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Theoretical Studies on the Acid-Catalyzed Hydrolysis of Sulfinamide

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Ab initio calculations were carried out on the gas phase acid-catalyzed hydrolysis reactions of sulfinamide using the 3-21G* basis sets. Single point calculations were also performed at the MP2/6-31G* level. The first step in the acid-catalyzed hydrolysis of N-methylmethanesulfinamide, I, involves protonation. The most favorable form is the O-protonated one, II, which is then transformed into a sulfurane intermediate, III, by addition of a water molecule. The reaction proceeds further by an intramolecular proton transfer from O to N (TS 2), which is followed by N-S bond cleavage (TS3) leading to the final products. The rate determining step is the N-S bond cleavage (TS3) at the RHF/3-21G* level, whereas it becomes indeterminable at the MP2/6-31G* //3-21G* level of theory. However, the substituent effect studies with N-protonated N-arylmethanesulfinamide, XIII, at the MP2/6-31G*//3-21G* level support the N-S bond breaking step as rate limiting.

Introduction

Nucleophilic substitution reactions are one of the most important class of reactions in mechanistic organic chemistry, and substitutions at carbon centers have been studied extensively both experimentally and theoretically.[1] In a direct displacement (S_N2) reaction at carbon, an attacking nucleophile forms a trigonal bipyramid type transition state (TS), which eventually leads to a product with inversion. Nucleophilic displacement at a second row element, sulfur is known to proceed through more complex processes.[2] Two possible pathways have been proposed for the nucleophilic displacement at sulfur: two-step mechanism involving an addition intermediate (sulfurane), and concerted displacement (S_N2) involving a TS without intermediate formation. Addition intermediate formation has been ruled out in the base-catalyzed hydrolysis of N-mesitylbenzenesulfinamides based on the substituent effect studies,[3] and also the base-catalyzed reactions of cyclic sulfinate esters are reported to occur by a concerted S_N2 mechanism.[4] However, synthesis of a sulfurane-like intermediate[5] has led to predict the possible existence of such intermediate.

A useful means of elucidating the reaction mechanism involving sulfur atom is the test of ^{18}O exchange[6]; ^{18}O exchange is possible only through sulfurane intermediate formation. Recently Okuyama *et al.*,[7] have reported the ^{18}O exchange in the acid-catalyzed reactions of sulfinamide and proposed the existence of such an intermediate. They argued that the reaction proceeds through a sulfurane intermediate and the rate determining step changes depending on the substituent, based on the experimental results of pH-rate profiles for various substituents which showed a break

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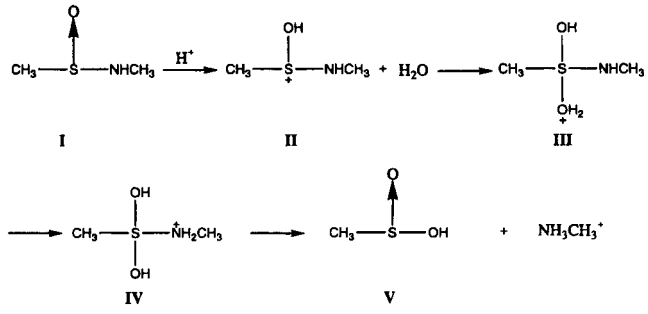


Scheme 1.

at pH=3.

In the theoretical investigation of a reaction involving sulfur atom, it is considered essential to take account of d-orbital for hypervalent bonding of the sulfur atom.[8] There are some reports on theoretical attempts to explain mechanism of the reactions of sulfinate esters. However, these were mostly concerned with discussions of MO energy levels of the optimized reactant structures[9] and structures of sulfurane intermediate.[10]

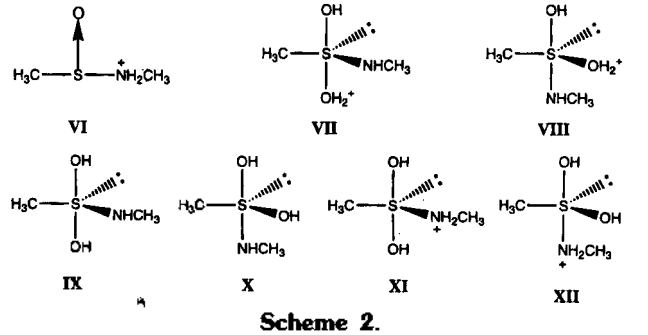
An interesting aspect of the sulfinamide structure is that there are three basic sites available, *i.e.*, nitrogen, oxygen and sulfur, for the possible protonation. Scorrano *et al.*,[11] reported that the protonation of $CH_3S(O)NH_2$ takes place on the oxygen atom, whereas in a recent work involving IR and ^{14}N NMR experiments Stefaniak *et al.*,[12] proposed the protonation on the nitrogen atom.

In this work, we aim to gain further information regarding the site of protonation and the reaction mechanism through MO theoretical investigations of the acid-catalyzed hydrolysis of a simple sulfinamide, N-methylmethanesulfinamide, as shown in Scheme 1.

Calculation

Ab initio calculations were carried out on the gas-phase acid-catalyzed hydrolysis of N-methylmethanesulfinamide, I. The programs used were Gaussian 92[13a] and 94[13b] with the 3-21G* basis sets[14] which include d-orbitals for sulfur atom. The structures of the species on the reaction pathway shown in scheme 1 and those of other relevant derived species are presented in Scheme 2. Geometries of all reactants were fully optimized.

Since in the first step of the reaction, protonation can take place at either O or N, both II and VI were considered. Starting from the most stable protonated species, the structures of all the stationary point species on the reaction path



Scheme 2.

were optimized. The transition states were located by first calculating several possible structures with the reaction coordinate method[15] and then searching with OPT=CALCALL option using the highest energy point structure. Similar optimizations were carried out for the species in Scheme 2. All positive (stable species) and only one negative (TS) vibrational frequencies were confirmed in the identification of the stationary point species.

For the substituent effect studies[7] on the reactions of N-arylbenzene-sulfinamides, we adopted a more simple model compound, N-protonated N-arylmethanesulfinamide, XIII, in order to avoid excessive computer time required for the large sized species. Since the two critical steps, TS2 and TS 3, occurred in the processes subsequent to the formation of XI, we simply began the search of the rate-determining step from XI. Thus, the structure of XI was simplified to XIII by replacing $N\text{-}CH_3$ with N-aryl, and the activation energies were calculated with electron-donor (Z=p-OCH_3, p-CH_3) as well as -acceptor substituents (Z=p-Cl). For each structure, single point calculations were carried out at the MP2/6-31G* level of theory (MP2/6-31G*//3-21G*).[16] The results at this level will be referred to hereafter simply as the MP2 results.

Results and Discussion

Structures and Energies of Stable Molecules. The 3-21G* optimized structure of the reactant, N-methylmethanesulfinamide, I, is shown in Figure 1. The bond lengths of the S-C, S=O and S-N bonds are 1.78, 1.48 and 1.66 Å, respectively, and bond angles <C-S=O and <O=S-N are approximately tetrahedral with 106.6 and 112.1°, respectively. The possible sites of protonation on I are the oxygen, nitrogen and sulfur atoms, but the sulfur protonated structure has a relatively high energy[11] so that it was excluded from our discussion. Thus, two protonated structures, II (protonated on O) and VI (protonated on N), are optimized and their geometries and energies are given in Figure 1 and Table 1 respectively. Geometry changes upon protonation of the neutral reactant are that: (i) For II, the S-O bond is elongated by 0.1 Å in contrast to contraction of S-C and S-N bonds by 0.02 and 0.07 Å, respectively. (ii) For VI, the S-N bond becomes stretched as much as 0.24 Å. Due to this large increase in the bond length in VI, VI is less stable by 19.0 kcal mol^{-1} compared with II. This is in agreement with the results of *ab initio* calculations[11] on the protonation of $CH_3S(O)NH_2$; the O-protonated form was reported to be more stable by 10.6 kcal mol^{-1} than the N-protonated one. In order to obtain additional information about the protonation site, we examined the HOMO structure of I in Figure 2. We note in this figure that contribution of the N atom is small relative to that of S and O atoms. We therefore conclude that the protonation of I occurs at O and we used II as a starting point for the rest of the calculations on the reaction pathway.

Geometries and energies for other relevant species on the reaction path are also given in Figure 1 and Table 1. The second step is the addition of a water molecule to II. The most likely place to approach for H_2O is toward the most positively charged S atom. At this stage, a loose complex, II-H_2O, is formed, which has a hydrogen bond between the oxygen atom of H_2O and the N-H bond in II. The length of

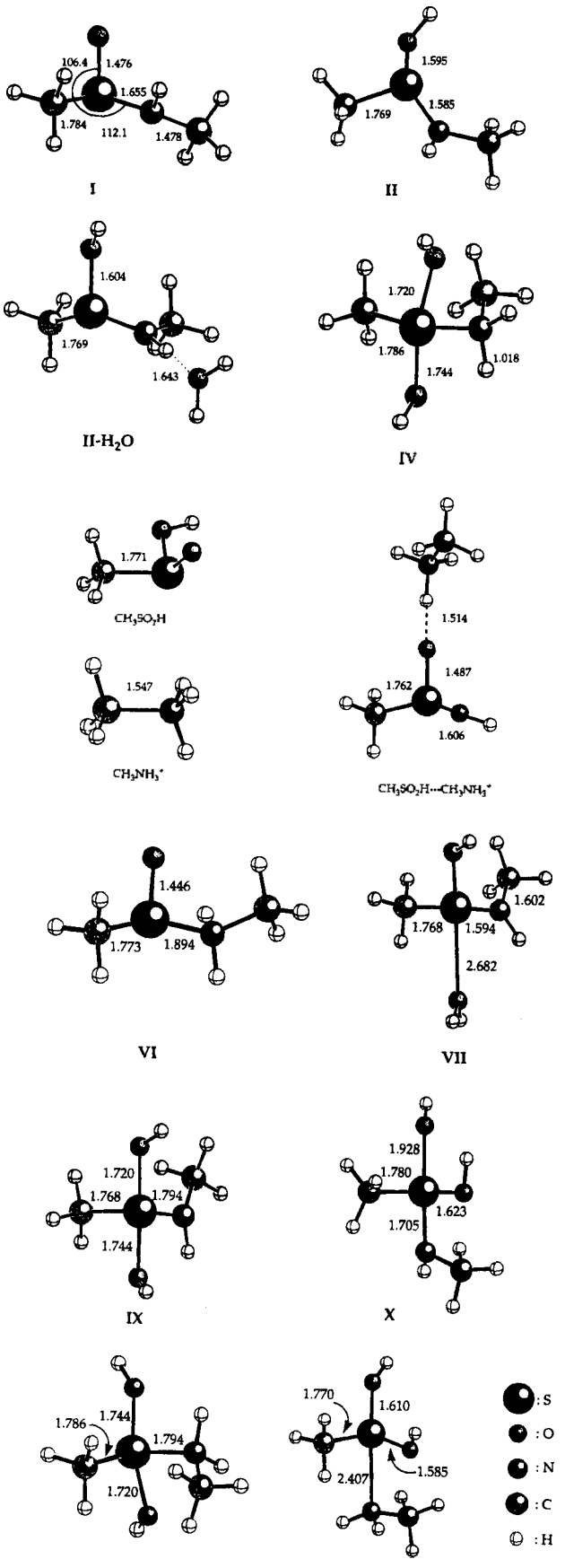


Figure 1. 3-21G* optimized structures of stationary point (bond lengths in Å and angles in degree).

Table 1. Calculated energies of the species shown in Figures 1 and 3

Structure	E(3-21G*)	E(MP2/6-31G*//3-21G*)
I	−603.57188	−607.29409
II	−603.94755	−607.64749
II-H_2O	−679.57142	−683.87233
V	−584.47962	−587.98408
VI	−603.92138	−607.64265
VII	−679.56457	−683.86460
VIII	−	−
IX	−679.12933	−683.45668
X	−679.12295	−683.45095
XI	−679.49563	−683.81366
XII	−679.54573	683.84783
TS1	−679.56403	−683.86565
TS2	−679.48741	−683.80104
TS3	−679.47957	−683.80459
CH_3NH_2	−94.68166	−95.50455
$CH_3NH_3^+$	−95.05934	−95.86715
CH_3SO_2H	−584.47962	587.98408
$CH_3SO_2H_2^+$	−584.82642	−588.30935

the H-bond, H_2O---H-N, in this complex is 1.64 Å and the complexation energy was relatively large (−17.80 kcal mol^{-1} at the MP2 level, and at the 3-21G* level it is even larger, −23.8 kcal mol^{-1}). When the H_2O in this complex covalently bonds to S, a sulfurane intermediate, III, is formed. For III, two isomers are possible depending on the spatial arrangement of the ligands: One with -OH and $-H_2O^+$ groups bonded at the apical sites, VII, and the other with -OH and $-NHCH_3$ at the apical sites, VIII. At the 3-21G* level, only VII exists and VIII breaks down. The stability of a hypervalent molecule has been shown to depend on the apicophilicity[17] of the more electronegative ligand, *i.e.*, the stability increases as the more electronegative ligands occupy the apical positions. Thus, the preference of VII relative to VIII is understandable in terms of the apicophilicity rule, which has often been applied in rationalizing the relative stabilities of the phosphorane structures.[18] The bond length of $S\text{-}OH_2^+$ in VII is 2.68 Å, which is in good accord with that of S-O (2.69 Å) in sulfurane intermediate calculated by Okuyama *et al.*[10] Reference to Table 1 reveals

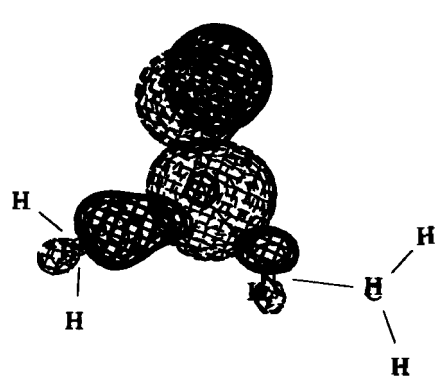


Figure 2. Highest occupied molecular orbital(HOMO) shape of reactant, I.

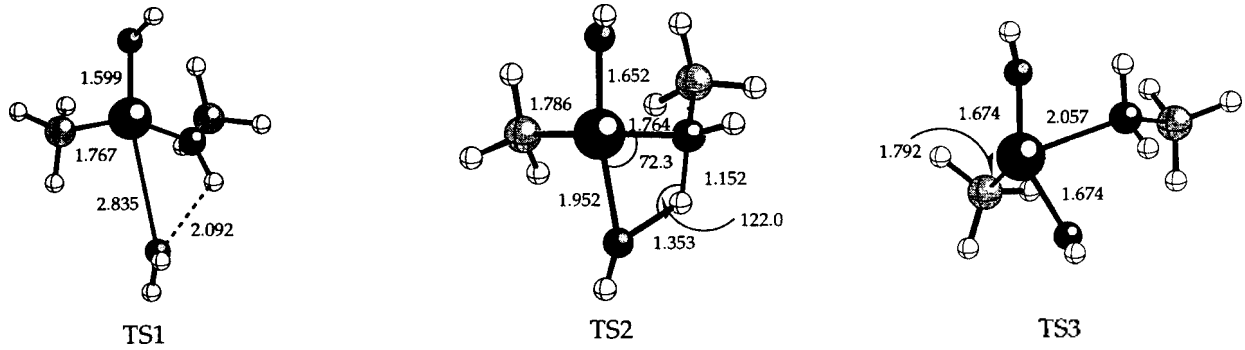


Figure 3. 3-21G* optimized structures of transition states (bond lengths in Å and angles in degree).

that for the unprotonated neutral analogs, the two isomers IX and X, are stable enough to exist irrespective of the ligand type with IX being more stable by 3.6 kcal mol^{-1} than X. Thus, protonation of OH in IX into OH_2^+ (VII) results in a large increase in the apicophilicity for OH_2^+ and brings enhanced stability to the protonated form, VII. This suggests that the increase in the apicophilicity accompanying the protonation is a result of the increase in the electronegativity of the oxygen atom upon protonation.[19]

The next step is the formation of IV by a shift of proton on $-OH_2^+$ to the nitrogen atom. Again two isomers are possible for IV: one is that with the two -OH groups at the apical sites, XI, and the other is that with the -OH and $-NH_2CH_3^+$ groups at the apical positions, XII. According to the MP2 results, XII is more stable by 21.4 kcal mol^{-1} than XI. This is again the result of a large increase in the apicophilicity of $-NHCH_3$ ligand upon protonation. A topological rearrangement, Berry pseudorotation[20] or turnstile rotation,[21] can occur within the hypervalent molecule like sulfurane, and ligand exchange takes place between axial and equatorial ligands. However, XI differs structurally from XII only by the exchange of an equatorial OH with and an apical $^+NH_2CH_3$; XI cannot be transformed into XII by a simple topological rearrangement and furthermore proton transfer from OH_2^+ in VII to $+NH_2CH_3$ transforms it into XI not into XII.

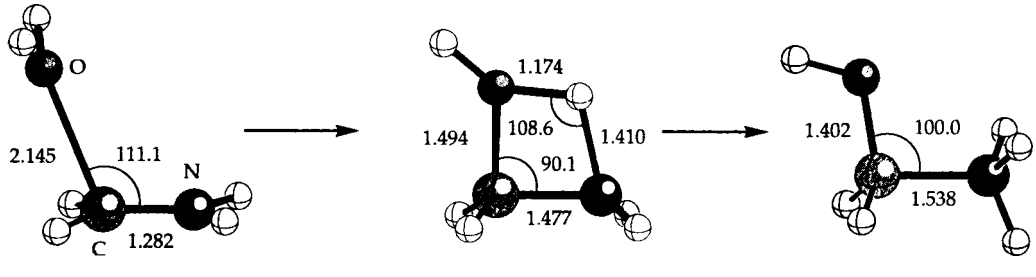
As a final product, a hydrogen-bonded complex formed between $CH_3SO_2H_2^+$ and CH_3NH_2 may be envisaged. However, the 3-21G* results gave a complex formed between V and $CH_3NH_3^+$. In order to confirm these result, calculations were performed on reaction (1). The reaction energy of (1)

$$CH_3SO_2H_2^+ + CH_3NH_2 = CH_3SO_2H + CH_3NH_3^+ \quad (1)$$

at the MP2 level was -23.4 kcal mol^{-1}, indicating a large exothermicity involved. Due to the large stability of the products, a barrierless proton transfer is believed to occur from $CH_3SO_2H_2^+$ to CH_3NH_2.

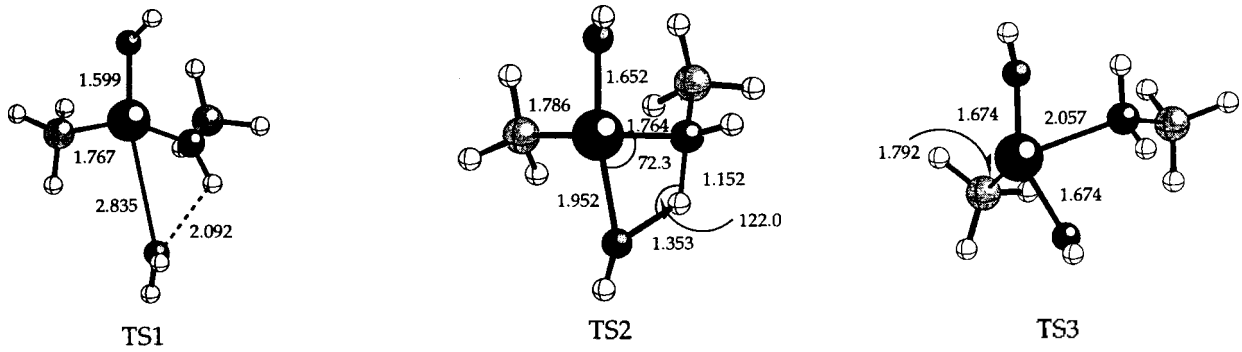
Transition Structures and Minimum Energy Reaction Pathway. The transition structures found on the reaction pathway are presented in Figure 3. The first TS, TS1, occurs when the sulfurane intermediate is formed by covalent bonding of H_2O within the complex (II-H_2O). The TS1 has an elongated hydrogen bond (to 2.1 Å) and a decreased bond length of S-O (2.8 Å) indicating little progress in bond formation. The activation energy was very small (4.6 kcal mol^{-1}) for this process.

The second TS, TS2, has a four-center structure, which is formed by a 1,3-[O,N]-proton shift as a proton on the apical $-OH_2^+$ group migrates toward the equatorial nitrogen atom. In this structure, bond length of the bonds between the migrating proton and O and N are 1.35 and 1.15 Å, respectively, with <OHN=122° and <OSN=72.3°. The MP2 activation energy was 39.9 kcal mol^{-1}, which is much higher than that (29.3 kcal mol^{-1} at the MP2 level) for the four-center TS involved in the proton shift within $^+OH_2$-CH_2-NH_2 in Scheme 3. The large difference (*ca.* 10 kcal mol^{-1}) in the activation energies found between the two TSs are the result of the longer bond length for S-O and S-N in the TS2 compared to the corresponding C-O and C-N bonds in the



E(3-21G)	-169.48531(0.00)	-169.44311(26.48)	-169.49216(-4.30)
E(MP2/6-31G*)	-170.87862(0.00)	-170.83199(29.26)	-170.89265(-8.80)

Scheme 3.



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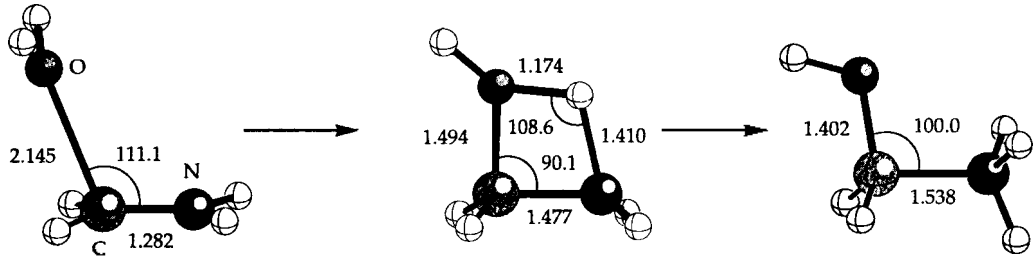

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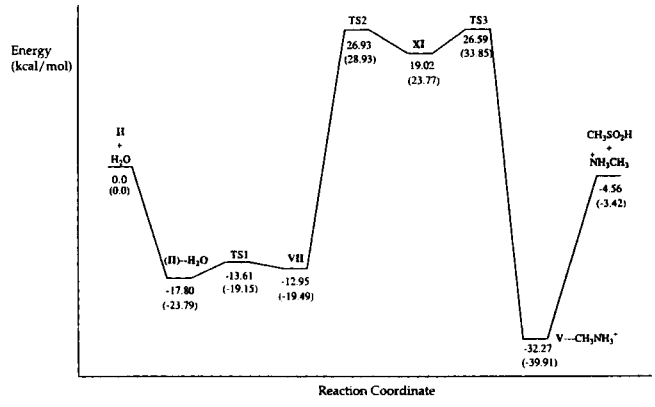


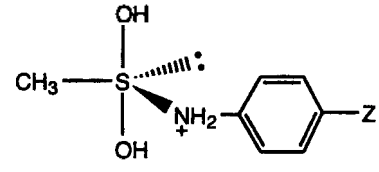
Figure 4. MP2/6-31G*//3-21G* energy profile for the acid catalyzed hydrolysis of I. Energies are relative to the sum of the energy of II and H_2O. Values in parentheses are those from 3-21G* calculations.

4-center TS shown in Scheme 3. Moreover, the reaction involving sulfur is endothermic, in contrast the reaction of the carbon analog is exothermic. In accordance with the Hammond postulate[22] the TS for the exothermic reaction (carbon analog) occurs at an earlier position (lower degree of bond-making and -breaking in the TS; compare bond lengths in the TS2 and the TS in Scheme 3) on the reaction coordinate.

TS3 corresponds to the rate determining step in the final product formation by the cleavage of the S-N bond of the sulfurane intermediate, XI. The S-N bond was stretched in this TS to 0.26 Å and the activation barrier for the bond cleavage of the intermediate was 7.6 kcal mol^{-1} at the MP2 level.

The energy profile showing the energies of all the species calculated on the reaction path is presented in Figure 4. The profile starts from II since the path from I to II was omitted from the profile due to a large energy change is involved. According to the results at the 3-21G* level of theory, the overall rate determining step (the highest energy TS on the reaction coordinate) corresponds to the transformation of IV to V. The barrier height for this step is relatively low, but it should be noted that the level of IV itself is high (23.8 kcal mol^{-1} higher than the reactant). Considering the barrier heights at the level of IV, TS3 is somewhat higher than TS 2. At the MP2 level of theory, however, the energy profile somewhat differs from that based on the results at the 3-21G* level. The order of stability for TS1 and III is now reversed so that the existence of the TS1 is doubtful. Another difference is that at the MP2 level the TS2 level becomes higher marginally (by 0.3 kcal mol^{-1}) than TS3. The levels of TS2 and TS3 are in fact nearly the same and suggests that the relative height may become variable depending on the level of theory used and also by a small changes in the TS structures.

Substituent Effects on the Breakdown of N-protonated N-arylmethanesulfinamide, XIII. Our MP2 results indicates that the level difference between the two highest points on the energy profile, *i.e.*, between TS2 and TS3, is marginal and indeed it is difficult to give a definitive answer for the highest point on the reaction coordinate, *i.e.*, the overall rate-determining step. One way of checking the real rate-determining step is to examine the substituent effects. In fact, such substituent effect studies were carried using acid-catalyzed hydrolysis of N-arylphenylsulfinamide.[7] We have therefore attempted a theoretical study of substituent effects involved in the TS2 and TS 3, which are the two critical barriers in the overall reaction. We investigated the effects of substituents on the proton transfer (TS2) and N-S bond cleavage (TS3) steps by calculating activation energy changes due to variation of substituents in a model compound of N-protonated N-arylmethanesulfinamide, XIII. Substituent was varied from that



Z=OCH_3, CH_3, H, Cl

XIII

of an electron donor to that of an electron acceptor and calculations were performed both at the 3-21G* and MP2 levels. The energy levels for the two TSs are summarized in Table 2. The S-N bond cleavage step is shown to be located at a higher energy level than the proton transfer step at both levels of theory irrespective of the substituent in the ring. As the substituent is varied from an electron donor to an electron acceptor, there is practically no change in the activation energy for the proton transfer step, whereas the activation energy for the N-S bond cleavage step becomes lower. The Hammett $\rho^+\sigma^+$[23] correlation, Eq. 2, was found to

$$-\frac{\delta\Delta E^{\neq}}{2.3RT}=\rho^{+}\sigma^{+} \qquad (2)$$

be satisfactory with ρ^+=1.19 and correlation coefficient of 0.97. The results of this theoretical substituent effect studies are consistent with the experimental results and provide a definitive answer to the question of which step, TS2 or TS3, is the overall rate determining one.

Nevertheless, in view of indeterminate nature of the rate

Table 2. Calculated energies[a] of N-protonated N-(Z)-arylmethanesulfinamide and transition states[b]

Z	Structure	E(3-21G*)	E(MP2/6-31G*//3-21G*)
	TS2	- 982.19322	- 989.13424
OCH_3	XIII	- 982.20316	- 989.14697
	TS3	- 982.18154	- 989.13162
	TS2	- 907.76067	- 914.11685
CH_3	XIII	- 907.77060	- 914.12965
	TS3	- 907.74984	- 914.11524
	TS2	- 868.93723	- 874.94369
H	XIII	- 868.94706	- 874.95640
	TS3	- 868.92712	- 874.94272
	TS2	- 1325.75145	- 1333.97042
Cl	XIII	- 1325.76103	- 1333.98289
	TS3	- 1325.74212	- 1333.97005

[a] in hartree. [b] TS2 and TS3 are the transition states for the 1,3-[O, N]-H-shift and N-S bons breaking step, respectively.

determining step based on the simple MP2 level energies of TS2 and TS3, higher level studies may prove to be useful. In addition, in order to compare with the experimental results which were conducted in the aqueous solution, we need to account for the solvent effects. Further works on such problems are in progress in this laboratory.

Conclusion

Following conclusions are derived from the results of the ab initio studies on the acid-catalyzed hydrolysis of sulfinamide.

1) The first step in the acid-catalyzed hydrolysis of N-methylmethanesulfinamide, I, is protonation, which occurs at the O rather than at the N atom leading to the more stable protonated species, II.

2) Addition of H_2O to II takes place at an apical site forming a sulfurane intermediate, VII, which is then transformed into XI by a 1,3-H-shift. Lastly, products are formed by N-S bond cleavage. The rate determining step is the N-S bond cleavage at the 3-21G* level, whereas it is rather indeterminable between the 1,3-H-shift and the N-S bond cleavage at the MP2 level. The rate determining step is sensitive to the level of theory used in the calculations.

3) The proton transfer to methyl amine occurs in a barrierless process leading to the final products, CH_3SO_2H and $^+NH_3CH_3$.

4) The rate determining step in the breakdown of the protonated intermediate, N-protonated N-arylmethanesulfinamide, XIII, is the S-N bond cleavage irrespective of the substituent in the ring. The Hammett coefficient, ρ^+, for this step is +1.19 reflecting a decrease in positive charge on the N atom in the transition state.

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