(1/T_2)_A$ is the measured half-width at half-height of the water peak. The term "pH" refers to the pH meter reading at room temperature. The curves show values calculated from eqs 13 and 17 using rate constants deduced in this work. Data acquired at other [S(IV)] and pH values are not shown but gave similar results (see Supporting Information).

These spectral features are consistent with the oxygen exchange scheme ABC, where A = H_2O (0 ppm), B = SO_3H^- (195 ppm), and C = HSO_3^- (175 ppm). The rate of oxygen exchange between A and B increases with decreasing pH, producing the coalescence of SO_3H^- and water resonances below pH 3.5. The rate of B−C exchange increases with pH, causing the two bisulfite resonances to be coalesced at and above pH 5. We interpret the observed decrease of $1/T_2 - 1/T_1$ of the water with increasing temperature at low pH as the exchange narrowing of the coalesced SO_3H^- and water resonances.

Oxygen Exchange between HSO_3^- and SO_3H^-. The rate law for oxygen exchange out of the HSO_3^- site was found by examining the broadening of the HSO_3^- peak as a function of pH, temperature, and S(IV) concentration. The broadening of the HSO_3^- peak at and below pH 3.5 was analyzed using the slow-exchange limit for two site chemical exchange[22] between site C and the combined A−B site. At these acidities exchange between SO_3H^- and H_2O was fast on the NMR time scale while exchange between either of these sites and HSO_3^- met slow-exchange conditions. Under these conditions the half-width at half-height of the HSO_3^- peak, $(1/T_2)_C$, is given by[22] $(1/T_2)_C = 1/T_{2C} + 1/\tau_C$, where $1/T_{2C}$ is the half-width at half-height due to relaxation processes other than chemical exchange and $1/\tau_C$ is the pseudo-first-order rate constant for oxygen exchange out of site C. Figure 2 shows the line width of the HSO_3^- peak at

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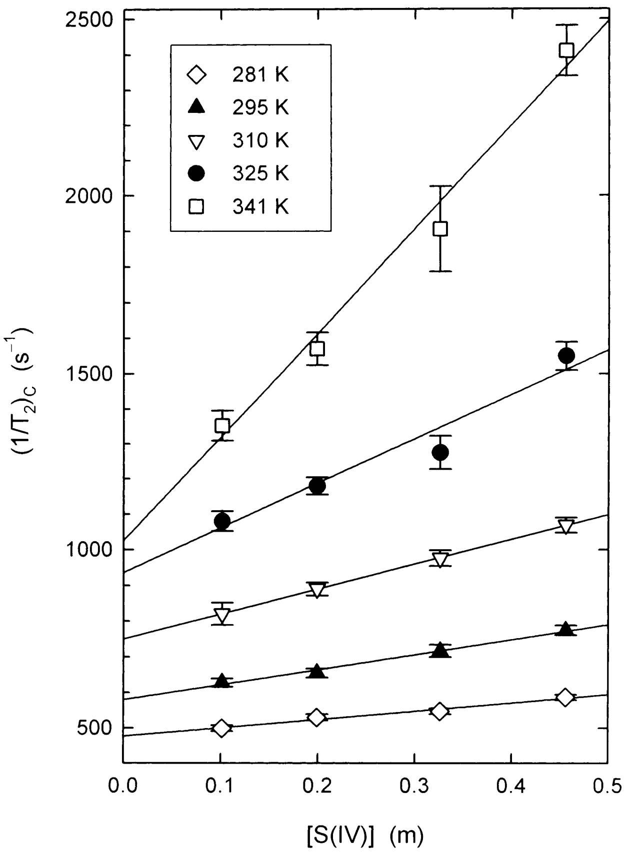

Figure 2. Dependence of the half-width at half-height of the HSO_3^- peak (site C) upon the concentration of S(IV). Data at each temperature were obtained from the same set of four sodium bisulfite solutions. At 25 °C the ionic strength of every solution was 1.0 m, and the H^+ activity as measured by a pH meter ranged from 9.6×10^{-4} to 1.00×10^{-3}. Weighted least-squares fittings of the data at each temperature are shown as solid lines. Data acquired at 274, 287, 303, 318, and 333 K gave similar results (see Supporting Information).

pH 3 and various temperatures as a function of the S(IV) concentration. The plots are essentially linear and have nonzero *y*-intercepts that increase with temperature. Since $1/T_{2C}$ of a quadrupolar nucleus should decrease as temperature increases,[23] $1/\tau_C$ must be the sum of terms that are zero and first order in S(IV).

At least one term in $1/\tau_C$ must be of negative order in $[H^+]$ to account for the broadening of the HSO_3^- peak with increasing pH. A given pH change had a much greater effect upon the line width of the peak in spectra of 0.2 m solutions than in those of 0.1 m solutions, suggesting that the term that is first order in S(IV) is also a function of $[H^+]$. The following comparison of the data of Figure 2 to the change in line width resulting from a pH change of about 0.4 unit in 0.10 m S(IV) solutions shows the [S(IV)]-independent term in $1/\tau_C$ to be essentially independent of $[H^+]$. By extrapolation of 274 K data[24] to [S(IV)] = 0, an upper limit to $1/T_{2C}$ of about 450 s^{-1} is obtained. Because $1/T_{2C}$ decreases as the temperature is raised, it must be less than 450 s^{-1} at 341 K. The total line width at 341 K and [S(IV)] = 0 is about 1050 s^{-1}, so the [S(IV)] independent term in $1/\tau_C$ must be greater than 600 s^{-1} at 341 K. Near this temperature the line width increase produced by changing the pH of 0.1 m solutions from pH 2.58 to pH 3.01 was only 50−100 s^{-1}, some of which is due to the term in $1/\tau_C$ that is first order in S(IV). Hence, the [S(IV)]-independent term must be between 0 and −0.2 power in the hydrogen ion concentration.

To determine the exact hydrogen ion dependence of $1/\tau_C$ we prepared plots of $(1/T_2)_C$ vs $[S(IV)]/\{(a_{H^+})_{298K}\}^p$ for several values of *p*. If $1/\tau_C = N + L[S(IV)]/[H^+]^n$, with *N* and *L* constant, then the plot should be a straight line when $p = n$, provided the activity coefficients have the same values in all the solutions at any given temperature. Graphs of $(1/T_2)_C$ data from solutions having S(IV) concentrations ranging from 0.10 to 0.46 m and pH values ranging from 2.58 to 3.52 were most linear when $p = 1$, suggesting that the $L[S(IV)]/[H^+]^n$ term in $1/\tau_C$ can be written as $L'[SO_3^{2-}]$. However, all the graphs showed systematic deviations from linearity. The data were fitted better when a third term, first order in SHO_3^-, was added to $1/\tau_C$ to give

$$1/\tau_C = N + L'[SO_3^{2-}] + R[SHO_3^-] \qquad (5)$$

In Figure 3, both the experimental values of $(1/T_2)_C$ and those determined from preliminary weighted linear least-squares fits at each temperature to the slow exchange expression, with $1/\tau_C$ given by eq 5, are plotted against $[SO_3^{2-}]$. The quantity $1/T_{2C} + N$ was treated as an adjustable parameter in the least-squares analyses.

Reactions consistent with the rate law of eq 5 are

$$(HSO_3^-)^* + SHO_3^- \xrightleftharpoons{k_6} (SO_3H^-)^* + SHO_3^- \qquad (6)$$

$$(HSO_3^-)^* \xrightleftharpoons[k_{-7}]{k_7} (SO_3^{2-})^* + H^+ \qquad (7)$$

$$(HSO_3^-)^* + SO_3^{2-} \xrightleftharpoons[k_{-8}]{k_8} (SO_3^{2-})^* + SHO_3^- \qquad (8)$$

$$(HSO_3^-)^* + SO_3H^- \xrightleftharpoons{k_9} (SO_3^{2-})^* + SO_2 + H_2O \qquad (9)$$

$$(SO_3^{2-})^* + H^+ \xrightleftharpoons{k_{-10}} (SO_3H^-)^* \qquad (10)$$

$$(SO_3^{2-})^* + SHO_3^- \xrightleftharpoons{k_{-11}} (SO_3H^-)^* + SO_3^{2-} \qquad (11)$$

The asterisk is used to tag the oxygen atoms. Reactions 6, 8, and 11 are not elementary reactions because they contain SHO_3^-. Other reactions that exchange oxygens out of the HSO_3^- site were omitted from the above mechanism either because they are slow compared with reactions 6−11 or are mechanistically improbable.[25] In particular, the mechanism includes no reactions that exchange oxygen atoms between sites C and A. We expect the fastest reaction of this type to be $HSO_3^- + H^+ = SO_2 + H_2O$, but the rate law contains no term that is first order in H^+.

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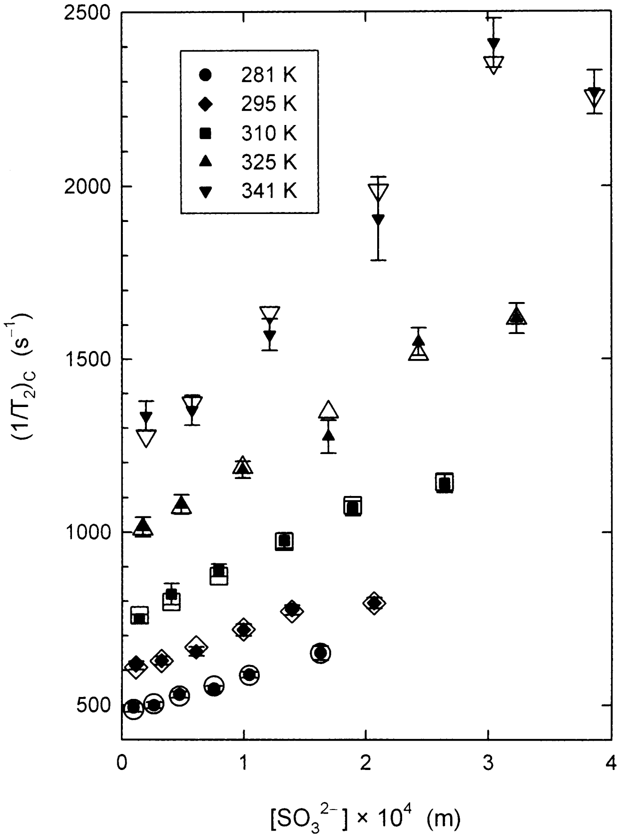

Figure 3. Dependence of the half-width at half-height of the HSO_3^- peak (site C) upon the concentration of SO_3^{2-}. At each temperature the data were obtained from the same set of six sodium bisulfite solutions. At 25 °C the ionic strength of each solution was 1.0 m, and in order of increasing $[SO_3^{2-}]$ the pH meter reading was 2.58, 3.01, 3.00, 3.01, 3.02, and 3.52. The solid symbols and error bars represent the experimental data. The open symbols are points obtained from the weighted linear least-squares fitting of the data at each temperature with the function $(1/T_2)_C = 1/T_{2C} + N + L'[SO_3^{2-}] + R[SHO_3^-]$. The quantity $1/T_{2C} + N$ was treated as a single, adjustable parameter. Data acquired at 274, 287, 303, 318, and 333 K gave similar results (see Supporting Information).

One obtains $1/\tau_C$ from reactions 6−11 by writing the expression for $d[(HSO_3^-)^*]/dt$, from which $[(SO_3^{2-})^*]$ is eliminated by the steady-state approximation. An expression consistent with the empirical rate law is obtained if it is assumed that $k_{-10} \gg k_{-7}$ and $k_{-11} \gg k_{-8}$.[26] Since reaction 10 belongs to the class of rapid reactions involving proton addition to an oxygen of the conjugate base of an inorganic oxyacid, k_{-10} probably exceeds 5×10^{10} M^{-1} s^{-1}.[27] Our data show[26] that proton addition to a sulfite oxygen atom proceeds much more rapidly than protonation of the sulfur atom, i.e., $k_{-10} \gg k_{-7}$, as otherwise these two reactions would lead to rapid isomerization. It is also likely that $k_{-11} \gg k_{-8}$, because reactions 8 and 11 are the general acid−base catalysis analogues of reactions 7 and 10. With these assumptions we obtain[26]

$$1/\tau_C = k_7 + k_8[SO_3^{2-}] + \{k_6 + k_9(1 + 1/Q_4)^{-1}\}[SHO_3^-] \qquad (12)$$

Comparison of this expression with eq 5 yields $N = k_7$, $L' = k_8$, and $R = k_6 + k_9(1 + 1/Q_4)^{-1}$. By assuming Arrhenius behavior for k_7, k_8, and R and that $1/T_{2C}$ is proportional to $1/T_1$ of water,[28] we found k_7, k_8, and R as functions of temperature by a single, 7-parameter weighted-least-squares fitting of the $(1/T_2)_C$ data, with $(1/T_1)_A$, $[SO_3^{2-}]$, $[SHO_3^-]$, and T as the independent variables. We obtained

$1/T_{2C} = (0.364 \pm 0.052)(1/T_1)_A$,

$\ln k_7/s^{-1} = (11.89 \pm 0.23) + (-1658 \pm 74)/T$ (covariance $= -17.29$),

$\ln k_8/(m^{-1}\ s^{-1}) = (19.41 \pm 0.54) + (-1622 \pm 166)/T$, (covariance $= -88.51$), and

$\ln R/(m^{-1}\ s^{-1}) = (26.0 \pm 2.6) + (-6452 \pm 856)/T$ (covariance $= -2205$), where T is in kelvin.

Combination of k_7 and Q_7[29] yielded $\ln k_{-7}/(m^{-1}\ s^{-1}) = (29.59 \pm 0.23) + (-3098 \pm 69)/T$, with a covariance of -15.8.

It should be possible to observe the proton resonance of HSO_3^- if the only mechanisms for exchange of the sulfur-bound proton are those that also produce the slow oxygen exchange with SO_3H^- (including HSO_3^- dissociation). For 0.2 m S(IV) at pH 3.0 and 25 °C the value of $1/\tau_C$ is about 650 s^{-1}. Proton exchange at this rate would yield a broad but distinct proton NMR peak if the resonance is no less than 1600 s^{-1} (1.3 ppm on our instrument) from the water resonance. However, we were unable to detect any solute peak in proton NMR spectra of a 0.2 m sodium bisulfite solution of pH 3 nor in spectra of 0.2, 0.4, and 1 m solutions of pH 2, in which $1/\tau_C$ is small. Suppression of the water peak using the two pulse sequence, lowering the temperature to nearly 0 °C, and shifting the water peak by adding $DyCl_3$ up to 0.02 m all failed to produce an observable solute resonance. The 500 MHz proton NMR spectra of 1 m sodium bisulfite solutions of pH 2 and pH 4.6 also exhibited no solute peak.[30]

Oxygen Exchange between SO_3H^- and H_2O. We investigated oxygen exchange between SO_3H^- and H_2O by studying the broadening of the water peak in the ^{17}O spectra. Because the population of oxygen in water greatly exceeded its populations in either isomer of bisulfite ion, the treatment of Swift and Connick[31] is applicable. Neglect of direct HSO_3^-−H_2O exchange (vide supra) yields as a good approximation

$$\left(\frac{1}{T_2}\right)_A = \frac{1}{T_{2A}} + \frac{p_B}{p_A}\frac{1}{\tau_{BA}} - \frac{p_B}{p_A}\left(\frac{1}{\tau_{BA}}\right)^2 \frac{X + \dfrac{1}{\tau_{BA}}}{\left(X + \dfrac{1}{\tau_{BA}}\right)^2 + Y^2} \qquad (13)$$

where

$$Y = \Delta\omega_B + \frac{p_C}{p_B}\left(\frac{1}{\tau_{CB}}\right)^2 \frac{\Delta\omega_C}{\left(\dfrac{1}{T_{2C}} + \dfrac{1}{\tau_{CB}}\right)^2 + (\Delta\omega_C)^2}$$

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[26] Details may be found in the Supporting Information.

[27] Eigen, M. *Angew. Chem., Int. Ed. Engl.* **1964**, *3*, 1.

[28] See Figure 6S in the Supporting Information for $(1/T_1)_A$ data.

[29] $Q_7 = Q_2(1 + Q_4)$.

[30] McKenna, S. T. Private communication, 2002.

[31] Swift, T. J.; Connick. R. E. *J. Chem. Phys.* **1962**, *37*, 307.

$$X = \frac{p_C}{p_B}\frac{1}{\tau_{CB}}\frac{\left(\frac{1}{T_{2C}}\right)^2 + \frac{1}{T_{2C}}\frac{1}{\tau_{CB}} + (\Delta\omega_C)^2}{\left(\frac{1}{T_{2C}} + \frac{1}{\tau_{CB}}\right)^2 + (\Delta\omega_C)^2} + \frac{1}{T_{2B}}$$

and the symbols have the following meanings:

$(1/T_2)_A$ = the half-width at half-height (line width) of the A (water) peak;

$1/T_{2i}$ = the natural line width of site *i*, i.e., the line width the peak would have in the absence of chemical exchange;

$1/\tau_{ij}$ = the pseudo-first-order rate constant for oxygen exchange from site *i* to site *j*;

p_i = the fraction of ^{17}O nuclei that are in site *i*;

$\Delta\omega_i$ = the precession frequency of the ^{17}O nuclei in site *i* in the absence of chemical exchange minus the spectral frequency at which the water peak has its maximum height.[32]

The pseudo-first-order rate constant for oxygen exchange between the SO_3H^- site and H_2O, $1/\tau_{BA}$, was evaluated from eq 13. The value of $1/T_{2A}$ was assumed to equal $(1/T_1)_A$. We set $1/T_{2C}$ equal to the value obtained from the fitting of the HSO_3^- line width data (vide supra) and estimated that $1/T_{2B}$ was equal to $(1/T_1)_A \pm 100\%$, but $1/\tau_{BA}$ was relatively insensitive to these values.[33] Equation 5 was used to calculate $1/\tau_{CB}$. In calculating the population ratios p_C/p_B and p_B/p_A, we assumed that resonances of the minor species $S_2O_5^{2-}$, SO_2, and SO_3^{2-} were coalesced with that of SO_3H^-, so that the B site comprised these species.[34] (In solutions with S(IV) concentrations greater than 4 m the $S_2O_5^{2-}$ did contribute significantly to peak areas and the $S_2O_5^{2-}$ and bisulfite resonances were coalesced.) The values of $\Delta\omega_B$ and $\Delta\omega_C$ were approximately 33 500 and 30 200 s^{-1}, respectively, and were corrected for small changes resulting from the coalescence of the A and B resonances at low pH.[35]

For any $(1/T_2)_A$ two values of $1/\tau_{BA}$ are obtained upon solving eq 13. When both were real and positive, we chose the correct value by examining Figure 1 to see whether the water peak broadened (smaller value) or narrowed (larger value) as the temperature increased. In spectra of pH 5 solutions the HSO_3^- and SO_3H^- peaks were coalesced; in these cases we calculated a second value of $1/\tau_{BA}$ from the width of the S(IV) peak. Because the exchange between bisulfite ion and water was in the slow-exchange limit at pH 5, the half-width at half-height of the S(IV) peak is $(1/T_2)_S = 1/T_{2S} + 1/\tau_{SA}$, where the combined S(IV) site is labeled with the letter S. To obtain $1/\tau_{BA}$ we replaced $1/\tau_{SA}$ with $[p_B/(p_B + p_C)](1/\tau_{BA})$ and calculated $1/T_{2S}$, the line width of the S(IV) peak in the absence of oxygen exchange with water, using the two-site exchange expression

$$\frac{1}{T_{2S}} = \left(\frac{p_B}{p_B + p_C}\right)\frac{1}{T_{2B}} + \left(\frac{p_C}{p_B + p_C}\right)\frac{1}{T_{2C}} + \frac{p_B^{\,2}p_C^{\,2}}{(p_B + p_C)^4}(\Delta\omega_B - \Delta\omega_C)^2(\tau_{BC} + \tau_{CB}) \quad (14)$$

for the width of the exchange narrowed S(IV) peak.[22] Values of $1/\tau_{BA}$ determined in this manner agreed well with those obtained from the water peak line width data.

Betts and Voss[3] measured the rate of oxygen exchange between S(IV) species and water in basic solutions and found a rate law consistent with the existence of three single-step oxygen exchange reactions:

$$SO_3H^- + H^+ \underset{k_{15}}{\overset{k_{-15}}{\rightleftarrows}} SO_2 + H_2O, \quad (15)$$

$$(SO_3H^-)^* + SHO_3^- \overset{k_{16a}}{\rightleftarrows} (SO_2)^* + (H_2O)^* + SO_3^{2-} \quad (16a)$$

and

$$(SO_3H^-)^* + SHO_3^- \overset{k_{16b}}{\rightleftarrows} S_2(O_2)^*O_3^{2-} + (H_2O)^* \quad (16b)$$

In acidic solutions, the pseudo-first-order rate constant, $1/\tau_{BA}$, for oxygen exchange between sites B and A due to the above reactions has the form

$$\frac{1}{\tau_{BA}}\left(\frac{p_B}{p_{SO_3H^-}}\right) = \frac{1}{3}(k_{-15}[H^+] + k_{16}[SHO_3^-]) \quad (17)$$

where $p_{SO_3H^-}$ is the fraction of oxygen nuclei present in SO_3H^- and $k_{16} = k_{16a} + k_{16b}$. To compare our data with this rate law, we examined the dependence of $1/\tau_{BA}$ upon $[H^+]$ and $[SHO_3^-]$. The dependence of $(1/\tau_{BA})(p_B/p_{SO_3H^-})$ upon hydrogen ion concentration for six solutions having $[SHO_3^-]$ = 0.19 m is shown in Figure 4. The variation of the ordinate with $[H^+]$ is due almost entirely to changes in $1/\tau_{BA}$, because the values of $(p_B/p_{SO_3H^-})$ all fall between 1.04 and 1.07. At high acidity $1/\tau_{BA}$ approaches first order in $[H^+]$ but shifts to a smaller order at lower acidities. At each temperature the data are fitted well (dashed curves) by the expression

$$\frac{1}{\tau_{BA}}\left(\frac{p_B}{p_{SO_3H^-}}\right) = G[H^+] + F \quad (18)$$

where *F* and *G* are temperature-dependent parameters. The data in Table 1 show that $1/\tau_{BA}$ is independent of [S(IV)] at pH 3, where *F* is insignificant, and therefore, *G* must be zero order in S(IV), in agreement with eq 17.

Above pH 3 the *F* term is nonnegligible, and $1/\tau_{BA}$ increases with increasing [S(IV)]. Figure 5 shows plots of the function $(1/\tau_{BA})(p_B/p_{SO_3H^-}) - G[H^+]$ vs $[SHO_3^-]$ at each temperature for solutions having a pH of 5, all at 1.0 m ionic strength except for the solution having $[SHO_3^-]$ = 0.69 m, which had an ionic strength of 0.9 m. The data are not highly precise because the H_2O peak is only slightly broadened at pH 5. Nevertheless, the data in Figure 5 do suggest that *F* is proportional to $[SHO_3^-]$. Although the points from the 0.19 m solution lie above lines drawn through the origin, a nonzero *y*-intercept in Figure 5 would correspond to a term in *F* that contains $[SHO_3^-]$ to zero or a negative power. Such a term could be explained by adding the reaction $SO_3H^- \rightarrow$

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(32) This is not Swift and Connick's definition of $\Delta\omega_i$, but it is a good approximation because the chemical shifts of the S(IV) peaks relative to water were large in comparison to changes in the position of the water peak.

(33) Reference 25, pp 93−96.

(34) Reference 25, pp 75−77.

(35) Reference 25, pp 98−103.

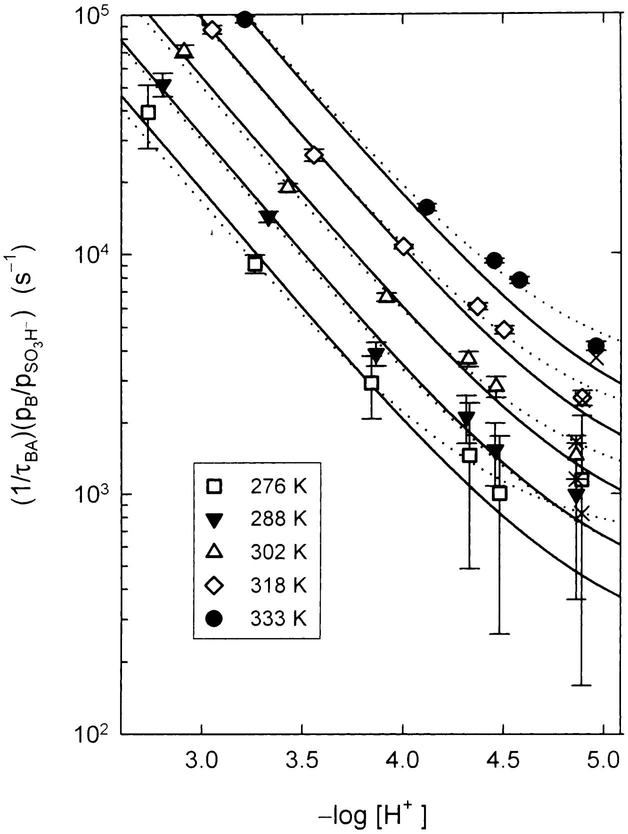

Figure 4. Product of the pseudo-first-order rate constant for exchange of ^{17}O from site B to H_2O (site A) and the population ratio of all oxygens in site B to oxygens in SO_3H^-, plotted as a function of $-\log [H^+]$ for six different sodium bisulfite solutions of [S(IV)] = 0.20 m and ionic strength 1.0 m. Solid and open symbols denote values obtained from analysis of the broadening of the water peak in the ^{17}O NMR spectra of the solutions, while the × symbols denote values obtained through analysis of the broadening of the coalesced S(IV) peak (located at ca. 192 ppm) in the spectrum of the solution of highest pH. Uncertainties on the S(IV) data are not shown but are smaller than the uncertainties in the corresponding water peak data. Each dotted curve represents the weighted linear least-squares fitting of the expression $F + G[H^+]$ to the displayed water peak data at a single temperature, while the solid curves show the values of $(k_{-15}[H^+] + k_{16}[SO_3H^-])/3$ obtained by a single fitting of the water peak $1/\tau_{BA}$ data at all temperatures, pH values, and S(IV) concentrations with the function given in eq 17. Data acquired at 282, 295, 310, 325, and 341 K gave similar results (see Supporting Information).

$SO_2 + OH^-$ to the proposed oxygen exchange mechanism but is ruled out by Betts and Voss' data.[3] They found no evidence for a term of this sort, although it would necessarily have been the dominant term in their basic solutions. Even if their largest oxygen exchange rate were attributed to such a term, it is easily shown that this term would be negligible at pH 5. It is thus likely that the points in Figure 5 corresponding to $[SHO_3^-] = 0.19$ m contain a systematic error. The data from this solution are also graphed as the pH 5 data in Figure 4, where the likely systematic error appears as $1/\tau_{BA}$ values that seem too large.

Having tentatively established that the rate law of eq 17 accounts for our data, the $1/\tau_{BA}$ data at every temperature, pH, and bisulfite ion concentration were fitted with the form of eq 17 in which the Arrhenius parameters of k_{-15} and k_{16} served as regression parameters. Weighted nonlinear least-squares fitting of the data yielded $\ln k_{-15}/(m^{-1}\ s^{-1}) = (30.54 \pm 0.11) + (-3511 \pm 36)/T$, with a covariance of −4.12, and $\ln k_{16}/(m^{-1}\ s^{-1}) = (19.52 \pm 0.37) + (-3141 \pm 120)/T$, with a covariance of −44.34, where T is in kelvin. Results of this fitting are shown as the solid curves in Figures 4 and 5. To confirm the rate law of eq 17, the line broadenings predicted by these values of k_{-15} and k_{16} were calculated. The results, shown as the solid curves of Figure 1, compare favorably with the experimental line broadenings.

Oxygen Exchange between Bisulfite Ion and Disulfite Ion ($S_2O_5^{2-}$). No separate $S_2O_5^{2-}$ resonance was observed in the ^{17}O NMR spectra of any of our solutions. In particular, in spectra of a solution in which both $S_2O_5^{2-}$ and SHO_3^- made an appreciable contribution to peak areas ([S(IV)] = 4.7 M), the $S_2O_5^{2-}$ and SHO_3^- resonances were apparently coalesced with each other but not with the water peak. By what mechanism is oxygen exchanged between bisulfite ion and disulfite ion? The mechanism proposed earlier for exchange between SHO_3^- and $S_2O_5^{2-}$, reaction 16b, also produces oxygen exchange between bisulfite ion and water. We attempted to determine whether an exchange process such as (16b) can account for the simultaneous existence of a coalesced S(IV) peak and a separate water peak due to the large chemical shift of water relative to the S(IV) species or whether the peak pattern requires the existence of an additional $SHO_3^- - S_2O_5^{2-}$ oxygen exchange pathway that does not produce oxygen exchange between these species and water, such as $SO_2 + SHO_3^- \rightleftarrows S_2O_5^{2-} + H^+$.

We acquired spectra of a solution in which [S(IV)] = 4.7 M and pH = 4.5 at several temperatures between 258 and 323 K, conditions for which the populations of oxygen atoms in the SHO_3^- and $S_2O_5^{2-}$ environments were approximately equal.[36] Analysis of the line width and chemical shift data revealed that the chemical shift of $S_2O_5^{2-}$ is roughly 164 ppm and that the psuedo-first-order rate constant for oxygen exchange from SHO_3^- to $S_2O_5^{2-}$ exceeds 1500 s^{-1} at 263 K. The spectral features described above do not require a $SHO_3^- - S_2O_5^{2-}$ oxygen exchange mechanism other than reaction 16b yet do not exclude such reactions. Moreover, k_{16b} is likely greater than or equal to k_{16a}. Details may be found in the Supporting Information.

Discussion

Several possible explanations exist for our inability to observe the HSO_3^- peak in proton NMR spectra. First, our assignment of the 175 and 195 ppm resonances to HSO_3^- and SO_3H^-, respectively, may be incorrect, in which case both HSO_3^- and SO_3H^- would exchange protons rapidly with water, the former via reaction 1 and the latter via reaction 10. This possibility seems ruled out by the results of Littlejohn et al., who showed that the temperature dependence of the intensity of the Raman H−S stretch of bisulfite solutions matched qualitatively that of the ^{17}O NMR resonance at 175 ppm.[21] A second, more likely reason is that the HSO_3^- and H_2O peaks in the proton spectrum were

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[36] The spectrometer on which the spectra of the 4.7 M and 0.800 m solutions were acquired was similar to the spectrometer described in the Experimental Section but had a magnetic field strength of 4.2 T, corresponding to an ^{17}O Larmor frequency of 24.4 MHz. It accepted 20 mm (outside diameter) sample tubes.

Table 1. Effect of S(IV) Concentration upon $(1/\tau_{BA})(p_B/p_{SO_3H^-})$ at pH 3 and Various Temperatures

			$10^{-3}(1/\tau_{BA})(p_B/p_{SO_3H^-})$ (s^{-1})					
$-\log [H^+]^a$	[S(IV)] (m)	$p_B/p_{SO_3H^-}{}^a$	288 K	295 K	310 K	318 K	333 K	340 K
2.89	0.101	1.04	47 ± 12	52 ± 10	71 ± 7	80 ± 6	81 ± 4	83 ± 5
2.88	0.199	1.06	51 ± 6	60 ± 5	79 ± 4	87 ± 3	96 ± 3	93 ± 3
2.89	0.326	1.07	51 ± 5	62 ± 4	76 ± 3	82 ± 2	92 ± 3	94 ± 3
2.90	0.456	1.09	50 ± 3	54 ± 4	75 ± 3	80 ± 2	85 ± 3	87 ± 3

[a] At 298 K.

coalesced or fortuitously superimposed. Third, if there exists any mechanism, such as $H^*SO_3^- + H^+ \rightleftarrows HSO_3^- + (H^+)^*$ or $H^*SO_3^- + H_2O \rightleftarrows HSO_3^- + H^*HO$, that exchanges protons between HSO_3^- and H_2O without leading to oxygen exchange between HSO_3^- and other species, then our estimate of $1/\tau$ for proton exchange would be too low.

Isomerization of HSO_3^- to SO_3H^- proceeds primarily via proton removal from HSO_3^-. In our solutions, proton transfer to SO_3^{2-} (reaction 8) was more rapid above pH 3.5 than proton transfer to a water molecule (reaction 7), while isomerization via reactions 6 and 9 was a minor contributor under all conditions. From the ratio k_8/k_7 one calculates the exponent β in Brønsted's equation[37] for base catalysis of HSO_3^- dissociation to be 0.6 at 298 K, a value typical of general base catalysis. General acid−base catalysis is of course expected when the rate-determining step involves proton transfer. The rate of addition of H^+ to SO_3^{2-} to form HSO_3^- is well below the diffusion limit, in contrast to the rate of association expected for the same two ions to form the oxyacid. The rate constant for acid dissociation of SO_3H^- is about 50 times greater than that for the dissociation of HSO_3^- at room temperature. Dissociation and recombination of SO_3H^- are sufficiently fast to make all three SO_3H^- oxygens equivalent on the NMR time scale provided the S−O and S−O−H resonances are separated by no more than a few thousand hertz.

Agreement between the experimental data and the predicted curves in Figures 1, 4, and 5 is quite good considering that only four adjustable parameters were used to fit data covering a wide range of temperature, $[SHO_3^-]$, and pH. The poorer quality of fit at high and low temperatures suggests some inaccuracy in the temperature measurements, but the directions of the deviations are incompatible with a consistent systematic error. In some parts of Figure 1 the predicted water peak broadenings are systematically too small. Most likely these deviations arose from an underestimate of the inhomogeneity correction. The deviations of experimental data from the predicted curves of Figure 5 were discussed earlier. No significant improvement in fitting the data was obtained by adding other reasonable oxygen exchange mechanisms.

Table 2 lists the rate constants evaluated in this work and the corresponding enthalpies and entropies of activation. The uncertainties assigned to our values are unusually small because they are standard deviations of least squares parameters and, therefore, may underestimate the actual uncertainties significantly.

The activation entropies in Table 2 are reasonable for reactions of ions in aqueous solution.[38] The entropy of activation for the dissociation of the HSO_3^- isomer, $\Delta S_7^{\ddagger} = -38$ cal/(mol K), seems unusually negative, but the net entropy change for this reaction is −45 cal/(K mol).[7,39] In an acid dissociation reaction most of the overall entropy change should appear in $\Delta S^{\ddagger}$ because the activated complex will have the proton already well separated from the anion.

In their study of oxygen exchange between SO_3^{2-} and water, Betts and Voss[3] found evidence for an exchange process that is second order in S(IV), which they attributed to the dimerization of bisulfite ion (reaction 3). We also detected an exchange process that is second order in S(IV), but ascribe it to two reactions: 16a and 16b. Although neither our data nor those of Betts and Voss distinguish between reactions 16a and 16b, we think it likely that reaction 16a, the general acid−base catalysis analogue of reaction 15, contributes appreciably to oxygen exchange with water. Not only would general acid−base catalysis be expected for reaction 15, but the ratio k_{-15}/k_{16} is consistent with the Brønsted relation for acid−base catalysis.[37] The experimental value of this ratio is reproduced when Brønsted's exponent α is about 0.5. Tolmachev and Scherson[5] also found evidence for general acid catalysis of the formation of SO_2 from bisulfite ion. Nevertheless, this reasoning in no way rules out reaction 16b. Reaction 9, one of the two elementary reactions that contribute to reaction 16a, is unimportant because the upper limit to k_9 is about 90 m^{-1} s^{-1} at 298 K, compared with a value of k_{16} of about 8000 m^{-1} s^{-1}. Because isomerization of HSO_3^- is slow, the reactions of SO_3H^- with HSO_3^- must not contribute significantly to k_{16}.

In Table 3 our rate constants for reactions that exchange oxygen between bisulfite ion and water are compared with those obtained by other workers. The distinction between molar and molal units is probably unimportant compared to uncertainties in the rate constant values. The existence of two isomers of bisulfite ion necessitated a reinterpretation of the data of Eigen et al.[2] Reaction 15 is much more rapid than both reaction 16 and the isomerization reaction at the acidities at which Eigen et al. worked, so their measured relaxation time, τ_{II}, may be attributed to reaction 15 only, i.e., $\tau_{II} = \{k_{-15}([H^+] + [SO_3H^-] + Q_{15})\}^{-1}$. Their relaxation time data then yielded a value of k_{-15}, from which we calculated k_{-1} at 0.1 m ionic strength. This value was also

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(37) (a) Bell, R. P. *Acid−Base Catalysis*; Clarendon: Oxford, U.K., 1941; Chapter V. (b) *The Proton in Chemistry*, 2nd ed.; Cornell: Ithaca, NY, 1973; Chapter 10.

(38) Frost, A. A.; Pearson, R. G. *Kinetics and Mechanism*; Wiley: New York, 1953; Chapter 7.

(39) Wagman, D. D.; Evans, W. H.; Parker, V. B.; Schumm, R. H.; Halow, I.; Bailey, S. M.; Churney, K. L.; Nuttall, R. L. *J. Phys. Chem. Ref. Data* **1982**, *11*, Suppl. 2.

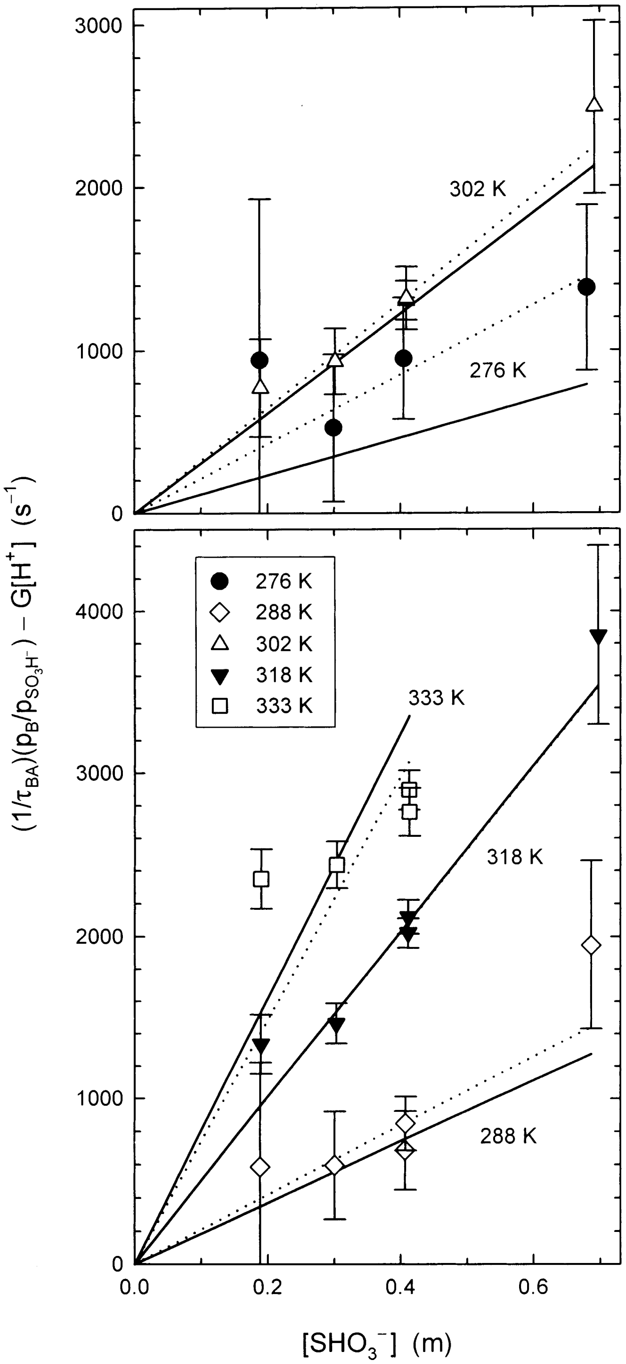

Figure 5. Graph of $(1/\tau_{BA})(p_B/p_{SO_3H^-}) - G[H^+]$ vs the calculated concentration of bisulfite ion for five different sodium bisulfite solutions having room-temperature pH values ranging from 4.97 to 5.13. The most concentrated solution ($[SHO_3^-] = 0.69$ m) had an ionic strength of 0.90 m, while the other four had ionic strengths of 1.0 m. Each dashed line represents the weighted least-squares fitting of the data at a single temperature, while the solid lines represent the values of $k_{16}[SHO_3^-]/3$ obtained by a single fitting of the data at all temperatures, pH values, and S(IV) concentrations with the function given in eq 17. Data acquired at 282, 295, 310, 325, and 341 K gave similar results (see Supporting Information).

corrected to ionic strength 1.0 m using Pitzer's equations[40] and the ionic interaction parameters of Rosenblatt[41] to estimate the activity coefficients of the reactants and activated complex of reaction 15 for a solution composition of 0.2 m $NaHSO_3$ and 0.8 m NaCl.[42]

Our experimental value of k_{-1} agrees well with that of Eigen et al. (compare the fifth and sixth entries of Table 3) but is less than one-third of Reynolds and Yuan's value[4] and is 1 order of magnitude smaller than the value reported by Tolmachev and Scherson.[5] Although our rate law agrees with that of Betts and Voss,[3] our rate constants differ substantially from theirs. Betts and Voss' reported value of k_{-1} exceeds ours by about a factor of 20 but really differs by a factor of 60 because their reported rate constants are inexplicably smaller, by a factor of 3, than those we calculated from their data. Betts and Voss' value of k_{-1} is nearly equal to that of a diffusion-controlled reaction, surprisingly large for a reaction that involves the breaking of a sulfur−oxygen bond.

Reynolds and Yuan's value of k_{-1} is presumably less precise than the others in Table 3 because it was determined from measurements at just two pH values. Rate constants determined by their polarographic method contain a systematic error if, as seems likely, the conversion of bisulfite ion to SO_2 is catalyzed by the buffer. Tolmachev and Scherson's data are not fitted well by their general acid catalysis model. In particular, the slope of the pH dependence of their Figure 3 does not match the expected value, and the precision of the fitting of their rate data as a function of H^+ and acetic acid concentrations decreased markedly when the data set was enlarged to include more than one pH. Furthermore, although both groups worked at high ionic strengths, neither made activity coefficient corrections in analyzing their data. Consequently the rate constants found by these groups can only be taken as quite approximate.

We were especially uneasy with discrepancies between our results and those of Betts and Voss because of the simplicity of their method. Surprisingly, oxygen exchange rates calculated[26] from our rate constants agree with Betts and Voss' rate vs pH data at a fixed [S(IV)] of 0.30 M (their Figure 1). For example, at pH 9.80 and $[SO_3^{2-}] = 0.30$ M we calculate $-\log[\text{rate}/(\text{m}^{-1}\ \text{s}^{-1})] = 3.89$, while Betts and Voss' Figure 1 gives $-\log[\text{rate}/(\text{M}^{-1}\ \text{s}^{-1})] = 3.85$. Betts and Voss' plot of −log(rate) vs $1/T$ at $[S(IV)] = 0.30$ M (their Figure 3) also agrees well with one calculated from our rate constants. We also carried out an oxygen exchange experiment[43] to verify Betts and Voss' rate data: we prepared a 0.30 m sodium sulfite solution by dissolving sodium sulfite in ^{17}O-enriched water, adjusted the pH to 10.0 with HCl, and then measured the areas of the SO_3^{2-} and H_2O peaks[44] in the ^{17}O NMR spectrum at 14 different times between 0 and 105 h. Analysis[45] of these data yielded $-\log[\text{rate}/(\text{m}^{-1}\ \text{s}^{-1})] = 4.50$ at 21.3 °C, compared with Betts and Voss' value of $-\log[\text{rate}/(\text{M}^{-1}\ \text{s}^{-1})] = 4.22$ at 24.7 °C. Although the

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(40) Pitzer, K. S. *J. Phys. Chem.* **1973**, *77*, 268.

(41) Rosenblatt, G. M. In *Flue Gas Desulfurization*; Hudson, J. L., Rochelle, G. T., Eds.; ACS Symposium Series 188; American Chemical Society: Washington, DC, 1982; p 57.

(42) Reference 25, pp 129−131.

(43) This experiment was done on the Bruker NMR spectrometer described in the Experimental Section.

(44) The SO_3^{2-} resonance was observed at 210 ppm.

(45) Duffield, R. B.; Calvin, M. *J. Am. Chem. Soc.* **1946**, *68*, 557.

Table 2. Summary of Rate Constants Obtained in This Study

rate const	value at 298 K	Arrhenius parameters ln *A*	E_a/R (K)	covariance[a]	$\Delta H_{298}^{\ddagger}$ (kcal mol^{-1})	$\Delta S_{298}^{\ddagger}$ (cal K^{-1} mol^{-1})
k_7	$(5.6 \pm 0.1) \times 10^2$ s^{-1}	11.89 ± 0.23	1653 ± 74	−17.3	2.7 ± 0.1	-37.9 ± 0.5
k_{-7}	$(2.08 \pm 0.06) \times 10^8$ m^{-1} s^{-1}	29.59 ± 0.23	3098 ± 69	−15.8	5.6 ± 0.1	-1.7 ± 0.5
k_8	$(1.17 \pm 0.05) \times 10^6$ m^{-1} s^{-1}	19.41 ± 0.54	1622 ± 166	−88.5	2.6 ± 0.3	-22 ± 1
k_{-15}	$(1.40 \pm 0.01) \times 10^8$ m^{-1} s^{-1}	30.54 ± 0.11	3511 ± 36	−4.12	6.38 ± 0.07	0.2 ± 0.2
k_{16}[b]	$(8.0 \pm 0.3) \times 10^3$ m^{-1} s^{-1}	19.52 ± 0.37	3141 ± 120	−44.3	5.6 ± 0.2	-21.7 ± 0.7

[a] Covariance of ln *A* and $-E_a/R$. [b] $k_{16} = k_{16a} + k_{16b}$ (see text). For comparison, the single oxygen-exchange experiment at pH 10.0 and 21.3 °C yielded $k_{16} = 5 \times 10^3$ m^{-1} s^{-1}.

Table 3. Comparison of Rate Constants of Reactions That Exchange Oxygen Atoms between Bisulfite Ion and Water

$$SHO_3^- + H^+ \xrightarrow{k_{-1}} SO_2 + H_2O$$

k_{-1}	Reference	T (°C)	ionic strength
$(2.5 \pm 0.3) \times 10^{9\ a,c}$	3	24.7	0.9 M
$(1.15 \pm 0.01) \times 10^{8\ b,d}$	this work	24.7	1.0 m
$(1.2 \pm 0.15) \times 10^{9\ a}$	5	23.3 ± 0.3	0.5 M
$1._9 \times 10^{8\ a,d,e}$	2	20	0.1 m
$1._2 \times 10^{8\ b,f}$	2	20	1.0 m
$(9.7 \pm 0.1) \times 10^{7\ b,d}$	this work	20.0	1.0 m
$3.7 \times 10^{8\ a}$	4	not reported	1.0 M

$$2\ SHO_3^- \xrightarrow{k_A} SO_2 + H_2O + SO_3^{2-} \qquad 2\ SHO_3^- \xrightarrow{k_B} S_2O_5^{2-} + H_2O$$

$k = k_A + k_B$	reference	T (°C)	Ionic strength
$700 \pm 200^{\ a,c}$	3	24.7	0.9 M
$6600 \pm 240^{\ b,g}$	this work	24.7	1.0 m

[a] Units are M^{-1} s^{-1}. [b] Units are m^{-1} s^{-1}. [c] Value reported in ref 3. The data from ref 3 yield a value three times greater (see text). [d] Calculated using $k_{-1} = k_{-15}/(1 + Q_4^{-1})$. [e] Obtained by first calculating k_{-15} using data from ref 2 (see text). The value of k_{-1} in ref 2 was reported to only one significant figure. [f] Estimated value, obtained by applying approximate activity coefficient correction to value at ionic strength 0.1 m. [g] Calculated using $k = k_{16}/(1 + Q_4^{-1})$.

factor of 2 discrepancy is puzzling, Betts and Voss' rate vs pH data at 0.3 M S(IV) are generally confirmed.

Our rate constants do not reproduce Betts and Voss' oxygen exchange rates for other S(IV) concentrations (their Figures 2 and 4). While Betts and Voss found an overall reaction order in S(IV) of 1.15 ± 0.03, our results predict that the observed order in S(IV) would be 2 at their pH. Betts and Voss allowed the ionic strengths of their solutions to range from 0.90 to 1.80 M and at 0.90 M adjusted ionic strength by replacing the 2−1 electrolyte Na_2SO_3 with a 1−1 electrolyte. When Betts and Voss' data are corrected for ionic strength differences,[26] their observed order in S(IV) increases to about 1.5 and their rate constants come closer to ours, but a substantial discrepancy remains.

In most of Betts and Voss' experiments a boric acid buffer (no concentrations given) was used to stabilize the pH. Possibly the boric acid was providing general acid catalysis so that at low sulfite concentrations the reaction was first order in sulfite ion and boric acid while at high sulfite ion concentrations it approached second-order sulfite ion dependence. Boric acid is a known general acid catalyst.[46] This interpretation would be consistent with our finding at pH 10 of a rate ca. 2-fold lower than the Betts and Voss rate. Moreover, in two experiments where they adjusted the pH with hydrochloric acid rather than boric acid buffer, Betts and Voss' rates were ca. 3-fold lower than in their experiments with boric acid buffer. In the three experiments where their pH was adjusted with ammonia, the rates were about the same as with boric acid buffer, but ammonium ion could have increased the rate by general acid catalysis as its acid ionization constant is close to that of boric acid.

The uncertainty in the S(IV) dependence along with their extremely high value of k_{-1} makes Betts and Voss' results questionable. This uncertainty could be removed by measuring the [SO_3^{2-}] dependence of the oxygen exchange rate under more carefully controlled conditions.

Our rate constant, k_{-15}, is only 1000 times smaller than that of a diffusion controlled reaction. It differs markedly

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(46) Bell, R. P.; Edwards, J. O.; Jones, R. B. In *The Chemistry of Boron and its Compounds*; Muetterties, E. L., Ed.; Wiley: New York, 1967; p 218.

from the rate constant of the analogous reaction between hydrogen ion and bicarbonate ion, which has a room-temperature value of $6 \times 10^4\ M^{-1}\ s^{-1}$.[47] It is known that the hydrogen in HCO_3^- is bonded to an oxygen atom. For this reason Eigen, Kustin, and Maass suggested that the HSO_3^- isomer is responsible for the high rate of reaction 1, but our results show that SO_3H^- reacts more rapidly with H^+ to produce SO_2 and H_2O. The great difference in rates between the bisulfite and bicarbonate reactions may be due to the small amount of atomic rearrangement needed for the O−S−O remnant of bisulfite ion to attain the bent SO_2 structure compared with the amount required to transform the O−C−O fragment to linear CO_2.

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Supporting Information Available: Plots of data for solutions and temperatures not shown in Figures 1−5, a figure showing $(1/T_1)_A$ vs T, details of the analysis of the rate law derived from reactions 6−11, details of the analysis of oxygen exchange between bisulfite ion and disulfite ion, and details of the comparison of our rate constants to those of ref 3. This material is available free of charge via the Internet at http://pubs.acs.org.

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(47) Gibbons, B. H.; Edsall, J. T. *J. Biol. Chem.* **1963**, *238*, 3502.