Computational Studies on the Reaction between Monoethanolamine and Nitrogen Oxides

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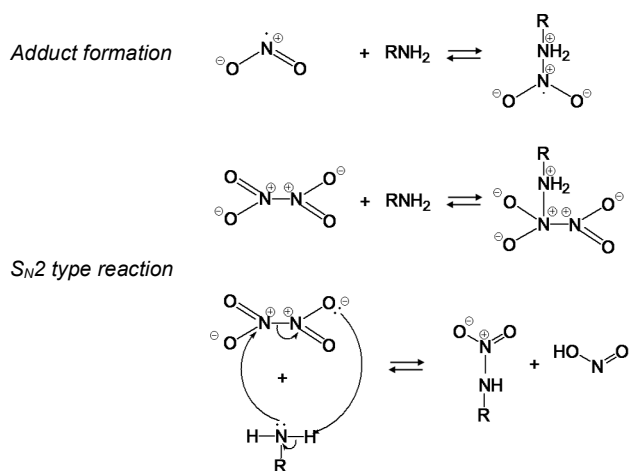
The flue gas emitted by power plants is composed of mainly N_2 and CO_2 with a small amount of the harmful gases SO_2 and NO_2. The greenhouse gas CO_2 is removed by absorption process using alkanolamines such as monoethanolamine (MEA).[1] SO_2 can also be captured by forming a Lewis acid-base complex with amines.[2] While both CO_2 and SO_2 can form stable adducts with MEA, it should be expected that NO_2 would behave differently since it is a paramagnetic gas, and in equilibrium with N_2O_4 at ambient temperature. It is possible for MEA to react with N_2O_4, too. There are patent reports on the removal of NO_2 by amines.[3] However, no research has yet been reported on the mechanism of the NO_2 elimination reaction by amines, which motivated us to investigate the reaction between NO_2 and MEA by quantum mechanical calculations.

As MEA can react with both NO_2 and N_2O_4, possible reactions are classified as shown in Scheme 1: (1) MEA- NO_2 or MEA-N_2O_4 complex formation, and (2) dissociation of N_2O_4 by MEA to $HO(CH_2)_2N$-NO_2 and nitrous acid. N_2O_4, a planar structure with D_{2h} symmetry, has a long and weak N-N bond in which d(N-N) is 1.75 Å. Its dissociation energy is only 57 kJ/mol (13.6 kcal/mol).[4] N_2O_4 is easily hydrolyzed to produce HNO_3 and HNO_2. As it is, it is expected that MEA could also break the N-N bond by an S_N2 type reaction.

In this work, all calculations were carried out using the Gaussian 03 suite of programs.[5] Geometry optimization and energy calculations were performed on the computational level of Hartree-Fock, and density functional theory (DFT)[6] with the B3LYP functional, respectively. For the energy calculation, we used the aqueous solvation model, PCM, developed by Tomasi *et al*.[7] The adopted basis set was 6-31 + G(d,p), and the cavities of the solvation model were given Bondi radii.[8]

Optimization and energy calculations for the MEA-NO_2 complex yielded a positive Gibbs energy, +7.6 kcal/mol. Although there are some stable compounds having an N-NO_2 bond,[9-11] the MEA-NO_2 complex is not likely to form spontaneously. Similarly, the MEA-N_2O_4 complex was very unstable, and each species was separated, and did not form a chemical bond during calculations.

As both NO_2 and N_2O_4 cannot form stable complexes with MEA, a nucleophilic reaction between MEA and N_2O_4 was investigated. The reaction pathway for a reaction between MEA and N_2O_4 is monitored by a "coordinate driving" method,[12,13] with a key parameter being d(N-N), a distance between

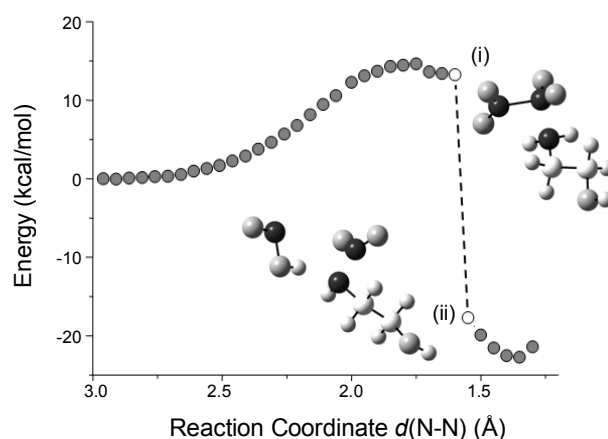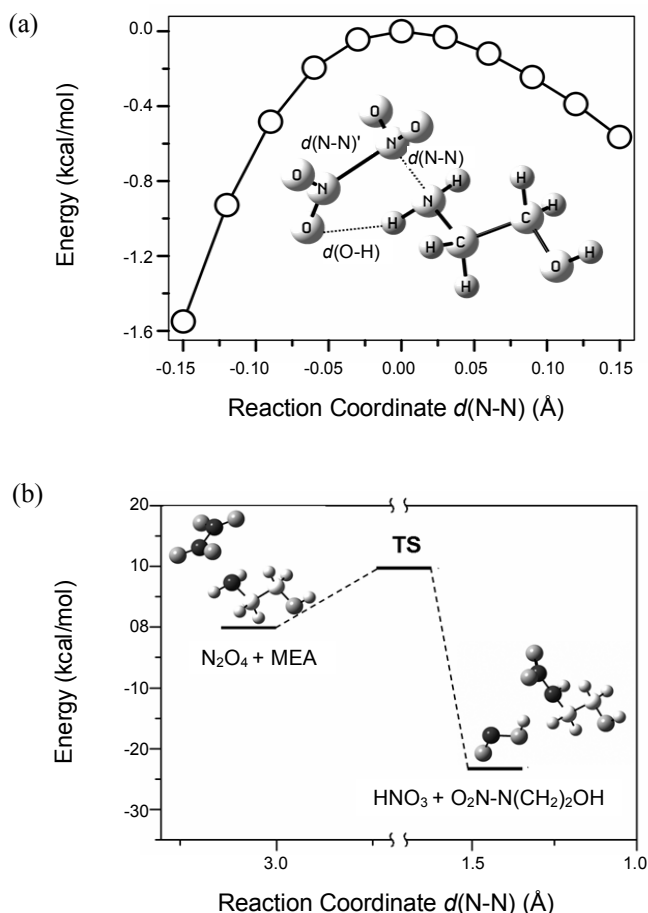**Scheme 1.** Reactions considered in this work are displayed with formal charges and electron rearrangement. R- is $HO(CH_2)_2$- for MEA

Figure 1. Energy vs. reaction coordinate d(N-N) for the reaction between MEA and N_2O_4, which produces HNO_3 + $HO(CH_2)_2$ NH-NO_2. There is a discontinuous change between the points (i), corresponding to pseudo-TS, and (ii), a product.

the nitrogen atom in MEA and a nitrogen atom in N_2O_4, as shown in Figure 1. The value of d(N-N) was fixed to 3.07 Å, and all other geometric parameters were optimized. In this manner, the energy profile was obtained by reducing d(N-N)

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Table 1. Selected inter-atomic distances of the N_2O_4-MEA complexes

distance (Å)	reactants	Pseudo-TS	TS	products
d(N-N)	2.99	1.75	1.60	1.33
d(N-N)'	1.57	1.62	1.81	3.70
d(O-H)	3.09	2.39	1.98	0.95

(a)

(b)

Figure 2. (a) IRC plot around TS, and (b) energies for the reactants, TS, and products for the reaction between MEA and N_2O_4.

to 1.2 Å. The resulting relative energies are plotted against the reaction coordinate. The energy of the initial optimized chemical structure with the fixed key parameter is defined as zero. The reaction was involved with one energy barrier at 1.75 Å. When d(N-N) was reduced further above the pseudo-TS (transition state), and the chemical connectivity of the system was changed greatly at 1.55 ~ 1.6 Å, the energy dropped from 13.3 kcal/mol to −17.7 kcal/mol. This unusual result indicated that the reaction coordinate and the application of the "coordinate driving" method to this work was not pertinent, or needed other factors to make it so.[14]

Instead of monitoring the reaction profile, the transition state (TS) was determined using the pseudo-TS structure obtained by the coordinate-driving method. The obtained TS structure (Figure 2a) had only one negative eigenvalue, corresponding to an imaginary vibration of i292.4 cm^{-1} along the

line connecting two reacting N atoms. Intrinsic reaction coordinate (IRC) calculations performed at ten points around the TS confirmed that the energy values at these points were lower than that of the TS (Figure 2a).[5] The energy *vs.* reaction coordinate is plotted in Figure 2b; here, structures for reactants, TS, and products, are displayed. The activation energy was 9.7 kcal/mol. Optimization and energy calculations were also carried out for both reactants and products. The calculated reaction energy was −22.5 kcal/mol, showing that the proposed reaction is spontaneous. Vibrational frequency analyses showed that all the stationary points of the reaction models had no imaginary frequencies, which confirmed that the obtained geometries were at their energy minima.

The important interatomic distance changes of d(N-N), d(N-N)', and d(O-H) (Figure 2a), the distances of the bonds which are formed or broken during the reaction, are listed in Table 1. It is seen that N_2O_4 maintains its structure with d(N-N)' a little elongated at TS, while MEA and N_2O_4 are partially bonded, with d(N-N) = 1.33 Å. It is also found that the H atom in MEA transferred to the oxygen atom in N_2O_4 to produce a nitrous acid, HNO_2.

In short, NO_2 seems to be eliminated in a fundamentally different manner from CO_2 and SO_2. While these two gases form stable adducts, NO_2 can be removed indirectly by an N_2O_4 elimination pathway. It is possible that NO_2 is also eliminated by H_2O to give nitiric acid,[15] and N_2O_5, like N_2O_4, can react with MEA. For the latter case, the only difference is that nitric acid rather than nitrous acid is produced; in all, the computed reaction energy was −43.8 kcal/mol.

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15. As a CO_2 absorption process using alkanolamine operates at 40 ~ 60 $^{\circ}$C, the reaction between NO_2 and H_2O was calculated at 50 $^{\circ}$C and 25 $^{\circ}$C, respectively. The energies were almost the same, with −0.46 kcal/mol at 50 $^{\circ}$C, and −0.43 kcal/mol at 25 $^{\circ}$C. In a real CO_2-absorption process, amines are used as an aqueous solution. As it is, NO_2 elimination may take place competitively by amines and water.