Gas-Phase Ion-Molecule Reactions in Tetrahydrothiophene[†]

Kenzo HIRAOKA,^{*a)} Takashi SHODA,^{a)} Shinichi YAMABE,^{b)} and
Edgar W. IGNACIO^{c)}

(Received January 20, 1998; Accepted May 21, 1998)

Gas-phase ion-molecule reactions have been investigated using a pulsed-electron beam mass spectrometer. The proton affinity (PA) of tetrahydrothiophene (THT), C₄H₈S, has been newly determined to be 205.4 kcal mol⁻¹ by measuring the equilibria of the proton transfer reaction between 2-methyltetrahydrofuran and THT. The thermochemical data for the hydration reaction of protonated tetrahydrothiophene, C₄H₈SH⁺(H₂O)_{n-1} + H₂O = C₄H₈SH⁺(H₂O)_n, with *n* = 1–3 were measured. The small and *n*-insensitive enthalpy changes ($-\Delta H_{n-1,n}^\circ$), 11.5, 10.4 and 9.5 kcal mol⁻¹, with *n* = 1, 2, and 3, respectively, have been obtained. The fall-off of $-\Delta H_{n-1,n}^\circ$ vs. *n* is small due to the positive charge dispersal in the protonated THT. The rate of proton transfer reaction from the proton-hydrates H₃O⁺(H₂O)_n to THT was found to be roughly the collision rate in agreement with the findings due to Viggiano *et al.* [*J. Chem. Phys.*, **88**, 2469 (1988)]. *Ab initio* calculations have been carried out, and those energies (PA and $\Delta H_{n-1,n}^\circ$) have been reproduced satisfactorily.

1. Introduction

It is noteworthy that the gas-phase proton affinity of H₂O (PA = 166.5 kcal mol⁻¹) was smallest among the oxygen-, nitrogen-, and sulfur-containing organic bases¹⁾ while water is the best solvent for proton (*i.e.*, acids). For example, free energy changes of transfer of H⁺ from liquid water to liquid methanol, ethanol, and acetonitrile are 2.5, 2.7, and 11.1 kcal mol⁻¹, respectively.²⁾ The smallest proton affinity of H₂O is due to the highly localized positive charge in the three H atoms in H₃O⁺, *i.e.*, the O atom in H₃O⁺ is negatively charged.³⁾ For the hydration, the highly localized positive charge in three H atoms of H₃O⁺ makes it possible to form a strong hydrogen-bond network in which a number of H₂O molecules take part in through the enhancement effect.⁴⁾ That is, the hydrogen bonding is self-tightened by the H₂O molecules from the inner hydration shells to the outer ones. In contrast, while the aprotic solvent molecules (B) such as acetonitrile (PA = 188.4 kcal mol⁻¹) have much higher proton affinities, the heats of hydration of the protonated bases (BH⁺) are smaller than that of H₃O⁺.²⁾

In this work, the ion-molecule reactions of a soft base molecule, tetrahydrothiophene (THT), have been investigated using a pulsed-electron beam mass spectrometer. The measured gas-phase proton affinity (PA = 205.4 kcal mol⁻¹) of THT was found to be larger than ammonia (PA = 204.0 kcal mol⁻¹), while the hydration energies of the protonated THT were smaller than 12 kcal mol⁻¹. This is in accord with the fact that THT is a weak base in an aqueous solution.

2. Experimental and Computational

The experiments were made with a pulsed-electron beam mass spectrometer which has been described previously.^{5)–7)} An ion source of solid stainless steel heated with a sheath heater was used. Mixtures of reagent compounds of interest in a carrier gas were prepared in a gas-handling system and allowed to flow into the ion source. Ionizing pulses of 2-keV electron beam initiated reaction sequences leading to the equilibria of interest. Ions escaping from the field-free ion source into an evacuated region were mass analyzed by a quadrupole mass spectrometer (ULVAC MSQ-400) and collected in a multichannel analyzer as a function of their arrival time after the electron pulse. The ion counts collected in a multichannel analyzer were transferred to a microcomputer, and time profiles of the ion counts were recorded on the x-y plotter.

The proton affinity of THT was measured by observing the proton-transfer equilibria between THT and 2-methyltetrahydrofuran (2-MTHF, C₅H₁₀O).

In this measurement, 10–100 μTorr of THT and 2-MTHF were introduced into the ~4 Torr CH₄ reagent gas. The measured equilibrium constants were found to be independent of the mixed ratio of THT and 2-MTHF.

In the present study, equilibria for the following hydration reaction have been also dealt with.

In the measurements of the equilibria for reaction (2), small amounts of H₂O and THT were added through stainless steel capillaries into the ~4 Torr methane carrier gas. The partial pressures of H₂O and THT were 10–100 mTorr and ~30 μTorr, respectively. The partial pressure of THT had to be suppressed much lower than that of H₂O in order to avoid the formation of proton-bound dimer cation H⁺(THT)₂. Under these experimental conditions, the protonated THT was produced by the proton transfer reaction (3).

[†] This paper is dedicated to Professor Masahiko Tsuchiya
^{*a)} Faculty of Engineering, Yamanashi University (Takeda-4, Kofu 400-8511, Japan)

^{b)} Department of Chemistry, Nara University of Education (Takabatake-cho, Nara 630-8528, Japan)

^{c)} Department of Chemistry, College of Science and Mathematics, MSU-Iligan Institute of Technology (Iligan City 9200, Philippines)

Under the present experimental conditions, the major initial products were $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$. These proton hydrates are converted slowly to $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_m$. The produced hydrated $\text{C}_4\text{H}_8\text{SH}^+$ decomposed unimolecularly to reach the equilibrium concentrations. It took about one ms to establish the equilibria for $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_n$ ions after the electron pulse. The time required to establish equilibria for reaction (2) was found to increase with n . For $n=3$, it took more than 1.5 ms after the electron pulse to establish the equilibria and a great care must be taken to measure the equilibrium constants.

Geometries of $\text{C}_4\text{H}_8\text{S}$, $\text{C}_4\text{H}_8\text{SH}^+$, and $\text{C}_4\text{H}_8\text{SH}^-(\text{H}_2\text{O})_n$ ($n=1, 2$, and 3) were determined by ab initio calculations. The RHF/6-31G* method was used for geometry optimizations and the subsequent vibrational analyses. Zero-point vibrational energies were scaled down by 0.9135 as recommended.⁶⁾ Electronic energies were obtained by single-point calculations of a density functional method, B3-LYP,⁹⁾ with the 6-311+G(2df, 2p) on the RHF/6-31G* geometries. The wave-function is the most accurate one for practical large-size systems.¹⁰⁾ The B3-LYP/6-311+G(2df, 2p)/RHF/6-31G* calculations were carried out, using the GAUSSIAN 94 program.¹¹⁾

3. Results and Discussion

3.1 Proton affinity of tetrahydrothiophene

The proton affinity (PA) of THT has not been measured yet. As a reference compound for the determination of the proton affinity of THT, we introduced several oxygen-containing compounds such as alcohols and ketones into the ion source with a presence of THT. After many attempts, we found that PA of THT was

Fig. 1. Van't Hoff plot for the proton transfer reaction, $\text{C}_5\text{H}_{10}\text{OH}^- - \text{C}_4\text{H}_8\text{S} = \text{C}_4\text{H}_8\text{SH}^- - \text{C}_5\text{H}_{10}\text{O}$.

Fig. 2. Van't Hoff plots for the clustering reactions, $\text{C}_4\text{H}_8\text{SH}^-(\text{H}_2\text{O})_{n-1} + \text{H}_2\text{O} = \text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_n$.

Table 1. Thermochemical Data of Proton Transfer Reaction, $(2\text{-MTHF})\text{H}^+ + \text{THT} = (\text{THT})\text{H}^+ + 2\text{-MTHF}$ and Hydration Reactions of Protonated Tetrahydrothiophene $((\text{THT})\text{H}^+)$ Obtained Experimentally and Theoretically
Enthalpy changes are in kcal mol^{-1} , and entropy ones are in $\text{cal mol}^{-1} \text{K}^{-1}$.

Reaction	Measured		Computed*	
	$-\Delta H^\circ$	$-\Delta S^\circ$	$-\Delta H_e$	$[D_e]$
$(2\text{-MTHF})\text{H}^+ + \text{THT} = (\text{THT})\text{H}^+ + 2\text{-MTHF}$	1.8	0.4	—	—
$(\text{THT})\text{H}^+ + \text{H}_2\text{O} = (\text{THT})\text{H}^+(\text{H}_2\text{O})$	11.5	20	13.70	[11.33]
$(\text{THT})\text{H}^+(\text{H}_2\text{O}) + \text{H}_2\text{O} = (\text{THT})\text{H}^+(\text{H}_2\text{O})_2$	10.4	20	12.33	[9.97]
$(\text{THT})\text{H}^+(\text{H}_2\text{O})_2 + \text{H}_2\text{O} = (\text{THT})\text{H}^+(\text{H}_2\text{O})_3$	9.5	21	11.22	[8.85]

* Theoretical values of ΔH° are at $T=300 \text{ K}$, and those of D_e are at $T=0 \text{ K}$ (electronic and zero-point vibrational energies).

quite close to that of 2-MTHF. Figure 1 represents van't Hoff plots for the proton transfer reaction (1). The observed straight line with the positive slope indicates that PA (THT) is larger than PA (2-MTHF), *i.e.*, reaction (1) is exothermic. Thermochemical data for reaction (1) obtained from Fig. 1 are $\Delta H^\circ = -1.8 \text{ kcal mol}^{-1}$ and $\Delta S^\circ = -0.4 \text{ cal mol}^{-1} \text{K}^{-1}$. Using the value of PA (2-MTHF) = $203.6 \text{ kcal mol}^{-1}$,¹²⁾ the proton affinity of THT is determined to be $205.4 \text{ kcal mol}^{-1}$. The negative enthalpy and entropy changes for reaction (1) are in accord with the general trend known as the compensation effect, *i.e.*, exothermic reactions often result in the decrease in entropy changes. A theoretical value of PA ($=204.3 \text{ kcal mol}^{-1}$) has been obtained which is in good agreement with the present experimental one ($=205.4 \text{ kcal mol}^{-1}$). The agreement demonstrates that the B3-LYP/6-311+G(2df, 2p)/RHF/6-31G* computational method is a practical and accurate way for estimating or furthermore revising experimental PA values.

3.2 Hydration reaction of protonated tetrahydrothiophene

Figure 2 shows the van't Hoff plots for reaction (2). The enthalpy changes $-\Delta H_{n-1,n}^\circ$ (and entropy changes $-\Delta S_{n-1,n}^\circ$) for the reaction obtained from the figure are $11.5 \text{ kcal mol}^{-1}$ ($20 \text{ cal mol}^{-1} \text{K}^{-1}$), $10.4 \text{ kcal mol}^{-1}$ ($20 \text{ cal mol}^{-1} \text{K}^{-1}$), and $9.5 \text{ kcal mol}^{-1}$ ($21 \text{ cal mol}^{-1} \text{K}^{-1}$) for $n=1, 2$, and 3, respectively (Table 1). It is worthwhile noting that the $-\Delta H_{n-1,n}^\circ$ values show a rather gradual decrease with n . In our previous work,¹³⁾ we could not get the $n=3$ thermochemical data ($n=1$ and 2 only). Since then, careful measurements have been repeated. A proton transfer described in the next sub-section tends to interfere with observation of the $\text{C}_4\text{H}_8\text{SH}^+$

(H₂O)₃ cluster. We have succeeded in determining the $n=3$ data here along with information of the proton transfer.

In Table 1, theoretical binding energies are also displayed. They were calculated at $T=300$ K and were found to be *ca.* 2 kcal mol⁻¹ larger than experimental ones (*e.g.*, 11.5 kcal mol⁻¹ (exptl) and 13.70 kcal mol⁻¹ (theory) with $n=1$). At $T=0$ K, D_e values are smaller than experimental ones. At present, it is not clear which is more reliable, experimental or calculated energies. But, theoretical energies reproduce well their gradual decrease (by *ca.* 1 kcal mol⁻¹).

3.3 Proton transfer reaction from H₃O⁺(H₂O)_{*n*} to THT

Reactions of cluster ions provide insight into the transition from gas phase to solution chemistry and are important in understanding the chemistry of the earth's upper atmosphere. For example, the primary ion NO⁺ in the upper atmosphere is converted to the proton hydrates *via* reaction (4).¹⁴⁾

When the partial pressure of water is more than 3 orders of magnitude higher than that of THT, the protonated THT and its hydrates are produced by the reaction of proton hydrates with THT (reaction (3)). Figure 3 shows the temporal profiles of the normalized intensities of ions observed in 30 μ Torr THT and 99.6 mTorr H₂O in 4.05 Torr CH₄ at 325.4 K. In the figure, the half-life for the formation of C₄H₈SH⁺(H₂O)_{*n*} is seen to be about 0.4 ms. This value just corresponds to the calculated half-life of the formation of C₄H₈SH⁺(H₂O)_{*n*} by reaction (3) on the assumption that the reactions proceed by collision rates ($\sim 10^{-9}$ cm³ molecule⁻¹s⁻¹). Viggiano *et al.* have found that the proton transfer reactions from H₃O⁺(H₂O)₁₋₁₀ to hard Brønsted bases such as methanol, ammonia, pyridine, acetonitrile, and acetone take place with collision rates.^{15), 16)} Our finding argues that the proton transfer reaction from H₃O⁺(H₂O)_{*n*} to a soft base, THT, also proceeds with a collision rate.

In Fig. 3, it is difficult to determine the branching ratio (*i.e.*, *m* distribution) of the product ions C₄H₈SH⁺(H₂O)_{*m*} in reaction (3). Figure 4 shows the decay curves

Fig. 3. Percent of total ionization of ions observed in 4.05 Torr of CH₄, 30 μ Torr of C₄H₈S, and 99.6 mTorr of H₂O. Ion source temperature = 325.4 K; electron pulse width = 20 μ s; electron energy = 2 keV.

Fig. 4. Temporal profiles of C₄H₈SH⁺ ($m/z=89$), C₄H₈SH⁺(H₂O)₁ ($m/z=107$), C₄H₈SH⁺(H₂O)₂ ($m/z=125$), and C₄H₈SH⁺(H₂O)₃ ($m/z=143$) in 4.07 Torr of CH₄, 30 μ Torr of C₄H₈S, and 97.3 mTorr of H₂O at 325.4 K. The integration times for the ions C₄H₈SH⁺(H₂O)_{*n*} with $n=0-3$ are 60, 60, 160, and 200 s, respectively.

Fig. 5. Enthalpy diagram for the reactants (left) and products (right). Enthalpy differences (in kcal mol⁻¹) are relative to the enthalpy of H₃O⁺.

for the C₄H₈H⁺(H₂O)_{*m*} after the electron pulse (pulse width: 20 μ s). This gives a clearer idea for the sequence to reach the final intensities in equilibrium for C₄H₈SH⁺(H₂O)_{*m*}. It can be seen that the decay rates for C₄H₈H⁺(H₂O)_{*m*} become slower with decrease of the number (*m*) of H₂O ligands. In other words, the ion C₄H₈SH⁺(H₂O)₃ is converted slowly to C₄H₈SH⁺(H₂O)_{*n*} with $n < 3$ and they approach to the equilibrium intensities.

Figure 5 shows the enthalpy diagram for the reactants (left) and products (right), identified by the ionic species. Relative enthalpies (in kcal mol⁻¹) are based on H₃O⁺. In Fig. 3, the H₃O⁺(H₂O)₄ ion is one of the major proton hydrates. However, this cluster ion may not be the precursor for the formation of C₄H₈SH⁺(H₂O)₃ in Fig. 4 because the reaction, H₃O⁺(H₂O)₄ + C₄H₈S $\rightarrow$ C₄H₈SH⁺(H₂O)₃ + 2H₂O, is endothermic by 15.5 kcal mol⁻¹ in Fig. 5. Thus, the formation of C₄H₈SH⁺(H₂O)₃ in Fig. 4 may be partly due to the slightly

endothermic reaction (3) with $n=3$ and mainly to the exothermic association reaction (3) with $n=2$, $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2 + \text{C}_4\text{H}_8\text{S} = \text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_3$. The exothermicity of the latter reaction ($-\Delta H^\circ = 15.1 \text{ kcal mol}^{-1}$) is larger than the bond dissociation energy, $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_2 \cdots \text{H}_2\text{O}$ ($9.5 \text{ kcal mol}^{-1}$), and thus at least some part of the intermediate complex, $[\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_3]^*$, may decompose unimolecularly to the smaller cluster ion $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_2$.

Viggiano *et al.* pointed out that the dominant reaction channel for the proton transfer reaction between $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ and various oxygen and nitrogen bases is the least exothermic path.¹⁵⁾ In Fig. 3, the major proton hydrates are $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ with $n=2-4$. As shown in Fig. 5, reaction (3) with $n \leq 2$ becomes exothermic for the formation of observed $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_n$ with $n \leq 3$. Since the reactions of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ with $n=3$ and 4 to form $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_3$ are endothermic, the major reactant ions of proton hydrates for the formation of $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_n$ with $n \leq 3$ must be $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ with $n \leq 2$ under the conditions shown in Figs. 3 and 4. Some fractions of $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_n$ ions with $n=2$ and 3 formed by reaction (3) may lose H_2O ligands sequentially to approach the concentrations in equilibrium. This explains the fact that it takes a long time to establish the equilibria for reaction (2) as shown in Figs. 3 and 4.

3.4 Discussion based on computational results

Figure 6 shows geometries of $\text{C}_4\text{H}_8\text{S}$ and $\text{C}_4\text{H}_8\text{SH}^+$. The proton is attached to $\text{C}_4\text{H}_8\text{S}$ in its axial direction.

Fig. 6. Geometries of (a) $\text{C}_4\text{H}_8\text{S}$ and (b) $\text{C}_4\text{H}_8\text{SH}^+$, optimized by RHF/6-31G*. Empty small circles stand for hydrogen atoms. Distances are in angstrom. Values in parentheses denote Mulliken atom electronic net charges (positive, cationic).

In $\text{C}_4\text{H}_8\text{SH}^+$, the cationic character is delocalized well and the hydration might occur either at the S-H proton or at the $\text{C}_\alpha\text{-H}$ proton. In the previous work,¹³⁾ geometry optimizations were made partially and the basis sets (STO-3G and RHF/6-31G) were small. Through RHF/6-31G* full geometry optimizations, two hydration geometries have been obtained (Fig. 7). The S-H hydration (a) has been confirmed to be more stable than the bifurcated C-H hydration (b). In Fig. 7(a), the S-H bond ($=1.336 \text{ \AA}$) is elongated due to the hydrogen bond relative to that ($=1.327 \text{ \AA}$) of the free $\text{C}_4\text{H}_8\text{SH}^+$ in Fig. 6(b). Computations show that there is no isomer of $\text{H}_3\text{O}^+(\text{C}_4\text{H}_8\text{S})$. This absence is understandable in terms of a very large difference between PA (THT) $= 205.4 \text{ kcal mol}^{-1}$ and PA (H_2O) $= 166.5 \text{ kcal mol}^{-1}$.¹²⁾ Theoretical PA values of H_2O , $(\text{H}_2\text{O})_2$, and $(\text{H}_2\text{O})_3$ have been calculated to be PA (H_2O) $= 164.5 \text{ kcal mol}^{-1}$, PA $(\text{H}_2\text{O})_2 = 194.7 \text{ kcal mol}^{-1}$, and PA $(\text{H}_2\text{O})_3 = 209.2 \text{ kcal mol}^{-1}$. While PA (THT) $= 205.4 \text{ kcal mol}^{-1}$ is entirely different from PA (H_2O) $= 166.5 \text{ kcal mol}^{-1}$, the former value is similar to PA $(\text{H}_2\text{O})_2$ and PA $(\text{H}_2\text{O})_3$. The presence of $\text{H}_3\text{O}^+(\text{H}_2\text{O})_n$ ($\text{C}_4\text{H}_8\text{S}$) ($n=1$ and 2) is predictable. Figure 8 exhibits three isomeric geometries. According to PA values of THT and water dimer, $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_2$ is more stable than $\text{H}_3\text{O}^+(\text{H}_2\text{O})$ ($\text{C}_4\text{H}_8\text{S}$). Noteworthy is the extremely small activation energy for (c) $\rightarrow$ (b), ($7.52-5.18$) kcal mol^{-1} . When THT encounters $\text{H}_3\text{O}^+(\text{H}_2\text{O})$, the proton transfer takes place almost at a collision rate. $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_2$ is generated exothermically and with high probability. It has been found also that the above $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_2$ is more stable than a model with S-H and C-H hydrations, $(\text{H}_2\text{O}) \cdot \text{H-CC}_3\text{H}_7\text{SH}^+(\text{H}_2\text{O})$ by $3.1 \text{ kcal mol}^{-1}$.

Fig. 7. Two models of $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})$. ΔE is the RHF/6-31G* energy differences, where a positive value indicates a less stable structure.

Fig. 8. Three isomeric geometries of $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_3$, $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_2$, TS, and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$ ($\text{C}_4\text{H}_8\text{S}$). TS means a transition state of the proton transfer. At TS, the reaction-coordinate vector corresponding to the sole imaginary frequency, $\nu^\ddagger$, is exhibited.

PA ($(\text{H}_2\text{O})_3$) is larger than PA (THT), and consequently $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_3$ should be less stable than $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$ ($\text{C}_4\text{H}_8\text{S}$). In fact, Fig. 9 verifies the instability of (a) or stability of (b). The activation energy ($=2.37 - (-5.11)$ kcal mol^{-1}) of the proton transfer (b) $\rightarrow$ (a) is appreciably larger than that in Fig. 8. The energy does not correspond to the kinetics of the collision rate. We have been suffering detection of $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_3$. This species is unstable and spontaneously either isomerizes to $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$ ($\text{C}_4\text{H}_8\text{S}$) or decomposes $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_2 + \text{H}_2\text{O}$.

There is a story of the proton transfer between soft and hard bases which is different from that (hard-hard bases) of Viggiano.¹⁵⁾ When PA values are not so different, generally the former has a double well potential, but the latter may have a skewed single well.

Acknowledgment

EWI thanks the Department of Science and Technology-Engineering and Science Education Project (DOST-ESEP) for financial support, and the Nara University of Education Information Processing Center for the generous allocation of computer time on the Convex SPP/1200/XA computer.

References

- 1) R. G. Keesee and A. W. Castleman, Jr., *J. Phys. Chem. Ref. Data*, **15**, 1011 (1986).

Fig. 9. Geometries of (a) $\text{C}_4\text{H}_8\text{SH}^+(\text{H}_2\text{O})_3$ and $\text{H}_3\text{O}^+(\text{H}_2\text{O})_2$ ($\text{C}_4\text{H}_8\text{S}$). The TS of proton transfer has $\Delta E = +2.37$ kcal mol^{-1} and $\nu^\ddagger = 1230.1i \text{ cm}^{-1}$.

- 2) Y. Marcus, *Pure Appl. Chem.*, **55**, 977 (1983).
- 3) K. Hiraoka, H. Takimoto, and S. Yamabe, *J. Phys. Chem.*, **90**, 5910 (1986).
- 4) K. Hiraoka, S. Mizuse, and S. Yamabe, *J. Chem. Phys.*, **92**, 3943 (1988).
- 5) P. Kebarle, in "Techniques for the Study of Ion-Molecule Reactions," ed. by J. M. Farrar and W. H. Saunders, Jr., Wiley, New York (1988).
- 6) P. Kebarle, *J. Am. Soc. Mass Spectrom.*, **3**, 1 (1992).
- 7) K. Hiraoka, *J. Chem. Phys.*, **87**, 4048 (1987).
- 8) A. P. Scott and L. Radom, *J. Phys. Chem.*, **100**, 16502 (1996).
- 9) A. D. Becke, *Phys. Rev. A*, **38**, 3098 (1988); R. G. Parr and W. Yang, "Density-Functional Theory of Atoms and Molecules," Oxford University Press, New York (1989).
- 10) J. B. Foresman and A. E. Frisch, "Exploring Chemistry with Electronic Structure Methods," 2nd Ed., Gaussian Inc., Pittsburgh (1995), Chapter 7.
- 11) GAUSSIAN 94, Revision C. 4, M. J. Frisch, W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. A. Robb, J. R. Cheeseman, T. Keith, G. A. Petersson, A. Montgomery, K. Raghavachari, M. A. Al-Laham, V. G. Zakrzewski, J. V. Ortiz, J. B. Foresman, J. Cioslowski, B. B. Stefanov, A. Nanayakkara, M. Challacombe, C. Y. Peng, P. Y. Ayala, W. Chen, M. W. Wong, J. L. Andres, E. S. Replogle, R. Gomperts, R. L. Martin, D. J. Fox, J. S. Binkley, D. J. Defrees, J. Baker, J. P. Stewart, M. Head-Gordon, C. Gonzalez, and J. A. Pople, Gaussian Inc., Pittsburgh, PA (1995).
- 12) S. G. Lias, J. F. Liebman, and R. D. Levin, *J. Phys. Chem. Ref. Data*, **13**, 695 (1984).
- 13) K. Hiraoka, H. Takimoto, and S. Yamabe, *J. Am. Chem. Soc.*, **109**, 7346 (1987).

- 14) E. E. Ferguson, F. C. Fehsenfeld and D. L. Albritton, in "Gas-Phase Ion Chemistry," ed. by M. T. Bowers, Academic Press, New York (1979).
- 15) A. A. Viggiano, F. Dale, and J. F. Paulson, *J. Chem. Phys.*, **88**, 2469 (1988).
- 16) P. M. Hierl, A. F. Ahrens, M. Henchman, A. A. Viggiano, and F. Paulson, *J. Am. Chem. Soc.*, **108**, 3140 (1986).

Keywords: Tetrahydrothiophene, Proton affinity, Ion molecule reaction, Hydration