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Reactions of NO_2 with CH_3NHNH and CH_3NNH_2: A direct molecular dynamics study

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Abstract

Reactive collisions between $CH_3NNH_2 + NO_2$ and $CH_3NHNH + NO_2$ were observed via direct molecular dynamics simulations. The simulations, which are classical trajectories whose dynamics were dictated by forces derived from quantum mechanics-based calculations, were conducted: (1) to confirm the importance of reaction paths expected to play a role in the ignition and combustion of monomethylhydrazine/nitrogen tetroxide (MMH/NTO) and monomethylhydrazine/red fuming nitric acid (MMH/RFNA) systems, and (2) for their potential to identify unexpected mechanisms. A number of different H-atom abstraction paths were observed, with four isomeric (CH_4N_2) products being formed: $CH_3N{=}NH$, CH_3NHN, $H_2C{=}NNH_2$, and CH_2NHNH. All abstractions were barrierless, including those from the methyl group. Reaction exothermicities, which were characterized via QCISD/6-311+G(d,p)//MPWB1K/6-31+G(d,p) calculations, ranged from 2 to 36 kcal/mol. The results suggest that finite rate chemical kinetics mechanisms for MMH/NTO and MMH/RFNA systems should include steps for the production and decomposition of CH_3NHNH, $H_2C{=}NNH_2$, CH_2NHNH, and CH_3NHN in addition to those for CH_3NNH_2 and $CH_3N{=}NH$.

Keywords: Monomethylhydrazine; CH_3NNH_2; CH_3NHNH; NO_2; Hypergolic propulsion

1. Introduction

Hypergolic bipropellants are fuel-oxidizer combinations that ignite spontaneously upon mixing at low temperatures and pressures. They facilitate the design of rocket propulsion systems for applications in which variable and/or intermittent thrust capabilities are needed. Among the most commonly fielded bipropellant combinations is monomethylhydrazine/nitrogen tetroxide, which is also referred to as MMH/NTO or $CH_3NHNH_2/(NO_2)_2$ [1]. For applications where the freezing point of $(NO_2)_2$ is too high, red fuming nitric acid (RFNA) is often proposed as an alternative. The two main components of RFNA are nitric acid (HNO_3) and NO_2, with typical mixtures having approximately 85 wt% and 14 wt%, respectively, of each.

As part of an effort to develop a capability to simulate via computational fluid dynamics hypergolic propulsion systems fueled with $CH_3NHNH_2/(NO_2)_2$ or CH_3NHNH_2/RFNA, a chemical kinetics mechanism for modeling their gas-phase combustion processes has been developed by the US Army Research Laboratory [2–4]. In both systems, abstractions of H-atoms from CH_3NHNH_2 and its dehydrogenated daughters by NO_2 have been identified as playing a critical role in the systems' evolution during the pre-ignition phase of the combustion process [3–5]. However, a large number of paths for such reactions can be postulated and it was considered possible that preconceptions about them might lead to important reactions being overlooked.

Seeking to validate the importance of steps in the chemical kinetics mechanism that was developed for MMH/NTO or MMH/RFNA systems, and to identify others that might be important, direct molecular dynamics (MD)

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simulations were conducted. The direct MD technique is a quasiclassical MD method in which the potential energy surface (PES) is generated "on the fly" rather than fit beforehand to an analytic function [6–10]. In contrast to traditional quantum mechanics (QM)-based methods for studying reactions, i.e., internal reaction coordinate walks on 0 K PESs, where the portion of the PES probed is generally limited to relatively small regions near a researcher's preconceived notions about the path a reaction will take, the ability of the direct MD technique to partition the energy generated by a highly exothermic process to vibrational, rotational and translational kinetic energies of a reacting subsystem increases the chance for surprises. A study of the reaction of C^+ with H_2O offers a case in point. Presuming that this reaction proceeded through a low-energy intermediate $[HCOH]^+$, early studies based on traditional methods focused on the energetics of C^+ insertion into the O—H bond [11,12]. A study by Ishikawa and coworkers based on direct MD [13], however, revealed that the reaction rarely proceeded through $[HCOH]^+$. Rather, in the vast majority of the simulations that were run, the dynamics were dictated by an ion-dipole interaction that induced C^+ to attack the oxygen lone pairs. This led to the formation of a high-energy intermediate $[COH_2{}^+]$ and $COH^+ + H$ as final products.

Reported here are observations for reactions which ensue following low energy (1–2 kcal/mol) collisions between NO_2 and the first daughters of H-atom abstraction from CH_3NHNH_2; namely CH_3NNH_2 and CH_3NHNH. The relevance of the observations to MMH/NTO and MMH/RFNA chemical kinetics mechanisms is discussed.

2. Methods

In this study, the solution of the classical equations of motion in Newtonian form determines the nuclear trajecto-

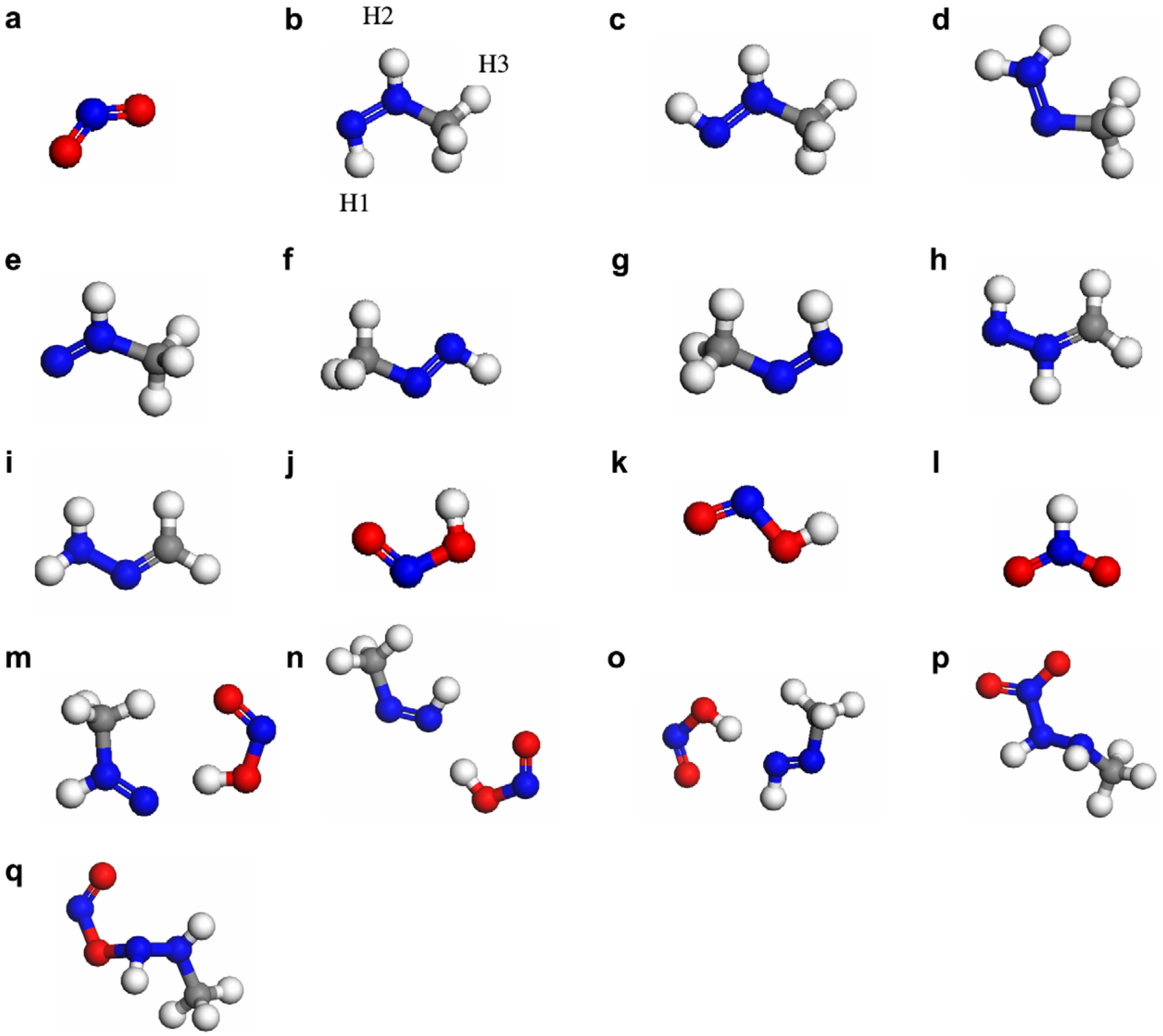

Fig. 1. MPWB1K/6-31+G(d,p) optimized geometries of reactants, intermediates, and products identified in direct MD simulations: (a) NO_2, (b) *anti*-CH_3NHNH, (c) *syn*-CH_3NHNH, (d) CH_3NNH_2, (e) CH_3NHN, (f) *anti*-$CH_3N{=}NH$, (g) *syn*-$CH_3N{=}NH$, (h) CH_2NHNH, (i) $H_2C{=}NNH_2$, (j) *cis*-HONO, (k) *trans*-HONO, (l) HNO_2, (m) CH_3NHN–*cis*-HONO complex, (n) *syn*-$CH_3N{=}NH$–*cis*-HONO complex, (o) *anti*-$CH_3N{=}NH$–*cis*-HONO complex, (p) $CH_3NHNH(NO_2)$, (q) $CH_3NHNH(ONO)$.