

Exploration of the Dehydrogenation Pathways of Ammonia Diborane and Diammoniate of Diborane by Molecular Dynamics Simulations Using Reactive Force Fields

Peng Gao^{a,b}, Zhenguo Huang^c and Haibo Yu^{a,b,d*}

^a School of Chemistry and Molecular Bioscience, University of Wollongong, NSW 2522, Australia

^b Molecular Horizons, University of Wollongong, NSW 2522, Australia

^c School of Civil and Environmental Engineering, University of Technology Sydney, NSW 2007, Australia

^d Illawarra Health and Medical Research Institute, Northfields Avenue, Wollongong, NSW 2522, Australia

* Corresponding author: hyu@uow.edu.au

1. Temperature ramping simulations of AADB and DADB.

The instantaneous temperatures and pressures were shown as a function of the simulation time (Figure S1: AADB and Figure S1: DADB).

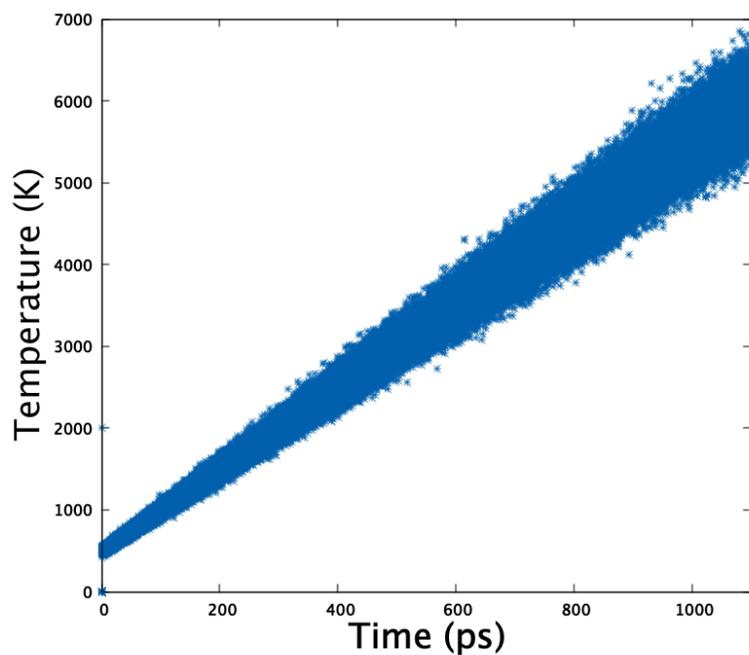


Figure S1a. Temperature as a function of simulation time for simulation of AADB.

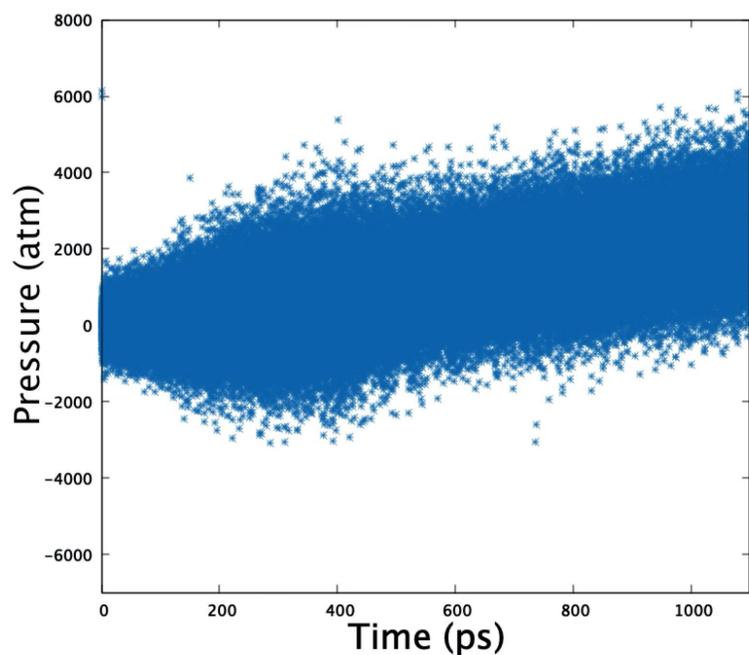


Figure S1b. Pressure as a function of simulation time for simulation of AADB.

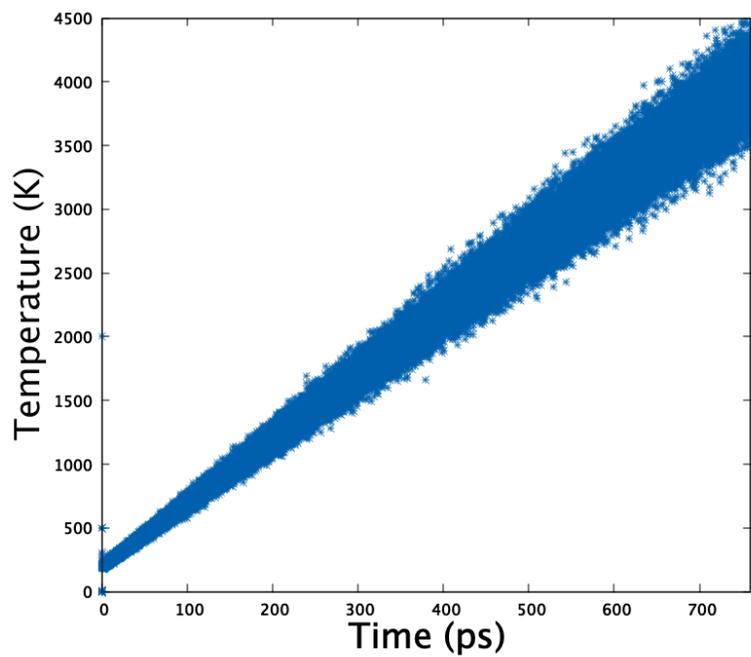


Figure S2a. Temperature as a function of simulation time for simulation of DADB.

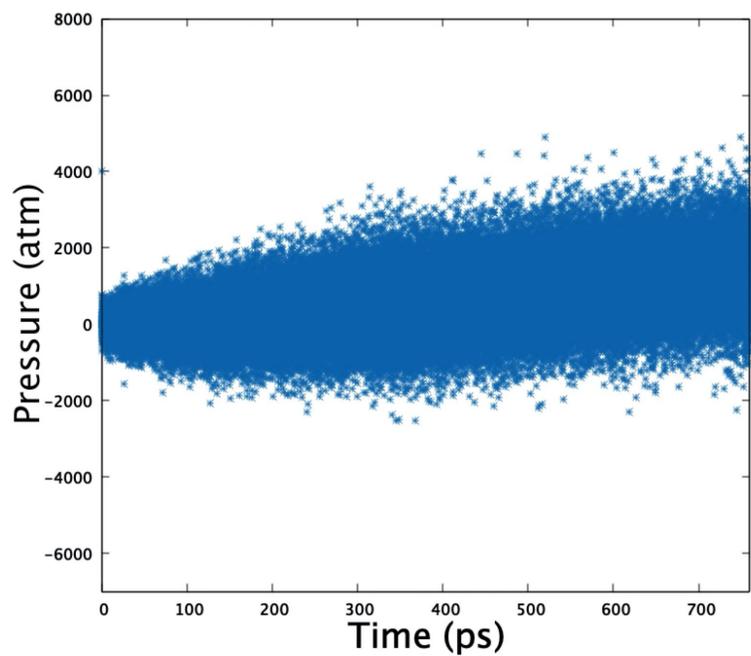


Figure S2b. Pressure as a function of simulation time for simulation of DADB.

2. The flowchart of the developed molecular recognition package. The package can be accessed at: https://github.com/tcsnfrank/Molecular_recognition

```
Load r[1-n];      #Load the trajectory of all the atoms
## Calculate the distance of the atoms and store bonding connections between atoms
for i & j in range(1:n)      #(i!=j)
    If r[i]-r[j]<rijcut:
        Bond[i].append(j)
        Bond[j].append(i)
## Recognize molecules based on bonding connections between atoms
1). Set an atom (atom[i]) as a beginning to find the whole molecule[k] (including atom[i])
2). Find all the atoms[.] have connection with atom[i]; Add atom[.] to molecule[k].
3). Find all the atoms[.] have connection with atom[.] except atoms already in molecule[k].
4). Keep searching until all the atoms[...] have been included in molecule[k].
5). Set another atom[j] that does not belong to any molecules which have been detected.
6). Restart a new searching from step 2).
## Analyze the molecular information from atomic composition of molecules
for molecule[k] in Molecules:
    for atoms[i] in molecule[k]:
        if atoms[i]_ID=="B":
            B_NO+=1
        if atoms[i]_ID=="H":
            H_NO+=1
        if atoms[i]_ID=="N":
            N_NO+=1
    .....
    molecule[k][formula]=B(B_NO)N(N_NO)H(H_NO)...
## Calculate the fingerprint of the molecules to define the structure of the molecules
Fetch the atom types and numbers that the atoms in molecule[k] has bond connection. This method can
distinct isomers except chrial molecules.
## Calculate the number of the boron species B(B_NO)N(N_NO)H(H_NO)... molecule
if molecule[k][formula]=B(B_NO)N(N_NO)H(H_NO)...:
    B(B_NO)N(N_NO)H(H_NO)..._NO+=1
## Perform above calculation for trajectories of different timestep
Plot B(B_NO)N(N_NO)H(H_NO)..._NO vs simulation time
```

To assign the atoms to a specific molecule, the empirical bond lengths were used as the criterion in the connectivity analyses: B-N: 1.8 Å; B-H:1.4 Å; N-H: 1.4 Å; H-H: 1.2 Å.

3. The averaged molecular weight (MW) versus temperature for the temperature ramping simulations of AADB and DADB.

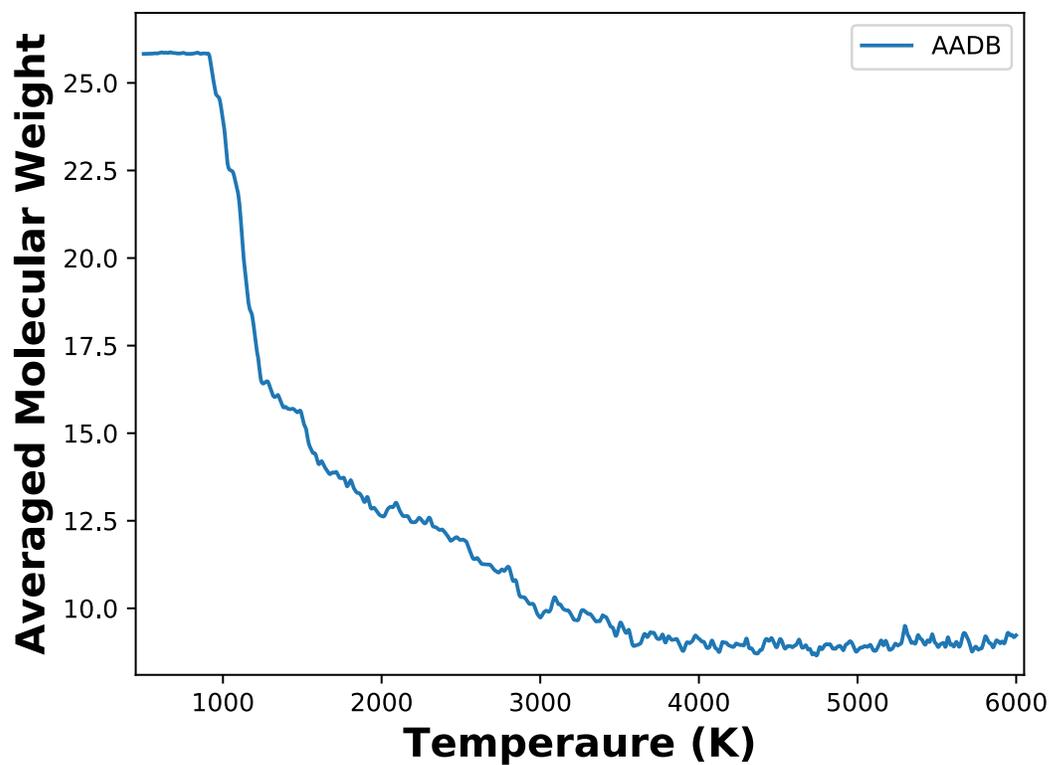


Figure S3. The plots of the averaged molecular weight (MW) versus temperature for the temperature ramping simulation of AADB.

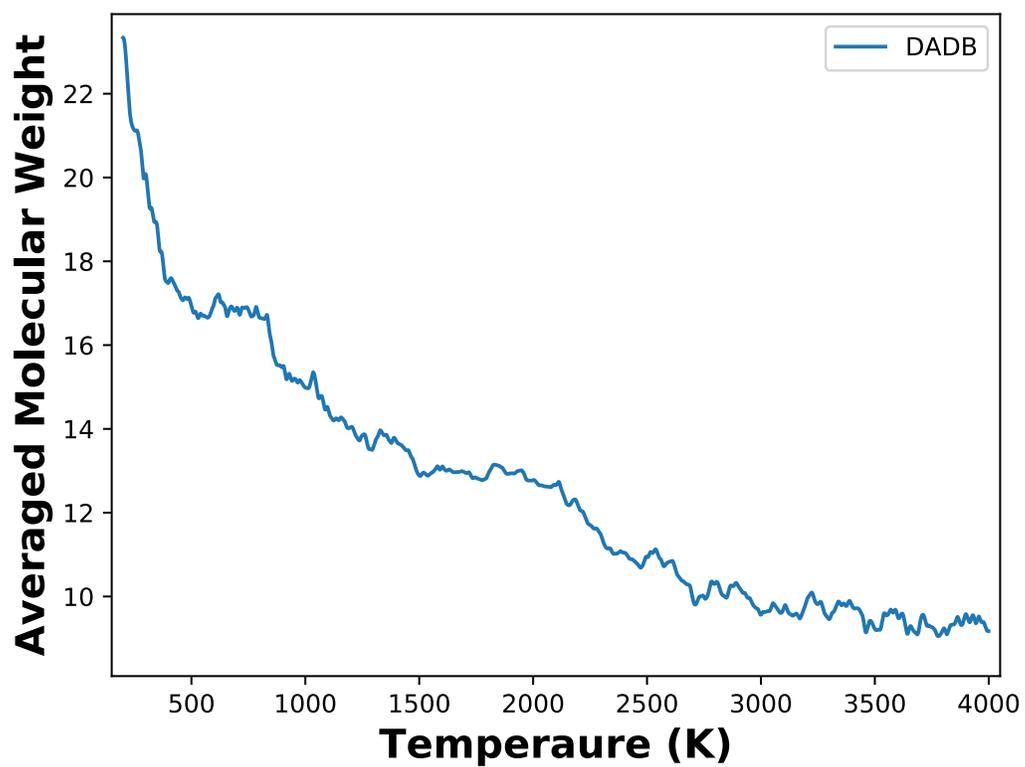


Figure S4. The plots of the averaged molecular weight (MW) versus temperature for the temperature ramping simulation of DADB.

4. The total number of molecules versus temperature for the temperature ramping simulations of AADB and DADB.

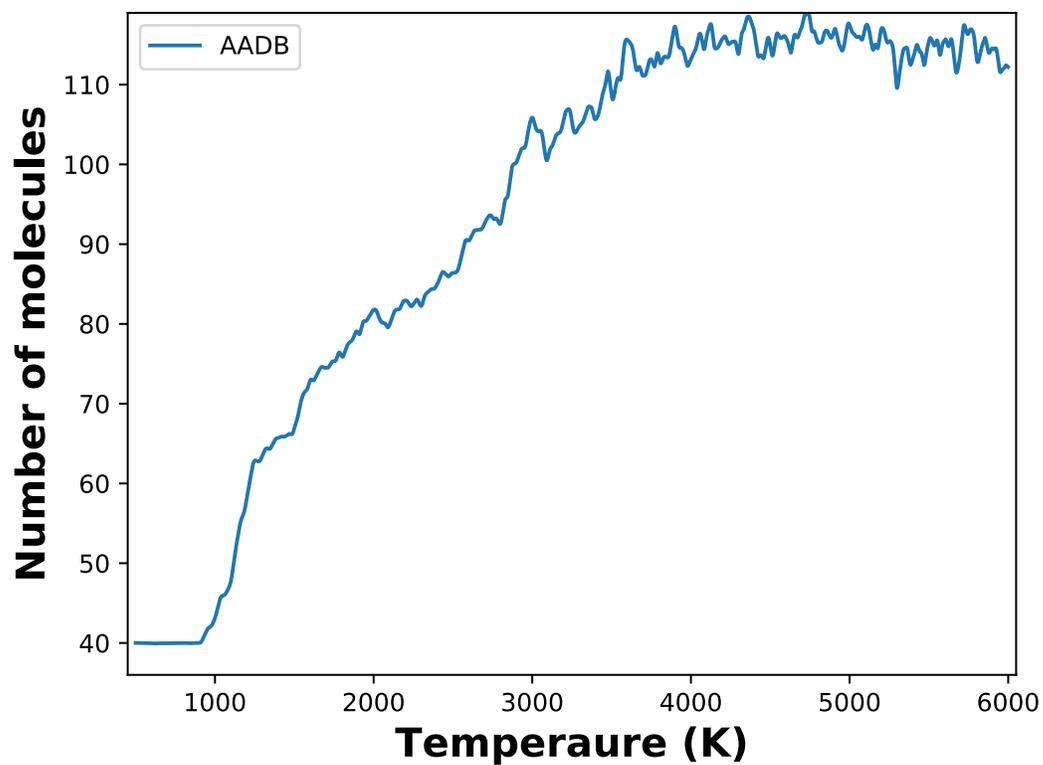


Figure S5. The plots of the total number of molecules versus temperature for the temperature ramping simulation of AADB.

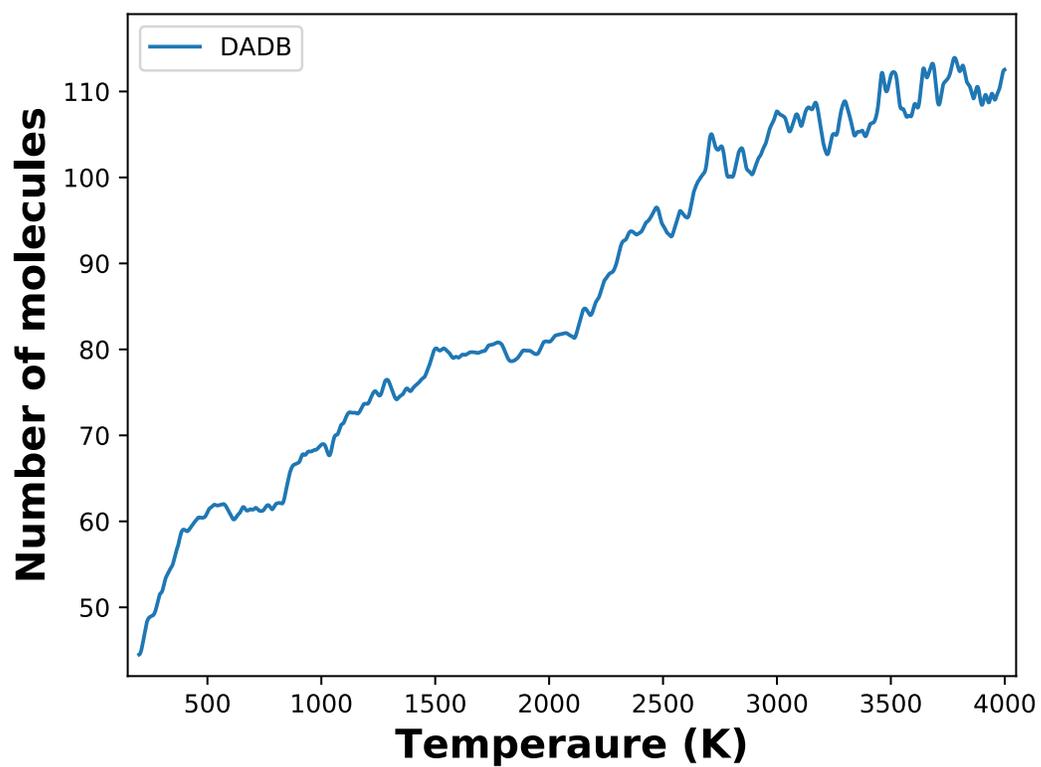


Figure S6. The plots of the total number of molecules versus temperature for the temperature ramping simulation of DADB.

5. Hydrogen release for the simulations of AADB and DADB at various constant temperatures.

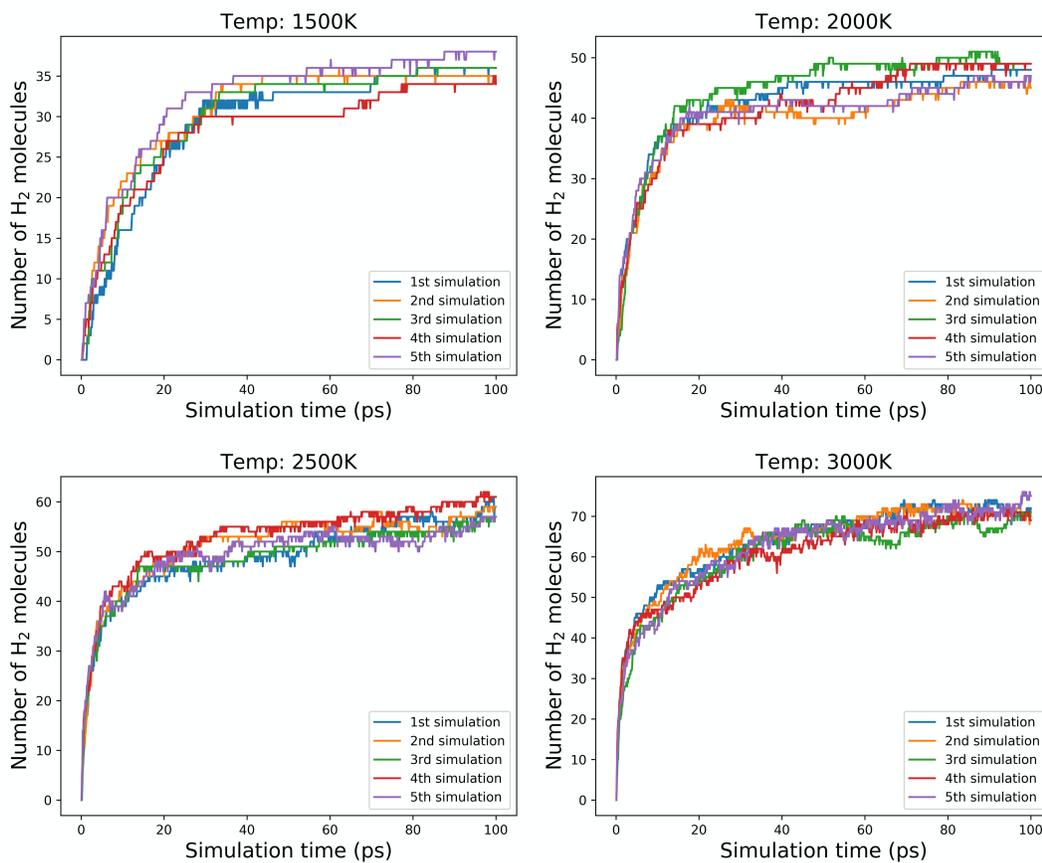


Figure S7. Hydrogen release versus time for the simulations of AADB at 1500K, 2000K, 2500K and 3000K. For each temperature, five independent simulations were carried out.

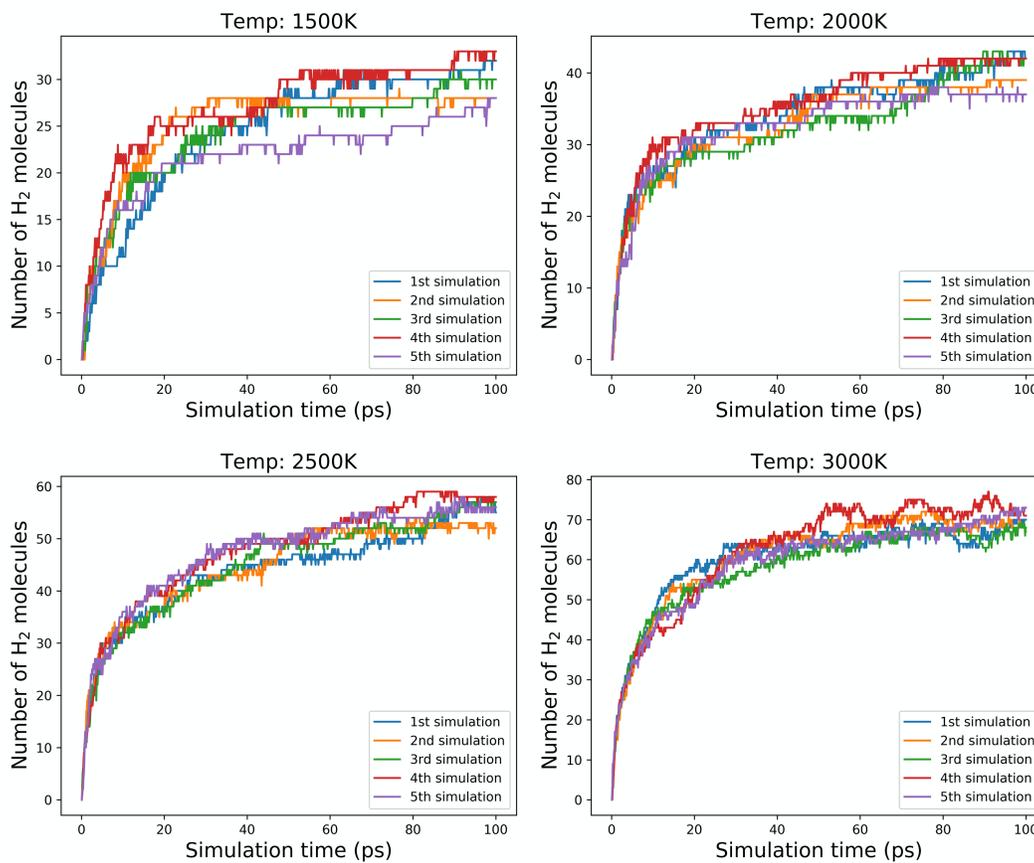


Figure S8. Hydrogen release versus time for the simulations of DADB at 1500K, 2000K, 2500K and 3000K. For each temperature, five independent simulations were carried out.

6. The averaged molecular weight for the simulations of AADB and DADB at various constant temperatures.

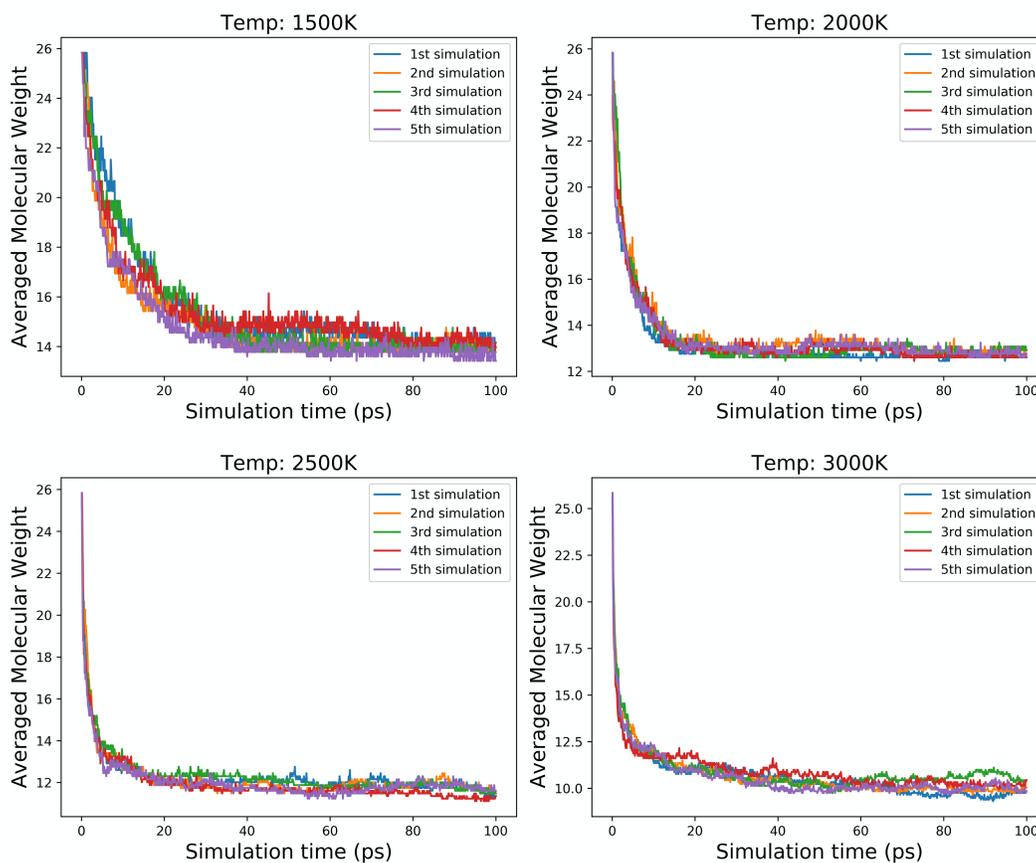


Figure S9. The averaged molecular weight (MW) versus time for the simulations of AADB at 1500K, 2000K, 2500K and 3000K. For each temperature, five independent simulations were carried out.

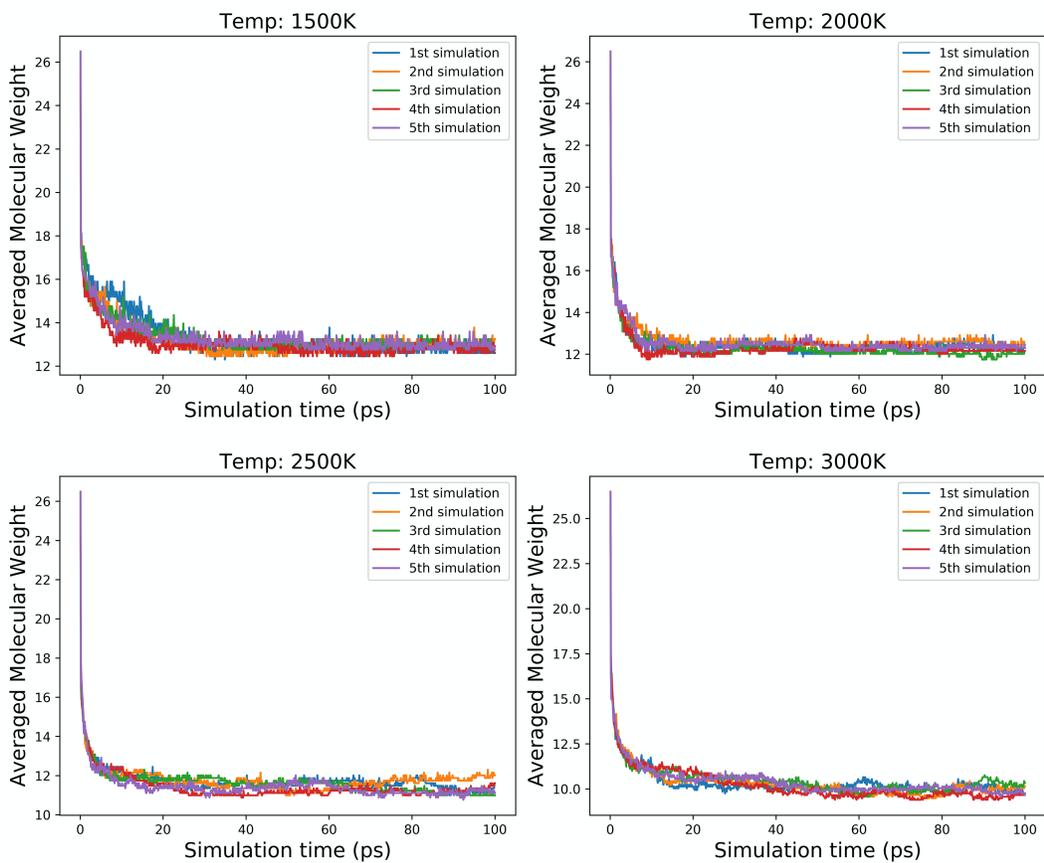


Figure S10. The averaged molecular weight (MW) versus time for the simulations of DADB at 1500K, 2000K, 2500K and 3000K. For each temperature, five independent simulations were carried out.

7. The total number of molecules for the simulations of AADB and DADB at various constant temperatures.

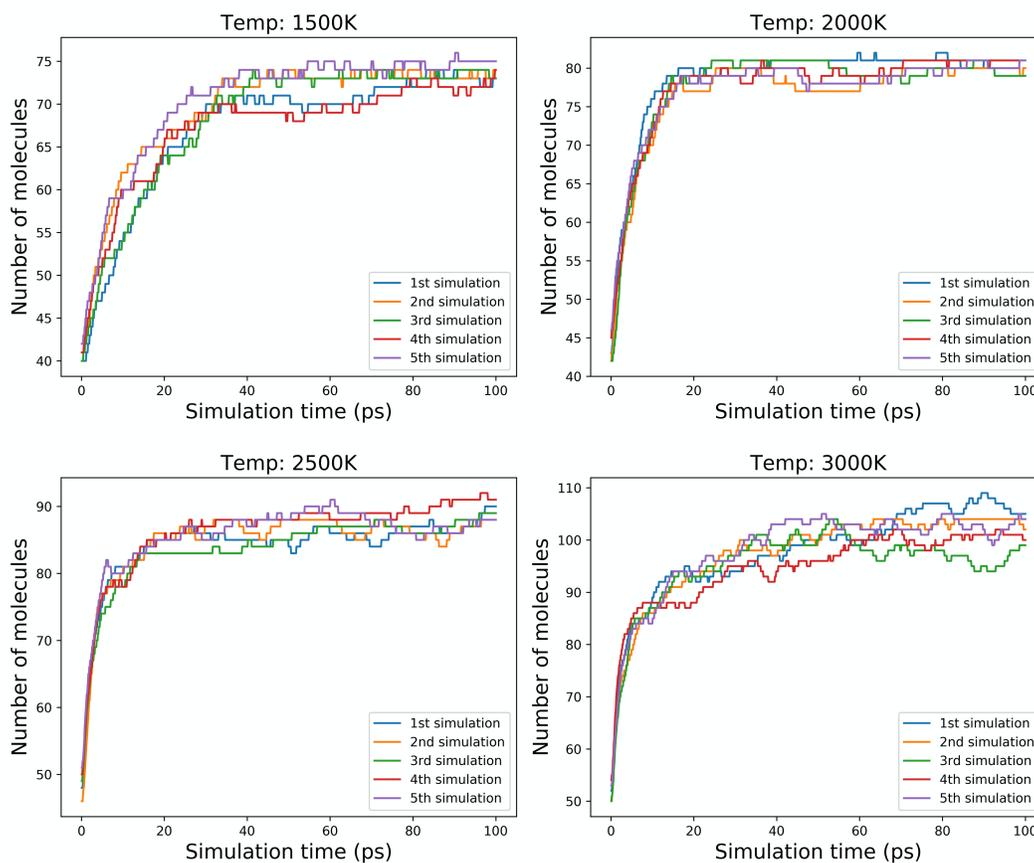


Figure S11. The total number of molecules versus time for the simulations of AADB at 1500K, 2000K, 2500K and 3000K. For each temperature, five independent simulations were carried out.

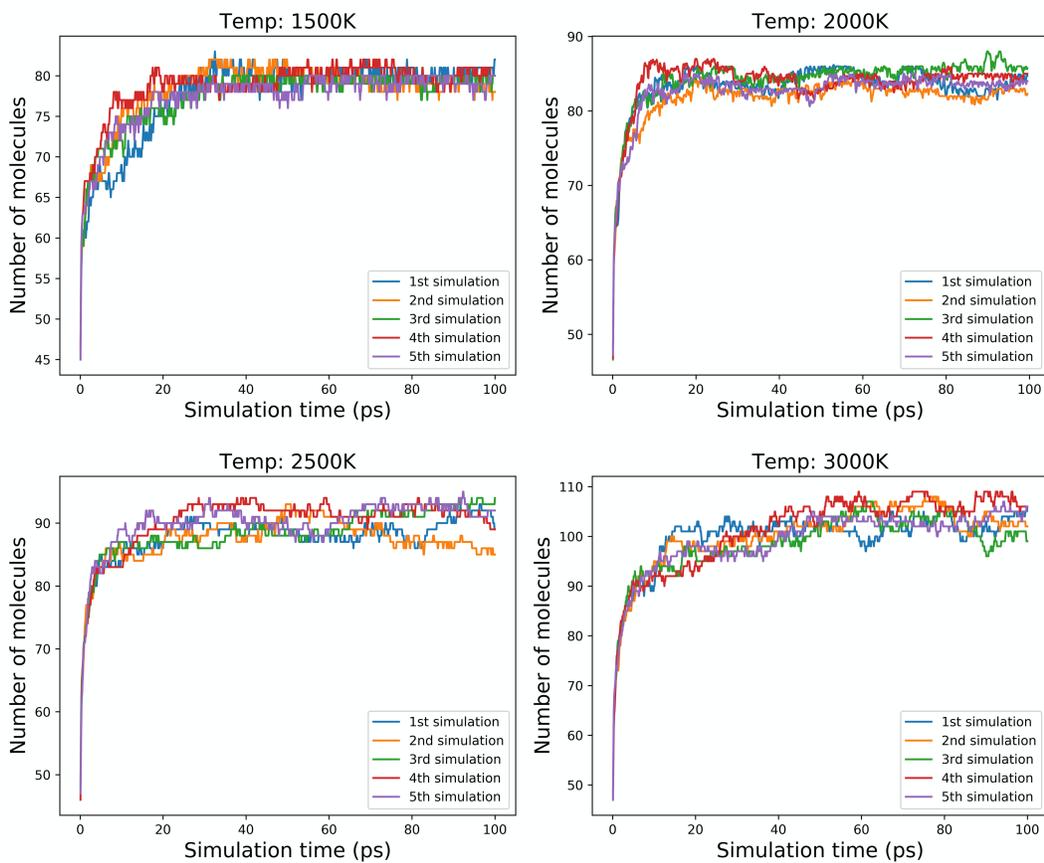


Figure S12. The total number of molecules versus time for the simulations of DADB at 1500K, 2000K, 2500K and 3000K. For each temperature, five independent simulations were carried out.

8. The distributions of the electron density for the states during the cleavage of B-N bond in DADB.

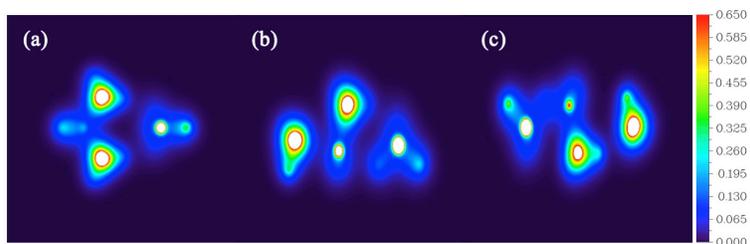


Figure S13. The distributions of the electron density for the states during the cleavage of B-N bond in DADB (via TS3). (a) Reactant; (b) Transition state (TS3); (c) Product. All the calculations were carried out at M062X/6-311++G(d,p).

Table S1. Chemical formula for the compositional analysis results

| AADB | DADB |
|---|--|
| NB ₂ H ₇ : BH ₃ -NH ₂ -BH ₂ | BNH ₅ : BH ₂ -NH ₃ |
| NB ₂ H ₆ : BH ₂ -NH ₂ -BH ₂ / BH ₃ -NH-BH ₂ | BNH ₄ : BH ₂ -NH ₂ |
| NB ₂ H ₅ : BH ₂ -NH-BH ₂ | BNH ₃ : BH ₂ -NH / BH-NH ₂ |
| N ₂ B ₂ H ₆ : BH ₂ -NH ₂ -BH-NH | BNH ₂ : BH-NH / B-NH ₂ |
| N ₂ B ₂ H ₄ : BH-NH-BH-NH | BN ₂ H ₆ : NH ₃ -BH-NH ₂ |
| NB ₂ H ₃ : BH ₂ -N-BH | BNH ₂ : BH-NH |
| NB ₂ H ₄ : BH ₂ -NH-BH | BN ₂ H ₅ : NH ₂ -BH-NH ₂ |
| NBH ₃ : BH ₂ -NH | B ₂ NH ₅ : BH ₂ -NH-BH ₂ |
| NBH ₂ : BH-NH | BN ₂ H ₄ : NH ₂ -BH-NH |
| NB ₂ H ₄ : BH ₂ -N-BH ₂ | BN ₂ H ₃ : NH ₂ -B-NH |
| N ₂ B ₃ H ₇ : BH ₂ -N-BH-NH ₂ -BH ₂ / BH ₂ -N-BH ₂ -NH-BH ₂ | N ₂ B ₂ H ₆ : NH ₂ -B-NH- BH ₃ |
| N ₂ B ₃ H ₉ : BH ₂ -N-BH ₂ -NH ₂ -BH ₃ | N ₂ B ₂ H ₆ : NH ₂ -BH-NH- BH ₂ |
| | N ₂ B ₂ H ₄ : NH ₂ -B-N- BH ₂ |
| | N ₂ B ₂ H ₄ : NH ₂ -BH-N- BH |