UC-114
LBL-28337
Preprint

Lawrence Berkeley Laboratory
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APPLIED SCIENCE DIVISION

Submitted to Inorganic Chemistry

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March 1990

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LBL-28337

The Chemistry of the Isomers and Dimer of Bisulfite Ion

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This work was supported by the Assistant Secretary for Fossil Energy, Office of Coal Utilization Systems, U.S. Department of Energy under Contract No. DE-AC03-76SF00098 through the Pittsburgh Energy Technology Center, Pittsburgh, PA.

Abstract

Raman measurements of the isomers of bisulfite ion have been used to determine the equilibrium quotient, Q_1, for the isomerization process. From the Raman peak areas of the isomers, a value of $Q_1 = 5.7$ is obtained at 298 K for solutions with an ionic strength of < 0.4 m. The effects of temperature and pH on Q_1 have been investigated and are reported. The bisulfite ion dimerization process to form $S_2O_5^{2-}$ has also been studied by Raman spectroscopy. A value of $Q_2 = 0.062\ M^{-1}$ is found for the dimerization reaction in a solution of [S(IV)] = 1 m at an ionic strength of 1 m and 298 K. The effects of ionic strength, concentration, temperature, and pH on Q_2 are discussed.

The chemistry of sulfur dioxide dissolved in aqueous solutions has been under investigation for many years, but is still not completely understood[1,2,3]. Knowledge of the behavior of SO_2 dissolved in aqueous solutions is of vital importance in understanding the chemistry that occurs in atmospheric aerosols and in aqueous flue gas desulfurization systems. Bisulfite ion can exist in two isomeric forms in aqueous solutions[4]. In one isomer, the hydrogen is bound to one of the oxygen atoms, and in the other isomer, the hydrogen is bound to the sulfur atom.

$$HOSO_2^- \rightleftharpoons HSO_3^- \qquad (1)$$

The equilibrium quotient for this process, Q_1, is given as

$$Q_1 = [HOSO_2^-] / [HSO_3^-]. \qquad (2)$$

At high concentrations, bisulfite ion can dimerize to form $S_2O_5^{2-}$, referred to as the pyrosulfite or disulfite ion (SHO_3^- will be used to refer to bisulfite ion when not referring to a specific isomer).

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

The equilibrium quotient for dimerization can be expressed as

$$Q_2 = [S_2O_5^{2-}] / [SHO_3^-]^2 \qquad (4)$$

There is evidence[2,5] for another dimer which acts as an intermediate in the formation of $S_2O_5^{2-}$.

$$HSO_3^- + HOSO_2^- \rightleftharpoons (SHO_3^-)_2 = S_2O_5^{2-} \qquad (5)$$

This intermediate, referred to as Golding's dimer, appears to exist in appreciable amounts at low bisulfite ion concentrations[5].

Only one study has been done on the isomerization of bisulfite ion. Horner and Connick[4] used O^{17} NMR to elucidate the relative amounts of the two isomers in solution by comparing the NMR peaks of the isomers with the NMR peak of water. There have been several studies of the dimerization process under a variety of conditions[3,6,7,8]. The agreement between the studies has less than satisfactory. The studies have utilized either UV spectroscopy or a combination of UV and Raman spectroscopy to determine the concentrations of the sulfur oxyanions in solution. In addition,

most studies have been made in the temperature range of 20 to 25°C. The results are summarized in Table I.

In an attempt to improve the understanding of the aqueous chemistry of dissolved sulfur dioxide, we have performed a study of aqueous solutions of bisulfite ion over a range of conditions using Raman spectroscopy. The results obtained are compared with earlier studies.

Experimental Section

Analytical grade reagents were used in the preparation of the solutions. Deionized water was used in preparation of the solutions. Solutions were degassed with high purity nitrogen or argon before the addition of sodium metabisulfite. The pH of the solutions were checked with a Corning model 130 pH meter with a Sensorex S200C combination pH electrode that was periodically calibrated with standard buffer solutions. Hydrogen ion concentrations were calculated from the pH reading, assuming that $pH = -\log_{10}(a_{H^+})$. The values of pH mentioned here are those read from the pH meter.

Raman spectra of the solutions were obtained using a Spex 1403 double monochromator interfaced to a Spex Datamate data aquisition system. Samples were illuminated with approximately 0.2 w of 514.5 nm radiation from a Coherent Innova 90-5 argon ion laser. A polarization scrambler was placed between the sample and the monochromator entrance slit. The samples were contained in a 1 mm diameter Pyrex capillary tube, which formed the inner tube of a double-walled coaxial cell. Deionized water from a circulating thermostatted bath was flowed at a constant rate between the inner and outer walls of the cell. The temperature of the circulating water was maintained within ±1°C of the desired temperature. This arrangement permitted Raman spectra to be collected from samples at temperatures of 2 to 67°C. Dry nitrogen was directed at the outer wall of the cell when operating at low temperatures to avoid problems with condensation. The temperatures within the inner tube of the coaxial cell were determined by inserting a fine chromel-alumel thermocouple into the inner tube at each of the settings used on the thermostatted bath.

Two methods were used to transfer the sample to the cell that would minimize the potential for oxidation. In one arrangement, the sample section of the cell was filled by slowly flowing the solution through plastic tubing directly from the flask where it was kept under an inert atmosphere. In the second arrangement, a 5 cc syringe was filled with the sample under an inert atmosphere and was used to inject the solution into the cell through a short length of plastic tubing.

Raman spectra were obtained by filling the cell and repeatedly scanning the spectral region of interest. To quantify the spectra, either potassium perchorate or boric acid was added to the

solutions as a reference. ClO_4^- concentrations were .07 m or less and boric acid concentrations were generally 0.20 m. Use of boric acid avoided problems with interference with the 967 cm^{-1} sulfite peak at higher pH conditions and minimized the effect of the reference compound on ionic strength. Ionic strength of the solutions was adjusted by adding NaCl. The bisulfite solutions were studied over a ionic strength range of 0.1 to 5.3 m.

The concentrations of the species in solution were determined by comparing the areas of their Raman peaks with the area of the 934 cm^{-1} ClO_4^- peak or the 876 cm^{-1} boric acid peak. Use of peak heights was found to be inferior to peak areas in quantifying the spectral peaks. The Raman intensity, I, of a peak due to a particular specie A in solution should be proportional to its concentration,

$$I = c\,[A]. \qquad (6)$$

The proportionality constant, c, will depend on the specie, the wavelength of light illuminating the sample, and the particular peak under observation. For the purposes of this study, the compounds of interest were referenced to the 934 cm^{-1} ClO_4^- peak. This peak was assigned a relative scattering efficiency (RSE) of 1.00. The RSEs of the other peaks were obtained by comparing their areas with the area of the 934 cm^{-1} ClO_4^- peak, with corrections made for differences in concentration. The areas were obtained over the same wavenumber range for all the spectra.

$$RSE = \frac{\text{area of peak of A / concentration of A}}{\text{area of } ClO_4^- \text{ 934 cm}^{-1} \text{ peak / concentration of } ClO_4^-} \qquad (7)$$

The RSEs of H_3BO_3, ClO_4^-, and SO_4^{2-} were compared over temperatures of 2 to 67°C and a range of concentrations. The variability of the RSEs was found to be small and within the experimental uncertainty. The RSEs for peaks of interest in this study are listed in Table II. Connick and co-workers[3] found that the scattering efficiency of the HSO_3^- 2530 cm^{-1} band to be relatively constant over a range of conditions. It was assumed that the other peaks used in this study had similar insensitivity to the solution conditions.

Alcohols have been used as oxidation inhibitors in some studies of bisulfite ion[3,7]. No alcohols were used in these studies as they often have Raman bands in the 1000-1100 cm^{-1} region. These bands could interfere with the measurement of the bisulfite bands in this region. No other oxidation inhibitors were used.

Bisulfite solutions were studied at three pH regimes in an effort to observe the possible effects of hydrogen ion, hydrated sulfur dioxide, and sulfite ion on Q_1 and Q_2. Solutions in the low pH regime (pH ~2) were prepared by adding small amounts of concentrated hydrochloric acid to bisulfite solutions. The potential for loss of sulfur dioxide from the solutions in the purge gas,

causing a shift in pH and S(IV) concentration, limited the accuracy to the measurements of these solutions. Solutions of about pH 4.5 were prepared by adding sodium metabisulfite to solutions without pH adjustment. High pH solutions (pH 6 to 7) were prepared by dissolving a mix of sodium metabisulfite and sodium sulfite in water.

Results and Discussion

Measurement of Q_1

The Raman peaks from the SO_3 stretch is in the range of 1000 - 1100 cm^{-1} for many compounds containing SO_3 groups, including bisulfite ion. The bisulfite ion Raman peaks in the 1000 - 1100 cm^{-1} range have not, until now, been definitely assigned. Connick and co-workers[3] have discussed the bisulfite ion peak assignments. We obtained Raman spectra of dilute bisulfite ion solutions over a temperature range of 1.5°C to 67°C. By comparing the change in the 1023 and 1052 cm^{-1} band intensities with temperature to the change in the 2530 cm^{-1} band intensity with temperature, we were able to make the peak assignments. The peak area for the 1023 cm^{-1} peak was obtained by measuring the area over the range of 990 cm^{-1} to 1100 cm^{-1} and subtracting the area of the 1052 cm^{-1} peak, measured over the range of 1038 cm^{-1} to 1070 cm^{-1}. The 2530 cm^{-1} peak has been assigned to the H-S stretch in the HSO_3^- isomer[3,9], and the band due to the SO_3 stretch of this isomer should exhibit similar temper-ature dependence to that of the H-S stretch. It was found that the 730 cm^{-1} band, which has been assigned to the $HOSO_2^-$ isomer[9], was too weak to use in making comparisons with the 1023 and 1052 cm^{-1} bands. As shown in Figure 1, the 1052 cm^{-1} peak and the 2530 cm^{-1} peaks have similar responses to temperature relative to the 1023 cm^{-1} peak. Thus, we can assign the 1023 cm^{-1} peak to the $HOSO_2^-$ isomer and the 1052 cm^{-1} peak to the HSO_3^- isomer. Additional confirmation can be obtained by comparing the relative change in the 1023 and 1052 cm^{-1} band intensities with the temperature dependence of the isomers given by Horner and Connick[4].

$$\ln Q_1 = (1438 \pm 151/T) - 3.232 \pm .527 \qquad (8)$$

They based their assignment of the NMR peaks on the oxygen exchange rates that they observed for the peaks. Figure 2 shows Raman spectra of the two peaks at temperatures of 20°C and 67°C. From the equation given by Horner and Connick, the change in the relative intensities of the peaks is consistant with the assignment of the 1023 cm^{-1} peak to $HOSO_2^-$ and the 1052 cm^{-1} peak to HSO_3^-.

Raman spectra of deuterated bisulfite ions were obtained by dissolving $Na_2S_2O_5$ in D_2O to generate $DOSO_2^-$ and DSO_3^-. The spectra of these solutions show peaks at 1030 cm^{-1} and 1050 cm^{-1} due to $DOSO_2^-$ and DSO_3^-, respectively. As might be expected, the peak of $DOSO_2^-$ exhibits a greater isotope shift than that for DSO_3^-. The peak due to the D-S stretch is found at 1850 cm^{-1}, compared to 2530 cm^{-1} for the H-S stretch in HSO_3^-. When the sum of the band intensities of the

deuterium isomers was compared with the ClO_4^- reference band intensity, no temperature dependent trend was observed, as with the SHO_3^- isomers. The temperature dependence of the deuterated bisulfite ion peaks is similar to that observed for SHO_3^-.

To determine the values of Q_1 for the solutions studied, it was necessary to establish the relative scattering efficiencies of the peaks of the isomers. If the scattering efficiencies of the peaks of the isomers are substantially different, the sums of the peak areas should systematically change with temperature when normalized to a reference peak. Raman spectra of 0.15 m - 0.32 m bisulfite solutions were taken at temperatures of 1.5, 20, 49 and 67°C, using ClO_4^- or H_3BO_3 references. Within the uncertainty of the measurements, there was no observable variation in the ratio of the sum of the bisulfite peak areas to the reference peak area. Based on these observations, the scattering efficiencies of the peaks were assumed to be the same and the value of the RSEs for the bisulfite ion isomers were calculated to be both 0.45 ± 0.04, compared to the 934 cm^{-1} ClO_4^- peak. Similar values were obtained for the deuterated isomers. The areas of the peaks of the isomers were then used to calculate Q_1 as a function of temperature for SHO_3^- and SDO_3^-. A plot of $\ln(Q_1)$ vs. 1/T is shown in Figure 3 for the bisulfite isomers in H_2O and D_2O. Least squares fits to the data yield the following equations.

For H_2O: $\ln Q_1 = (1458 \pm 152/T) - 3.160 \pm .504$ (9)

For D_2O: $\ln Q_1 = (1567 \pm 79/T) - 3.604 \pm .265$ (10)

The data used in determining these equations were collected from solutions at pH ~4.5, ionic strength <0.4 m, and $[SHO_3^-] < 0.3$ m. For the measurements in D_2O, the conditions were pH ~4.5, ionic strength = 0.2 m and $[SDO_3^-] = 0.15$ m. The H_2O data compare well with equation 8 obtained by Horner and Connick[4]. We observed no definite dependence of Q_1 on ionic strength over the range of μ = 0.1 to 0.4 m. There was no evidence that Q_1 was dependent on the bisulfite ion concentration.

To obtain an independent measure of the scattering efficiencies for the Raman peaks of the two isomers, the values of $Q_1(T)$ from the equation given by Horner and Connick were compared with the isomer peak areas. The peak area ratio divided by the isomer ratio calculated from equation 8 of Horner and Connick is shown in Figure 4 as a function of the isomer ratio. While there is significant scatter in the points, the average value is close to 1. A least squares fit yields

$$(1023/1052)_{observed} \ / \ (HOSO_2^-/HSO_3^-)_{calculated} = 1.08 \pm .28 \qquad (11)$$

for pH ~4.5, $[SHO_3^-]$ in the range of 0.1 - 0.3 m, and ionic strength < 0.4 M. On this basis, the RSEs of the two isomers are equal within the uncertainty of the data. This is consistant with the measurements of the sums of the peak areas as a function of temperature.

The number of measurements taken at pHs other than ~4.5 were limited. The measurements done at high pH (6 - 7) suffered from weak signals since much of the S(IV) (where S(IV) is used to refer to all sulfur oxyanions or oxides with sulfur in the +4 state) was in the form of SO_3^{2-}. The low

pH measurements, obtained at pH ~2, had the problem of S(IV) being in the form of SO_2(aq) and from loss of S(IV) by entrainment in the purge gas as SO_2. The data obtained are shown in Figure 5, along with the data from pH ~4.5. The high pH data agree reasonably well with the pH ~4.5 data. The low pH data appear to be shifted upward somewhat and suggest a higher proportion of $HOSO_2^-$ at low pH conditions. However, the data are too limited and the potential for error too large to put much confidence in these observations. It should be noted that the $HOSO_2^-$ isomer could be more easily attacked by H^+ than the HSO_3^- isomer.

$$HOSO_2^- + H^+ \rightleftharpoons SO_2(aq) + H_2O \qquad (12)$$

Horner and Connick[4] observed a much larger H exchange with $HOSO_2^-$ than with HSO_3^- and based their assignment of isomers on this. Direct interconversion of the isomers would involve transfer of a hydrogen from the sulfur to one of the oxygens, or vice versa. Horner and Connick propose the process

$$(HSO_3^-)^* + SO_3^{2-} \rightleftharpoons (SO_3^{2-})^* + SHO_3^- \qquad (13)$$

where SO_3^{2-} is an intermediate in the conversion.

Measurement of Q_2

The poor agreement between previous studies[2,3,6,7,8] attempting to determine Q_2, is due, in part to the difficulty in determining the molar absorptivity, a, of $S_2O_5^{2-}$, as indicated in Table I. Connick and co-workers[3] used Raman spectroscopy in conjunction with UV absorption measurments to avoid some of the difficulties. By using Raman spectroscopy, we were able to avoid the necessity of determining the value of the molar absorptivity of $S_2O_5^{2-}$. In addition to the disagreement of the literature values of Q_2 at room tempeature, there is poor agreement in the measurements at other temperatures. Connick et al[3] observed a small decrease in Q_2 with increasing temperature, while Bogolitsyn and co-workers[8] observed a substantial increase in Q_2 with temperature.

To determine the amount of the S(IV) in the form of $S_2O_5^{2-}$ in our experiments, the RSE for $HOSO_2^-$ was used to determine the concentration of $HOSO_2^-$ from the 1023 cm^{-1} peak. HSO_3^- could be calculated from the appropriate value of Q_1 and corrections were made for SO_2(aq) and SO_3^{2-}, as necessary. The remaining S(IV) was assumed to be in the form of $S_2O_5^{2-}$. The peak area of the 1052 cm^{-1} peak was corrected for HSO_3^- using values of Q_1 calculated from equation 9 to obtain the contribution from $S_2O_5^{2-}$. The 235 cm^{-1} peak of $S_2O_5^{2-}$ did not show significant interference from other S(IV) species, but it was necessary to correct for the background signal since it is nearer the laser line than the other peaks. Blank spectra of either water or a sodium chloride solution were obtained before or after the collection of the $S_2O_5^{2-}$ spectra for correction purposes. The 655 cm^{-1} $S_2O_5^{2-}$ peak is free of interference, but is weaker than the 235 and 1052 cm^{-1} peaks. Values of Q_2 could then be calculated. To determine the RSE values for $S_2O_5^{2-}$ peaks, the corrected areas of the

235 and 1052 cm^{-1} peaks were measured and the calculated $S_2O_5^{2-}$ concentrations were used. Some spectra were taken without any reference compounds and the RSEs for $HOSO_2^-$, HSO_3^-, and $S_2O_5^{2-}$ were used to calculate Q_2 . The values obtained agreed well with the values of Q_2 calculated with references.

It has been established in earlier studies[3,7] that Q_2 shows a strong dependence on ionic strength. Guggenheim's modification[10] of Bronsted's equation for the effect of ionic strength on reaction rates can be stated as:

$$\log k/k_o = \frac{A z_1 z_2 \mu^{1/2}}{1 + \mu^{1/2}} + B\mu, \qquad (14)$$

where k is the rate constant at ionic strength μ, k_o is the rate constant at zero ionic strength, A is the Debye-Huckel coefficient, z_1 and z_2 are the charges on the reacting species, and B is a constant dependent on the ions and the medium. The dependence of Q_2 on ionic strength could be expected since the rate of the $S_2O_5^{2-}$ formation reaction:

$$HSO_3^- + HOSO_2^- \xrightarrow{k_f} S_2O_5^{2-} + H_2O \qquad (15)$$

should show an increase with increasing ionic strength, while the reverse reaction:

$$S_2O_5^{2-} + H_2O \xrightarrow{k_r} HSO_3^- + HOSO_2^- \qquad (16)$$

should not. Thus, the equilibrium constant,

$$Q_2 = k_f / k_r$$

would show an increase with an increase in ionic strength. The presence of an intermediate in reactions 14 and 15 should not effect the ionic strength behavior. After compilation of the values of Q_2 derived from the spectra collected over a range of conditions, it was apparent that there was considerable scatter of the values of Q_2 obtained at the same ionic strength, temperature, and pH. Plotting theses values of Q_2 as a function of [S(IV)] showed a definite dependence on the S(IV) concentration. This is shown in Figure 6 for S(IV) in H_2O (open squares) and D_2O (solid squares) at an ionic strength of about 5 m and at temperatures of 20 - 25°C and pH ~4.5.

By selecting data at constant S(IV) concentration, we are able to determine the ionic strength dependence. Values of $\log(Q_2)$ are plotted against the square root of ionic strength in Figure 7 for a series of runs with [S(IV)] = 1 m at pH ~4.5 and a temperature of 20°C. NaCl was used to adjust the ionic strength. These data were compiled with other data obtained under similar conditions and the average values of Q_2 obtained are:

$$Q_2 = .062 \pm .011\ M^{-1} \quad (\mu = 1 \text{ and } [S(IV)] = 1\ m)$$
$$Q_2 = .25 \pm .03\ M^{-1} \quad (\mu = 5 \text{ and } [S(IV)] = 1\ m)$$
$$Q_2 = .11 \pm .03\ M^{-1} \quad (\mu = 5 \text{ and } [S(IV)] = 5\ m)$$

for conditions of pH ~4.5 and temperatures of 20 - 25°C. The values that we obtain agree reasonably well with those of Connick and co-workers.[3] They note that if the data of Bourne et al[7] are recalc-

ulated using a larger value of the $S_2O_5^{2-}$ molar absorptivity at 255 nm, the results of the two studies are consistant. While the numerical values of Q_2 obtained by Connick et al[3] differ substantially from our results at conditions of high S(IV) concentrations, the differences in the amount of $S_2O_5^{2-}$ observed are considerably smaller. The fraction of S(IV) in the form of $S_2O_5^{2-}$ for our results was compared with the data published by Connick et al. The agreement between the studies is good up to about 2M, beyond which the results diverge. This could be due to either the uv molar absorptivity or the Raman scattering efficiency of $S_2O_5^{2-}$ possessing a dependence on the S(IV) concentration. Results from both studies were obtained at an ionic strength of about 5 m and at 20 - 25°C. If a dimer intermediate between SHO_3^- and $S_2O_5^{2-}$ exists, it would increase in concentration as the SHO_3^- concentration increases. If it has a uv absorption at the wavelength used by Connick et al, the observed signal would indicate a higher concentration than the actual $S_2O_5^{2-}$ concentration. However, none of the uv studies have observed any behavior at the 255 nm wavelength that suggests a contribution from the dimer intermediate.

High concentration bisulfite ion solutions were studied over a range of pH 1.9 to 6.1. Little or no dependence on pH was observed in the values of Q_2 calculated in this range at $\mu = 1$ and $\mu = 5$, suggesting that neither $SO_2(aq)$ nor SO_3^{2-} are directly involved in the equilibrium between SHO_3^- and $S_2O_5^{2-}$. The values of Q_2 are shown in Figure 8 as a function of pH for S(IV) concentration of 1 m and ionic strength $\mu = 1$.

The $S_2O_5^{2-}$ equilibrium constant measurements were made over the temperature range of 1.5°C to 67°C. When the values of Q_2 are plotted against 1/T, as shown in Figure 9, for $\mu = 1$ (open squares) and $\mu = 5$ (closed squares). The data shown were obtained at a S(IV) concentration of 1 m and summed over all pHs studied since there was no observable pH dependence. Observing the behavior of Q_2 in Figure 9, the $\mu = 1$ data show little dependence on temperature. The $\mu = 5$ data show a temperature dependence similar to that observed by Connick et al[3], but are in poor agreement with the results of Bogolytsin et al[8]. The $\mu = 5$ data give values of $\Delta H = -2.0$ kcal and, at 25°C, $\Delta S = -11$ eu. The two ionic strengths show essentially the same value of Q_2 at high temperatures (~60°C). The low temperatures and high ionic strengths appear to have a stabilizing effect on $S_2O_5^{2-}$, perhaps by stabilizing the Golding's dimer intermediate involved in its formation. This intermediate would be expected to be more weakly bound and more susceptible to dissociation than $S_2O_5^{2-}$.

Rhee and Dasgupta[5] derived values for the equilibrium constants K_D and K_P in the process:

$$SHO_3^- + SHO_3^- \overset{K_D}{\rightleftharpoons} (SHO_3^-)_2 \overset{K_P}{\rightleftharpoons} S_2O_5^{2-} + H_2O \qquad (17),$$

where

$$Q_2 = K_D \cdot K_P \qquad (18).$$

The numbers they obtain indicate that a significant amount of bisulfite ion should be in the form of Golding's dimer at [S(IV)] ~ .1 m. We collected Raman spectra of bisulfite ion solutions over a concentration range of [S(IV)] = 0.010 to 0.25 m at 293 K. The was no observable concentration-dependent change in either the positions or areas of the bisulfite isomer peaks relative to the ClO_4^- reference in these spectra, with the exception of some broadening of the 1052 cm^{-1} peak in the 0.010 m and 0.025 m spectra. Studies of the SHO_3^- - $S_2O_5^{2-}$ system are needed that could provide definitive evidence the the intermediate.

Betts and Voss[11] made a study of oxygen exchange in aqueous solutions of sulfite ions and attempted to determine the kinetics for the conversion of bisulfite ion to $S_2O_5^{2-}$. They did not consider the possibility of an intermediate in the process, which could affect the chemistry they observed. If their observed second order dependence is correct, the oxygen exchange could proceed by the intermediate instead of $S_2O_5^{2-}$. This process is different than that proposed by Horner and Connick[4] in reaction 13, and could be an additional pathway for oxygen exchange. It would be incorrect to use the oxygen exhange rate to determine the $S_2O_5^{2-}$ hydrolysis rate because of the presence of the intermediate. Direct observation of $S_2O_5^{2-}$ decay would be a more reliable measure of the kinetics of this process.

Table I

Literature Values of the Dimerization Quotient, Q_2

Temp., °C	Ionic Strength, m	$^{a}S_2O_5$*	Q_2, m	Reference
20	.07 - .32	4000 (255)	.07	Golding[2]
22	.3	143 (258)	2.0	Arkhipova & Chistyakova[6]
25	0	1980 (255)	.076	Bourne, Higuchi & Pitman[7]
	2.0		.34	
25	0	5790 (255)	.03	Connick, Tam & Van Deuster[3]
	1.0		.088	
	2.1		.132	
25	0	2400 (255)	.0059	Bogolitsyn, Skrebets, Romanenko & Komarov[8]

* Wavelength in parentheses (nm).

Table II

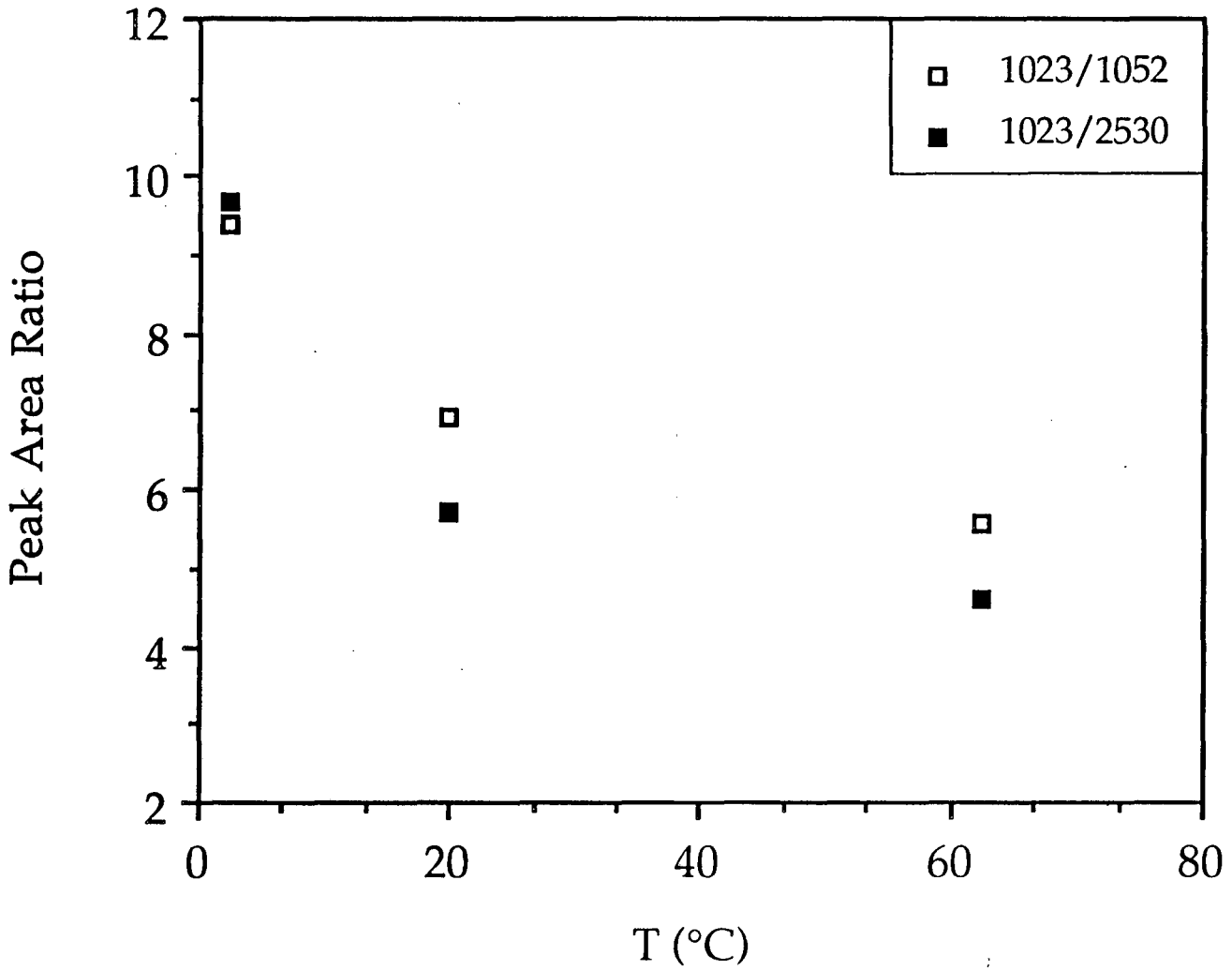
Relative Scattering Efficiencies of Compounds Involved in This Study

(Reference ClO_4^- = 1.00)

Compound		in H_2O	in D_2O
ClO_4^-	(934 cm^{-1})	1.00	1.00
H_3BO_3	(875 cm^{-1})	0.22 ± .01	—
SO_4^{2-}	(980 cm^{-1})	0.72 ± .04	0.70 ± .10
$HOSO_2^-$	(1023 cm^{-1})	0.45 ± .04	0.46 ± .05 *
HSO_3^-	(1052 cm^{-1})	0.45 ± .04	0.46 ± .05 **
HSO_3^-	(2530 cm^{-1})	0.45 ± .10	—
$S_2O_5^{2-}$	(235 cm^{-1})	4.4 ± 1.8	5.4 ± 2.0
$S_2O_5^{2-}$	(655 cm^{-1})	0.45 ± .20	—
$S_2O_5^{2-}$	(1052 cm^{-1})	0.6 ± .2	0.7 ± .2

* $DOSO_2^-$ peak is centered at 1030 cm^{-1}.

** DSO_3^- peak is centered at 1050 cm^{-1}.



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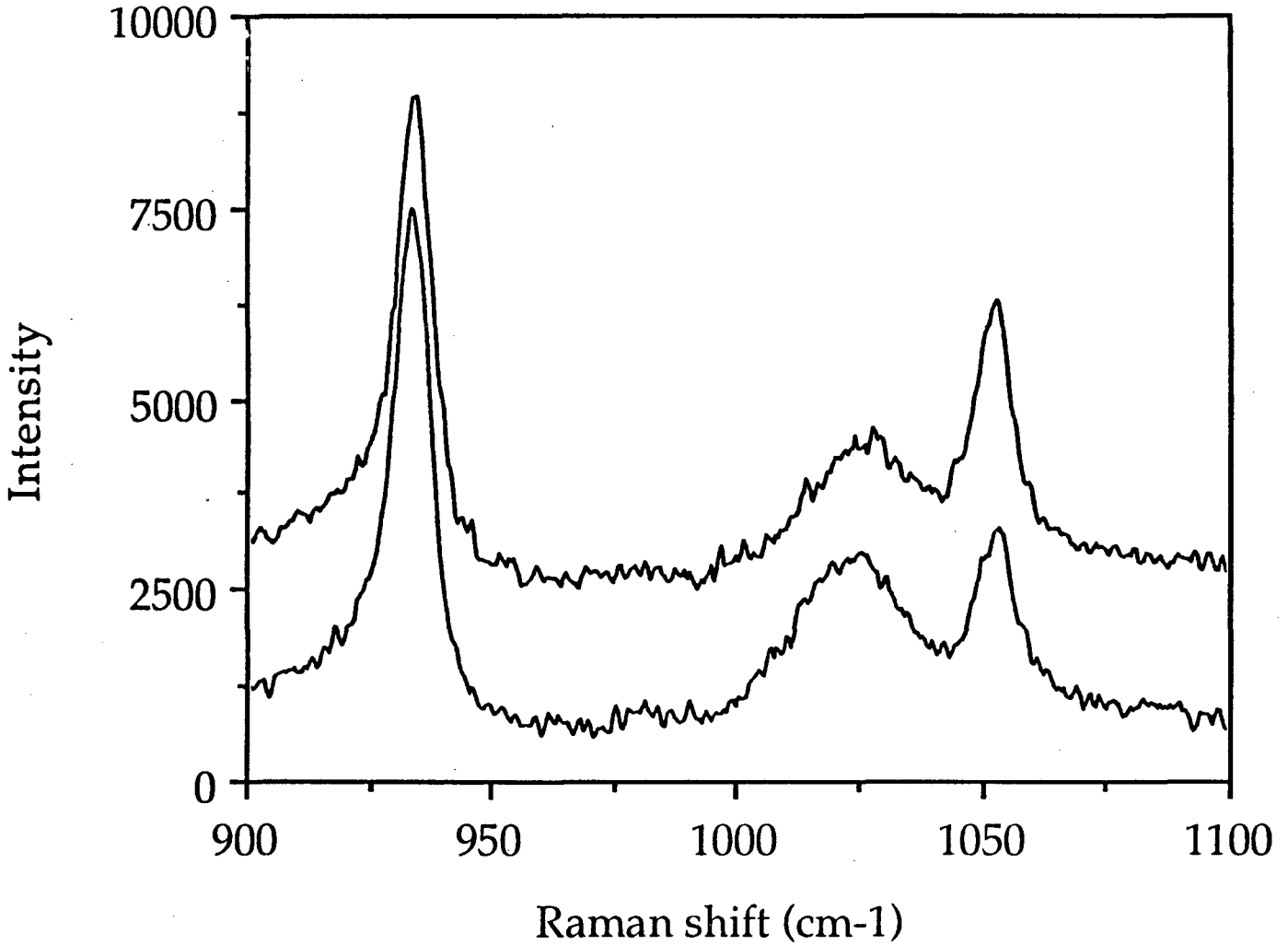
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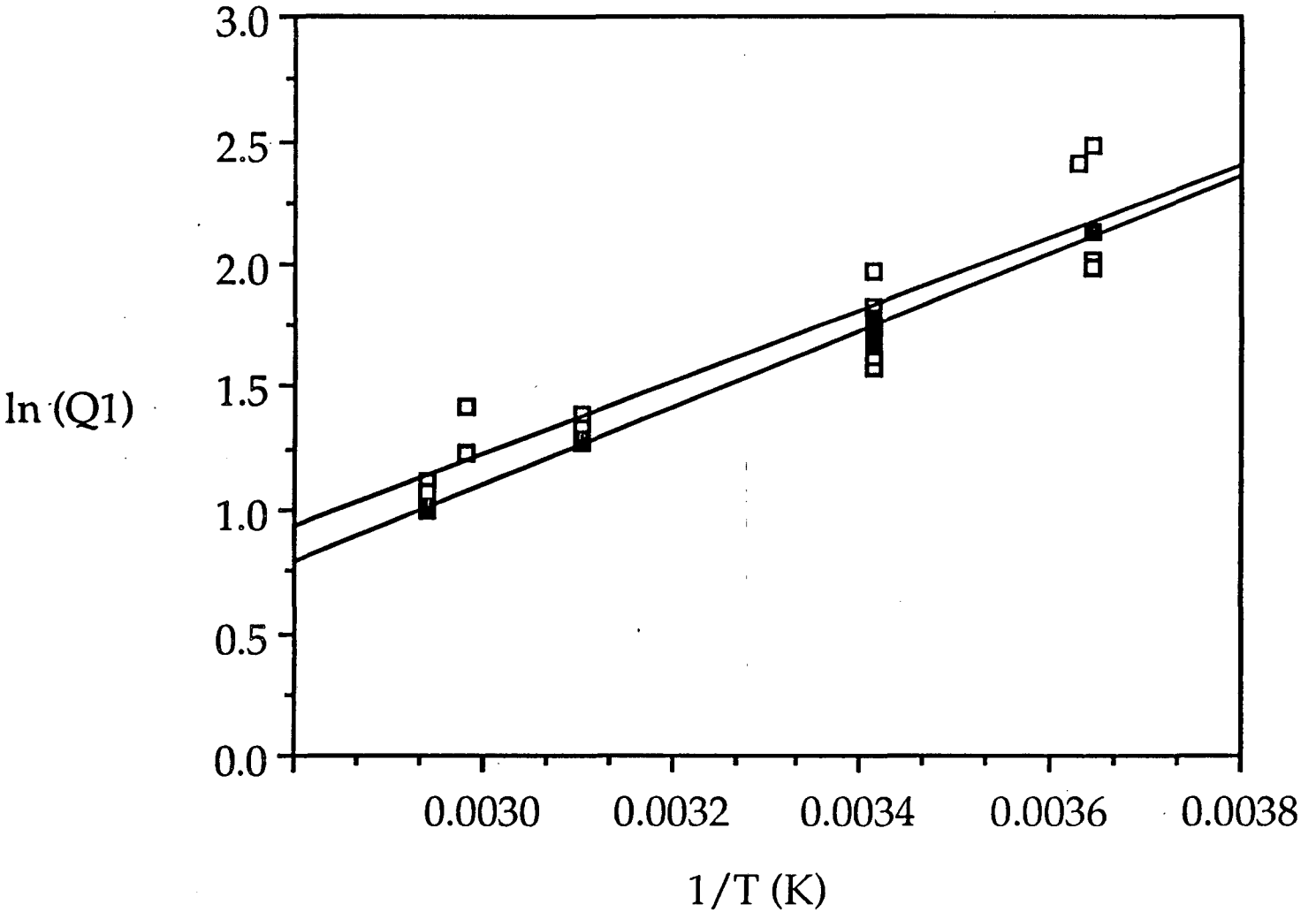
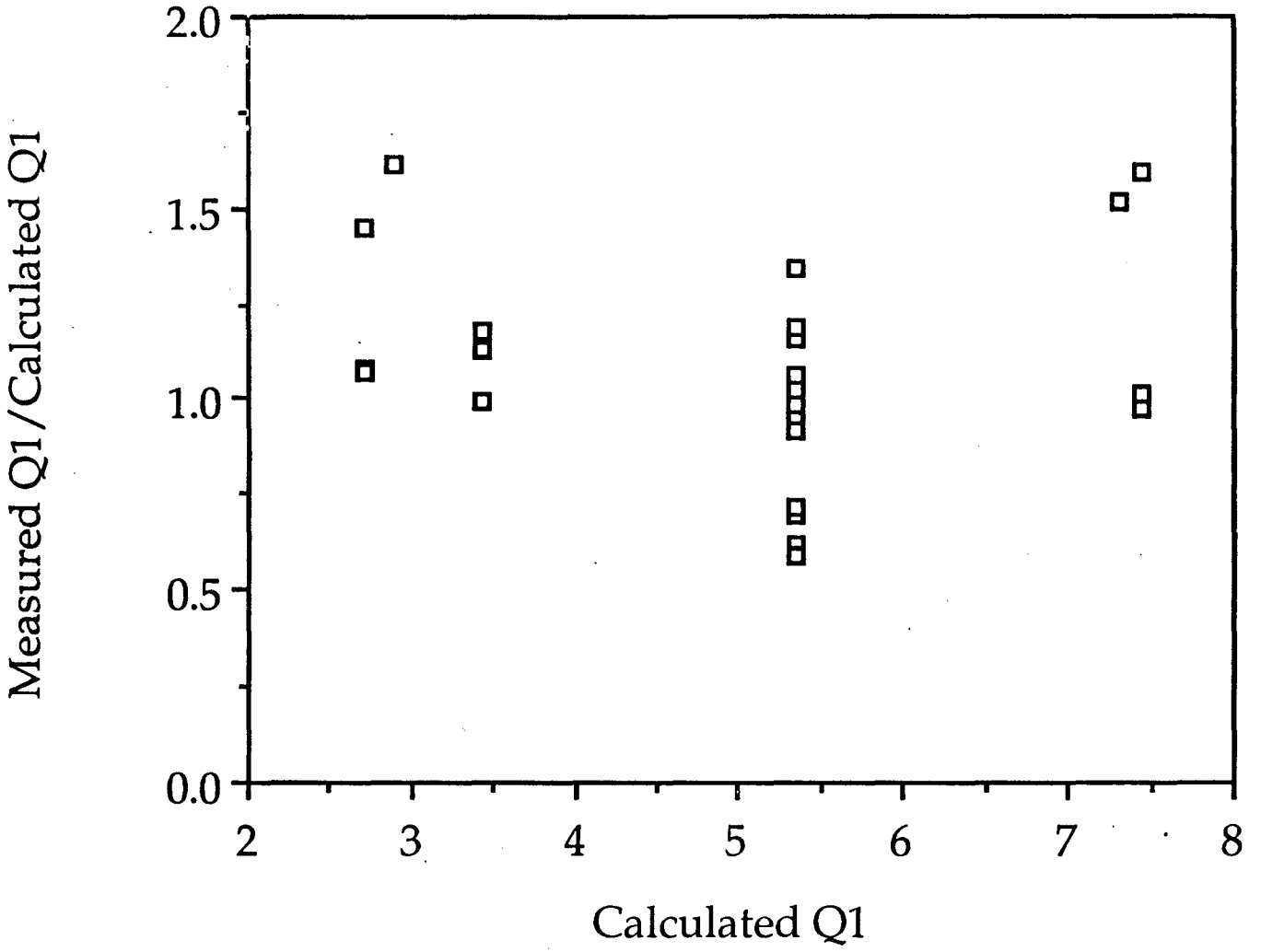
7500
5000
2500
0
Intensity
900
950
1000
1050
1100
Raman shift (cm-1)

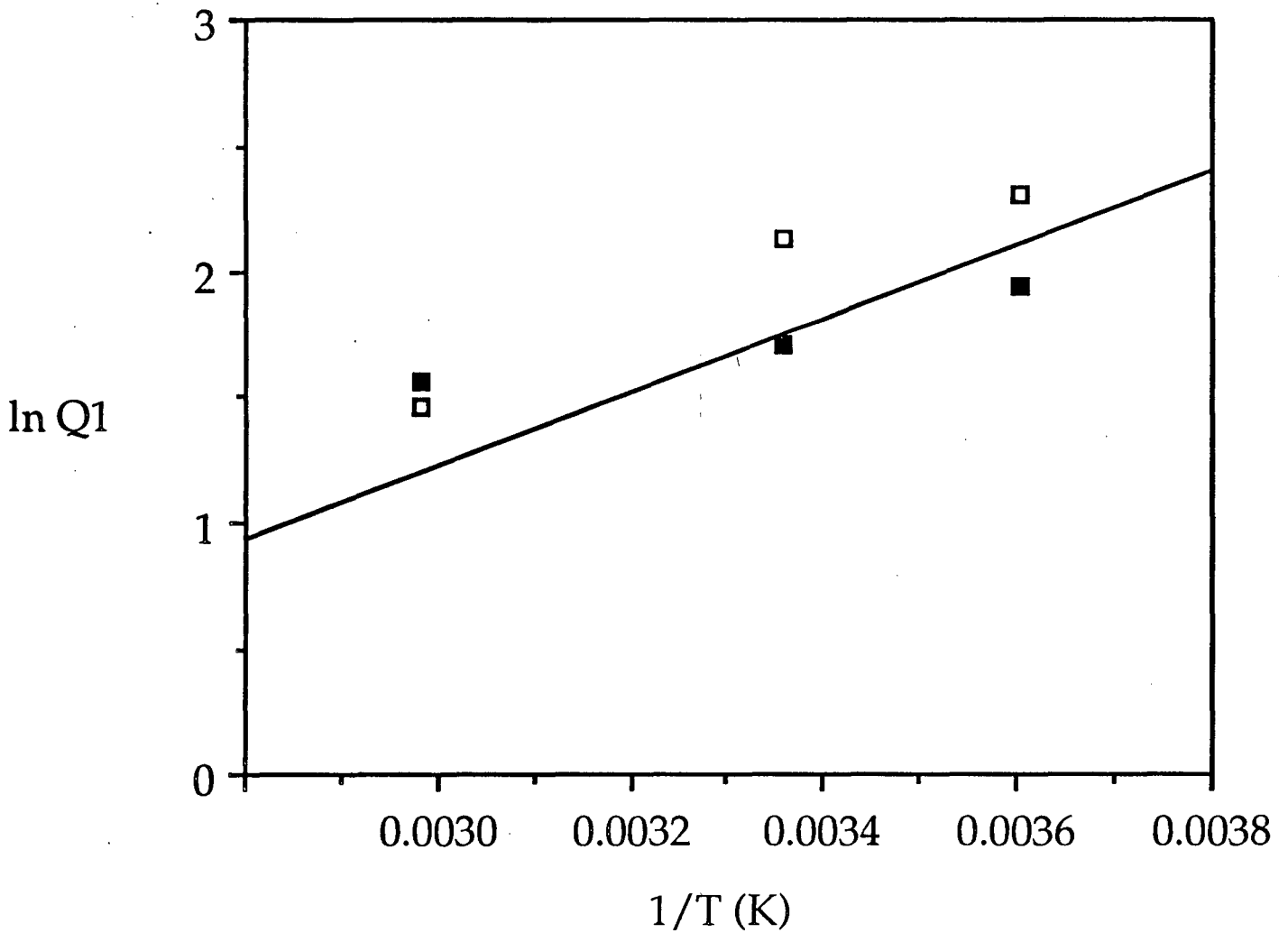
XBL 903-838



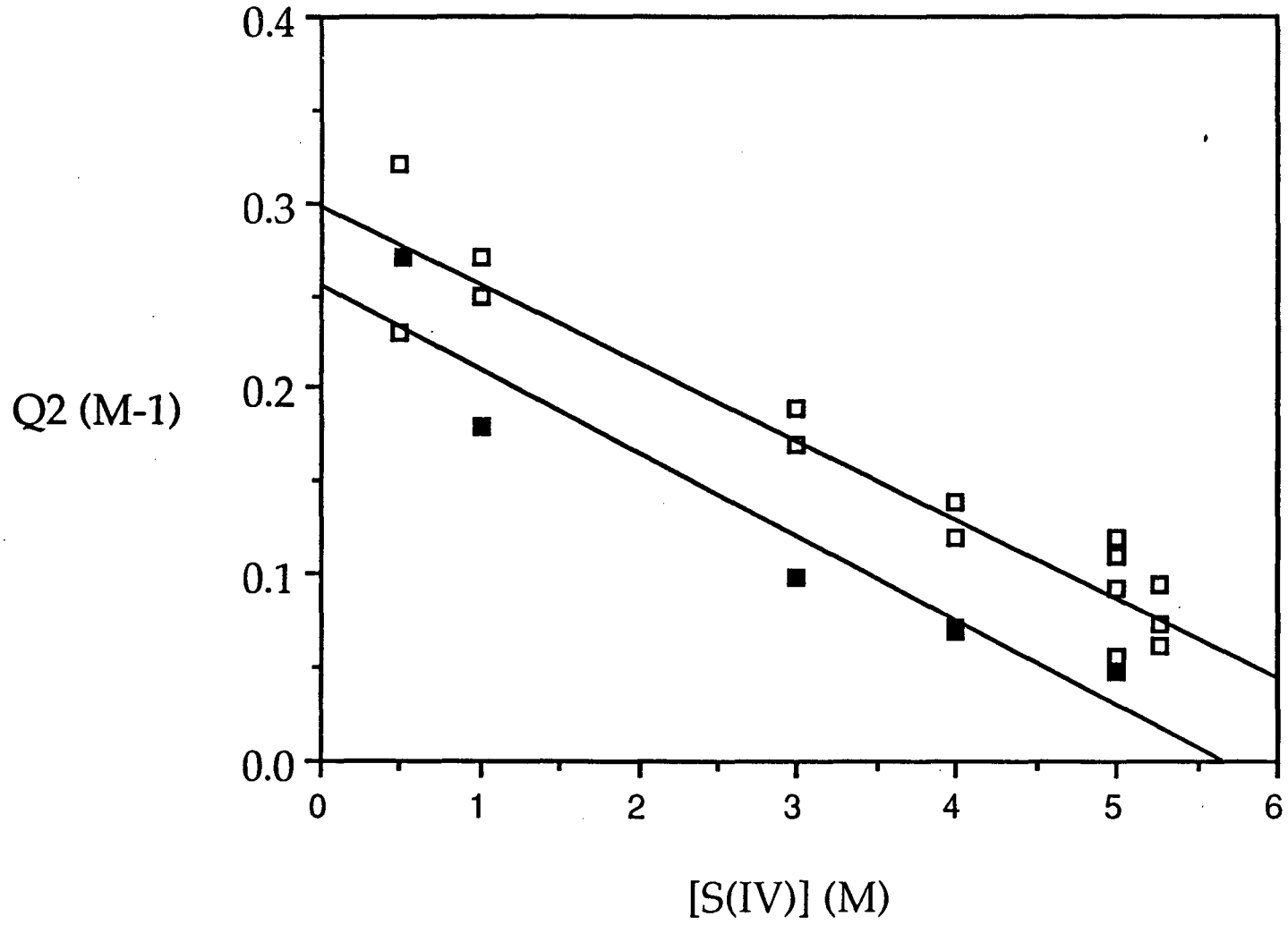
XBL 903-839


2.0
1.5
1.0
0.5
0.0
2
3
4
5
6
7
8
Measured Q1/Calculated Q1
Calculated Q1

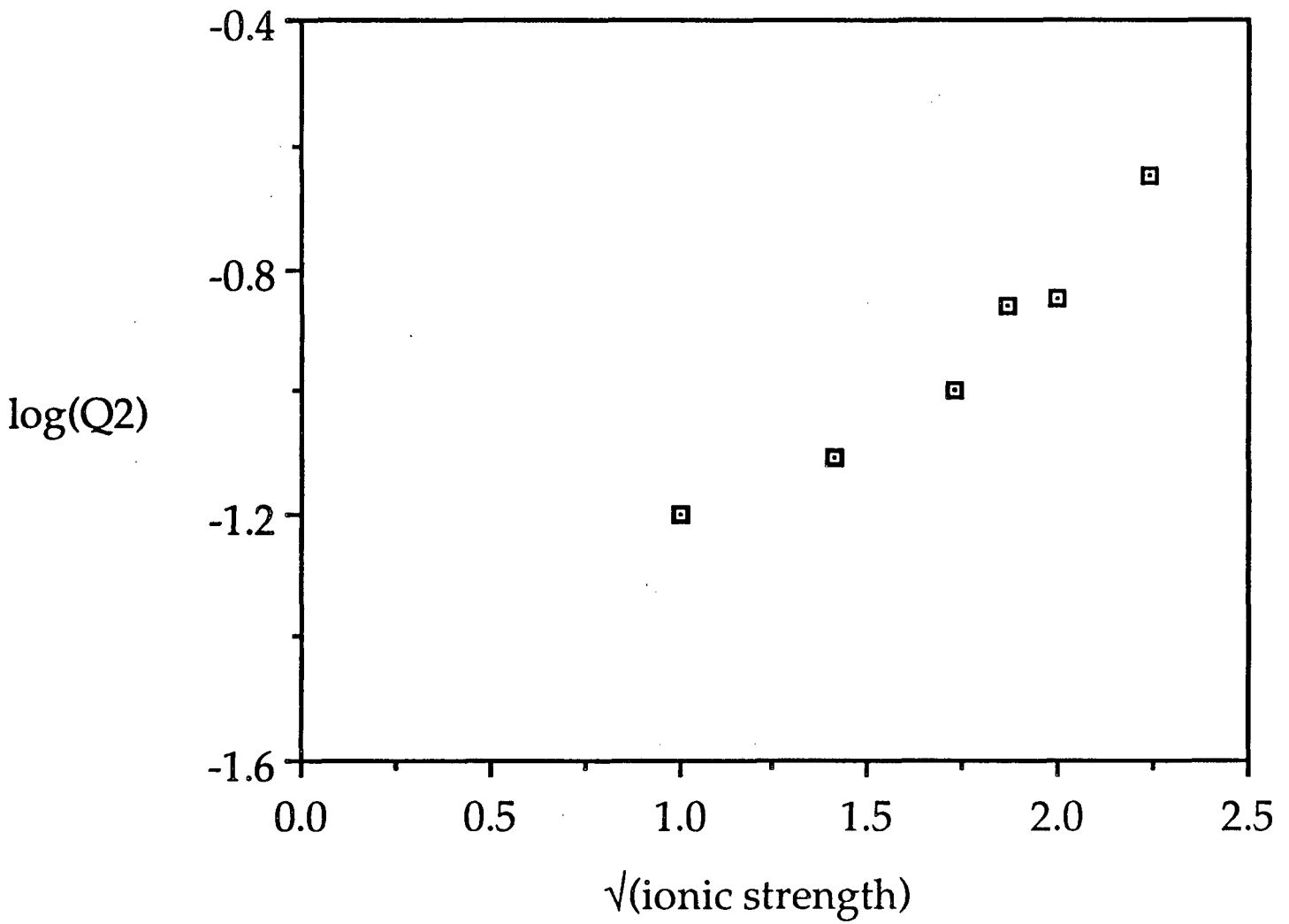
XBL 903-840



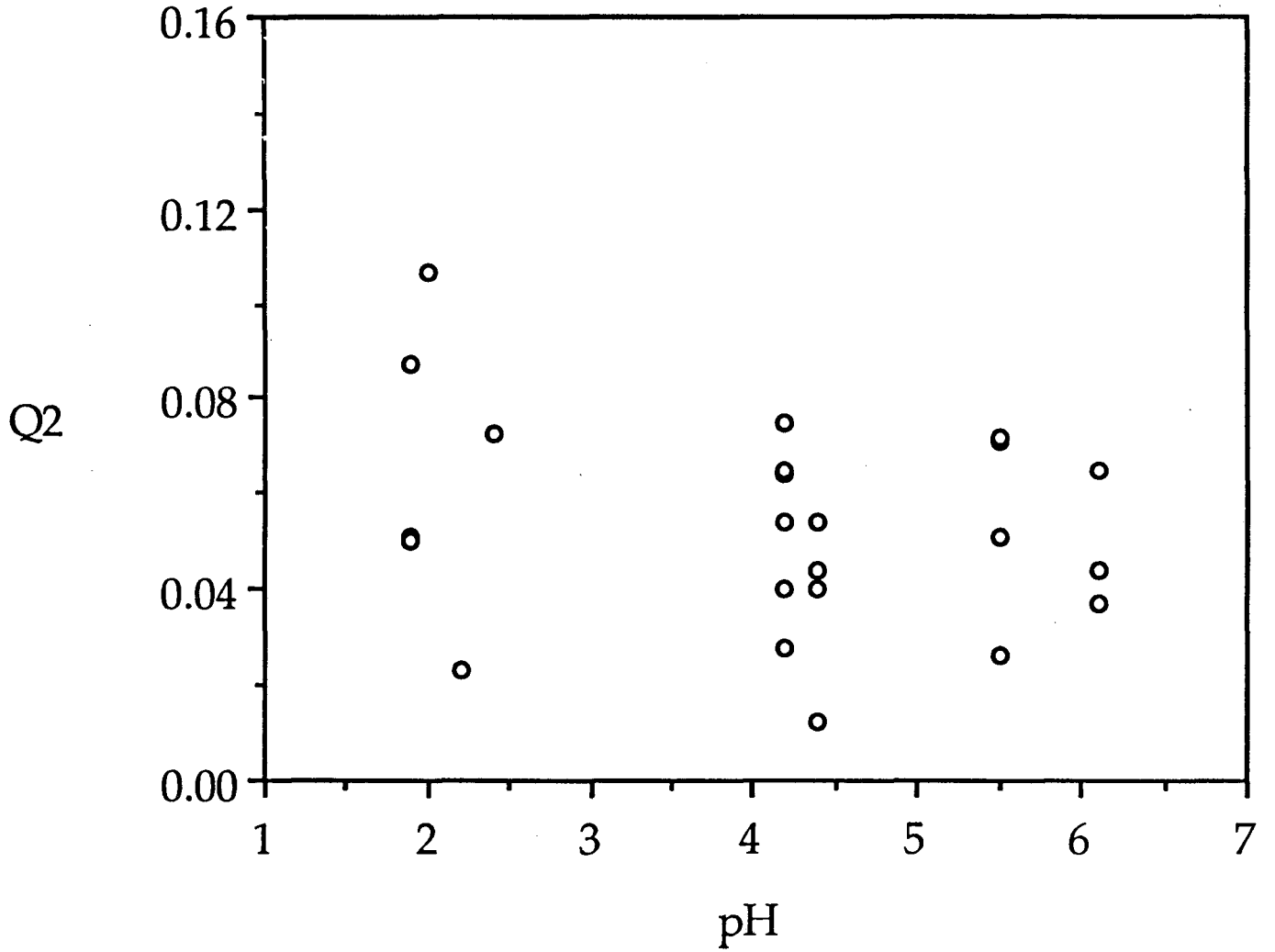
XBL 903-841



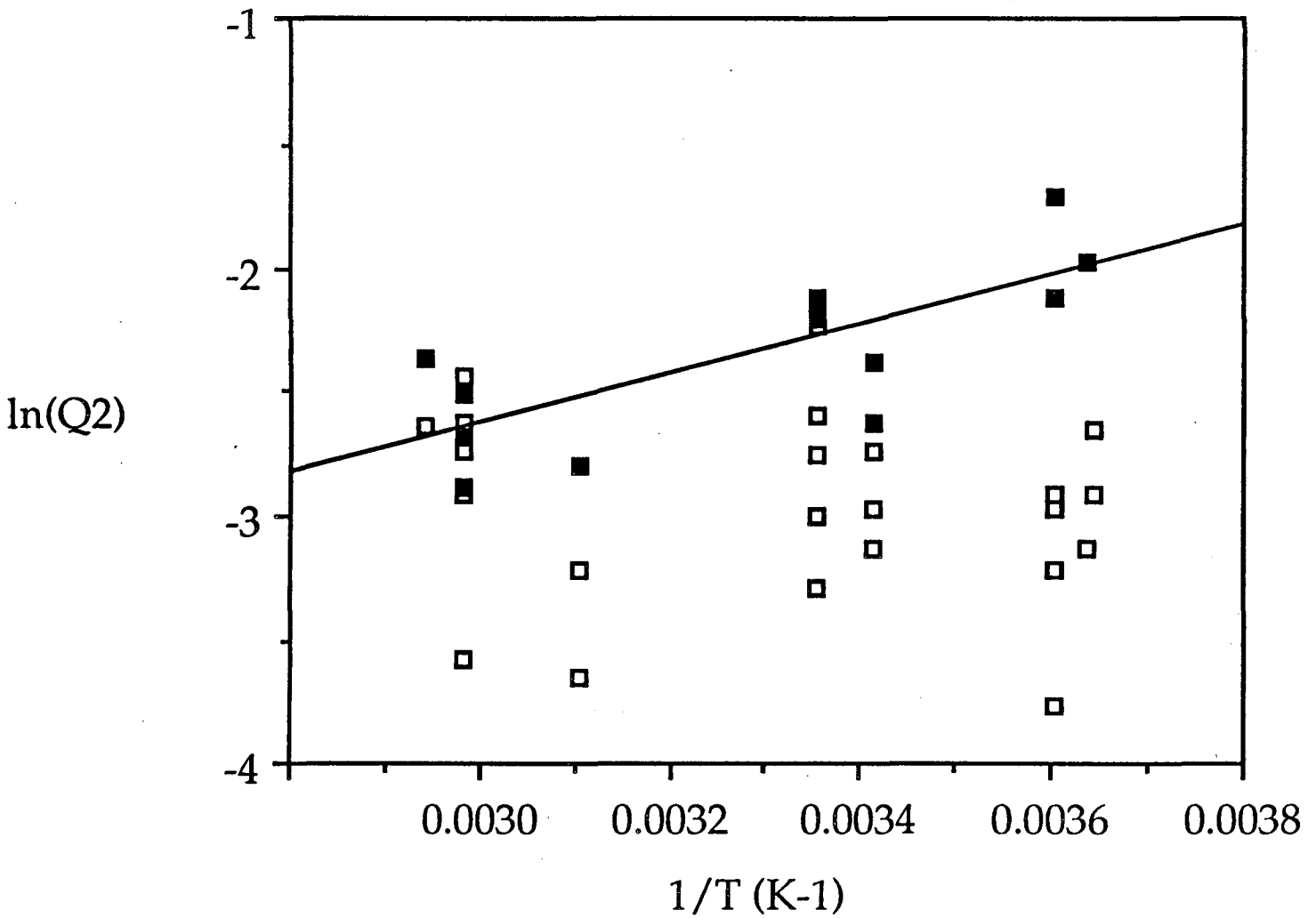
XBL 903-842



XBL 903-843



XBL 903-844



XBL 903-845

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