About the Stability of Sulfurous Acid (H_2SO_3) and Its Dimer

Andreas F. Voegele,[a] Christofer S. Tautermann,[a] Thomas Loerting,[a, b]
Andreas Hallbrucker,[a] Erwin Mayer,[a] and Klaus R. Liedl*[a]

Abstract: The characterization and isolation of sulfurous acid (H_2SO_3) have never been accomplished and thus still remain one of the greatest open challenges of inorganic chemistry. It is known that H_2SO_3 is thermodynamically unstable. In this study, however, we show that a C_i-symmetric dimer of sulfurous acid $(H_2SO_3)_2$ is 3.5 kcal mol^{-1} more stable than its dissociation products SO_2 and H_2O at 77 K. Additionally, we have investigated the kinetic stability of the sulfurous acid monomer with respect to dissociation into SO_2 and H_2O and the kinetic isotope effect (*KIE*) on this reaction by transition-state theory. At 77 K, the half-life of H_2SO_3 is 15×10^9 years, but for the deuterated molecule (D_2SO_3) it increases to 7.9×10^{26} years. At room temperature, the half-life of sulfurous acid is only 24 hours; however, a *KIE* of 3.2×10^4 increases it to a remarkable 90 years. Water is an efficient catalyst for the dissociation reaction since it reduces the reaction barrier tremendously. With the aid of two water molecules, one can observe a change in the reaction mechanism for sulfurous acid decomposition with increasing temperature. The most likely mechanism below 170 K is via an eight-membered transition-state ring; yet, above 170 K, a mechanism with a six-membered transition state ring becomes the predominant one. For deuterated sulfurous acid, this change in reaction mechanism can be observed at 120 K. Consequently, between 120 and 170 K, different predominant reaction mechanisms occur for the decomposition of normal and deuterated sulfurous acid when assisted by two water molecules. However, the much longer half-life of deuterated sulfurous acid and the stability of the sulfurous acid dimer at 77 K are encouraging for future synthesis and characterization under laboratory conditions.

Keywords: ab initio calculations · autocatalysis · isotope effects · kinetics · proton-transfer reaction

Introduction

In many inorganic chemistry textbooks it is still reported that the molecules sulfurous acid (H_2SO_3) and carbonic acid (H_2CO_3) cannot be isolated in (water-)free form.[1–5] However, this picture has been partially revised in the last couple of years since it has become possible to prepare and isolate carbonic acid by several methods[6–12] and to show its remarkable kinetic stability.[11, 13]

Attempts to isolate and characterize free H_2SO_3 from an aqueous SO_2 solution have not yet been successful. However, presumably a small fraction of SO_2 dissolved in water is present in the form of H_2SO_3.[3, 14] On cooling of such a solution, SO_2 hydrates form instead of H_2SO_3.[1–3] Solutions of SO_2 are weakly acidic and form two series of salts namely sulfites (SO_3^{2-}) and bisulfites (HSO_3^-). The bisulfite ion has been characterized by NMR spectroscopy by Horner and Connick,[15] who showed that there are two isomeric forms of the bisulfite ion. In one form the proton is attached to the oxygen atom ($SO_2(OH)^-$, bisulfite ion), whereas in the other form it is attached to the sulfur atom (HSO_3^-, sulfonate ion).[15] The equilibrium was determined to be in favor of the bisulfite ion; this was confirmed by ab initio studies of bisulfite and sulfonate water clusters.[15–18] Sülzle et al. report a successful generation of H_2SO_3 and showed that the bisulfite form is produced rather than the sulfonate form.[19] In the course of this study, H_2SO_3 was prepared in situ by a dissociative ionizing process with diethylsulfite, followed by a neutralization–reionization process experiment during mass-spectroscopic studies. The H_2SO_3 molecule produced in this experiment was extremely short-lived and was neither isolated nor characterized except by mass spectroscopy. Taking ab initio calculations into consideration, the question why it was hitherto impossible to isolate H_2SO_3 under normal conditions becomes clearer.[20–22] The Gibbs standard state free energy (ΔG^0) for the reaction

$$SO_2 + H_2O \rightarrow H_2SO_3 \tag{1}$$

---

[a] Prof. Dr. K. R. Liedl, Mag. A. F. Voegele, MMag. C. S. Tautermann,
Dr. T. Loerting, Prof. Dr. A. Hallbrucker, Prof. Dr. E. Mayer
Institute of General, Inorganic and Theoretical Chemistry
University of Innsbruck, Innrain 52a, 6020 Innsbruck (Austria)
Fax: (+43) 512-507-5144
E-mail: klaus.liedl@uibk.ac.at

[b] Dr. T. Loerting
Current address:
Department of Earth, Atmosphere and Planetary Sciences
Massachusetts Institute of Technology
77 Massachusetts Avenue, Cambridge, MA 02139-4307 (USA)

© 2002 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

is +14.6 kcal mol^{-1} at 298 K at the G2 level of theory. Thus, under standard conditions, H_2SO_3 is thermodynamically unstable and can be expected to dissociate into SO_2 and H_2O.[20] Additionally, it has been shown that water acts catalytically; thus, it lowers the reaction barrier between H_2SO_3 and $SO_2 + H_2O$. This catalytic effect not only accelerates the rate of decomposition but also explains why attempts to isolate sulfurous acid from aqueous SO_2 solutions failed. Castleman and co-workers have studied protonated sulfur dioxide–water clusters experimentally and characterized them mass-spectroscopically.[23, 24] Clusters of constitution $H_3SO_3^+$ are composed of two isomers, namely $H_2OH^+ \cdot SO_2$ and $SO_2H^+ \cdot H_2O$, but not of $S(OH)_3^+$; this shows that H_2SO_3 does not form in an aqueous environment. SO_2 and water mixtures have also been investigated by infrared and microwave spectroscopy,[25, 26] and a $SO_2 \cdot H_2O$ complex in which the planes of H-O-H and O-S-O are almost parallel was identified.[25] Apart from these studies, the anhydride of sulfurous acid SO_2 itself has gained much attention. Since SO_2 is one of the major pollutants in our atmosphere, it is not surprising that researchers have been focusing on the behavior and fate of SO_2 in our atmosphere.[27, 28] However, hydration of SO_2 to H_2SO_3 has not been observed in our atmosphere because of its slow rate.[29] Instead, SO_2 is oxidized, formally to SO_3, in several steps. Therefore, much research on mechanisms describing the oxidation of SO_2 has been done. It has been shown that oxidizing agents like $HO^{\bullet}$ and O_2 are responsible for the oxidation to SO_3.[20, 30–37] Then SO_3 is hydrated and forms sulfuric acid, H_2SO_4, in a multistep mechanism.[38–52] In this study we investigate the kinetic stability of H_2SO_3 and its deuterated form by transition-state-theory considerations. We evaluate which laboratory conditions are necessary to synthesize sulfurous acid and characterize H_2SO_3 spectroscopically. Additionally, we show for the first time that a symmetric sulfurous acid dimer is thermodynamically stable with respect to dissociation into $SO_2 + H_2O$.

Computational Methods

In order to calculate reaction rate constants, we have applied the variational transition-state-theory approach (VTST) with inclusion of quantum chemical effects like tunneling and corner cutting.[53–65] This approach requires a detailed knowledge of the potential-energy surface (PES). Calculation of a PES is computationally expensive, therefore the PES was calculated by employing the hybrid density-functional method B3LYP,[66–68] with the 6–31+G(d) basis set, which is known to yield a reasonably good description of the PES.[13, 52, 69–71] The minimum energy path (MEP), which is the path of least energy connecting products and reactants in internal mass-weighted coordinates, was determined by using the Page–McIver algorithm.[72, 73] The step size was set to 0.05 bohr, and at every third step along the MEP, second derivatives of the energy with respect to the nuclear coordinates were determined. To improve the quality of the PES, the B3LYP energy surface was interpolated to three high level stationary points (i.e., the reactants, the transition state, and the products) according to an interpolation scheme that also maps the harmonic frequencies and moments of inertia onto the high-level data.[74, 75] The three stationary points (reactants, transition state, and products) have been determined at several higher levels of theory, namely MP2/aug-cc-pVxZ (x = D, T),[76, 77] CCSD(T)/aug-cc-pVxZ//MP2/aug-cc-pVxZ [x = D, T; shorthand notation CCSD(T)/VxZ],[78] and Gaussian theory [G2(MP2)].[79, 80] Comparison of these high-level methods showed that they are in good agreement with each other within chemical accuracy. Harmonic vibrational frequencies were determined at the B3LYP/6–31+G(d) and the MP2/aug-cc-pVxZ (x = D, T) levels of theory. Quantum-chemical corrections have been applied to the variational transition-state-theory result by the microcanonical-optimized multidimensional-tunneling approach. In this approach, the Arrhenius prefactor of the rate constant is multiplied by a transmission coefficient κ. The transmission coefficient is evaluated by different methods, which consider that the system tunnels along shorter paths in the course of the reaction that are more demanding in terms of energy. The methods we consider are the small-curvature-tunneling (SCT) and large-curvature-tunneling (LCT) approaches within the framework of semiclassical theory.[81] The SCT approximation[55, 82] allows moderate corner-cutting along a curved MEP and is calculated by means of the centrifugal dominant small-curvature semiclassical adiabatic ground-state tunneling method according to the concept of Marcus and Coltrin.[54, 55, 61, 83, 84] The LCT correction assumes that tunneling occurs along straight-line connections between the reactant and the product valley; this leads to tunneling paths far off the MEP in the nonadiabatic region of the PES. We employed the large-curvature ground-state approximation version 4 (LCG4)[85] to calculate LCT effects. Due to the involvement of proton transfer in the course of H_2SO_3 decomposition, we also investigated the influence of the substitution of "normal" hydrogen (i.e. ^1_1H) by deuterium (^2_1H). Due to the difference in mass between ^1_1H and ^2_1H, molecules carrying either of the two isotopes have different zero-point energies. The mass difference will usually result in a smaller transmission coefficient for D transfer compared with H transfer. Therefore we determined the rate constant $k_{D_2SO_3}$ for the deuterated reaction, which was done in analogy to $k_{H_2SO_3}$. The MEP was recalculated at the B3LYP/6–31+G(d) level of theory with ^2_1H instead of ^1_1H and then interpolated to G2(MP2). Rate constants and transmission coefficients were calculated by VTST and the microcanonical optimized multidimensional tunneling approach, respectively. The kinetic isotope effect (*KIE*) was calculated as the ratio between "normal" and deuterated reaction-rate constants $KIE = \frac{k_{H_2SO_3}}{k_{D_2SO_3}}$

All stationary points were determined with the Gaussian 98 program package,[86] and the kinetics calculations were performed with Polyrate 8.5[87] and Gaussrate 8.6,[88] which is an interface between Gaussian 98 and Polyrate 8.5.

Results and Discussion

Sulfurous acid: As already outlined in the introduction, there are two isomeric forms with stoichiometry H_2SO_3 when sulfur is in the oxidation state S^{IV}.[15] Since the "sulfurous acid" isomer is more stable than the sulfonic acid isomer, we have concentrated only on sulfurous acid. In fact Li and McKee reported that the standard state free energy (ΔG^0) for the reaction $SO_2 + H_2O \rightarrow H_2SO_3$ is 14.6 kcal mol^{-1} at 298.15 K at the G2 level of theory.[20] This is already highly endergonic, so the sulfonic acid isomer would be even more endergonic. The standard-state free-energy change reported by Li and McKee is in very good agreement with our G2(MP2) result of ΔG^0(298.15 K, 1 bar) = 15.1 kcal mol^{-1}. Another level of theory namely CCSD(T)/VTZ yields a ΔG^0(298.15 K) of 12.6 kcal mol^{-1}, which is 2 kcal mol^{-1} lower than the G2 results. It is difficult to judge which of the results is most accurate in describing the zero-point energy: while G2 uses scaled Hartree–Fock harmonic frequencies with a small basis set, we used Møller–Plesset perturbation theory with a large basis set [MP2/aug-cc-pVTZ]. However, we used the CCSD(T)/VTZ energies because we believe in using the larger basis set. Figure 1 shows changes in free energy and in standard-state free energy as a function of temperature. At

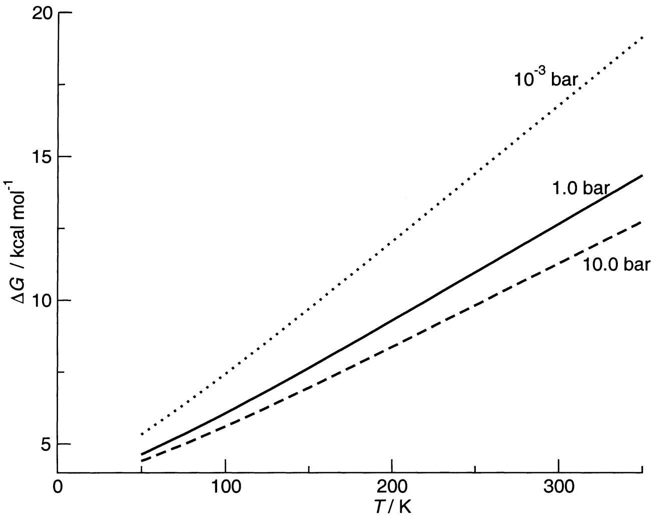
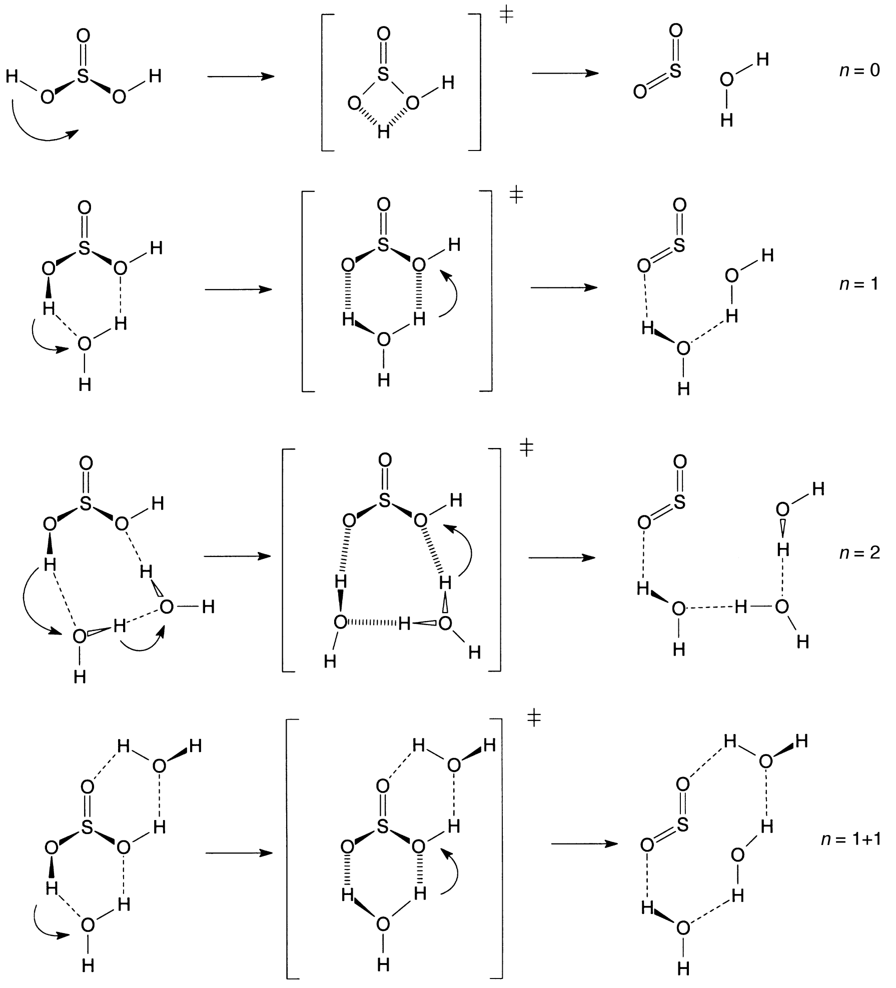


Figure 1. Free-energy change for the formation of H_2SO_3 according to the reaction $SO_2 + H_2O \rightarrow H_2SO_3$. Three different pressures were investigated, namely 0.001, 1.0 (standard state), and 10.0 bar. The energies were determined at the CCSD(T)/aug-cc-pVTZ//MP2/aug-cc-pVTZ level of theory, and zero point corrections were obtained with MP2/aug-cc-pVTZ.

77 K, ΔG^0 for this reaction is $+5.4$ kcal mol^{-1}; this demonstrates that at this temperature H_2SO_3 is only slightly unstable. The structure predicted in this study does not deviate significantly from the one reported by Li and McKee.[20] The orientation of the hydrogen atoms is *cis*-like to the double-bond oxygen, as indicated in Scheme 1. We also identified a *trans*-like H_2SO_3 molecule, which is 0.98 kcal mol^{-1} higher in energy with a *cis*–*trans* isomerisation barrier of 2.38 kcal mol^{-1} (determined at the CCSD(T)/VTZ level of theory).

Mechanism of H_2SO_3 decomposition: The mechanism of H_2SO_3 decomposition is shown schematically in Scheme 1 ($n = 0$). The transition state during H_2SO_3 decomposition is comprised of a four-membered ring that suffers from high ring strain, which in turn explains the high reaction barrier of 30.0 kcal mol^{-1}. In the presence of only one water molecule, the mechanism proceeds via a six-membered transition state as shown in Scheme 1 ($n = 1$). This transition state does not suffer so much from ring train, and therefore the reaction barrier is 12.5 kcal mol^{-1} lower than for $n = 0$. From the mechanistic point of view, one proton from H_2SO_3 is transferred to the assisting water molecule and not directly to the leaving –OH group. The water molecule in turn transfers one of its own protons to the –OH leaving group. Such a mechanism is termed water-mediated proton transfer, and a similar mechanism has been described by Li and McKee.[20] For cases with two water molecules there are several mechanisms: the probably two most important ones are drawn in Scheme 1 and termed $n = 2$ and $n = 1+1$. The $n = 2$ mechanism is the continuation of the previous mechanisms with an increase in size of the transition-state ring. The transition state ring is eight-membered, and one of the protons is transferred via both water molecules to the leaving group. In contrast to this mechanism, the $n = 1+1$ mechanism can be seen as an "improved" version of the $n = 1$ reaction. One water molecule is actively involved in the proton transfer and the other water molecule is only a spectator. This spectator stabilizes the transition state and therefore lowers the reaction barrier. Table 1 summarizes the reaction barriers for the different reaction mechanisms.



Scheme 1. Reaction mechanisms for the decomposition of H_2SO_3. The left-hand structures correspond to the reaction complexes, the middle ones to transition states and the right-hand ones to the products. In the series $n = 0$, $n = 1$, and $n = 2$ the transition-state ring size increases systematically from 4 to 8, whereas in the $n = 1+1$ system, the second water molecule acts as a spectator molecule that stabilizes the transition state by formation of hydrogen bridges; this results in a lower reaction barrier than in the pure $n = 1$ case. (The arrows indicate the motion of protons during the reaction.)

Table 1. Energy barriers and reaction energies of the reactions H_2SO_3 + $n\,H_2O \rightarrow (n{+}1)\,H_2O$ + SO_2 at the G2(MP2) and CCSD(T)/aug-cc-pVxZ//MP2/aug-cc-pVxZ (x = D, T) levels of theory. All values are in kcal mol^{-1}.

n	Method	Energy Barrier	Reaction Energy
0	G2(MP2)	30.0	– 8.09
	CCSD(T)/VDZ	27.4	– 6.82
	CCSD(T)/VTZ	28.6	
1	G2(MP2)	17.4	– 5.42
	CCSD(T)/VDZ	17.7	– 4.47
2	G2(MP2)	12.4	– 8.32
1+1	G2(MP2)	8.44	– 5.05

The reaction barrier for $n = 1{+}1$ is 4.0 kcal mol^{-1} lower than the barrier for $n = 2$; this makes the $n = 1{+}1$ mechanism preferable. Taking a look at the reaction paths of the different mechanisms shows that the shape of the minimum energy path (MEP) with $n = 2$ water molecules is higher but narrower than the $n = 1{+}1$ mechanism (see Figure 2). The shape of the MEP has an effect on the probability of tunneling, which will be discussed in more detail below. Extending the theoretical consideration of H_2SO_3 decomposition to a "real event" (either in solution, gas-phase, or crystal) this process is autocatalytic. Every single decomposition event releases one molecule of water that can act as a catalyst to destroy the next H_2SO_3 molecule and so forth. In the gas-phase, however, reaction mechanisms with a low number of water molecules will occur since the probability that several water molecules come into contact with H_2SO_3 is small.

Rate of decomposition and kinetic isotope effects: Figure 3A shows the rates of H_2SO_3 decomposition for the different reaction channels. Pure H_2SO_3 decomposes at a rate of $7.8 \times 10^{-6}\,s^{-1}$ at 300 K. This corresponds to a half-life of approximately 24 hours. The reaction rates of "water-contaminated" H_2SO_3 increase up to $7.1 \times 10^{4}\,s^{-1}$ ($n = 1{+}1$), which corresponds to a half-life of only 10 µs and is 9×10^{9} times faster than the uncatalyzed reaction. The value for the rate constant (for mechanism $n = 1{+}1$) at room temperature is only lower than the value of H_2SO_3 decomposition determined experimentally by Eigen et al. for an aqueous solution by a factor of 90.[89] An extension of the $n = 1{+}1$ mechanism to an $n = 1{+}m$ mechanism will presumably lead to a result that is comparable to experiment and will be the subject of future studies.

At lower temperatures, the $n = 2$ mechanism is faster than the $n = 1{+}1$ mechanism, whereas at higher temperatures we observe a crossover, and the $n = 1{+}1$ mechanism becomes predominant. These large differences in the reaction rates are caused mainly by the much stronger acceleration of the $n = 2$ mechanism due to tunneling as compared with the $n = 1{+}1$ mechanism. The higher barrier in the $n = 2$ case together with the much lower tunneling enhancement than in the $n = 1{+}1$ case lead to the very rare case of a crossing in the reaction-rate constants as a function of the temperature alone. This means

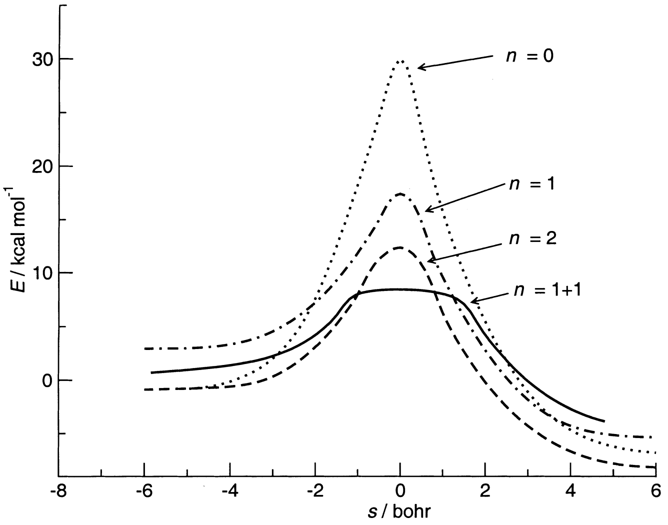


Figure 2. Potential energy along the minimum-energy path as a function of the reaction coordinate s for the reactions H_2SO_3 + $n\,H_2O \rightarrow SO_2$ + $(n{+}1)\,H_2O$ for n between 0 and 2. The reaction barrier decreases for an increasing number of water molecules n. While the barrier becomes lower and narrower for $n = 1$ and 2 relative to the uncatalyzed reaction, for $n = 1{+}1$ (one spectator water molecule) the reaction barrier is the lowest but becomes wider again. The negative side of s corresponds to "reactant-like" species, the positive side to "product-like" species and $s = 0$ to the transition state. Reaction barriers for H_2SO_3 decomposition are $n = 0$: 30.0 kcal mol^{-1}, $n = 1$: 17.4 kcal mol^{-1}, $n = 2$: 12.4 kcal mol^{-1}, and $n = 1{+}1$: 8.44 kcal mol^{-1}. Values determined at the G2(MP2) level of theory.

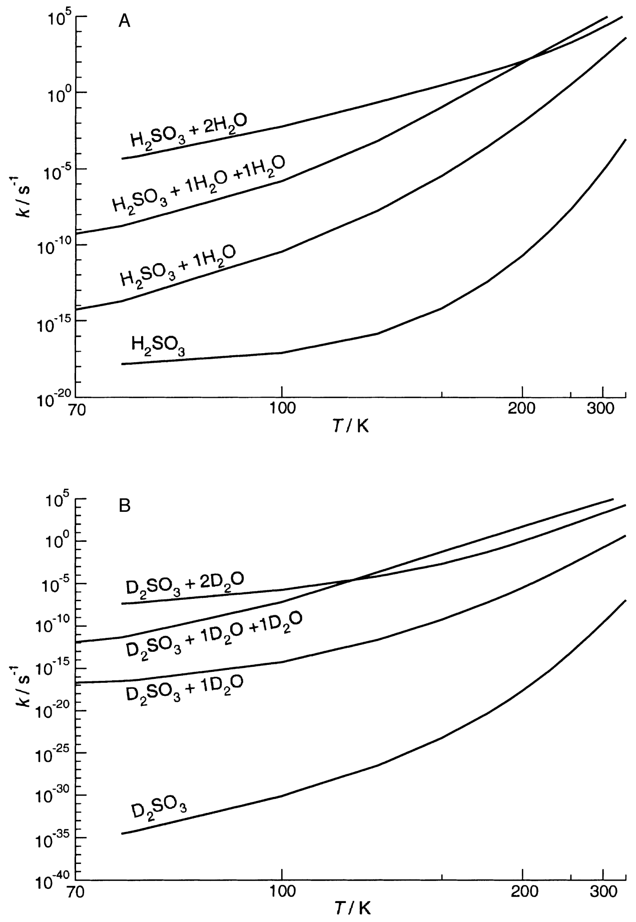


Figure 3. Reaction rates of sulfurous acid decomposition, as a function of temperature, as catalyzed with no, one, or two water molecules. A) reaction rate constants with the $^{1}_{1}$H isotope, B) reaction rates for the deuterium ($^{2}_{1}$H) isotopes. In both cases quantum-mechanical tunneling is important. The contribution of tunneling is lower for the deuterium-substituted reaction channels, thus the cross-over between $n = 2$ and $n = 1{+}1$ occurs at lower temperatures.

that the chemical mechanism changes on reduction of the temperature while keeping all other experimental parameters constant, and goes over an eight-membered instead of a six-membered transition state. However, if we consider possible laboratory conditions, for instance the temperature of liquid nitrogen (77 K), we observe that pure sulfurous acid is kinetically stable for 15×10^9 years ($k = 1.5 \times 10^{-18}\,\mathrm{s}^{-1}$) but two water molecules lower this half-life to a few hours ($k = 4.7 \times 10^{-5}\,\mathrm{s}^{-1}$). As already indicated, tunneling plays a very important role in the course of H_2SO_3 decomposition because it accelerates the reaction rate by several orders of magnitude. Therefore, we have substituted ${}^1_1\mathrm{H}$ by deuterium (${}^2_1\mathrm{H}$) and investigated the kinetic isotope effect on the reaction rates (see Figure 3B). The reaction-rate constants with deuterated species are significantly lower, and the kinetic isotope effects (*KIE*) are relatively big for some of the reactions. The *KIE*s are given in Table 2. In terms of kinetic stability, the *KIE* increases the half-life of pure H_2SO_3 6.3×10^{16}-fold at 77 K and 3.2×10^4-fold at 300 K. These rates of decomposition correspond to half-lives of 8.0×10^{26} years at 77 K and still 90 years at 300 K.

Table 2. Kinetic isotope effects $\left(\frac{k_\mathrm{H}}{k_\mathrm{D}}\right)$ for the decomposition of H_2SO_3 catalyzed by $n = 0$ to $n = 2$ water molecules.

T [K]	*KIE*			
	$n = 0$	$n = 1$	$n = 1{+}1$	$n = 2$
77	5.3×10^{16}	6.2×10^3	4.0×10^2	1.2×10^3
100	1.1×10^{13}	6.8×10^3	25	3.5×10^3
150	1.2×10^9	6.5×10^3	2.2	1.6×10^3
175	7.8×10^7	5.1×10^3	1.97	4.4×10^2
200	9.5×10^6	3.7×10^3	1.86	1.2×10^2
300	3.2×10^4	1.2×10^3	1.69	10.5
350	8.3×10^3	9.2×10^2	1.65	7.1

The cross-over between mechanisms $n = 2$ and $n = 1{+}1$ has major consequences for the reaction mechanism. First of all, the predominant mechanism at lower temperatures is via an eight-membered transition state that is favored over a six-membered transition state. At approximately 170 K both mechanisms are equally important, at higher temperatures the six-membered transition-state mechanism becomes the more dominant one. Even more interesting is the fact that for the deuterated species this cross-over occurs at a much lower temperature (approx. 120 K). Thus, in the temperature range between 120 and 170 K the predominant mechanism for the ${}^1_1\mathrm{H}$- and ${}^2_1\mathrm{H}$-substituted molecules are different. From an experimental point of view, this would mean that in this range the observed *KIE* would be a ratio between two different reaction channels. Therefore, the *KIE*s between 120 and 170 K reported in this study will not coincide with experimentally observable *KIE*s.

Sulfurous acid dimer: The sulfurous acid monomer turned out to be thermodynamically unstable with respect to SO_2 and H_2O over the complete temperature range investigated, even though the ΔG^0 at 50 K was only $+4.6\,\mathrm{kcal\,mol^{-1}}$. However, we investigated whether there is a sulfurous acid dimer that is stable compared to the decomposition products SO_2 and H_2O. We found a highly symmetric supermolecule with a center of inversion (point group C_i) that is shown in Figure 4.

Figure 4 also shows the change in standard-state free energy for the decomposition of the sulfurous acid dimer $(H_2SO_3)_2$ into the monomer H_2SO_3 and into the constituents SO_2 and H_2O according to the reactions

$$(H_2SO_3)_2 \rightarrow 2\,H_2SO_3 \qquad (2)$$

$$(H_2SO_3)_2 \rightarrow 2\,SO_2 + 2\,H_2O \qquad (3)$$

For reaction (2), ΔG^0 is positive throughout the whole investigated temperature range. The entropy of the dimer is lower than that of the two monomers; however, the gain in enthalpy due to the formation of four hydrogen bridges clearly overcomes the entropic effect. Even though the four hydrogen bridges are not linear, which normally lowers the strength of hydrogen bonds significantly, the sum of all four hydrogen bridges is $-21.8\,\mathrm{kcal\,mol^{-1}}$, which is on average still $-5.5\,\mathrm{kcal\,mol^{-1}}$ each. Due to the symmetry of the molecule, the protons can change their position and hop between the two H_2SO_3 entities. This hopping occurs at a frequency of about 5 GHz at 77 K, and the barrier for the proton transfer is

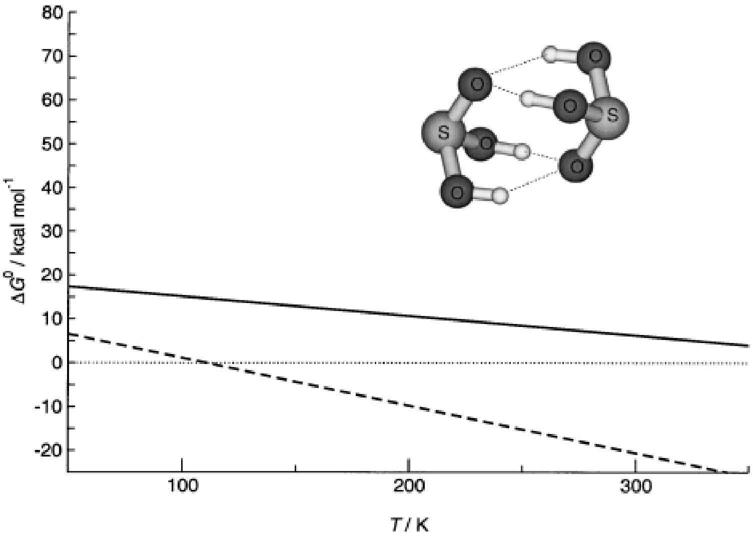


Figure 4. Standard-state free-energy change (ΔG^0) for the decomposition of the H_2SO_3 dimer. The solid line shows ΔG^0 for the decomposition of the dimer into the monomers $[(H_2SO_3)_2 \rightleftharpoons 2\,H_2SO_3]$, whereas the dashed line represents decomposition of the dimer into the constituents SO_2 and H_2O $[(H_2SO_3)_2 \rightleftharpoons 2\,H_2O + 2\,SO_2]$. The insert shows the structure of the highly symmetric sulfurous acid dimer with its four hydrogen bridges. The dimer is stable relative to the monomers within the total temperature range and is also stable compared with SO_2 and H_2O below 110 K. Harmonic infrared spectroscopic frequencies (intensity in $\mathrm{km\,mol^{-1}}$): 3523.03 (1244), 3466.84 (0.1), 1276.10 (163), 1153.21 (170), 1095.90 (485),783.08 (330), 777.35 (439), 636.74 (17), 626.98 (96), 471.53 (42),374.76 (12), 364.12 (7.1), 213.13 (43), 96.01 (1.0), 62.91 (0.3)—calculated at the MP2/aug-cc-pVDZ level of theory.

© 2002 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim

12.0 kcal mol^{-1} at both the G2(MP2) and the CCSD(T)/VDZ level. Additionally such a symmetric supermolecule as the sulfurous acid dimer shows a ground-state tunneling splitting, which is a small difference in the ground-state energy potential occurring in symmetric molecules.[90] The ground-state tunneling splitting determined for $(H_2SO_3)_2$ is 2.2 Hz (equivalent to 1.6×10^{-19} J or 7.3×10^{-11} cm^{-1}), which is clearly outside the experimentally accessible range and cannot be used for characterization.[91, 92] Therefore the infrared spectroscopic frequencies are shown in the legend of Figure 4 and can be used for later spectroscopic identification. If we take a look at the standard-state free-energy change for reaction (3), we find that ΔG^0 is positive at temperatures below 110 K. At 77 K, the thermodynamic stability of the $(H_2SO_3)_2$ supermolecule is -3.5 kcal mol^{-1} with respect to SO_2 and H_2O. Thus, H_2SO_3 is not only kinetically stable, as shown above, but the dimer is also thermodynamically stable below 110 K with respect to dissociation into $2\,SO_2$ and $2\,H_2O$. Compared with decomposition into a $(SO_2 \cdot H_2O)_2$ complex, the dimer is energetically higher by a $\Delta G^0(77\,K)$ of 9.6 kcal mol^{-1} [G2(MP2)]. However, we do not believe that decomposition into this complex does actually happen because this process seems to be kinetically difficult. In fact, we were not able to find a fully converged transition state for this reaction, but our best guess for the reaction barrier with an almost converged transition state is 19.7 kcal mol^{-1} at the B3LYP/6–31+G(d) level and might be even larger for higher levels of theory. A conservative TST guess based on such a barrier suggests a rate of decomposition of approximately 10^{-30} s^{-1}, which would mean a half-life of 10^{22} years. The dimer seems to be stable against attack of single water molecules, thus the direct decomposition of the dimer is highly unlikely. The alternative mechanism of decomposition by dissociation into the monomer units that might decompose into sulfur dioxide and water or the $SO_2 \cdot H_2O$ complex (probably catalyzed by additional water molecules) is thermodynamically unlikely at temperatures below 100 K due to the stability of the dimer compared with the monomer units.

Conclusion

In this study we have demonstrated that H_2SO_3 is kinetically stable at low temperatures. Even though sulfurous acid is destroyed autocatalytically by water, it has a half-life of 1.1 million years at 77 K in the presence of one water molecule. However, there are striking similarities between carbonic acid and sulfurous acid in their thermodynamic and kinetic behavior. While the monomers of both H_2SO_3 and H_2CO_3 are thermodynamically unstable with respect to dissociation (into $SO_2 + H_2O$ and $CO_2 + H_2O$, respectively),[93, 94] the dimers are stable.[11, 95] In recent studies it was possible to sublime and recondense solid carbonic acid, and thus, to prove the stability of H_2CO_3 in the gas phase[11] and to show its remarkable kinetic stability. The long half-life of H_2SO_3 at low temperatures demonstrated in this study should encourage experimentalists to perform experiments under similar conditions with lower temperatures than those that were successful for synthesizing carbonic acid. For carbonic acid, several different cryogenic techniques have been successfully applied to synthesizing it in crystalline form.[8–11] For instance, high energy and proton irradiation of cryogenic CO_2/H_2O mixtures,[8] of pure solid CO_2,[10] and protonation of bicarbonate and carbonate[9, 11] at temperatures around 200 K are conditions under which it is possible to synthesize carbonic acid. The chance of being successful in synthesizing sulfurous acid from cryogenic SO_2 under laboratory conditions is increased if deuterium is used instead of protons and if lower temperatures are applied. At 77 K, the half-life of H_2SO_3 is increased from 1.5×10^{10} years to 7.9×10^{26} years due to deuteration. Even in the presence of a small fraction of water ($n = 1$), the half-life of deuterated sulfurous acid is 710 million years, which is 700 times longer than that of “normal”, water-free sulfurous acid. Thus, in a similar way to carbonic acid, it might be possible to prepare and characterize H_2SO_3 from cryogenic SO_2, SO_2/H_2O, or HSO_3^-/ice by proton (deuterium) irradiation.

An interesting fact that can be observed is the change in reaction mechanism for the decomposition reaction of sulfurous acid due to deuteration. In the temperature range 120 K to 170 K, the mechanism of decomposition assisted by two water molecules changes upon deuteration from a six-membered transition state to an eight-membered transition state. This is largely caused by a much larger tunneling effect in one of the mechanisms. The fact that a sulfurous acid dimer is thermodynamically more stable by 3.5 kcal mol^{-1} at 77 K compared with the decomposition products SO_2 and H_2O is encouraging for experimentalists attempting to synthesize H_2SO_3. If they are successful in preparing H_2SO_3 by, for instance, one of the described techniques it is very likely that the dimer forms spontaneously out of the monomers, since this process should be barrierless. This dimer has C_i symmetry and is stabilized by altogether four hydrogen bonds; the protons can hop from one H_2SO_3 entity to the other. Once the dimer has formed, it is thermodynamically unlikely that it will dissociate back into monomers. Since this dimer is extremely stable, and it is more stable against water attack than the monomer, the chance to characterize H_2SO_3 either as a monomer or a dimer is increased.

Acknowledgement

Support from the Austrian Science Fund (FWF, project number P14357-TPH) is acknowledged. We are grateful to one of the referees for valuable suggestions.

---

[1] R. T. Sanderson, *Inorganic Chemistry*, Reinhold, New York, **1967**.
[2] D. Lyons, G. Nickless, *Inorganic Sulphur Chemistry* (Ed.: G. Nickless), Elsevier, Amsterdam, **1968**, pp. 509–533.
[3] A. F. Holleman, N. Wiberg, *Lehrbuch der anorganischen Chemie, Vol. 91–100*, de Gruyter, Berlin, **1985**.
[4] C. E. Mortimer, *Chemistry*, Wadsworth, California, USA, **1986**.
[5] N. N. Greenwood, A. Earnshaw, *Chemistry of the Elements*, Butterworth–Heinemann, **1997**.
[6] J. K. Terlouw, C. B. Lebrilla, H. Schwarz, *Angew. Chem. Int. Ed.* **1987**, *26*, 354–355; *Angew. Chem.* **1987**, *99*, 352–353.
[7] H. Falcke, S. H. Eberle, *Water Res.* **1990**, *24*, 685–688.
[8] M. H. Moore, R. K. Khanna, *Spectrochim. Acta* **1991**, *47A*, 255–262.

[9] W. Hage, A. Hallbrucker, E. Mayer, *J. Am. Chem. Soc.* **1993**, *115*, 8427–8431.

[10] J. R. Brucato, M. E. Palumbo, G. Strazzula, *Icarus* **1997**, *125*, 135–144.

[11] W. Hage, K. R. Liedl, A. Hallbrucker, E. Mayer, *Science* **1998**, *279*, 1332–1335.

[12] R. Ludwig, A. Kornath, *Angew. Chem. Int. Ed.* **2000**, *39*, 1421–1423; *Angew. Chem.* **2000**, *112*, 1479–1481.

[13] T. Loerting, C. Tautermann, R. T. Kroemer, I. Kohl, A. Hallbrucker, E. Mayer, K. R. Liedl, *Angew. Chem. Int. Ed.* **2000**, *39*, 891–8944; *Angew. Chem.* **2000**, *112*, 919–922.

[14] *CRC Handbook of Chemistry and Physics*, 80th ed (Ed.: D. R. Lide), CRC Press, Boca Raton, **2000**.

[15] D. A. Horner, R. E. Connick, *Inorg. Chem.* **1986**, *25*, 2414–2417.

[16] A. Strömberg, O. Gropen, U. Wahlgren, O. Lindqvist, *Inorg. Chem.* **1983**, *22*, 1129–1133.

[17] R. E. Brown, F. Barber, *J. Phys. Chem.* **1995**, *99*, 8071–8075.

[18] A. Smith, M. A. Vincent, I. H. Hillier, *J. Phys. Chem. A* **1999**, *103*, 1132–1139.

[19] D. Sülzle, M. Verhoeven, J. K. Terlouw, H. Schwarz, *Angew. Chem. Int. Ed. Engl.* **1988**, *27*, 1533–1534; *Angew. Chem.* **1988**, *100*, 1591–1592.

[20] W.-K. Li, M. L. McKee, *J. Phys. Chem. A* **1997**, *101*, 9778–9782.

[21] E. Bishenden, D. J. Donaldson, *J. Phys. Chem. A* **1998**, *102*, 4638–4642.

[22] A. H. Otto, R. Steudel, *Eur. J. Inorg. Chem.* **2000**, 617–624.

[23] A. W. Castleman, Jr., K. H. Bowen, Jr., *J. Phys. Chem.* **1996**, *100*, 12911–12944.

[24] Q. Zhong, S. M. Hurley, A. W. Castleman, Jr., *Int. J. Mass. Spectrom.* **1999**, *185/186/187*, 905–911.

[25] K. Matsumura, F. J. Lovas, R. D. Suenram, *J. Chem. Phys.* **1989**, *91*, 5887–5894.

[26] F. Fleyfel, H. H. Richardson, J. P. Devlin, *J. Phys. Chem.* **1990**, *94*, 7032–7037.

[27] T. E. Graedel, P. J. Crutzen, *Chemie der Atmosphäre, Bedeutung für Klima und Umwelt*, Spektrum, Heidelberg, **1994**.

[28] K. Capaldo, J. J. Corbett, P. Kasibhatla, P. Fischbeck, S. N. Pandis, *Nature* **1999**, *400*, 743–746.

[29] T. Loerting, R. T. Kroemer, K. R. Liedl, *Chem. Commun.* **2000**, 999–1000.

[30] J. V. McArdle, M. R. Hoffmann, *J. Phys. Chem.* **1983**, *87*, 5425–5429.

[31] Y.-Y. Lee, W.-C. Kao, Y.-P. Lee, *J. Phys. Chem.* **1990**, *94*, 4534–4540.

[32] L. Schriver, D. Carrere, A. Schriver, K. Jaeger, *Chem. Phys. Lett.* **1991**, *181*, 505–511.

[33] O. Timpe, R. Schlögl, *Ber. Bunsen.-Ges.* **1993**, *97*, 1076–1085.

[34] M. A. Vincent, I. J. Palmer, I. H. Hillier, E. Akhmatskaya, *J. Am. Chem. Soc.* **1998**, *120*, 3431–3439.

[35] D. Fulle, H. F. Hamann, H. Hippler, *Phys. Chem. Chem. Phys* **1999**, *1*, 2695–2702.

[36] H. Chaabouni, L. Schriver-Mazzuoli, A. Schriver, *J. Phys. Chem. A* **2000**, *104*, 3498–3507.

[37] F.-Y. Leung, A. J. Colussi, M. R. Hoffmann, *J. Phys. Chem. A* **2001**, *105*, 8073–8076.

[38] T. S. Chen, P. L. Moore Plummer, *J. Phys. Chem.* **1985**, *89*, 3689–3693.

[39] X. Wang, Y. G. Jin, M. Suto, L. C. Lee, *J. Chem. Phys.* **1988**, *89*, 4853–4860.

[40] C. E. Kolb, J. T. Jayne, D. R. Worsnop, M. J. Molina, R. F. Meads, A. A. Viggiano, *J. Am. Chem. Soc.* **1994**, *116*, 10314–10315.

[41] T. Reiner, F. Arnold, *J. Chem. Phys.* **1994**, *101*, 7399–7407.

[42] M. Hofmann, P. v. R. Schleyer, *J. Am. Chem. Soc.* **1994**, *116*, 4947–4952.

[43] K. Morokuma, C. Muguruma, *J. Am. Chem. Soc.* **1994**, *116*, 10316–10317.

[44] J. A. Phillips, M. Canagaratna, H. Goodfriend, K. R. Leopold, *J. Phys. Chem.* **1995**, *99*, 501–504.

[45] R. Steudel, *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1313–1315; *Angew. Chem.* **1995**, *107*, 1433–1435.

[46] E. R. Lovejoy, D. R. Hanson, L. G. Huey, *J. Phys. Chem.* **1996**, *100*, 19911–19916.

[47] J. T. Jayne, U. Pöschl, Y.-m. Chen, D. Dai, L. T. Molina, D. R. Worsnop, C. E. Kolb, M. J. Molina, *J. Phys. Chem. A* **1997**, *101*, 10000–10011.

[48] E. V. Akhmatskaya, C. J. Apps, I. H. Hillier, A. J. Masters, N. E. Watt, J. C. Whitehead, *Chem. Commun.* **1997**, 707.

[49] E. J. Meijer, M. Sprik, *J. Phys. Chem. A* **1998**, *102*, 2893–2898.

[50] L. J. Larson, M. Kuno, F.-M. Tao, *J. Chem. Phys.* **2000**, *112*, 8830–8838.

[51] L. J. Larson, F.-M. Tao, *J. Phys. Chem. A* **2001**, *105*, 4344–4350.

[52] T. Loerting, K. R. Liedl, *Proc. Natl. Acad. Sci. USA* **2000**, *97*, 8874–8878.

[53] H. Eyring, *J. Chem. Phys.* **1935**, *3*, 107–115.

[54] R. A. Marcus, M. E. Coltrin, *J. Chem. Phys.* **1977**, *67*, 2609.

[55] R. T. Skodje, D. G. Truhlar, B. C. Garrett, *J. Phys. Chem.* **1981**, *85*, 3019–3023.

[56] B. C. Garrett, D. G. Truhlar, *J. Chem. Phys.* **1983**, *79*, 4931–4938.

[57] D. G. Truhlar, W. L. Hase, J. T. Hynes, *J. Phys. Chem.* **1983**, *87*, 2664–2682.

[58] D. G. Truhlar, B. C. Garrett, *Ann. Rev. Phys. Chem.* **1984**, *35*, 159–189.

[59] D. G. Truhlar, A. D. Isaacson, B. C. Garrett, *Theory of Chemical Reaction Dynamics*, (Ed.: M. Baer), CRC Press, Boca Raton, USA, **1985**, pp. 65–137.

[60] M. M. Kreevoy, D. G. Truhlar, *Investigation of Rates and Mechanisms of Reactions*, (Ed.: C. F. Bernasconi), Wiley, New York, **1986**, pp. 13–95.

[61] K. K. Baldridge, M. S. Gordon, R. Steckler, D. G. Truhlar, *J. Phys. Chem.* **1989**, *93*, 5107–5119.

[62] *New Theoretical Concepts for Understanding Organic Reactions*, S. C. Tucker, D. G. Truhlar, *NATO ASI Ser. C* **1989**, *267*, 291–346.

[63] A. Gonzalez-Lafont, T. N. Truong, D. G. Truhlar, *J. Chem. Phys.* **1991**, *95*, 8875–8894.

[64] D. G. Truhlar, *The Reaction Path in Chemistry: Current Approaches and Perspectives*, (Ed.: D. Heidrich), Kluwer, Dordrecht, **1995**, pp. 229–255.

[65] D. G. Truhlar, B. C. Garrett, S. J. Klippenstein, *J. Phys. Chem.* **1996**, *100*, 12771–12800.

[66] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[67] P. J. Stephens, F. J. Devlin, C. F. Chabalowski, M. J. Frisch, *J. Phys. Chem.* **1994**, *45*, 11623–11627.

[68] A. D. Becke, *J. Chem. Phys.* **1997**, *107*, 8554–8560.

[69] C. Märker, P. v. R. Schleyer, K. R. Liedl, T.-K. Ha, M. Quack, M. A. Suhm, *J. Comput. Chem.* **1997**, *18*, 1695–1719.

[70] T. Loerting, K. R. Liedl, *Chem. Eur. J.* **2001**, *7*, 1662–1669.

[71] C. S. Tautermann, A. F. Voegele, T. Loerting, I. Kohl, A. Hallbrucker, E. Mayer, K. R. Liedl, *Chem. Eur. J.* **2002**, *8*, 66–73.

[72] M. Page, J. W. McIver, Jr., *J. Chem. Phys.* **1988**, *88*, 922–935.

[73] V. S. Melissas, D. G. Truhlar, B. C. Garrett, *J. Chem. Phys.* **1992**, *96*, 5758–5772.

[74] W.-P. Hu, Y.-P. Liu, D. G. Truhlar, *J. Chem. Soc. Faraday Trans.* **1994**, *90*, 1715–1725.

[75] Y.-Y. Chuang, D. G. Truhlar, *J. Phys. Chem. A* **1997**, *101*, 3808–3814.

[76] C. Møller, M. S. Plesset, *Phys. Rev.* **1934**, *46*, 618–622.

[77] T. H. Dunning, Jr., *J. Chem. Phys.* **1989**, *90*, 1007–1023.

[78] K. Raghavachari, G. W. Trucks, J. A. Pople, M. Head-Gordon, *Chem. Phys. Lett.* **1989**, *157*, 479–483.

[79] L. A. Curtiss, K. Raghavachari, G. W. Trucks, J. A. Pople, *J. Chem. Phys.* **1991**, *94*, 7221–7230.

[80] L. A. Curtiss, K. Raghavachari, J. A. Pople, *J. Chem. Phys.* **1993**, *98*, 1293–1298.

[81] M. S. Child in *International Series of Monographs on Chemistry, Vol 25*: *Semiclassical Mechanics with Molecular Applications*, Oxford Science Publications, Oxford, **1991**.

[82] R. T. Skodje, D. G. Truhlar, B. C. Garrett, *J. Chem. Phys.* **1982**, *77*, 5955–5976.

[83] D.-h. Lu, T. N. Truong, V. S. Melissas, G. C. Lynch, Y.-P. Liu, B. C. Garrett, R. Steckler, A. D. Isaacson, S. N. Rai, G. C. Hancock, J. G. Lauderdale, T. Joseph, D. G. Truhlar, *Comput. Phys. Commun.* **1992**, *71*, 235–262.

[84] Y.-P. Liu, G. C. Lynch, T. N. Truong, D.-h. Lu, D. G. Truhlar, B. C. Garrett, *J. Am. Chem. Soc.* **1993**, *115*, 2408–2415.

[85] A. Fernández-Ramos, D. G. Truhlar, *J. Chem. Phys.* **2001**, *114*, 1491–1496.

[86] *Gaussian 98*, (Revision A.9), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo,

S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

[87] *Polyrate 8.5.1*, J. C. Corchado, Y.-Y. Chuang, P. L. Fast, J. Villá, W.-P. Hu, Y.-P. Liu, G. C. Lynch, K. A. Nguyen, C. F. Jackels, V. S. Melissas, B. J. Lynch, I. Rossi, E. L. Coitiño, A. Fernandez-Ramos, R. Steckler, B. C. Garrett, A. D. Isaacson, D. G. Truhlar, University of Minnesota, Minneapolis, **2000**.

[88] *Gaussrate 8.6*, J. C. Corchado, Y.-Y. Chuang, E. L. Coitiño, D. G. Truhlar, University of Minnesota, Minneapolis, **2000**.

[89] M. Eigen, K. Kustin, G. Maass, *Z. Phys. Chem. Neue Folge* **1961**, *30*, 130–136.

[90] V. A. Benderskii, D. E. Makarov, C. A. Wight in *Advances in Chemical Physics*, *Vol.* LXXXVIII: *Chemical Dynamics at Low Temperatures*, Wiley, New York, **1994**.

[91] C. S. Tautermann, A. F. Voegele, T. Loerting, K. R. Liedl, *J. Chem. Phys.* **2002**, *117*, 1967–1974.

[92] C. S. Tautermann, A. F. Voegele, T. Loerting, K. R. Liedl, *J. Chem. Phys.* **2002**, *117*, 1962–1966.

[93] B. Jönsson, G. Karlström, H. Wennerström, B. Roos, *Chem. Phys. Lett.* **1976**, *41*, 317–320.

[94] B. Jönsson, G. Karlström, H. Wennerström, S. Forsѐn, B. Roos, J. Almlöf, *J. Am. Chem. Soc.* **1977**, *99*, 4628–4632.

[95] K. R. Liedl, S. Sekusak, E. Mayer, *J. Am. Chem. Soc.* **1997**, *119*, 3782–3784.

Received: March 13, 2002
Revised: July 29, 2002 [F3941]