Ab Initio Study of Intramolecular Proton Transfer in Formohydroxamic Acid

Deng-Hwa Wu and Jia-Jen Ho*

Department of Chemistry, National Taiwan Normal University, 88 Section 4, Tingchow Road, Taipei, Taiwan 117, ROC

Received: November 18, 1997; In Final Form: March 4, 1998

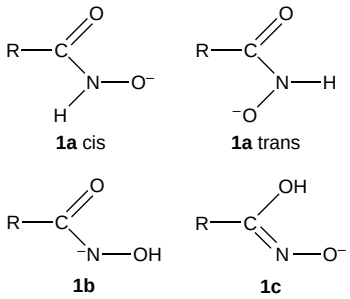
Interconversion of five isomeric tautomers of formohydroxamic acid via intramolecular proton transfer has been examined by ab initio theoretical calculation. The transfer potential surfaces, the global isomeric structures, and the transition geometries of intramolecular proton transfer were determined by the MP2/6-31+G** level of calculation. The energy was further analyzed by a single point calculation, MP2/6-31++G**//MP2/6-31+G**, and the use of G2 theory. Not counting the unstable charge separating species, the order of stability of these tautomers calculated at the HF level was **1E** > **1Z** > **2Z** > **2E**, and it shifted to **1Z** > **1E** > **2Z** > **2E** at the MP2 level, where **1Z** and **1E** are keto forms, while **2Z** and **2E** are iminol forms. Further investigation using G2 theory redirects the order to be **1Z** > **2Z** > **1E** > **2E**. The strength of the intramolecular hydrogen bond and the effect of dipole moment are the two major factors to dominate the acidity of formohydroxamic acid. Judging from the transition barrier of intramolecular proton-transfer we believe that formohydroxamic acid in dissociating proton in the gas phase is an N-acid.

Introduction

Compounds such as hydroxamic acids (RCONHOH) have been found for more than 100 years by researchers such as Lossen,[1] yet they still attract much attention.[2−4] The main reason for this interest is that this type of molecule contains the simplest structure (NH··O═C) that winds the DNA and RNA protein (secondary structure) into an α-helix skeleton. Formohydroxamic acid (HCONHOH) is the simplest formula among the hydroxamic acids. Several theoretical calculations were performed related to its structural analysis.[5−10] There are two tautomeric forms, keto, **1E** and **1Z**, and iminol, **2E** and **2Z**, shown in Figure 1. Some experimental studies on the structure of formohydroxamic acid using X-ray[11] and ^{17}O NMR[12] concluded that the most stable structure was **1Z**. Although low-level calculations suggested that the *E* tautomer existed preferentially in the gas phase, this preference was reduced at more sophisticated theoretical levels, and the *Z* structures became evident when correlated energy was included. Bauer and Exner et al.[13] reported that for the neutral molecule **1E** and **1Z** are favored over **2E** and **2Z**. Conformation **1Z** is assumed to be present in solution,[14,15] whereas **1E** is found in crystal structures.

Further studies were carried out to determine which proton (the N−H or O−H) being released forms the conjugated base. The alkylation position (N-alkylation or O-alkylation) is deterministic for the decrease in the acidities of hydroxamic acids and it can be used as a method to reveal which proton is being released. Gal et al.[16] measured gas-phase activities of acetohydroxamic acid as well as those of its *N*-methyl and *O*-methyl derivatives, concluding that it behaves essentially as an N-acid in the gas phase. Bordwell et al.[17] in their acidity measurement concluded that both aceto- and benzohydroxamic acids behaved as N-acids in DMSO solution. Recent theoretical calculations[18] showed that both formo- and acetohydroxamic acids should behave as N-acids in the gas phase, but as O-acids in aqueous solution. Bagno et al.,[19] from their hetronuclear (^{14}N, ^{15}N, and ^{17}O) relaxation time measurement, indicated that in aqueous solution acetohydroxamic acid is predominately an O-acid, whereas benzohydroxamic acid is predominately an N-acid.

A study of the stability of the anion formed from the release of a proton of hydroxamic acid (RCONHOH → H^+ + $RCONHO^-$) is also a good method to determine a N-acid or O-acid of hydroxamic acids. In an early review[20] most of the anions were considered to be formed from the release of a proton from the O−H bond, indicating that most of the hydroxamic acids were considered as O-acids. Plapinger[21] proposed that there existed at least two kind of anions in aqueous solution, one was **1a**, the other was **1b** or **1c**, from his analysis of the UV spectrum.



However, Exner[22] denied the existence of structure **1c** from his analysis of the IR spectrum of the sample in dioxane solution. He further analyzed the UV and IR spectrum for ph-CONHOH and N-alkylated and O-alkylated anions[23] and found that the frequency of C═O was clearly red-shifted but that there was no change for the O−H frequency. The explanation for this red-shifted C═O frequency was that the resonance effect existed between the C═O double bond and the lone-pair electron on the nitrogen atom produced from the dissociation of the N−H

* Corresponding author. Address for correspondence: Dr. Jia-Jen Ho, Department of Chemistry, National Taiwan Normal University 88 Sec. 4, Tingchow Rd. Taipei, Taiwan 117, ROC. Phone: (886)-2-930-9085. Fax: (886)-2-9324249. E-mail: jjh@scc.ntnu.edu.tw.

S1089-5639(98)00242-4 CCC: $15.00
Published on Web 04/22/1998

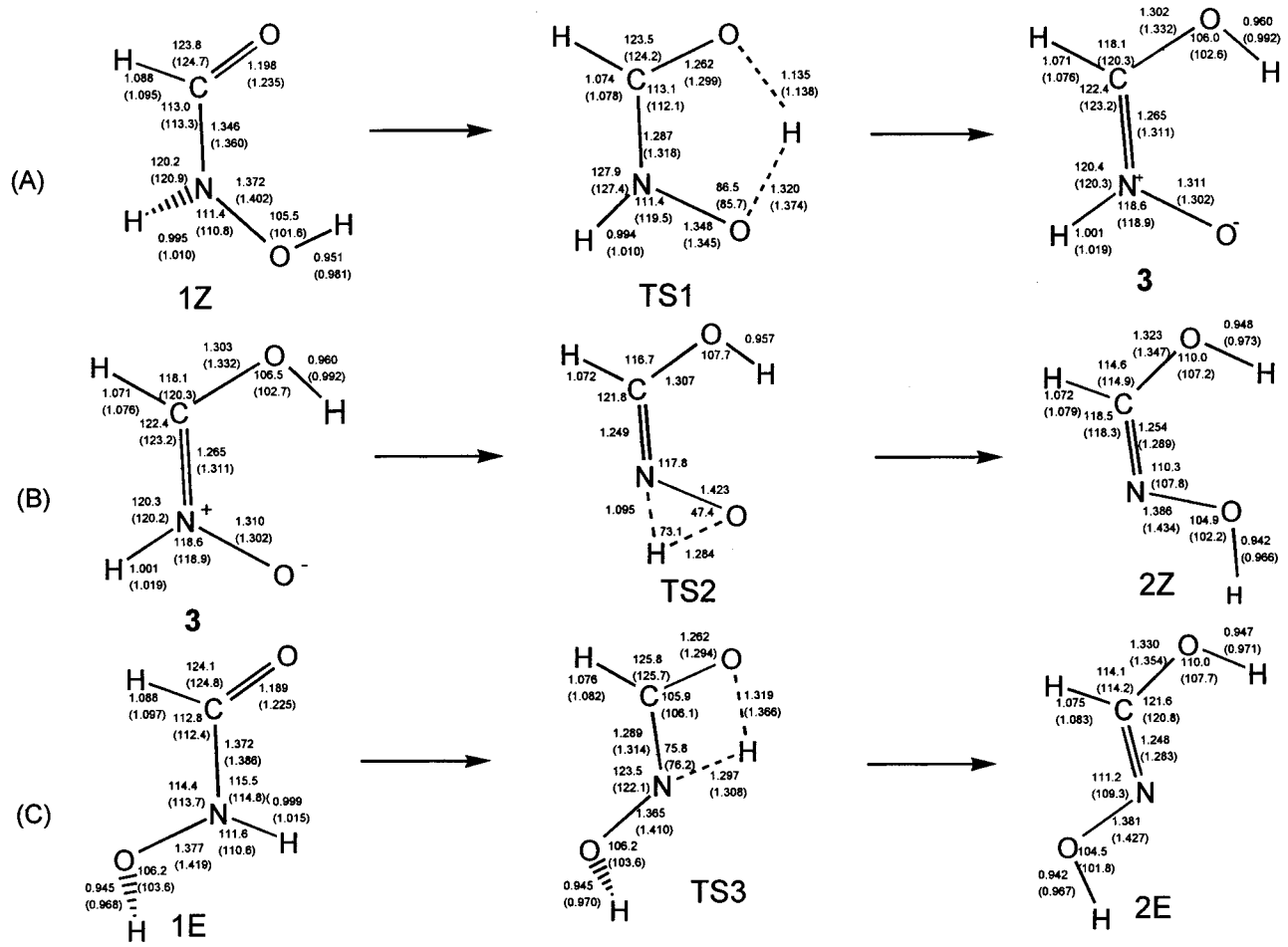


Figure 1. Optimized structures of formohydroxamic acid tautomers and their corresponding TS structures calculated at HF and MP2 levels (bond length in angstroms and angles in degrees). The MP2 data are listed in parentheses.

bond, while the O−H bond was not dissociated to maintain no change of O−H frequency. Therefore the existence of **1b** was confirmed for benzohydroxamic acid. Remko et al.[8] did a theoretical study of formohydroxamic acid isomers and their anions and concluded that the N-anion was more stable than the O-anion, hence hydroxamic acids were predicted to behave as N-acids in the gas phase.

The disagreement of the experimental conclusions leaves room for theoretical studies.[10,18,19,24] Most of these calculations drew their conclusion of N-acids or O-acids based on the stability comparison of the anions. Actually the confusion of these experimental results is strongly related to the experimental conditions, especially to the solvents being applied. Different substituent such as alkyl or aryl need different solvents such as DMSO, water, or water/methanol, which have different solvent effects on the reactants.

In the present work we calculated the energy hypersurfaces of intramolecular transfer of a proton on the N atom and the O atom to the carbonyl oxygen of formohydroxamic acids (HCONHOH). The barriers to different intramolecular proton transfer processes, the structures, and the energetics of species on the potential energy surfaces are properly characterized. It is also plausible to relate the answer to the puzzle of N-acid or O-acid of formohydroxamic acid in the gas phase to the barrier height of intramolecular proton transfer in the system.

Methods of Calculation

The Gaussian-94 set of ab initio computer codes[25] was employed for all calculations. Geometries were optimized with the gradient schemes included therein. To take into account the effect of electron correlation we employed second-order Moller−Plesset perturbation theory (MP2). The G2 theory[26] was also performed to calculate the energy for the local points and transition conformations on the potential energy hypersurfaces. The polarized split valence basis set including diffuse function, 6-31+G**, was used for the fact that Wiberg[27] verified this basis set yielding satisfactory agreement with experiments in his formic acid calculation. For single point energy calculation, MP2/6-31++G**//MP2/6-31+G** was also employed for stable tautomers of hydroxamic acids, since it was demonstrated to meet sufficiently the experimental result of acetohydroxamic acid.[16] When the fully optimized equilibrium structure of each tautomer was determined, the calculation of potential profile for intramolecular proton transfer was carried out. The energy profile was obtained for the system with no constraint of fixed R (the distance of the two heavy atoms) at the equilibrium length.

Results and Discussion

There are five forms of structure of formohydroxamic acid, two keto forms (**1E**, **1Z**) two iminol forms (**2E**, **2Z**) and one iminol form with separating charges, **3**, shown in Figure 1. Three transition structures (**TS1**, **TS2**, and **TS3**) for the proton transfer between pair of tautomers, **1Z** and **3**, **3** and **2Z**, and **1E** and **2E**, respectively, depicted in Figure 1 are also located. The calculated relative energies for the tautomers and TS structures fully optimized at HF/6-31+G** and MP2/6-31+G** levels are listed in Table 1. The calculated data following G2 theory

TABLE 1: Relative Energies[a] of the Tautomers and Transition Structures of Formohydroxamic Acid (kcal/mol)

	HF[b]	MP2[b]	MP2[c]	G2[d]
1Z	2.0(1.7)	0.02(−0.34)	0.03(−0.33)	−1.5(−1.9)
TS1	29.2	15.9	15.9	11.4
3	22.0(22.4)	13.4(13.8)	13.4(13.8)	10.8(11.2)
TS2	74.7		58.8[e]	50.6
2Z	3.5(3.7)	0.2(0.3)	0.2(0.4)	−0.2(−0.1)
1E	0.0(0.0)	0.0(0.0)	0.0(0.0)	0.0(0.0)
TS3	62.8	46.1	46.1	42.4
2E	6.9(6.6)	4.6(4.3)	4.7(4.4)	3.5(3.2)

[a] All energies are reported with respect to the **1E** form. The energies in parentheses are corrected for computed zero-point vibrational energies and contributions from translational and rotational terms in the HF level. [b] The energies are calculated by using the 6-31+G** basis set. [c] Energies calculated at the MP2/6-31++G**//MP2/6-31+G** level. [d] Energies calculated by using the G2 theory; see ref 27. [e] The energy calculated at the MP2/6-31++G**//HF/6-31+G** level. The difference between MP2//MP2 and MP2//HF is about 2.1−2.8 kcal/mol, with MP2//MP2 smaller.

TABLE 2: Calculated Gas Phase Proton Dissociation Energy[a] of the Acetohydroxamic Acid (kcal/mol)

basis set	ΔE, kcal/mol
HF/6-31+G**	361.7
MP2(FC)/6-31+G**	348.3
MP2(FULL)/6-31+G**	348.5
MP2/6-31++G**//MP2/6-31+G**	348.7
MP2/6-311+G**//MP2/6-31+G**	350.4
MP2/6-311++G**//MP2/6-31+G**	350.4
MP4/6-31++G**//MP2/6-31+G**	350.5
expt[b]	346.7 ± 2

[a] ΔE is the energy difference between **1E** (with H_1 substituted by a methyl group) and **1b**. [b] Experimental dissociation energy, corrected for computed zero-point vibration energy and contributions from translational and rotational terms in the HF level; see ref 16.

are also presented for comparison. To find the best method and basis set suitable for this calculation we tried several different basis sets and levels of calculation for the acetohydroxamic acid molecule, for which the thermodynamic experimental value was known. The results are listed in Table 2. The proton dissociation energy calculated at MP2(FC)/6-31+G** for fully optimized acetohydroxamic acid is 348.3 kcal/mol, which falls within the error range of the experimental value, 346.7 ± 2 kcal/mol. The MP2(Full)/6-31+G** does not give a better result, 348.5 kcal/mol. Single point calculations in extended basis sets, MP2/6-31++G**//MP2/6-31+G**, MP2/6-311+G**//MP2/6-31+G** and MP2/6-311++G**//MP2/6-31+G**, were also performed (listed in the fourth, fifth, and sixth rows of Table 2); however, none of them reduces the deviation of the calculated values from that of the experiment. Although, to our knowledge, there are still no such experimental thermodynamic data of formohydroxamic acid to compare with, we believe that the use of the MP2(FC)/6-31+G** level of calculation should provide reasonable precision to the real value of the system.

Among the five forms, the **3** form with charge separation is calculated to be the least stable, as predicted. We will neglect it in further discussion. From the HF result the most stable structure is **1E** followed by **1Z**, **2Z**, and **2E**. The two keto forms **1E** and **1Z** are nonplanar, whereas the two iminol forms **2E** and **2Z** are planar. Without considering ZPE (zero-point energy), the energy difference between the highest (**2E**) and the global minimum (**1E**) is less than 7 kcal/mol, and that between **2E** and the other two tautomers (**1Z**, **2Z**) is less than 3.5 kcal/mol, whereas with MP2(FC) calculation, the energy order of the tautomers is still the same but the energy differences

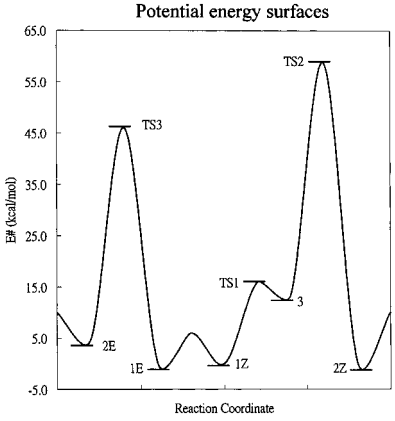


Figure 2. Schematic potential energy surfaces describing intramolecular proton transfer. Energies are calculated at the MP2/6-31++G**//MP2/6-31+G** level.

reduce from 7 kcal/mol (HF) to 4.6 kcal/mol and from 3.5 kcal/mol (HF) to 0.2 kcal/mol, respectively. With ZPE consideration **1Z** becomes more stable than **1E**; the energy order of others remains the same. Single point energy calculation, MP2/6-31++G**//MP2/6-31+G**, gives similar energy order as MP2-(FC), while in the G2 calculation the energy order shifts greatly, both **1Z** and **2Z** are more stable than **1E**. This result is in good agreement with the one done by Ventura[28] in which the energy gaps among **1E**, **1Z**, and **2Z** become smaller and smaller with the use of polarization functions included in the extended basis sets and the use of calculation methods containing a higher order of electron correlation effect. Recent results calculated by Exner et al.[8] also implied that **1Z** was the most stable tautomer. It is reasonable to accept that **1Z** is more stable than **1E** by the fact that there exists intramolecular hydrogen bonding in the **1Z** configuration. **1Z** is a keto form and **2Z** is an enol form, both with intramolecular H-bonding; while **1E** and **2E** are keto and enol forms, respectively, without intramolecular H-bonding. Accordingly, the keto form is more stable than the enol form and the H-bonding stabilization energy is greater than the energy difference between the keto and enol forms.[29] Therefore the calculated G2 result of stability order **1Z** > **2Z** > **1E** > **2E** agrees well with these statements. Besides, the calculated smaller dipole moment of **1Z** (3.425 D compared to 3.477 D of **1E**) also agrees with what was found from Wiberg[30]and Wang's[31] dipole moment studies of rotational tautomers, which say that the more stable tautomer always accompanies with smaller dipole moment. Three possible intramolecular proton transfer paths (labeled (A), (B), and (C)) of formohydroxamic acid tautomers are also shown in Figure 1. The geometries (including transition structures) are fully optimized at HF and MP2 levels using the 6-31+G** basis set. The differences in the calculated data between these two levels are very small (about 0.01 Å in bond length and 1° in angle) except at the lengths of the double bond (C═O in **1Z** and **1E**; C═N in **2E**, **2Z**, and **3**), the lengths of the O−H bond (which are greater than 0.03 Å), and the bond angles of ∠COH and ∠NOH (greater than 3°). The MP2 data of these bond lengths are longer than the corresponded HF data, while the bond angles are smaller. The transition structures of path A, **TS1**, path B, **TS2**, and path C, **TS3**, each has a different ring strain, and the barriers of these three paths are in the same order of TS ring strains, (B) > (C) > (A).

Figure 2 shows the potential energy surface for the intramolecular proton transfer of formohydroxamic acid isomers. The barriers for most of the processes are high, even the smallest one, **1Z** → **3**, needs 12.9 kcal/mol in the G2 level of calculation.

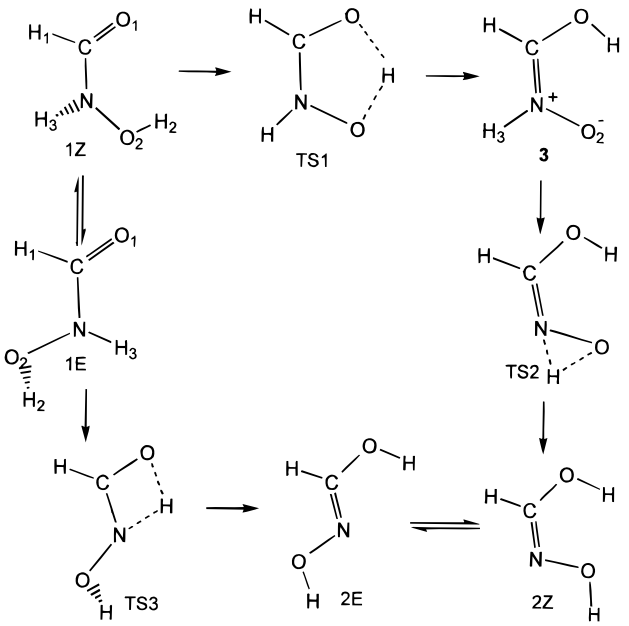


Figure 3. Possible pathways for the transform of **1Z** to **2Z**.

This value is much greater than that in the intermolecular proton transfer of protonated aldehyde dimer systems[32] (less than 5.0 kcal/mol in the MP4 level). It is obvious that intramolecular proton transfer is the transfer of a proton between two rigid heavy atoms, in which the distance is almost fixed from fully optimized equilibrium structure of formohydroxamic acid; whereas, the two heavy atoms in protonated aldehyde dimer systems were allowed to move to maintain the lowest energy possible during the intermolecular proton transfer. Besides, the protonation energy (PE) is also an important factor in determining the transfer barrier, the bigger the PE the higher the barrier. The PEs for aldehydes[32−34] are around 180−190 kcal/mol, while that of hydroxamic acids, according to Gal et al.,[16] are around 340−350 kcal/mol. Some other reasons such as the strength of intramolecular H-bonding are also related to the barrier in hydroxamic acids.

Intramolecular proton transfer in hydroxamic acids has not been studied before, although Ventura et al.[4,18] presented an analysis of the keto−enol tautomerism in formohydroxamic acid in comparison with the analogue problem in formamide. The detailed transformation from keto form (**1Z**) to enol form (**2Z**) was not presented in these studies. If the transformation of **1Z** to **2Z** were to take place in one step, the only possible path would be the direct transfer of H_3 in N to O_1. It seems very difficult since the distance between H_3 and O_1 is calculated to be 3.085 Å in the trans position, almost twice as much as the normal calculated hydrogen bond distance (about 1.5−2.0 Å).[35] There is no sufficient kinetic energy to initiate such direct transfer. From our calculation there are two possible pathways, each of which has one transition conformation. The first pathway is **1Z** → **3** → **2Z**, and the second is **1Z** → **1E** → **2E** → **2Z**, shown in Figure 3. The first pathway starts the transfer of the H_2 atom to the O_1 atom and passes the transition state (**TS1**), forming a charge-separated conformation, **3**, in which the O_2 atom is negatively charged and the H_3 atom is positive. Due to the charge attraction of the O_2 atom, the H_3 atom may initiate the transfer to the O_2 atom to form **2Z**; however, a very high barrier with three-member ring transition conformation **TS2** is a major concern. The second pathway starts from the rotation of the C−N bond to form **1E**, then goes through a proton transfer of H_3 from N to O_1 to form **2E** by passing through the relatively lower barrier of four-member ring transition state (**TS3**), and finally makes a C═N bond rotation to form **2Z**. From the height of these barriers in Figure 2, it is clear that the second pathway is easier to perform. The barrier of the rotation of C−N bonds is ignored here (about 10−15 kcal/mol),[36] since these barrier heights are much smaller in comparison with those in proton transfer. The intramolecular proton transfer in formohydroxamic acid in pathways A and C also shows the fact that the two heavy atoms (O_1 and O_2 in (A) and N and O_1 in (C)) prefer to move closer to assist the completion of proton transfer.[37] The comparison of these calculated distances in the transition structure and the equilibrium structure is listed in Table 3.

TABLE 3: Full Optimized Geometry[a] of Tautomers of Formohydroxamic Acid and Its Corresponding Transition State

		R(I−T)	*r*(I−H)	*r*(T−H)	ΔE_a,[e] kcal/mol
(A)[b]	**1Z**	2.650(2.649)	0.951(0.981)	2.135(2.039)	
	TS1	2.277(2.334)	1.320(1.374)	1.135(1.138)	12.9
	3	2.584(2.574)	2.043(1.935)	0.960(0.992)	
(B)[c]	**3**	1.310(1.302)	1.001(1.019)	1.993(2.004)	
	TS2	1.423	1.095	1.284	39.8
	2Z	1.386(1.434)	1.866(1.891)	0.942(0.966)	
(C)[d]	**1E**	2.254(2.293)	0.999(1.015)	2.492(2.523)	
	TS3	2.036(2.085)	1.297(1.308)	1.319(1.366)	42.4
	2E	2.252(2.292)	2.316(2.312)	0.947(0.971)	

[a] All distances in angstroms calculated by using the 6-31+G** basis set in the HF level, except values in parentheses are in at the MP2 level. [b] I, T, H represent O_2, O_1, H_2, respectively. [c] I, T, H represents N, O_2, H_3, respectively. [d] I, T, H represents N, O_1, H_3, respectively. [e] ΔE_a is the barrier height in each process of proton transfer, calculated at G2 theory.

Discussion

Formohydroxamic acid is the most fundamental species among all the hydroxamic acids, yet experimental data were scarcely available.[8] The theoretical calculation results become important. A debated issue of whether the formohydroxamic acid is an O-acid or an N-acid has existed for a long time, yet there is still no conclusion. From our calculation results we would like to address our thinking on this issue. For the higher level of calculation, structure **1Z** is the most stable conformation of formohydroxamic acid. Whether it is an O-acid or an N-acid depends on which hydrogen atom (attached to the N atom or the O_2 atom) can be more easily dissociated. From our study of intramolecular proton transfer (process **1Z** → **3**, with a much smaller barrier, 12.9 kcal/mol), we realize that the proton on the O_2 atom is likely to be confined and delocalized between O_1 and O_2 atoms; therefore, it is not easily dissociated. In contrast, as the proton on the N atom is less likely to experience intramolecular proton transfer (**1Z** → **1E** → **TS3** → **2Z**), it is relatively easy to dissociate. For that reason we support that formohydroxamic acid is an N-acid rather than an O-acid in the gas phase. If the proton is being dissociated from the N atom to form an anion, an electron resonance would also develop within N−C−O_1 bonds, which would release the instability of the two unshared electron pairs on the N atom. In contrast, if the proton dissociated from the O_1 atom, there would not be any electron resonance effect developed to lower the system, instead, the originally existed intramolecular hydrogen bonding would also disappear, and hence raise the instability of the forming anion. In addition, we performed calculations on structure **1b** and **1a** cis at the MP2/6-31++G**//MP2/6-31+G** level, and they reveal that **1b** is more stable than **1a** cis by 15.8 kcal/mol, which is a value very closed to the hydrogen resonance energy calculated by Dannenberg et al.[38]

on the acetylacetone molecule. All this strong evidence draws us to believe that formohydroxamic acid is an N-acid in the gas phase.

Acknowledgment. Support for this research from the National Science Council of the Republic of China (NSC-86-2113-M-003-013) is gratefully acknowledged. We are also grateful to the National Center for High-Performance Computing where the Gaussian package and the computer time were provided. We are also indebted to the reviewers for helpful suggestions concerning the manuscript.

References and Notes

(1) Lossen, H. *Justus Liebigs Ann. Chem.* **1869**, *150*, 314.
(2) (a) Stweart, A. O.; Martin, G. J. *J. Org. Chem.* **1989**, *54*, 1221. (b) Neihands, J. B. *Struct. Bonding (Berlin)* **1996**, *1*, 59.
(3) Sobolewski, A. L. *J. Photochem. Photobiol., A: Chem.* **1995**, *89* (2), 89.
(4) Ventura, O. N.; Rama, J. B.; Turi, L.; Dannenberg. J. J. *J. Phys. Chem.* **1995**, *99*, 131.
(5) Hilal, R.; Moustaf, H. *Int. J. Quantum Chem.* **1984**, *26*, 183.
(6) Nguyen, M. T.; Sana, M.; Lerory, G.; Dignam, K. J.; Hegarty, F. *J. Am. Chem. Soc.* **1980**, *102*, 573.
(7) Yuangi, T.; Wengui, D. *Int. J. Quantum Chem.* **1992**, *44*, 319.
(8) Exner, O.; Remko, M.; Mach, P.; Schleyer, P. v. R. *J. Mol. Struct. (Theochem.)*; **1993**, *279*, 139.
(9) Bagno, A.; Comuzzi, C.; Scorrano, G. *J. Am. Chem. Soc.* **1994**, *116*, 916.
(10) Turi, L.; Dannenberg, J. J. Rama, J.; Ventura, O. N. *J. Phys. Chem.* **1992**, *96*, 3709.
(11) Larsen, I. K. *Acta Crystallogr. B* **1988**, *44*, 527.
(12) Lipczynska-Kochany, E.; Iwamura, H. *J. Org. Chem.* **1982**, *47*, 5277.
(13) Bauer, L.; Exner, O. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 376.
(14) Artemenko, A. I.; Tikurova, I. V.; Anufriev, E. K.; Jehlicka, V.; Exner, O. *Collect. Czech. Chem. Commun.* **1981**, *46*, 729.
(15) Exner, O. Pecka, J. *J. Chem. Res.* **1988**, *(S)*, 404.
(16) Decouzon, M.; Exner, O.; Gal, J.-F.; Maria, P.-C. *J. Org. Chem.* **1990**, *55*, 3980.
(17) Bordwell, F. G.; Fried, H. E.; Hughes, D.; Lynch, T.-Y.; Satich, A. V.; Whang, Y. E. *J. Org. Chem.* **1990**, *55*, 3330.
(18) Ventura, O. N.; Rama, J. B.; Turi, L.; Dannenberg, J. J. *J. Am. Chem. Soc.* **1993**, *115*, 5754.
(19) Bagno, A.; comuzzi, C.; Scorrano, G. *J. Am. Chem. Soc.* **1994**, *116*, 916.
(20) Yale, H. L. *Chem. Rev.* **1943**, *33*, 209.
(21) Plapinger, R. E. *J. Org. Chem.* **1959**, *24*, 802.
(22) Exner, O.; Kakac. B. *Collect. Czech. Chem. Commun.* **1963**, *28*, 1656.
(23) Exner, O. *Collect. Czech. Chem. Commun.* **1964**, *29*, 1337.
(24) Yuang, J.; Wengui, D. *Int. J. Quantum Chem.* **1992**, *44*, 319.
(25) Gaussian 94 (Revision A.1), Gaussian, Inc., Pittsburgh, PA, 1995.
(26) Curtiss, L. A.; Raghavachari, K.; Trucks, G. W.; Pople, J. A. *J. Chem. Phys.* **1991**, *94* (11), 7221. (b) Curtiss, L. A.; Raghavachari, K.; Pople, J. A. *J. Chem. Phys.* **1995**, *103* (10), 4192.
(27) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1987**, *109*, 5935.
(28) Turi, L.; Dannenberg, J. J.; Rama, J.; Ventura, O. N. *J. Phys. Chem.* **1992**, *96*, 3709.
(29) (a) Turi, L.; Dannenberg, J. J. *J. Phys. Chem.* **1992**, *96*, 5819. (b) Turi, L.; Dannenberg, J. J. *J. Phys. Chem.* **1993**, *97*, 12197.
(30) Wiberg, K. B.; Laidig, K. E. *J. Am. Chem. Soc.* **1988**, *110*, 1872.
(31) Wang, X.; Houk, K. N. *J. Am. Chem. Soc.* **1988**, *110*, 1870.
(32) Chu, C. H.; Ho, J. J. *J. Am. Chem. Soc.* **1995**, *117*, 1076.
(33) Chu, C. H.; Ho, J. J. *J. Phys. Chem.* **1995**, *99*, 1151.
(34) Chu, C. H.; Ho, J. J. *J. Phys. Chem.* **1995**, *99*, 16590.
(35) (a) Scheiner, S.; Hillenbrand, E. A. *J. Phys. Chem.* **1985**, *89*, 3053. (b) Scheiner, S.; Wang, L. *J. Am. Chem. Soc.* **1992**, *114*, 3650. (c) Cybulsk, S. M.; Scheiner, S. *J. Am. Chem. Soc.* **1989**, *111*, 23. (d) Scheiner, S. *J. Chem. Phys*. **1982**, *77* (7), 4039.
(36) Blom, C. E.; Gunthard, H. H. *Chem. Phys. Lett.* **1981**, *84*, 267.
(37) Chalk, A. J.; Radom, L. *J. Am. Chem. Soc.* **1997**, *119*, 7573.
(38) Dannenberg, J. J.; Raphael, Rios, *J. Phys. Chem*. **1994**, *98*, 6714.