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Experimental and quantum mechanics investigations of early reactions of monomethylhydrazine with mixtures of NO_2 and N_2O_4

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ABSTRACT

The gas-phase chemistry of the hypergolic system CH_3NHNH_2 – monomethylhydrazine (MMH), with oxidizers NO_2/N_2O_4 at room temperature and 1 atm N_2 was investigated experimentally using a gold-coated chamber reactor, coupled with a Fourier transform infrared (FTIR) spectrometer. The IR-active species identified in the early reactions include HONO, monomethylhydrazinium nitrite (MMH·HONO), methyl diazene ($CH_3N{=}NH$), methyl nitrate (CH_3ONO_2), methyl nitrite (CH_3ONO), nitromethane (CH_3NO_2), methyl azide (CH_3N_3), H_2O, N_2O and NO. In order to elucidate the mechanisms by which these observed products are formed, we carried out quantum mechanics calculations [CCSD(T)/M06-2X] for the possible reaction pathways. Based on these studies, we propose that the oxidation of MMH in an atmosphere of NO_2 occurs via two mechanisms: (1) sequential H-abstraction and HONO formation, and (2) reaction of MMH with asymmetric $ONONO_2$, leading to formation of methyl nitrate. These mechanisms successfully explain all intermediates observed experimentally. We conclude that the formation of asymmetric $ONONO_2$ is assisted by an aerosol formed by HONO and MMH that provides a large surface area for $ONONO_2$ to condense, leading to the generation of methyl nitrate. Thus we propose that the overall pre-ignition process involves both gas-phase and aerosol-phase reactions.

1. Introduction

Hypergolic bipropellants are fuel-oxidizer combinations that ignite spontaneously upon mixing at ambient temperatures. They facilitate the design of rocket thrusters by simplifying the ignition system, and are widely used in propulsion systems in which variable and/or intermittent thrust capabilities are needed. Among the most commonly deployed bipropellant combinations is monomethylhydrazine/nitrogen tetroxide, which is also referred to as MMH/NTO or CH_3NHNH_2/N_2O_4 [1] For applications in which the freezing point of NTO is too high, an alternative oxidizer is red fuming nitric acid (RFNA), which is composed of nitric acid (HNO_3, ~85 wt%) and NO_2 (8–15 wt%).

Recently the impinging stream vortex engine (ISVE) has attracted significant attention due to its compact size and potential for efficient combustion, making it important to develop computational fluid dynamics (CFD) models to gain insight into the influence of design parameters on engine performance [2–5]. An important part of this effort is to develop a chemical kinetics mechanism for MMH/NTO or MMH/RFNA combinations.

To provide a starting point for such activities a detailed, finite-rate, chemical kinetics mechanism of MMH/RFNA was developed by the U.S. Army Research Laboratory (ARL) [6–9] for modeling the gas-phase combustion processes. The most recent version of this mechanism involves 513 reactions and 81 species [6]. Sources for the ARL mechanism include the following:

1. a set of reactions for H/C/N/O compounds developed by Anderson and co-workers for modeling the dark zones observed in solid-propellant combustion (43 species, 204 reactions) [10],
2. approximately 160 small-hydrocarbon-molecule reactions that were extracted from the GRI 3.0 database [11],
3. approximately 80 reactions involving HNO_3, NO_3, N_2O_4, and hydrocarbon/NO_x moieties that were identified via a literature search performed specifically for the mechanism development effort, and
4. approximately 50 reactions recommended by Catoire and co-workers for modeling the ignition and combustion of MMH/O_2 [12] and MMH/NTO [13] systems.

The validity and completeness of the ARL mechanism was tested by running CHEMKIN [14] simulations for MMH/NTO systems, and a reduced version of the mechanism was used in CFD simulations for the ISVE engine [2,5,8].

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One major concern with the ARL MMH/RFNA mechanism is the lack of relevant experimental studies for its validation [6]. As part of an effort to provide experimental support for this mechanism, we investigated the pre-ignition reactions between MMH and HNO_3 (the major constituent of RFNA) in an earlier work [15]. These experimental results suggested that the current MMH/RFNA mechanism omits some important early reactions between MMH and HNO_3 and corresponding species. Since NO_2/N_2O_4 is another important constituent in RFNA, its early gas-phase reactions with MMH are examined in this work.

The current ARL mechanism for MMH/NTO, a subset of the MMH/RFNA mechanism, contains reactions categorized in two domains:

1. single-bond fission events to strip fragments from MMH and generate free radicals, and
2. radical–radical reactions to form either closed-shell or open-shell species.

Given the low temperature (<100 °C) in the pre-ignition environment, direct bond fission from MMH to produce H, CH_3 or NH_2 is unlikely so that NO_2 is the major free radical available initially. Based on this assumption, the ARL mechanism considers the two types of initial reactions:

1. H-abstraction from MMH and sequential HONO formations, and
2. recombination between NO_2 and MMH free radicals generated by H-abstraction.

However, these reactions do not fully explain the formation of a condensate that has been observed in several previous studies involving examinations of a residue from gas-phase reactions in a stoichiometric mixture of MMH and NO_2/N_2O_4 [16]. The IR properties of this residue are quite similar to the IR properties of a residue obtained from reactions between liquid-phase MMH and gaseous NO_2/N_2O_4 [17] The IR properties of the residue from these two studies suggest that monomethylhydrazinium nitrate (MMH·HNO_3) is formed in addition to other species [16]. The formation of MMH·HNO_3 was also detected by Saad et al. [18], who examined liquid-phase reactions between MMH and N_2O_4 in a system diluted by CCl_4 at −20 °C. In a recent work by Catoire et al. [13], it is suggested that the MMH·HNO_3 detected as a major product in the residue by Semans et al. is not formed from reactions in the gas phase, since its elemental analysis matches rather poorly with that of the residue as determined by Breisacher et al. [19]. Catoire et al. suggests that nonionic compounds are formed and accumulate in a condensate. However, it appears that no experiments were carried out to confirm the formation of these nonionic compounds.

Based on the above discussion, there is a clear need to reexamine gas-phase reactions between MMH and NO_2/N_2O_4 at low temperatures in order to identify the relevant preignition products and reaction pathways. There are two objectives with the present work. First, we would like to experimentally identify *in situ* the species formed early in the preignition event from gas-phase reactions between MMH and NO_2/N_2O_4. Second, we would like to use quantum mechanics (QMs) tools to help elucidate the reaction pathways, since experimentally it is rather difficult to identify and quantify radicals, as well as to identify transition-state structures.

2. Methods

2.1. Chemicals

Monomethylhydrazine (MMH), purchased from Sigma–Aldrich and used without further purification, is a liquid with a concentration higher than 98%. Nitrogen dioxide (NO_2) is diluted in nitrogen (N_2) and stored in a pressurized cylinder. The mole concentration of NO_2 is 1%. In the gas phase, nitrogen dioxide and dinitrogen tetroxide always coexist due to the reversible dimerization reaction: $2NO_2 \leftrightarrow N_2O_4$ [20]. Since MMH and NO_2/N_2O_4 are highly toxic and corrosive, only small amounts of reactants were used in each test (i.e. ~0.2 μl MMH) and necessary protections (i.e., gloves, mask, etc.) were adopted.

2.2. Experimental setup and procedures

An overview of the experimental setup is shown in Fig. 1. The chamber reactor is made of stainless steel and has a 12 mm inner diameter and a path length of 65 mm. A thin layer of gold is coated on the chamber surface to minimize the potential of surface catalytic reactions. On each side of the cylindrical chamber is a ZnSe window for transmission of the modulated FT-IR beam from a Bruker IFS 66/S FT-IR spectrometer. $NO_2/N_2O_4/N_2$ mixture is injected into the chamber reactor through a Teflon tube, while MMH (~0.2 μl) is delivered by a 1 μl syringe. MMH is volatile (vapor pressure is 5 kPa at 20 °C) and evaporates rapidly upon injection. MMH vapor then mixes and reacts with NO_2/N_2O_4 in the chamber. The temporal evolution of IR-active species in the chamber, including initial reactants and products, is recorded by a time-resolved rapid scan on the FT-IR spectrometer. In each test a total of 390 spectra (the maximum memory limit), with a spectral resolution of 2.6 cm^{-1} and temporal resolution of 50 ms, are acquired. It should be noted that IR-inactive species such as N_2, O_2 and H_2, transparent to the IR beam, cannot be detected. Since the reactants are highly diluted in N_2 (~99%), the temperature and pressure variations in the chamber due to chemical reactions can be neglected.

Two types of tests, labeled as either oxidizer-rich or fuel-rich in the discussion below, were conducted.

- In the oxidizer-rich test, the reactor is purged with $NO_2/N_2O_4/N_2$ mixture and thus initially filled with the oxidizer. 0.2 μL MMH (3.8×10^{-6} mol) is quickly injected into the chamber and reacts with NO_2/N_2O_4.
- In the fuel-rich test, the chamber is purged with N_2 and 1 μL MMH (1.9×10^{-5} mol) is first injected into the chamber, which is then initially filled with MMH vapor and N_2. The mixture of oxidizers ($NO_2/N_2O_4/N_2$) is then pressurized into the chamber and reacts with MMH vapor upon mixing. The findings from these two types of tests are discussed separately in the results section.

Because residues may remain on the chamber wall after each test, the chamber wall is cleaned and conditioned through two steps before each new test. In the first step the chamber reactor

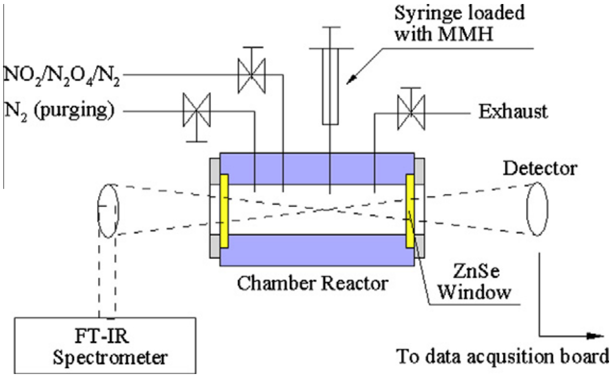

Fig. 1. A schematic view of the experimental setup.