

Identification of Pathways for Polyaromatic Growth Using Molecular Dynamics

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Abstract

Reaction pathways for polyaromatic growth in combustion environments are explored theoretically using molecular dynamic techniques. The reaction systems considered include cyclization reactions that involve H atom migration. Specifically we examine the absorption of acetylene on an aromatic ring radical. The Parallel Replica method for accelerating Molecular Dynamics calculations is used to screen reaction pathways. The information obtained through the use of Molecular Dynamics runs are then analyzed with quantum chemical methods and thermodynamic data for the key compounds.

Introduction

Polycyclic aromatic hydrocarbons play an important role in the formation of combustion generated particles such as soot, and their presence in atmospheric aerosols has been widely shown [1].

Formation and growth of aromatic species bridges the main combustion zone chemistry with soot formation. The role and the formation mechanism of polycyclic aromatic hydrocarbons in a variety of high temperature phenomena have recently received great attention. Theoretical investigations conducted by Frenklach and co-workers revealed new reaction pathways for aromatic ring growth [2-3], such as enhanced formation of five-, and six-membered aromatic rings, interconversion of five and six-member rings and migration of the cyclopent ring along the zig-zag aromatic edges. All these pathways are induced or assisted by hydrogen migration.

Unimolecular migration of hydrogen atoms is an important feature of hydrocarbon chemistry [4]. In many of those cases, migration of hydrogen becomes competitive, as compared with a gaseous analog because of molecular rigidity and atomic constraints imposed by the surface. Some examples of hydrogen migration may include dimerization of propargyl [5-6] and cyclopentadienyl [7] radicals, allene-propyne isomerization [8].

Motivated by the importance of these reactions, we illustrate in this paper the use of Molecular Dynamics (MD) for the study of the reaction pathways for six-member ring cyclization. Molecular Dynamics offers the

advantage of modeling complex systems and not requiring advanced knowledge of the available pathways.

In this study we use an accelerated dynamics method in which the system trajectory caught in his current state is stimulated to find an appropriate path for escape more quickly than it would with direct Molecular Dynamics.

The present theoretical investigation focus on the application of a molecular dynamics methodology to combustion related problems. The main trust of this paper is to illustrate the application of the method for purposes of evaluating alternative pathways for the cyclization reactions. Specifically we examine hydrogen migration during acetylene absorption on an aromatic ring radical. The escape events identified by running MD on the system are then analyzed using semiempirical quantum methods to calculate the thermodynamic properties of the key compounds.

After summarizing in the following section the methodological details of the computations performed, results from the quantum chemical calculations for the pathways identified during MD runs are reported.

Theoretical Approach

Molecular Dynamics in which one chooses an appropriate interatomic potential to describe the forces between atoms and then integrates the classical equation of motion, is the most direct approach among atomistic simulations.

Transition state theory can be employed to compute the rate constants provided the dividing surface of the

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Proceedings of the Third Joint Meeting of the U.S. Sections of The Combustion Institute

reaction is known. However, all the possible escape mechanisms cannot be guessed in advance.

The underlying mechanisms may be too numerous, too complicated, and/or have an interplay whose consequences are unpredictable. With the approach proposed, as in MD, no a priori information about what this escape path might look like is imposed on the procedure; the trajectory simply finds its own way out of the state.

With MD, the limitation in the accessible simulation time represents a substantial obstacle in making useful predictions. Resolving individual atomic vibrations requires a femtosecond time step in the integration of the equations of motion, so simulation of reaction mechanisms on microsecond or larger time scale is still very difficult even for small systems. For circumventing this time scale problem, we employed one of the methods developed by Voter and co-worker to accelerate dynamics, the Parallel Replica Molecular Dynamics (PRMD) [9].

Among accelerated dynamic methods, the PRMD [10] is the simplest and most accurate method. Starting with a N-atom system in a particular state the entire system is replicated on each of M available parallel processors. After a dephasing stage each processor carries out an independent MD trajectory for the entire N-atom system thus exploring phase space within the particular basin M times faster than a single trajectory would. Whenever a transition state is detected all processors are alerted to stop. The simulation clock is advanced.

The potential used for these simulations is the empirical bond-order potentials of Brenner [11], which is able to capture many of the essential features of chemical bonding in hydrocarbons. Tersoff had previously proposed effective many body empirical potential for all group IV elements in which the potential energy of the system is written as a sum of effective pair terms for each bond, the energetics of which depends on the local environment. These potentials are very accurate for Si and Ge but less reliable for C [12]. In fact, the Tersoff potential for C () which has been fit to the bulk properties of both diamond and graphite, does not distinguish the chemical character of the bond.

This shortcoming turns out to be particularly serious when dealing with structures presenting both types of bonding. Brenner [11] has re-parametrized the Tersoff potential and added nonlocal terms to properly account for the bond modifications induced by a change of bonding of neighboring atoms. The major improvement with respect to Tersoff is due to the fact that the bond energy takes into account the local environment via a many body term which depends not only on bond length and angle but also on the coordination of the atoms making the bond and of their nearest neighbor. Petukhov et al. have demonstrated the high accuracy of the

empirical many-body Brenner potential for carbon structures by a detailed comparison of its structures by a detailed comparison of its structural predictions with those of *ab-initio* studies for known reconstruction of diamond (100) and (111) surfaces [13].

Results

Surface growth of carbonaceous material is proposed to follow sequential hydrogen abstraction that creates a surface radical, acetylene addition to the radical formed, and ring cyclization.

This reaction pathway is here studied using Parallel Replica for a system composed of acetylene and 4-phenantryl radical.

For this small system the input configuration has been replicated on 7 processors. A minimization is performed to generate a reference configuration for transition checks. On each processor after a momentum randomization stage to eliminate correlations with other replicas, a classical trajectory is integrated.

Each replica trajectory is monitored for a transition event by performing a quench after each ΔT_{block} of integration time. When one processor (i) detects an event, all processors are notified to stop. The simulation clock is incremented by the sum of the trajectory times accumulated by all 7 replicas since the beginning.

On the processor that identified the transition state replica (i) is integrated forward for a prechosen time during which new transitions may occur. Replica (i) becomes the new configuration of the system and the sequence is repeated.

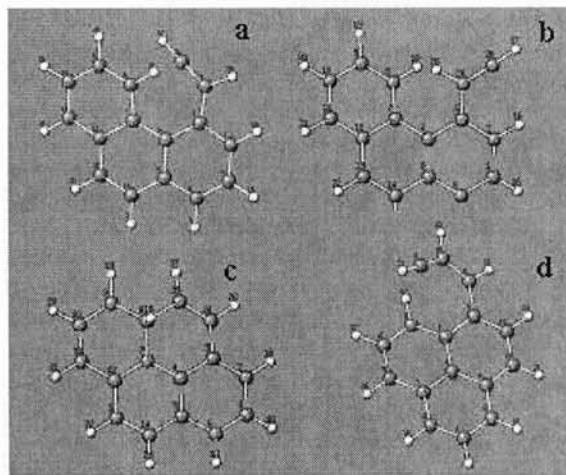


Figure 1: Snapshots of PRMD runs at 1700K

Figure 1 reports some snapshots from the parallel replica simulation at $T=1700$ K. Of the four replicas shown, three leads to ring closure.

This reaction has been already studied by Frenklach and co-workers who identified some possible reaction mechanisms [14]. The result using the current method

gives us new information that include the possibility of also forming substituted phenalene compounds.

With this in mind, the transition events identified during the MD runs have been then analyzed using quantum chemical methods. The geometries of the reactants, products and transition states have been optimized using the AM1 semiempirical quantum method.

Vibrational frequencies calculated at the same level have been used for characterization of stationary points and zero-point energy (ZPE) corrections.

All the energies quoted and discussed in the present paper include the ZPE correction. In order to obtain more reliable values for the energies, we have also carried out single-point calculations at the B3LYP level of theory (i.e. Becke's three-parameter non local exchange functional) with the non local correlation function of Lee, Yang and Parr), with the 6-31G(d,p) basis set [15-16-17]. All quantum calculations were done by using the Gaussian 98 program [18].

A potential energy diagram for this reaction system along with the identification of species nomenclature is reported in Fig.2.

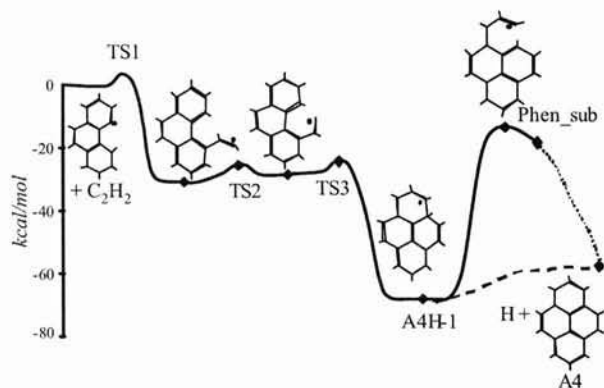


Figure 2: Relative energies diagram (SP_{B3LYP} + ZPE_{AM1}) (kcal/mol) for the reaction of acetylene with 4-phenanthryl.

The reaction begins with the formation of an adduct, 4-ethynyl phenanthrene (A₃C₂H₂) through a first transition state (TS1) that lies only 5 kcal/mol higher in energy than the reactants.

A second transition state leads to the rotation of the CH=CH group that finally through TS3 forms A₄H-1, that denotes radical formed by addition of H to pyrene with the unpaired electron located at position 1.

The reaction for the cyclization becomes A₃C₂H₂ = A₄H-1 this pathway is in agreement with the results obtained by Wang and Frenklach [19]. From A₄H-1 the system can then cyclize to form pyrene (A₄) through the loss of H atom (dashed line) or through further rearrangements to produce phenalene substituted

compound (P1). Figure 3 reports the optimized geometries for A₄H-1 and P1 computed at Am1 level of theory.

Inspection of the computed potential energy surfaces in Fig. 2 indicates that the reaction pathways for the formation of P1 experiences repulsion due to the sterically hindered aromatic bay. The presence of the repulsion implies close proximity of the chemisorbed CH=CH* radical group to the aromatic hydrogen.

The transition state for the formation of P1 lays 20 kcal/mol below the reactants. The energy plot shows that both the pathways are possible in high temperature environment.

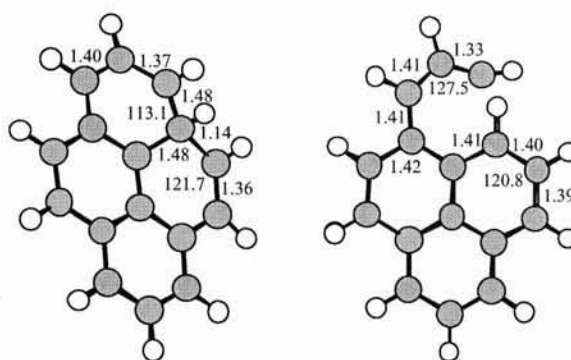


Figure 3: Geometries (bond lengths in angstroms, bond angles in degrees) of A₄H-1 and phen_{sub} optimized at AM1 level of theory.

Detailed kinetic modeling studies have shown that the high-temperature gas-phase formation of PAH involves many highly reversible reaction steps. These tightly balanced reaction steps play a particular important role in PAH formation and growth [20-22].

Their rates and their directions are determined to a large degree by the corresponding equilibrium constants. It has been shown by Frenklach and Warnatz (23) that uncertainties in the thermochemical data can affect significantly PAH concentration profiles. The accuracy of thermodynamic data of PAH molecules and radicals which in turn determines the accuracy of the equilibrium constants, becomes critical for developing detailed kinetic models.

Therefore, besides the analysis of reaction pathways, the thermodynamic properties of the key compounds have been calculated. Relative results of semi-empirical techniques were shown to be consistent compared to molecular mechanics and therefore the viability of group corrected semi-empirical techniques as developed by Wang and Frenklach [23] was supported. This last techniques has been used in this paper to correct the thermodynamic data obtained through AM1 calculations.

The thermodynamic properties are summarized in Table 1.

Table 1: Thermodynamic data of species considered in the present work (units: ΔH_f , kcal/mol; S, C_p cal/mol K)

Species	A ₃ C ₂ H ₂	A ₄ H-1	A ₄	Phen_sub
ΔH_f	119.02	63.05	53.75	121.63
S_f^0	107.5	101.7	97.3	110.7
$C_{p,300K}$	52.5	47.5	44.5	52.1
$C_{p,500K}$	81.9	78.6	74.3	81.6
$C_{p,700K}$	101.5	99.5	94.7	101.4
$C_{p,900K}$	114.7	113.5	108.5	114.7
$C_{p,1000K}$	119.7	118.8	113.7	119.8
$C_{p,1200K}$	127.6	127.1	121.8	127.7
$C_{p,1500K}$	135.8	135.5	130	135.9

Conclusions

Molecular dynamics method was used to study the six-member ring cyclization reaction pathways in combustion conditions. The reaction pathways analyzed in this paper are represented by the addition of acetylene to 4-phenanthryl radical and the ring cyclization to form pyrene.

This paper presents qualitatively results and shows the importance of Molecular Dynamics to evaluate reaction pathways, especially in combustion conditions. The Parallel Replica method for accelerating Molecular Dynamics calculations is used to screen reaction pathways. The information obtained through the use of Molecular Dynamics run are then analyzed with quantum chemical methods and thermodynamic data for the key compounds.

Work is now underway on quantifying the kinetics of the possible reaction pathways for both the zig-zag and armchair surfaces, and reactions involving H migration. We will present these results along with further details about the methods used in a forthcoming publication.

Acknowledgements

This research is funded by the University of Utah Center for the Simulation of Accidental Fires and Explosions (C-SAFE), funded by the Department of Energy, Lawrence Livermore National Laboratory, under subcontract B341493. The calculations presented in this paper were carried out at the Utah Center for High Performance Computing, University of Utah that is acknowledged for computer time support. The authors thank Dr. A. Voter for providing us with the PRMD code.

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