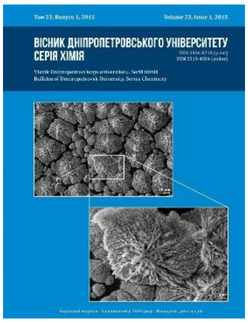
Vìsnik Dnìpropetrovs'kogo unìversitetu. Serìâ hìmìâ 23 (2015), 1, 1–7

Вісник Дніпропетровського університету. Серія хімія
Bulletin of Dnipropetrovsk University. Series Chemistry

p-ISSN 2306-871X, e-ISSN 2313-4984
journal homepage: http://chemistry.dnu.dp.ua


ВІСНИК ДНІПРОПЕТРОВСЬКОГО УНІВЕРСИТЕТУ
СЕРІЯ ХІМІЯ

UDC544.431.24

THEORETICAL STUDY ON ALKALINE HYDROLYSIS OF TRINITROTOLUENE: LATER STEPS

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Received 19 October 2014; revised 25 May 2015; accepted 28 May 2015; available online 07 October 2015

Abstract

Alkaline hydrolysis is an effective method to destroy such the pollutant as 2,4,6-trinitrotoluene (TNT) in solution and in well-mixed soil. The mechanism of hydrolytic transformation of polynegative complex, which is one of the products of early stages of TNT hydrolysis, was theoretically investigated at the SMD(Pauling)/M06-2X/6-31+G(d,p) level under alkali condition. The studied process consists of more than twenty steps and includes a six-membered cycle cleavage and sequenced [1,3]-hydrogen migration and C-C bond rupture. The highest energy barrier is observed for interaction of nitromethanide with hydroxide. The most exothermic steps are C–C bonds breaking. As a result final products such as formate, acetate, ammonium, and nitrogen are formed.

Key words: trinitrotoluene; DFT; hydrolysis; mechanism.

ТЕОРЕТИЧНЕ ДОСЛІДЖЕННЯ ЛУЖНОГО ГІДРОЛІЗУ ТРИНІТРОТОЛУОЛУ: ПІЗНІ СТАДІЇ

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Анотація

Лужний гідроліз – ефективний метод знищення такого забруднювача навколишнього середовища, як 2,4,6-тринітротолуол (ТНТ) у розчині і ґрунті. Механізм гідролітичного перетворення полізарядного комплексу, який є одним із продуктів ранніх стадій гідролізу ТНТ, теоретично досліджений у наближенні SMD(Pauling)/M06-2X/6-31+G(d,p) за лужних умов. Вивчений процес передбачає більше ніж двадцять кроків і включає розщеплення шестичленного циклу і послідовні [1,3]-міграцію Гідрогену і розрив С-С зв'язків. Найвищий енергетичний бар'єр спостерігається за взаємодії нітрометаніду з гідроксидом. Найбільш екзотермічні кроки реакції – це розрив С–С зв'язків. У результаті реакції гідролізу утворюються такі кінцеві продукти, як форміат, ацетат, амоніак і азот.

Ключові слова: тринітротолуол; ТФГ; гідроліз; механізм.

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doi: 10.15421/081501

Vìsnik Dnìpropetrovs'kogo unìversitetu. Serìâ hìmìâ 23 (2015), 1, 1–7

ТЕОРЕТИЧЕСКОЕ ИССЛЕДОВАНИЕ ЩЕЛОЧНОГО ГИДРОЛИЗА ТРИНИТРОТОЛУОЛА: ПОЗДНИЕ СТАДИИ

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Аннотация

Щелочной гидролиз является эффективным методом нейтрализации такого загрязнителя окружающей среды, как 2,4,6-тринитротолуол (ТНТ) в растворе и грунте. Механизм гидролитического превращения полизарядного комплекса, который является одним из продуктов ранних стадий гидролиза ТНТ, теоретически исследован в приближении SMD(Pauling)/M06-2X/6-31+G(d,p) в щелочных условиях. Изученный процесс состоит из более чем двадцати шагов и включает расщепление шестичленного цикла и последовательные [1,3]-миграцию водорода и разрыв С-С связей. Самый высокий энергетический барьер наблюдается при взаимодействии нитрометанида с гидроксидом. Наиболее экзотермические шаги реакции – это разрыв С–С связей. В результате реакции гидролиза образуются такие конечные продукты, как формиат, ацетат, аммоний и азот.

Ключевые слова: тринитротолуол; ТФП; гидролиз; механизм.

Introduction

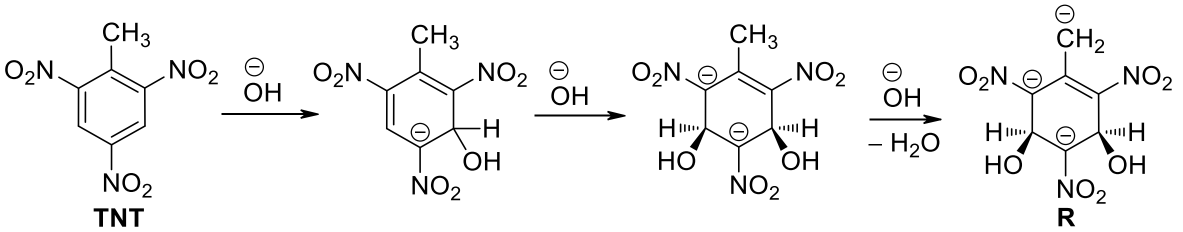
The nitroaromatic compound 2,4,6-trinitrotoluene(TNT) is a potential environmental contaminant released into the water and soil during manufacture, loading, and assembling. TNT and its metabolites are mutagenic and carcinogenic to a variety of organisms [1–4]. Thus its transformation under a variety of environmental conditions are consequently of great interest. Alkaline hydrolysis is one of the possible methods to safely remove this compound from contaminated soils, sediments and water due to its ability to transform TNT into water-soluble non-explosive and more biodegradable products [5]. Experimentally observed, or suggested on the data of spectroscopy and chromatography, products of TNT hydrolysis have included: nitrate, nitrite, ammonia, formate, acetate, oxalate, various nitroaromatics, and uncharacterized polymers [6–14]. It should be mentioned that alkaline hydrolysis of TNT is a very complicated multisteps process with several pathways, which is not well understood yet.

There are only a few theoretical studies of the process [15–17]. Recently a mechanism of the initial stages of this reaction was investigated [15; 16]. The results obtained were compared to available experimental data on the alkaline hydrolysis of TNT and suggested that the formation of Meisenheimer complexes and an anion of TNT are potential first-step intermediates in the reaction path. As the reaction proceeds, computational results indicate that polynegative complexes dominate the degradation pathway (Scheme). Also, later on the products of direct substitution of nitro-group by hydroxide arose. A second possible pathway was identified that leads to polymeric products through Janovsky complex formation [15].

We continue a theoretical investigation of alkaline hydrolysis of TNT. The purpose of the present study is to predict a hydrolysis mechanism that includes the structure of intermediates and hydrolysis products of TNT at later stages in the reaction pathway, starting from the most stable polynegative complex (**R**) formed at early stages of the hydrolysis.

Computational Methodology

All calculations were performed using the Gaussian 09 code [18]. The relevant stationary points (intermediates, transition states, and products) were fully optimized at the SMD(Pauling)/M06-2X/6-31+G(d,p) level [19; 20], due to this theoretical approach was successfully tested for calculation of earlier stages of TNT hydrolysis and was found to give



Scheme

Table1

SMD(Pauling)/M06-2X/6-31+G(d,p)calculated energetics for alkaline decomposition of complex R

Reaction	$\Delta G_{activation}$	$\Delta G_{reaction}$	Reaction	$\Delta G_{activation}$	$\Delta G_{reaction}$
R→INT1	24.39	12.66	**INT13→INT14**	24.73	11.12
INT1→INT2	10.60	–11.31	**INT14→INT15+INT8**	5.51	–19.72
INT2+OH^-→INT3	17.73	9.66	**INT15**+OH^-→**INT16**	20.16	10.36
INT3→INT4	23.57	19.75	**INT16→INT17**	20.16	11.19
INT4→INT5+$HCOO^-$	–4.18	–50.56	**INT17→INT8**+CH_3COO^-	–0.47	–42.74
INT5→INT6	25.02	15.86	**INT8**+OH^-→**INT18**	32.99	16.73
INT6→INT7+INT8	0.80	–20.55	**INT18→INT19**	–0.90	–4.23
INT7+OH^-→**INT9**	16.81	5.68	**INT19→INT20**+OH^-	3.94	–19.58
INT9→INT10	24.90	20.72	**INT20→INT21**	11.32	–30.98
INT10→INT11+$HCOO^-$	–0.19	–49.54	**INT21**+OH^-→**INT22**	24.65	16.86
INT11+H_2O→**INT12**+OH^-	–	11.49	**INT22→INT23**	22.48	0.28
INT12+OH^-→**INT13**	–	–12.33	**INT23**→NH_2O^-+$HCOO^-$	1.13	–22.59

computed results which are close to experimental ones [16]. Stationary points were further characterized as either local minima having all real frequencies, or as transition states possessing only one imaginary frequency, by calculation of the analytic harmonic vibrational frequencies at the same theory level as geometry optimization.

Results and Discussion

As have been mentioned earlier in the present article we continue the study of alkaline hydrolysis of TNT from the most stable poly-negative complex (**R**) formed at early stages of the hydrolysis [15]. The transformation of complex **R** directs on six-membered cycle opening and following C–C bond breaking with formation of structures of smaller molecular weight. The structures of intermediates and products are shown in Fig. 1. The values of Gibbs free barriers and Gibbs free energies of all stages of the process are listed in Table 1. The diagram of Gibbs free energy change for the whole studied process is demonstrated in Fig. 2.

The [1,3]-hydrogen shift in initial polynegative complex R from hydroxyl group at C3 to C2 atom led to formation of intermediate **INT1** (Fig. 1). Herewith C2–C3 bond becomes longer and easily breaks with energy barrier of 10.60 kcal/mol.

[1,3]-Hydrogen shift is endothermic reaction while as C–C bond rupture is exothermic one. Cycle-opened intermediate **INT2** can attach hydroxide forming unstable intermediate **INT3**, which undergoes a [1,3]-hydrogen shift and further terminated C–C bond breaking with formation of **INT5** and release of formate. The hydroxide attachment and hydrogen shift are both endothermic reactions and have free energy barriers of 17.73 kcal/mol and 23.57 kcal/mol, respectively. Elimination of formate is a barrierless process which results in release of more than 50 kcal/mol energy. Thus it is irreversible step.

The [1,3]-hydrogen shift in **INT5** proceeds with formation of unstable **INT6** which readily undergoes C–C bond breaking with formation of **INT7** and **INT8**. Further transformation of **INT7**, consisting of a hydroxide attachment, [1,3]-hydrogen shift, and formate release, leads to **INT11**. The energetic of the **INT7→INT11** process is the same as one for **INT2→INT5** transformation.

Due to an attachment of a proton from a water molecule, and a hydroxide **INT11** transforms into **INT13** through unstable **INT12**. These two processes do not have corresponding transition states. **INT13** is 0.8 kcal/mol more stable than **INT11**. Further **INT13** undergoes [1,3]-hydrogen shift and C–C bond rupture leading to **INT15** and **INT8**. Using now a well-known scheme (hydroxide attachment, hydrogen migration, and C–C bond breaking) **INT15** transforms into **INT8** with release of acetate. As always, C–C bond cleavage here is a highly exothermic process.

Structure of **INT8** (nitromethanide) is stable. A hydroxide attachment to it requires of 33 kcal/mol energy and is a rate-limiting step for whole the studied process. Through two unstable intermediates (**INT18** and **INT19**) nitromethanide transforms to **INT20**, which undergoes a hydrogen transfer with formation of highly stable **INT21**. Further hydroxide attachment, a hydrogen migration from carbon to nitrogen, and C–N bond rupture lead to hydroxylamine anion and formate. As can be seen from the Fig. 2the studied process starting from the complex **R** and ending by hydroxylamine anion and formate is approximately 120 kcal/mol exothermic. That suggests that six-membered cycle cleavage and further C–C bond rupture, with formation of structures of smaller molecular weight, is irreversible process in alkaline hydrolysis of TNT.

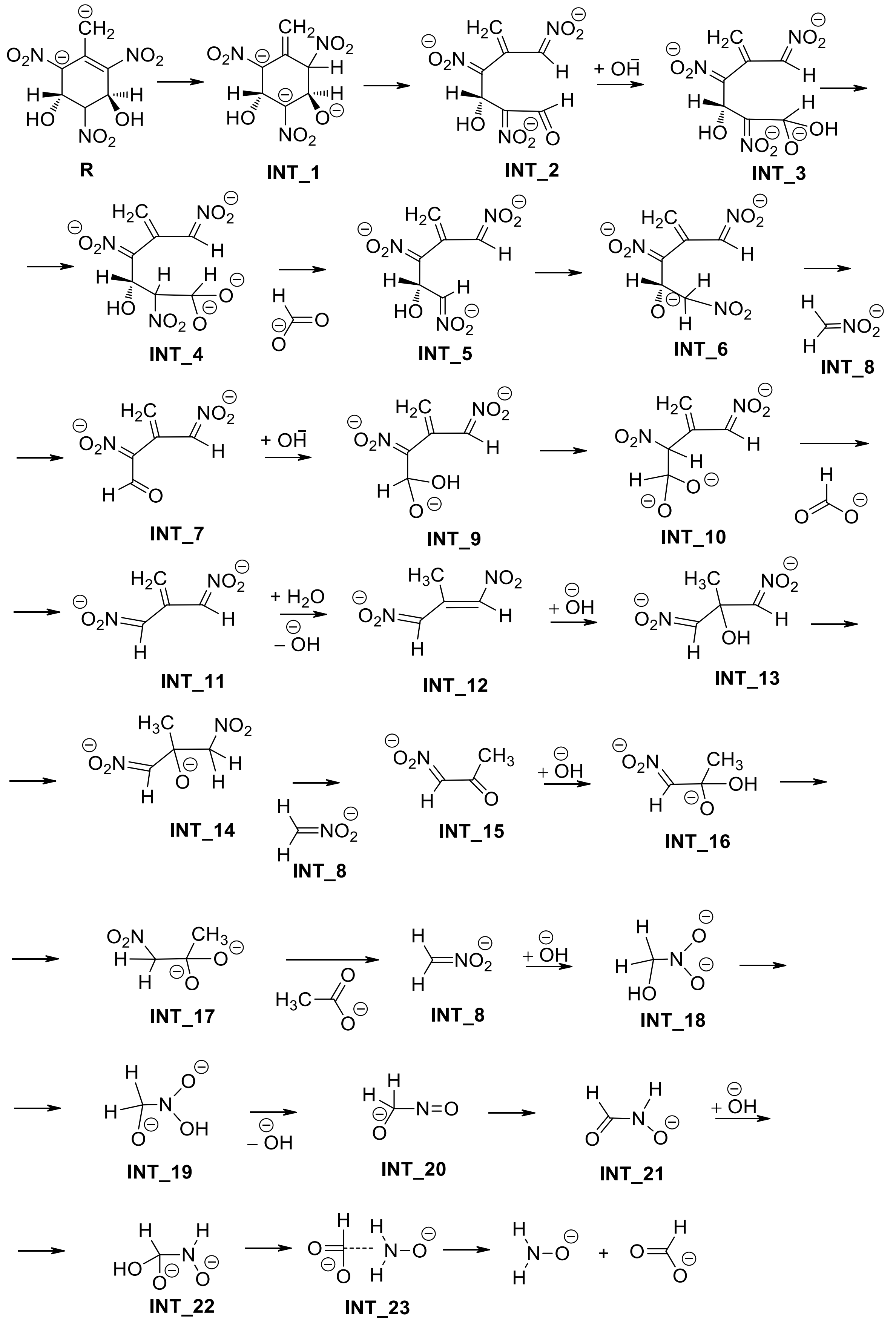


Fig.1. The reaction pathway for later stages of alkaline hydrolysis of TNT

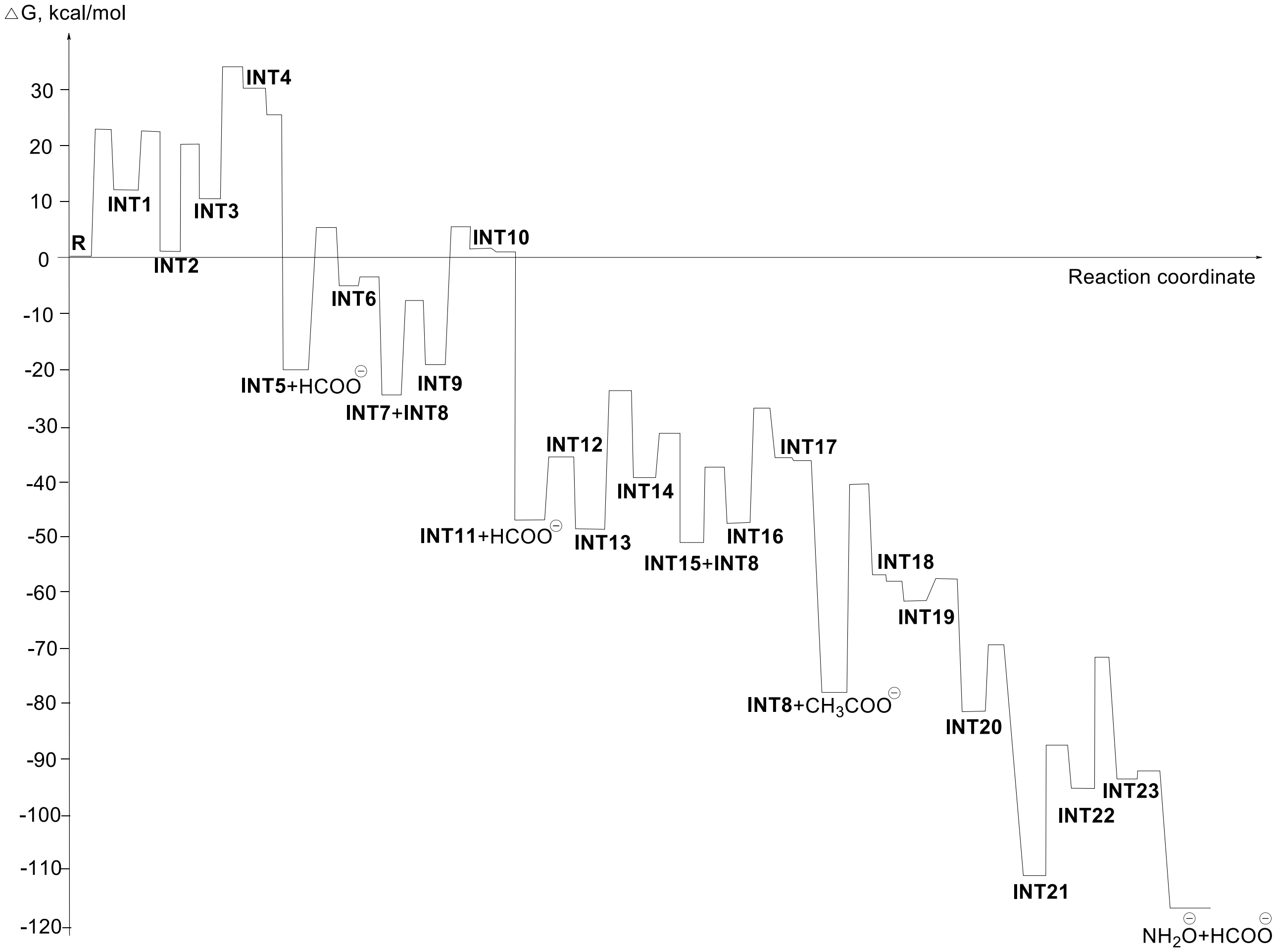


Fig.2. The diagram of Gibbs free energy change for later stages of alkaline hydrolysis of TNT

We did not study the transformation of hydroxylamine (NH_2O^-) in the present work since this compound is unstable in alkaline solution and its decomposition mechanisms were proposed earlier in literature [21]. The total reaction for four-steps mechanism may be written as the following:

$$3NH_2O^- \rightarrow N_2 + NH_3 + 3OH^-.$$

The B3P86/cc-pVDZ calculated enthalpy of reaction is −192 kJ/mol [21], that is approximately −45.89 kcal/mol. Thus, hydroxylamine easily transforms into nitrogen, ammonium, and hydroxide under alkaline condition.

Based on obtained results and literature data, one may conclude that the final products of TNT decomposition through the polynegative complexes are formate, acetate, ammonium, and nitrogen. These products are less toxic and less energetic than the parent TNT molecule. The first three compounds were experimentally observed in alkaline hydrolysis of TNT [11] that supports the proposed above mechanism. It should be noticed that studied pathway is one of several directions of complicated TNT hydrolysis process.

Conclusion

The first quantum-chemical study on later stages of alkaline hydrolysis of TNT, starting with polynegative six-membered cyclic complex and leading to final products, was provided at the SMD(Pauling)/M06-2X/6-31+G(d,p) level. The process in more than twenty steps follows through several [1,3]-hydrogen migrations and C–C bond ruptures. The rate-limiting step is an attachment of hydroxide to nitromethanide. The main amount of energy releases during C–C bond breaking. The observed final products (formate, acetate, ammonium, and nitrogen) are corresponding to experimental data.

Acknowledgement

This work has been supported by ERDC (grant number is W912HZ-13-P-0037). The computation time was provided by the Extreme Science and Engineering Discovery Environment (XSEDE) by National Science Foundation Grant NumberOCI-1053575 and XSEDE award allocation Number DMR110088 and by the Mississippi Center for Supercomputer Research.

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