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Supplemental Material for

Pyrolysis and oxidation of benzene and cyclopentadiene by NO_x: A ReaxFF molecular dynamics study

Ying Wang[a], Lei Zhou[a], Qian Mao[b,c*], Zhanyuan Wang[a], Haiqiao Wei[a*]

[a] State Key Laboratory of Engines, Tianjin University, Tianjin 300072, China

[b] Institute of Technology for Nanostructures, University Duisburg-Essen, Duisburg 47057, Germany

[c] Institute of Engineering Thermophysics, Chinese Academy of Sciences, Beijing 100190, China

*Corresponding authors: qian.mao@uni-due.de (Qian Mao); whq@tju.edu.cn (Haiqiao Wei)

1. Verification of the ReaxFF force field

The CHON-2019 force field [1] used in the present system is trained on the basis of the CHO-2016 force field by Ashraf and van Duin [2] and added the N atom type in the force field. Notably, CHO-2016 is trained for C/H/O chemistry, especially for the chemistry of small molecules, which is suitable to simulate the oxidation and pyrolysis of benzene and cyclopentadiene. In the present work, we focus on the bond dissociation energies (BDEs) of NO_x because the decomposition of NO_x is the initiation step at high temperatures. Table S1 shows the bond dissociation energies of NO_2 and NO with quantum chemistry methods [3] and all the 9 sets of C/H/O/N force fields (including CHON-2019 and 8 additional sets of force fields containing information on C/H/O/N species from the literature [4-11], which are represented by ReaxFF-1 to ReaxFF-8 respectively). CHON-2019 is the only force field which the relative differences in both BDE of NO and NO_2 are less than 10% compared to CBS-QB3.

Table R1. Bond dissociation energies of NO_2 and NO with quantum chemistry methods and the ReaxFF Force Field (Unit: kcal/mol)

	BDE of NO_2	relative difference from CBS-QB3 (%)	BDE of NO	relative difference from CBS-QB3 (%)
CBS-QB3	74.20	--	151.68	--
ReaxFF CHON-2019	73.42757	1.0410108	160.65	5.91376582

ReaxFF-1	115.09381	55.1129515	148.96428	1.7904272
ReaxFF-2	92.93069	25.2435175	128.98049	14.965394
ReaxFF-3	88.18082	18.8420755	156.28749	3.03763845
ReaxFF-4	88.03454	18.6449326	145.09197	4.3433742
ReaxFF-5	94.22266	26.984717	148.56242	2.0553666
ReaxFF-6	88.02452	18.6314286	145.09197	4.3433742
ReaxFF-7	84.12326	13.3736658	126.74232	16.440981
ReaxFF-8	63.35861	14.611038	169.94741	12.0433874

2. Oxidation of C_6H_6 and c-C_5H_6 by O_2

O_2 is one of the most common oxidants in the combustion process. $C_{18}H_{15}$ and $C_{13}H_{11}$ are the largest species that appear in C_6H_6 and c-C_5H_6 systems with the addition of O_2, indicating that O_2 inhibits the growth of species to some extent. Compared with the reactions that occur in the pyrolysis system, Fig. S1 shows that the types of the initial step are more varied as a result of the modification of the composition of the radical pool. O_2 is rarely involved in the oxidation of C_6H_6 or c-C_5H_6 directly, as can be seen from the last column. The chain-branching reaction via H and O_2 producing O and OH is the most important source to broad the radical pool.

$$O_2 + H = O + OH \quad \text{(R1)}$$

The reactions of O or OH with reactants are carried out by two routes: H-abstraction and addition reaction. H-abstraction is proposed:

$$C_6H_6 + O = C_6H_5 + OH \quad \text{(R2)}$$

$$C_6H_6 + OH = C_6H_5 + H_2O \quad \text{(R3)}$$

$$C_5H_6 + O = C_5H_5 + OH \quad \text{(R4)}$$

$$C_5H_6 + OH = C_5H_5 + H_2O \quad \text{(R5)}$$

For the addition reaction by OH, OH attacks on C_6H_6 and c-C_5H_6, leading to ring-opening via C-C β-scission as shown by pathways (1) and (2).

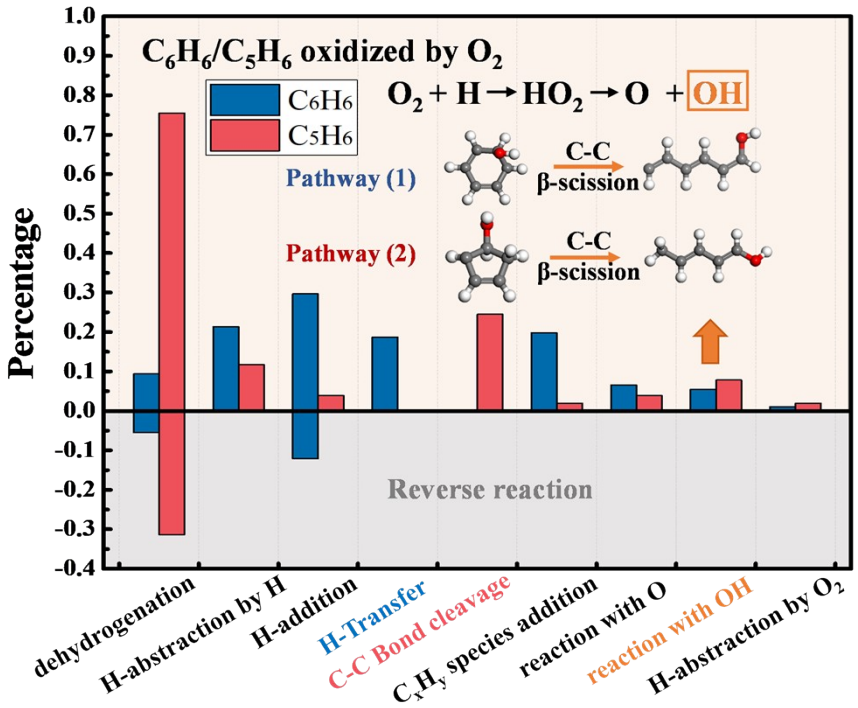

Fig. S1 Proportion of different first-step reactions of C_6H_6 (blue columns) and c-C_5H_6 (red columns) in the presence of O_2 at 2500 K.

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