Research Article

Theoretical Study on the Mechanism for the Formation of Nitro Compounds in Red Oil

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Received 1 July 2020; Revised 28 August 2020; Accepted 27 September 2020; Published 12 November 2020

Academic Editor: José M. G. Martinho

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The mechanisms involved in reactions between methane, n-hexane, n-butanol, cyclohexane, and nitric acid were explored by density functional theory calculations. All the calculations in gas phase and n-tri–...
nitric acid [14, 24]. And Gordon et al. studied the decomposition of red oil by simulating these accidents conditions experimentally [1, 7]. Kumar et al. also reported the thermal decomposition of red oil with nitric acid [25]. Some works were also performed under radiations [26–28].

However, there are majority of investigations concerned with red oil experimentally, which only focus on the degradation of TBP or TBP/HNO₃ system, as well as the factors that influence these reactions. The nitrogen-containing organic materials are the most undesirable waste tank components in the “red oil” accidents, since they are energetic species in their own right [3, 7]. However, there are limited investigations about them. Therefore, we performed quantum chemical computations to study the formation of nitro compounds when methane (CH₄), n-hexane (n-C₆H₁₄), n-butanol (n-C₄H₉OH), and cyclohexane (c-C₆H₁₂) are mixed with nitric acid (HNO₃) in TBP as solvent. The whole reactions taking place among these components are as the following:

\[
\text{CH}_4 + \text{HNO}_3 \rightarrow \text{CH}_3\text{NO}_2 + \text{H}_2\text{O}
\]

\[(1)\]

\[
\text{n-C}_6\text{H}_{14} + \text{HNO}_3 \rightarrow \text{CH}_3(\text{CH}_2)_2\text{NO}_2 + \text{H}_2\text{O}
\]

\[(2a)\]

\[
\text{n-C}_6\text{H}_{14} + \text{HNO}_3 \rightarrow \text{CH}_3\text{CH}(\text{NO}_2)(\text{CH}_2)_2\text{CH}_3 + \text{H}_2\text{O}
\]

\[(2b)\]

\[
\text{n-C}_6\text{H}_{14} + \text{HNO}_3 \rightarrow \text{CH}_2\text{CH}_2\text{CH}(\text{NO}_2)(\text{CH}_2)_2\text{CH}_3 + \text{H}_2\text{O}
\]

\[(2c)\]

\[
\text{n-C}_4\text{H}_{9}\text{OH} + \text{HNO}_3 \rightarrow \text{n-C}_4\text{H}_{9}\text{ONO}_2 + \text{H}_2\text{O}
\]

\[(3)\]

\[
\text{c-C}_6\text{H}_{12} + \text{HNO}_3 \rightarrow \text{c-C}_6\text{H}_{11}\text{NO}_2 + \text{H}_2\text{O}
\]

\[(4)\]

The reaction mechanisms of these reactions are discussed in the following sections, and we hope to forecast the feasible reactions in the red oil system consisting of more complex components and to provide guidance for the safety problem.

### 2. Computational Methods

All of the geometrical structures including reactants, transition states, and products involved in red oil were optimized at the B3LYP/6-311++G** level of theory. It has been proved that the B3LYP method can provide relative accurate geometries for both inorganic and organic systems [29, 30]. To verify the correct connections among the transition states, corresponding reactants, and products, the intrinsic reaction coordinates (IRC) were determined at the same level. In order to get more accurate relative energies, single point energies (SPE) of reactants, transition states, and products were calculated at the CCSD(T)/6-311+G** level based on the optimized geometries at the B3LYP/6-311++G** level. The single point energies were used for the discussions unless otherwise stated. All the calculations were performed with the Gaussian 09 set of programs.

The rate constants of all the pathways were obtained by using the Eyring expression:

\[
k = \frac{k_B T}{h} \left( \frac{P_0}{RT} \right)^{1-n} e^{\Delta S^F/(RT) - \Delta H^F/(RT)}
\]

in which \(k_B\) refers to the Boltzmann constant of \(8.617 \times 10^{-5} \text{J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\), \(h\) refers to the Planck constant of \(6.6260696 \times 10^{-34} \text{J} \cdot \text{s}\), \(T\) is the temperature, \(n\) is the sum of computation coefficient for all reactants, \(P_0\) is the pressure of 1.0 \times 10^5 \text{Pa}, \(R\) is molar gas constant of 8.314 \text{J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}, \Delta S^F and \Delta H^F are the entropy differences and enthalpy differences between the transition states and corresponding reactants, respectively.

### 3. Results and Discussion

Observing the reactions (1) to (4) listed above, it is easily found that the nitro compounds are produced through the nitro-substitution. However, alkanes or butanol cannot react with nitric acids directly, so an active species is needed to trigger the C-H bond cleavage and then react with nitric acids. It was pointed out above that the red oil system is under γ-ray irradiation. Therefore, it was associated that HNO₃ can decompose into nitrogen dioxide radical (NO₂) and nitrogen trioxide radical (NO₃) under irradiation, which initiate the subsequent reactions. Thus the reactions are divided into three steps. In the following sections, we only discussed the results obtained in the gas phase unless explicitly stated.

#### 3.1. Formation of Nitrogen Dioxide Radical (NO₂) and Nitrogen Trioxide Radical (NO₃)

As depicted in Figure 1, where \(R\), \(P\), and \(TS\) denote the reactant, product, and the transition state, respectively, Path \(n\) represents the reaction pathway, and the initial step is the generation of ·NO₂ and ·NO₃ radicals. There are three possible generation pathways: (i) the rupture of N-O(H) bond of HNO₃ leads to ·OH and ·NO₂ radicals (Path 1); then the OH radical reacts with HNO₃ leading to H₂O and NO₂ radical (Path 12a) or H₂O and ·NO₂ radical (Path 12b); (ii) the protonated HNO₃ after dehydration, reacts with NO₃⁻ ion leading to the NO₂ and ·NO₃ radicals (Path 2, Path 13); (iii) the dehydration reaction between HNO₃ molecules and leads to ·NO₂ and ·NO₃ radicals and H₂O molecule (Path 3, Path 13). Clearly, all the pathways to form radicals occur via bond cleavage under γ-ray irradiation. It should be pointed out that HNO₃ is ionized into H⁺ and NO₃⁻ ions in the red oil system, which result in HNO₃ molecule protonation firstly, and then protonated HNO₃ reacts with NO₃⁻ ion via Path 2 and Path 13. Besides, we failed to obtain the transition state of N₂O · · · NO₂, but it is well known that N₂O₃ is a highly reactive species, so its dissociation energy at the B3LYP/6-311+G** level is used for the following discussions.

For the present red oil system, the structures of transition states are depicted in Figure 2. The activation free energies of transition states TS₁₁, TS₁₂a, TS₁₂b, TS₂, and
Three activation energies are high, they can be overcome easily under γ-ray irradiation. The energies of the products are 190.32 kJ/mol, 84.95 kJ/mol, and 35.17 kJ/mol higher than corresponding reactants for Path 1, Path 2, and Path 3,
respectively. Surely, Path 3 → Path 12 is the most feasible pathway, forming the ·NO2 or ·NO3 radicals. The results can be understood from transition states listed in Figure 2 (TS1, TS2, and TS3). The original N-O bond changes from 1.416 Å in HNO3 to 1.588 Å in TS1 and 1.565 Å in TS2, while the N-O bond is 1.949 Å in TS3. The N-O bond lengths indicate the N-O bond interaction is weak in TS3, but the interactions are strong in TS1 and TS2, while the O-H bond interaction in TS3 (1.355 Å) is slightly weaker than that of TS2 (O-H bonds lengths are 1.276 Å and 1.274 Å). Therefore, it is easier for TS3 to form radicals.

3.2. Attacks of Radicals to Alkanes or Butanol. The second step (Figure 3) is the attack of ·NO2 or ·NO3 radical on the alkanes or butanol, which leads to direct intermolecular H-shift from carbon or oxygen atom to ·NO2 or ·NO3 radical. All of the reactions can be written as follows:

\[ R + \cdot \text{NO}_2 \rightarrow R + \cdot \text{HNO}_2 \]

where R represents reactants (alkanes or butanol). When the ·NO2 radical attacks the hydrogen atom of OH or CH, the isomer products cis-HONO, trans-HONO, and HNO2 can be formed. The activation energies of the reactions R + ·NO2 are listed in Table 1, in which the symbols a, b, and c mean the products HNO2 in different geometrical structures, respectively. The reaction pathways b and c are more competitive than Path a. Meanwhile, Path b plays a slightly more important role than Path c. Though the activation energies of these three pathways differ greatly, the reaction mechanisms are similar. There is only the oxygen atom acting as an attacking atom in the ·NO3 radical. From the viewpoints expressed above, we mainly discussed the reactions of ·NO2 radical in Path b or ·NO3 radical reacting with alkanes or butanol.

The reaction mechanisms between ·NO2 radical and alkanes or butanol can be described as follows. The reactions of R + ·NO2 occur via the formation of van der Waals complexes first. ·NO2 radical attaches to H-atom of alkanes or butanol via hydrogen bond interaction in these van der Waals complexes. Then, H-atom transfers from alkanes or butanol to ·NO2 radical through the transition states TSn leading to other van der Waals complexes. In these van der Waals complexes, there is a hydrogen bond interaction between HNO2 molecule and the alkane or butanol radical. At last, the HNO2 molecule and alkane or butanol radical formed via the van der Waals’ force weaken. The reaction mechanisms of R + ·NO3 are a bit different from those of reactions R + ·NO2. The ·NO3 radical attacks H-atom of alkanes or butanol leading to transition states TSn directly, then producing HNO3 and a radical.

The geometrical structures of transition states (TS4 – TS10) are shown in Figure 2 and the activation energies, enthalpies, and free energies (ΔE*, ΔH* and ΔG*) of these transition states are listed in Table 2. However, we failed to get the transition state of reaction c-C6H12 + ·NO3 at B3LYP/6-311++G** level. Thus, the transition state of c-C6H11 · · · H · · · O3 is not listed here. It is found that the relative energies of reactions R + ·NO2 are higher than those of reactions R + ·NO3, which can be explained by the changes of C-H or O-H bond lengths in transition states. The O-H bond lengths in transition states RNO2 are shorter than those in transition states RNO3. On the contrary, the H-C bond lengths in transition states RNO2 are longer than those in transition states RNO3.

3.3. Formation of Nitro Compounds. These radicals formed from the above steps combine with each other and form nitro compounds spontaneously (Figure 4, where the symbol L means the last reaction between radicals to generate the nitro product). For the reactions n-C6H14 + HNO3, it has the isomer products CH3(CH2)3NO2, CH2CH(NO2) (CH2)3CH3, and CH3CH2CH(NO2)(CH2)3CH3.

Single point energies in the gas phase (Table 3) calculated at the CCSD(T)/6-311++G** level show that the products of these reactions are 129.2 kJ/mol, 145.3 kJ/mol, 154.5 kJ/mol, 153.6 kJ/mol, 238.70 kJ/mol, and 17.2 kJ/mol more stable than corresponding reactants, respectively, for reactions (1) to (4).

3.4. Energies along the Reaction Pathways and Rate Constants. According to the discussions above, the differences among the mechanisms of reactions R + ·NO2/·NO3 are the second step. We mainly discussed the energies and rate constants in the second step in this section. Figure 5 provides the single point energies along the reaction pathways, where the symbols M1n and M2n represent van der Waals complexes, and the energies of reactants are set to zero for reference. As seen from these figures, the products of reactions R + ·NO3 are more stable than the corresponding reactants, and the stability of the products in the reactions R + ·NO3 is in the order P9 > P7b > P7c > P7a > P5. However, the energy barriers of transition states RNO3 are less than ~15 kJ/mol. The energies of products in reactions R + ·NO2 are higher than those of corresponding reactants, except for reaction c-C6H12 + ·NO2. The energy barriers of the products increase as follows: P8 (27.24), P6b (38.54), P6c (38.87), P6a (47.93), and P4 (57.70). Meanwhile, the energy barriers of transition states RNO2 are over 100 kJ/mol, which are difficult to overcome at room temperature, expect for TS10 (22.92 kJ/mol). Therefore, the reactions R + ·NO2 are more competitive than reactions R + ·NO3 and all the reactions R + ·NO3 are kinetically feasible.

The rate constants (K) of the reactions to form transition states at 298 K are listed in Table 4. It shows that TBP contributes to the reactions. The rate constants of the dissociation of N2O5 are 1.14 × 10−8 s−1 and 5.38 × 105 s−1 in gas phase and TBP solvent, respectively. Surely, N2O5 can decompose easily at room temperature. The rate constants of the reactions to form transition states from 300 K to 500 K are shown in Figure 6. There is a linear relationship between ln(K) and 1/T. As can be seen in Figure 6(a), though the rate constant of TS1 or TS2 increases more than that of TS3 with increasing temperature, the rate constants of TS3 are higher than the others at the temperature from 300 K to 500 K.
Hence, Path 3 \(\rightarrow\) Path 12 plays the main role for the formations of \(\cdot\)NO\(_2\) and \(\cdot\)NO\(_3\) radicals. This is consistent with the conclusion in Section 3.2. Comparing the rate constants of transition states RNO\(_2\) and RNO\(_3\) in Figure 6(b), it can be seen that the rate constants differ greatly between them, and the attacking of alkanes or butanol by \(\cdot\)NO\(_3\) radical plays the dominant role, so we only discussed the rate constants of transition states RNO\(_3\). Here we only show the rate constants of transition state \(c\) \(-\) C\(_6\)H\(_{11}\) \(\cdot\) H \(\cdots\) NO\(_2\) in Figure 6(b) because we failed to get the transition state \(c\) \(-\) C\(_6\)H\(_{11}\) \(\cdot\) H \(\cdots\) NO\(_2\) (TS11). The rate constants of TS11 are much higher than that of \(c\) \(-\) C\(_6\)H\(_{11}\) \(\cdot\) H \(\cdots\) NO\(_3\) according to the rate constants trends. It could predict that the rate constants of TS11 are more than \(1.22 \times 10^3\) mol\(^{-1}\)L\(\cdot\)s\(^{-1}\) above 298 K. As a result, the rate constants of these transition states increase as TS11, TS9, TS7c, TS7b, TS7a, and TS5. The product \(c\) \(-\) C\(_6\)H\(_{11}\)NO\(_2\) is the most competitive among the products. Because the rate constants of reactions \(n\)-
Table 1: Activation free energies (in kJ/mol) of reactions between -NO2 radical and alkanes or butanol in different pathways*.

| Reactants                        | ΔG^‡  | ΔG^‡  | ΔG^‡  |
|---------------------------------|-------|-------|-------|
| R4                              | 172.94| 151.92| 165.91|
| R6a                             | 161.77| 140.93| 144.20|
| R6b                             | 148.81| 128.72| 127.67|
| R6c                             | 150.20| 129.26| 130.14|
| R8                              | 147.08| 129.92| 141.41|
| R10                             | 60.01 | 37.83 | 39.46 |

*Subscripts a, b, and c in ΔG^‡ denote the products of trans-HONO, cis-HONO, and HNO2, respectively.

Table 2: Activation energies, enthalpies, and free energies (ΔE^r, ΔH^r, and ΔG^r in kJ/mol) of transition states at B3LYP/6-311++G** level of theory in the gas phase.

| Transition states | ΔE^r  | ΔH^r  | ΔG^r  |
|-------------------|--------|-------|-------|
| TS4               | 124.77 | 122.34| 151.92|
| TS5               | 49.11  | 45.76 | 80.78 |
| TS6a              | 103.07 | 102.93| 140.93|
| TS6b              | 88.87  | 88.88 | 128.73|
| TS6c              | 89.55  | 89.66 | 129.26|
| TS7a              | 24.41  | 23.43 | 66.52 |
| TS7b              | 10.38  | 9.07  | 54.67 |
| TS7c              | 10.18  | 8.85  | 55.13 |
| TS8               | 90.61  | 89.45 | 129.92|
| TS9               | -0.13  | -2.72 | 46.25 |
| TS10              | 1.65   | 6.40  | 37.83 |

Figure 4: Formation of nitro compounds.

C6H14 + NO2 are in the order of TS7c ≈ TS7b > TS7a, the competitions of CH3CH(NO2)(CH2)3CH3 and CH3CH2CH(NO2)(CH2)2CH3 are close to each other, and both of them are less competitive than c-C6H11NO2 and n-C6H12NO2. The product CH3(CH2)3NO2 is only more competitive than CH3NO2, and the competition of CH3NO2 is negligible. The cyclic alkanes are the easiest to form nitro compound, followed by n-butanol, and n-alkanes are the least reactive to form the nitro compounds. That is consistent with the previous studies [1, 3, 7, 14]. It can be also found that the long n-alkanes are easier to react with nitric acid to form the nitro compound than those of the short ones.

3.5. Relative Stabilities of Carbon-Centered Radicals and Reactivities of the Alkanes. For the carbon-centered radicals, their relative stabilities (E) were obtained by using the expression [31]

$$E = \Delta H_0 + \sum \Delta H_1 + \sum_{n=2}^{2} \frac{\Delta H_n}{\sqrt{2^3 - 2}}$$

where ΔH is the energy contribution of a group to the relative stability. The number 0 represents the center C-atom (C0) of a radical that an H-atom is depleted. Number 1 is the C-atom attached to the C0-atom directly, and the other numbers n are the n’th C-atom attached to the C0-atom. The energy contributions of the groups and relative stabilities of carbon-centered radicals are represented in Tables 5 and 6.

As can be seen in Table 6, the relative stabilities of carbon-centered radicals are in the order of Path 10 > Path 6c > Path 6b > Path 6a > Path 4. It is
worth noting that the competitions for the formation of \( \text{CH}_3\text{CH(NO}_2\text{)(CH}_2\text{)}_3\text{CH}_3 \) and \( \text{CH}_3\text{CH}_2\text{CH(NO}_2\text{)(CH}_2\text{)}_2\text{CH}_3 \) are similar. In general, the lower the relativestabilities of carbon-centered radicals, the more competitive the reactions between nitric acid and alkanes. The exception is the \( \cdot \text{R}_10 \) radicals.

Herelativestability of carbon-centered radicals depends on the energy contributions of groups in the radical. The energy contributions of groups are related to their structures and relative positions to the \( \text{C}_0 \)-atom. As a result, for the chain and cyclic alkanes with the samenumber of C-atoms, the relative stabilities of their corresponding carbon-centered radicals may differ slightly. However, the competitions of reactions depend on their activation energies. Comparing the activation energies for the formation of \( \cdot \text{R}_6 \) and \( \cdot \text{R}_10 \) radicals (Table 6), their activation energies differ greatly.

Though there are small differences of relative stabilities between chain and cyclic carbon-centered radicals, there are still large differences in their reactivities. Therefore, the

### Table 4: The rate constants \( K_1 \) (TS1, TS2 in K s\(^{-1}\) and the others in mol\(^{-1}\) L s\(^{-1}\)) of reactions involved in the red oil system at 298 K in the gas phase or TBP solvent.

| Transition states | Rate constants |
|------------------|----------------|
|                  | Gas phase   | TBP solvent |
| TS1              | \( 1.07 \times 10^{-37} \) | \( 1.52 \times 10^{-35} \) |
| TS2              | \( 7.65 \times 10^{-30} \) | \( 4.19 \times 10^{-27} \) |
| TS3              | \( 9.28 \times 10^{-19} \) | \( 8.23 \times 10^{-15} \) |
| TS4              | \( 3.71 \times 10^{-16} \) | \( 2.43 \times 10^{-15} \) |
| TS5              | \( 1.08 \times 10^{-3} \)  | \( 6.46 \times 10^{-2} \)  |
| TS6a             | \( 3.13 \times 10^{-14} \) | \( 3.13 \times 10^{-14} \) |
| TS6b             | \( 6.58 \times 10^{-12} \) | \( 5.41 \times 10^{-11} \) |
| TS6c             | \( 3.48 \times 10^{-12} \) | \( 2.87 \times 10^{-11} \) |
| TS7a             | \( 0.34 \)    | \( 9.08 \)    |
| TS7b             | \( 40.65 \)   | \( 7.47 \times 10^3 \) |
| TS7c             | \( 33.77 \)   | \( 1.35 \times 10^3 \) |
| TS8              | \( 2.66 \times 10^{-12} \) | \( 1.32 \times 10^{-12} \) |
| TS9              | \( 1.21 \times 10^7 \)   | \( 1.70 \times 10^6 \)   |
| TS10             | \( 3.63 \times 10^4 \)   | \( 5.58 \times 10^3 \)   |
reactivities of the same type of alkanes (either chain or cyclic alkanes) reacting with nitric acid can be speculated by comparing the relative stabilities of carbon-centered radicals. The lower the relative stabilities of carbon-centered radicals are, the more reactive the alkanes are. However, the reactivities of different type of alkanes cannot be determined by the relative stabilities of their corresponding radicals.

4. Conclusion

The reactions of nitric acid with some alkanes or butanol in red oil were studied by the quantum mechanics method. All the calculations were performed in TBP solvent and gas phase. The calculated geometrical structures of the transition states showed that the TBP solvent can speed up all the reactions, and the rate constants of reactions provide insight into the formations of red oil components. The reactions are in three steps. The nitrogen dioxide radicals and nitrogen trioxide radicals form firstly, and then these radicals initiate the depletion of H-atom from alkanes or butanol; finally the generated radicals contact with each other and form the products. Though the energy barriers for the formations of ·NO₂ and ·NO₃ radicals are high, they could be overcome easily under γ-ray irradiation. The energy barriers of reactions R + ·NO₃ are much lower than those of reactions R + ·NO₂, so the reactions R + ·NO₃ are more competitive than the reactions R + NO₂. Among these products, c-C₆H₁₁NO₂ is more competitive than the others and is the easiest to form. CH₃CH(NO₂)(CH₂)₃CH₃ and CH₃CH₂CH(NO₂)(CH₂)₂CH₃ are less competitive than c-C₆H₁₁NO₂ and CH₃(CH₂)₃ONO₂. Since the energy barriers and rate constants of the rate-limiting step for the formation of CH₃CH(NO₂)(CH₂)₃CH₃ and CH₃CH₂CH(NO₂)(CH₂)₂CH₃ are close to each other, the competition of them will depend on the actual experimental environment. Besides, the product CH₃(CH₂)₂NO₂ is only more competitive than CH₃NO₂, and the competition of product CH₃NO₂ is negligible. The reactivities of the same type of alkanes reacting with nitric acid can be speculated by comparing the relative stabilities of carbon-centered radicals. The lower the relative stabilities of carbon-centered radicals are, the more reactive the alkanes are. However, the reactivities of different type of alkanes cannot be determined by the relative stabilities of their corresponding radicals. In general, long n-alkanes could be easier than...
the shorter ones to form nitrogen-containing organic materials that play roles in the "red oil" accidents [3, 7] as a uranium recycling medium.

Data Availability
The data used to support the findings of this study are available from the corresponding author upon request.

Conflicts of Interest
The authors declare that they have no conflicts of interest.

Authors’ Contributions
Xue-Hai Ju conceptualized the study; Meng-Ke Tian and Shuang-Ling Tang were involved in data curation; Shuang-Ling Tang and Hong-Bin Tang were responsible for project administration; Meng-Ke Tian wrote the original draft; Xue-Hai Ju wrote and reviewed the manuscript; and Shuang-Ling Tang and Hong-Bin Tang reviewed and edited the manuscript.

Acknowledgments
The authors thank the Joint Funding for Nuclear Technology Innovation Program of National Natural Science Foundation of China (No. U1867203) and Special Funding for Spent Nuclear Fuel Reprocessing of China.

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