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 N2 and CO2 with a small amount of the harmful gases SO2 and NO2. The greenhouse gas CO2 is removed by absorption process using alkanolamines such as monoethanolamine (MEA).1 SO2 can also be captured by forming a Lewis acid-base complex with amines.2 While both CO2 and SO2 can form stable adducts with MEA, it should be expected that NO2 would behave differently since it is a paramagnetic gas, and in equilibrium with N2O4 at ambient temperature. It is possible for MEA to react with N2O4 too. There are patent reports on the removal of NO2 by amines.3 However, no research has yet been reported on the mechanism of the NO2 elimination reaction by amines, which motivated us to investigate the reaction between NO2 and MEA by quantum mechanical calculations.

As MEA can react with both NO2 and N2O4, possible reactions are classified as shown in Scheme 1: (1) MEA- NO2 or MEA-N2O4 complex formation, and (2) dissociation of N2O4 by MEA to HO(CH2)2N-NO2 and nitrous acid. N2O4, a planar structure with D2h 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 N2O4 is easily hydrolyzed to produce HNO3 and HNO2. As it is, it is expected that MEA could also break the N-N bond by an SN2 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-NO2 complex yielded a positive Gibbs energy, +7.6 kcal/mol. Although there are some stable compounds having an N-NO2 bond,9-11 the MEA-NO2 complex is not likely to form spontaneously. Similarly, the MEA-N2O4 complex was very unstable, and each species was separated, and did not form a chemical bond during calculations.

As both NO2 and N2O4 cannot form stable complexes with MEA, a nucleophilic reaction between MEA and N2O4 was investigated. The reaction pathway for a reaction between MEA and N2O4 is monitored by a “coordinate driving” method,12,13 with a key parameter being d(N-N), a distance between the nitrogen atom in MEA and a nitrogen atom in N2O4, 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)
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 parameter is defined as zero. The reaction was involved with one energy barrier at 1.75 Å. 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 292.4 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). 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 nitric acid, and \(N_2O_4\) like \(NO_2\), 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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**Table 1.** Selected inter-atomic distances of the \(N_2O_4\)-MEA complexes

<table>
<thead>
<tr>
<th>distance (Å)</th>
<th>reactants</th>
<th>Pseudo-TS</th>
<th>TS</th>
<th>products</th>
</tr>
</thead>
<tbody>
<tr>
<td>(d(N-N))</td>
<td>2.99</td>
<td>1.75</td>
<td>1.60</td>
<td>1.33</td>
</tr>
<tr>
<td>(d(N-N'))</td>
<td>1.57</td>
<td>1.62</td>
<td>1.81</td>
<td>3.70</td>
</tr>
<tr>
<td>(d(O-H))</td>
<td>3.09</td>
<td>2.39</td>
<td>1.98</td>
<td>0.95</td>
</tr>
</tbody>
</table>

**References**

15. As a \(CO_2\)-absorption process using alkanolamine operates at 40 ~ 60 °C, the reaction between \(NO_2\) and \(H_2O\) was calculated at 50 °C and 25 °C, respectively. The energies were almost the same, with -0.46 kcal/mol at 50 °C, and -0.43 kcal/mol at 25 °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.