

Computational Studies on the Sulfur Dioxide Absorption by Organic Lewis Bases

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The flue gas emitted by burning of fossil fuels is a significant source of the atmospheric sulfur dioxide (SO₂). As SO₂ can produce eventually sulfuric acid after oxidation and reaction with water, it is considered as one of the main sources causing acid rain. To prevent the environmentally harmful gas from exposing to atmosphere, the flue gas desulfurization (FGD) processes such as limestone-scrubbing and chemical absorption are requested in the fire power plant. Currently, among many sorbents limestone (CaCO₃) is widely used for a scrubbing process which utilizes the chemical reaction between CaCO₃ and SO₂ to give solid CaSO₃. As this process gives a large amount of solid waste cakes as by-products as well, the new absorption methods using organic solvents as SO₂-removal agents have been explored because the absorbing agents can be regenerated repeatedly.¹⁻⁵

The SO₂ removal method by organic solvents is generally composed of two steps: 1) a fixation of SO₂ from the flue gas by the formation of a absorbent-SO₂ complex, and 2) thermal regeneration of absorbing agents and SO₂ stripping at the same time. The working process looks similar to that of an amine-CO₂ reaction which is an important CO₂ removal method from the flue gas. However, in the case of the SO₂ absorption and stripping, Lewis acid-base reactions involving dative bonds as shown in Scheme 1 happen while amines react with CO₂ to produce carbamates via covalent bonds.^{4,6} This difference in the reaction mechanism was experimentally verified that Lewis basicity parameterized by Gutmann donor number (D_N) was related to the reactivity of the SO₂ absorption while it did not for the CO₂ case.⁴

Various sulfur dioxide complexes at molecular level have been extensively studied by Kuczowski and coworkers.⁷⁻¹⁰ They classified sulfur dioxide complexes according to the types of interactions into charge-transfer complexes, van der Waals complexes, and hydrogen-bonded complexes.¹⁰ Gas phase complexes were investigated by microwave spectroscopy and *ab initio* calculations, and solid state structures by

X-ray crystallography. Leopold *et al.* also have extensively studied "partially formed bonds" in Lewis acid-base complexes containing BF₃ and SO₂ as Lewis acids.¹¹ The Lewis acid-base complexes are actually same as the charge-transfer complexes classified by Kuczowski and coworkers. Interestingly, the bond lengths of the partial dative bonds in the gas phase become significantly shorter in solid, and turn into nearly full dative bonds. This phenomenon has been attributed to more enhanced dipole moment interactions in

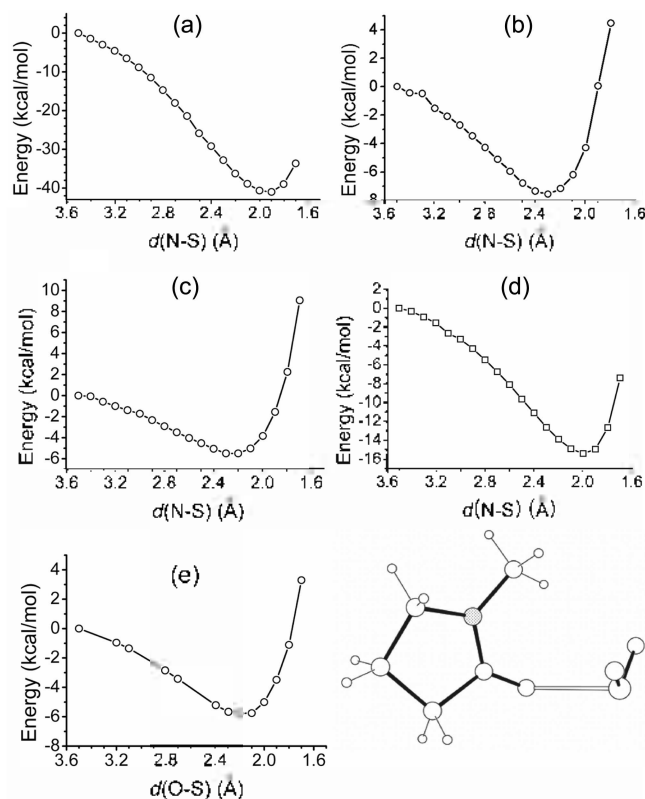
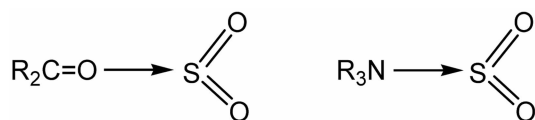


Figure 1. Energy profiles of the reactions between amine molecules and SO₂ in aqueous environments are plotted with respect to the constraint reaction coordinates. HF calculations in gas phases were used to optimize each structure, and then each energy value was determined by a higher level DFT calculation and applying a PCM solvation model (See Experimental Section). Plots for (a) TMA-SO₂, (b) TEA-SO₂, (c) MEA-SO₂, (d) pyridine-SO₂, and (e) NMP-SO₂. The energy-minimum structure of NMP-SO₂ is shown with a ball-and-stick model where a dotted ball is N atom, and the open bond indicates an O...S dative bond.



Scheme 1. Representative sulfur dioxide complexes formed with a dative bond, O-S or N-S bonding.

the condensed phase. However, it is noticeable that TMA- and DMA-SO₂ (TMA = trimethylamine, DMA = dimethylamine) complexes having 2.046(4), and 2.003(12) Å for *d*(N-S)s in solid, respectively, are *only* about 0.25 Å contraction from those in gas phases.^{7,11}

Considering that the SO₂ complexes have been studied for a long time, it is our surprise that there have been yet no theoretical investigations on the SO₂ complexes by the viewpoint of the SO₂ removal. Only chemical engineers have been interested in this issue, and studied the SO₂ removal process experimentally.¹⁻⁵ In this regard we have conducted quantum mechanical computations to trace the reaction between amines and SO₂, and to calculate binding energies of the stable Lewis acid-base complexes in both a gas phase and an aqueous environment. Lewis bases dealt with in this work were trimethylamine (TMA), triethylamine (TEA), monoethanolamine (MEA), pyridine, and methylpyrrolidone (NMP), where NMP did not form an SO₂ complex *via* an N-S bond but reacts with SO₂ by forming a O(carbonyl)-S bond (Figure 1e).

The constraint has been applied to the inter-atomic distances between each N atom in TMA, TEA, MEA, and pyridine and the S atom of SO₂. For the case of TMA, the distance started from the value close to a sum of van der Waals radii, 3.35 Å for N and S atoms, which was gradually reduced by 0.1 Å to 1.7 Å, near the sum of the covalent radii, 1.78 Å. The energy-minimum was obtained at 1.90 Å with a gradual stabilization after which the energy increased abruptly (Figure 1a). The overall energy profile indicates that the absorption reaction for TMA is a one-step reaction forming N-S bonding with no transition state, which was also observed for the previous reports on TMA-SO₂,⁷ and NH₃-BF₃.¹¹ Similar trends have been observed for the other amines, TEA, MEA and pyridine with the optimized N-S distances of 2-2.3 Å (Figures 1b, 1c and 1d). The NMP-SO₂ complex has an energy-minimum at an O-S distance of ~2.2 Å (Figure 1e).

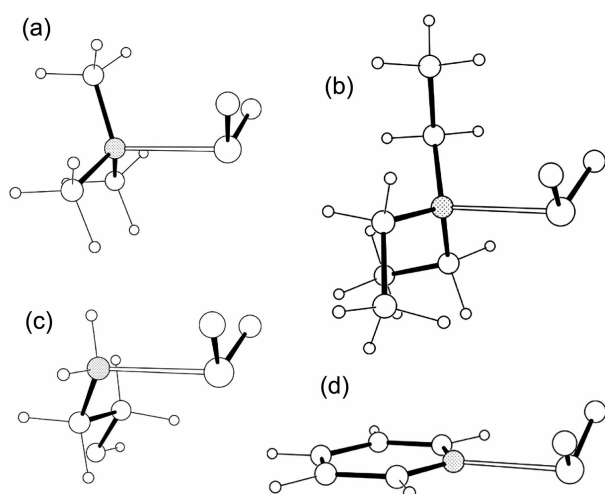


Figure 2. Final optimized structures of the SO₂-complexes with Lewis bases. (a) TMA. (b) TEA. (c) MEA, and (d) pyridine. Dotted balls are N atoms, and small balls are H atoms. Dative bonds are drawn with open sticks which link N and S atoms.

The energy-minimum structures found during studies on the reaction pathways were further optimized by DFT-B3LYP/6-311++G(d,p) computations. As the additional calculations were done for the gas phase complexes, parallel DFT studies with PCM (Polarized Continuum Model) were also carried out to check the variations of the structural and energetic values in aqueous environments. The final structures adjusted by PCM models are drawn in Figure 2, the final geometric values and binding energies corresponding to gas phase (*gas*) or solvated (*sol*) structures are listed in Table 1, and the definition of the geometric parameters are depicted in Figure 3.

Both distances of N-S and O-S bonds in a gas phase or with a solvation model range between the sum of covalent radii (N-S = 1.78 Å; O-S = 1.78 Å) and the sum of van der Waals (vdW) radii¹² (N...S = 3.35 Å; O...S = 3.32 Å), which is indicative of the "partially formed bonds".¹¹ The N-S distances of TMA- and pyridine-SO₂ complexes are well-matched to the experimental values in gas phases (2.26, and 2.61 Å, respectively).^{7,10} These values become smaller by about 0.29 Å with maintaining overall conformations when PCM models were applied. The calculated binding energy of the TMA-SO₂ complex (-9.07 kcal/mol) in a gas phase is very close to the experimental value (-9.1 kcal/mol).^{7,13} It becomes larger by 1.0 kcal/mol when a PCM model was applied. On the contrary of the TMA-SO₂ case, the binding energies for other amines become smaller. Others reported previously the binding energies obtained by various levels of *ab initio* calculations for a pyridine-SO₂ complex.¹⁰ However, the values are not sufficient for the quantitative description because the calculated values for TMA-SO₂ using same computational levels were significantly deviated from the experimental value. The bond distances, *d*(N-S)s obtained by PCM models lie between those in gas and in

Table 1. Binding energy, geometric parameters, and basicity parameters of various SO₂-amine complexes

Contents		TMA	TEA	MEA	pyridine
Binding energy (kcal/mol)	<i>gas</i>	-9.07	-7.08	-5.69	-6.14
	<i>sol</i>	-10.05	-6.80	-5.01	-4.42
<i>d</i> (N-S) (Å)	<i>gas</i>	2.422	2.461	2.570	2.536
	<i>sol</i>	2.188	2.279	2.178	2.195
α (°)	<i>gas</i>	176.47	174.01	123.62 ^a	176.37
	<i>sol</i>	178.82	174.53	117.28 ^a	178.57
β (°)	<i>gas</i>	101.71	104.63	100.32	100.53
	<i>sol</i>	106.35	107.94	105.33	104.16
γ (°)	<i>gas</i>	-0.32	29.84	16.22 ^b	87.70
	<i>sol</i>	-1.33	27.68	18.91 ^b	90.72
D_N (kcal/mol)		60.0 ¹⁴	61.0 ¹⁵	NA	33.1 ¹⁴
pK_a at 25 °C		9.9 ¹⁶	10.75 ¹⁷	9.51 ¹⁸	5.21 ¹⁷

^aMEA has a pseudo C₃ axis, and the direction of the electron lone pair at N is not coincident with the axis. ^bA torsion angle defined by H-N-S-X (See Figures 2 and 3).

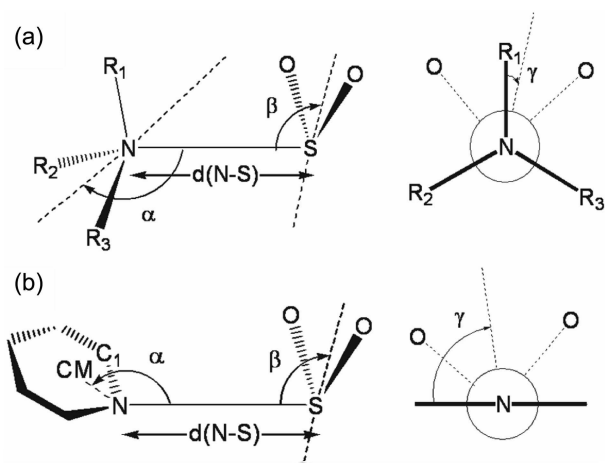


Figure 3. Definition of geometric parameters^{8,10} of (a) α , β , $d(\text{N-S})$, and γ of aliphatic amines, and (b) those of pyridine. The parameter α or β is the angle between the C_2 axis of SO_2 and N-S bond, respectively. The parameter γ is the torsion angle $R_1\text{-N-S-X}$. Here X is an arbitrary point on the C_2 axis. In the case of pyridine, the parameters, α and γ are the CM-N-S angle and the torsion angle, $C_1\text{-N-S-X}$, respectively. CM represents the center of mass of the aromatic ring.

solid phases, which implies that the calculated binding energies for TEA, MEA, and pyridine- SO_2 s are reasonable enough to describe stabilities in aqueous environment although the variation tendency is obverse to that of TMA- SO_2 .

As the strength of the Lewis basicity increases, stronger binding energies and shorter $d(\text{N-S})$ values would be expected. As shown in Table 1, there is a general correlation between the basicity and binding energy, however bond lengths do not follow this trend. For example, TMA, TEA, and MEA are more basic - they have larger D_N numbers and pK_a values- and have larger binding energies than pyridine, but the $d(\text{N-S})$ length of TEA is not shorter than that of pyridine. A plausible reason for the unexpected observation may be ascribed to the presence of the bulky ethyl groups in TEA which makes steric hindrance come into effect. Supporting evidences can be found in the geometric parameters, α and β (Figure 3). When there is steric hindrance two contacting groups would tend to be separated from each other, which will result in smaller α , and larger β values. In pyridine- SO_2 complex, SO_2 moiety does not feel a significant steric hindrance because it is almost vertical to the molecular plane of the pyridine ring with $\beta = 104.16^\circ$ (Table 1). For the MEA- SO_2 complex, as two hydrogen atoms bound to an N atom face SO_2 moiety, it is easily expected that the magnitude of the steric hindrance is much smaller than those in TMA and TEA. Based on these speculation and observation, we can say that the overall steric hindrance increases with the increasing order, pyridine < MEA < TMA < TEA. In short, the binding energy is correlated to the basicity or D_N , and the steric effect diminishes the binding energy somewhat with increased $d(\text{N-S})$ distances.

In summary, this work shows by computational appro-

aches that various absorption agents having primary, tertiary, and aromatic amines are able to form stable Lewis acid-base complexes with SO_2 without forming particular transition states. The dative bond lengths indicate the all the Lewis acid-base complexes in this study are partially bound complexes. The binding energies calculated in aqueous environments are increased by 10.8% for TMA- SO_2 , and decreased by 4.0%, 12.0%, and 28.0% for TEA-, MEA-, and pyridine- SO_2 s, respectively. If the binding energy of $\text{H}_2\text{O-SO}_2$ is similar to that of DMF- SO_2 (3.6 kcal/mol; DME = dimethylether),⁹ it is likely that they have a chance to form the complexes, and can be used in absorption of SO_2 as aqueous solvents. Finally, a relatively good correlation has been observed between the strengths of binding energies and the basicities of the amines.

Computational Section

To find out the reaction pathways, geometric parameters intimately involved in the reaction, that is, N-S, and O-S distances have been chosen as pseudo reaction coordinates. A series of quantum mechanical calculations were run by fixing the inter-atomic distances at each step, and the structures of the complexes was optimized.¹⁹ *Ab initio* (HF) in gas phase and DFT in solvation phase are used for the geometry optimization and energy calculation, respectively. HF method adopted basis set of 6-31+G(d,p) for C, H, N, and O atoms, and 6-31+G(2d) for S atom, while DFT used B3LYP functional with 6-311++G(d,p) basis set for C, H, N, and O atoms, and 6-311++G(2d) for S atom. The used solvation model for an aqueous solution was PCM (Polarized Continuum Model) developed by Tomasi and coworkers.²⁰ To define the cavity for a solute, Bondi radii¹² were adopted. For the energy calculation, zero potential energy (ZPE) was also considered.

The binding energy (B.E.) of a SO_2 -amine complex was defined as,

$$\text{B.E.} = E(\text{SO}_2\text{-amine complex}) - E(\text{SO}_2) - E(\text{amine}) \quad (1)$$

The each energy term is corresponding to an optimized SO_2 -amine complex, SO_2 , and amine, respectively. The calculations were performed by the same DFT methods mentioned above. The basis set superposition error (BSSE) was not corrected because the adapted basis sets in this work are sufficiently large and can relieve the error somewhat. Especially, MEA can have an internal hydrogen bond between the terminal -OH and - NH_2 groups, which may cause a significant BSSE, and may need an application of the counterpoise method.²¹ However, as it is beyond our objectives, it was not considered in this work.

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