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Detailed kinetic model for ammonium dinitramide decomposition

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ABSTRACT

Ammonium dinitramide (ADN; $[NH_4]^+[N(NO_2)_2]^-$) is the most promising oxidizer for use with future green solid and liquid propellants for spacecraft applications. To allow the effective development and use of ADN-based propellants, it is important to understand ADN reaction mechanisms. This work presents a detailed chemical kinetics model for the liquid phase reactions of ADN based on quantum chemical calculations. The thermal corrections, entropies, and heat capacities of chemical species were calculated from the partition function using statistical machinery based on the G4 level of theory. Rate coefficients were also determined to allow the application of transition state theory and variational transition state theory to reactions identified in our previous study. The new model employed herein simulates the thermal decomposition of ADN under specific heating conditions and successfully predicts heats of reaction and the gases that result from decomposition under those conditions. The thermal behavior predicted from the new model was an excellent match with the experimental behavior observed from thermal analysis using differential scanning calorimetry and Raman spectroscopy. The new kinetic model reveals the mechanism for the decomposition of ADN.

1. Introduction

Ammonium dinitramide (ADN; $NH_4N(NO_2)_2$) has attracted attention as a novel and environmentally friendly solid/liquid propellant oxidizer because it possesses both a good oxygen balance and a high energy content, and it does not contain halogen atoms [1–3]. Information regarding the decomposition and combustion behavior of propellant ingredients such as ADN is useful when developing comprehensive ignition and combustion models for rocket motors and gas generators that employ these materials. The combustion of energetic salts, including ADN, is typically characterized by a diverse range of physical and chemical processes that occur in a complex series of stages. In the case of ADN, the condensed phase reactions have the greatest effect on the combustion characteristics [4–6]. Some reliable energetic-salt gas-phase reaction models have been proposed to date, all of which work to explain observed combustion behavior [4,7–9]. More recently, models for the liquid phase reactions of these compounds have also been developed [10–14]. However, there are no detailed reaction models for the condensed phase reactions of ADN, only semi-detailed mechanisms [4].

To construct a detailed reaction model for the condensed phase reactions of ADN, it is important to understand the thermal decomposition pathways and the associated kinetics. There have been many studies regarding the reaction mechanisms of ADN [15–19]. Yang et al. [15] assessed ADN liquid phase decomposition and reported that it may proceed through one of two competing mechanisms: ADN → NH_4NO_3 (AN; ammonium nitrate) + N_2O or ADN → $NH_3 + HNO_3 + N_2O$. The competing mechanisms in the gas phase are ADN → NH_3 + dinitraminic acid (HDN) and ADN → $NH_3 + HNO_3 + N_2O$. However, in practice, it is difficult to experimentally distinguish the latter reaction from the series consisting of ADN → NH_3 + HDN followed by HDN → $N_2O + HNO_3$, and to distinguish ADN → AN + N_2O from the series of reactions ADN → NH_3 + HDN followed by HDN → $N_2O + HNO_3$ and $NH_3 + HNO_3$ → AN. There have been several experimental studies on the kinetics of ADN decomposition under various conditions [20–26] and the results have been summarized in several publications [15,16].

In our previous work [27], quantum chemistry calculations that incorporated solvent effects were used to investigate the decomposition pathways in aqueous ADN solutions. Optimized structures for reactants and products were obtained at the CBS-QB3 [28]//ωB97X-D [29]/6-311++G(d,p)/SCRF = (solvent = water) level of theory, considering the isomers ADN_I (NH_4–$N(NO_2)_2$) and ADN_{II} (NH_4–$ON(O)NNO_2$), and the four ADN_{II} conformers. Although ADN can potentially dissociate to either an anion–cation pair or an acid–base pair, the thermal assessment in this study determined that ionization is preferable to acid-base dissociation in aqueous

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solution. In the initial stage of decomposition, the ADN_{II} conformers and the dinitraminic anion (DN^-) decompose to $NO_2\bullet$ and de-$NO_2\bullet$ intermediates (NNO_2NH_4 and NNO_2^-), while neither ADN_I nor dinitraminic acid plays an important role. Following the initial decomposition, $NNO_2NH_4\bullet$ and $NNO_2^-\bullet$ transition to $NNO_2H\bullet$ and NH_3 through proton transfer, after which the NNO_2H decomposes to N_2O and $OH\bullet$, and the $OH\bullet$ combines with $NO_2\bullet$ from the initial reaction to yield HNO_3. This decomposition can be expressed using one global formula: $ADN \rightarrow N_2O + NH_4NO_3$ $(NH_3 + HNO_3)$.

The purpose of the present work is (i) to develop a detailed chemical model using kinetic data based on reactions identified in previous studies [24,25,27], (ii) to validate the model by comparison with data obtained from experimental thermal analysis and the literature [30], and (iii) to reveal the ADN decomposition mechanism theoretically.

2. Computational

2.1. Rate coefficients

The rate coefficient k_{TST}, for the generic reaction $A + B \rightarrow P$ (products in solution) can be calculated on the basis of traditional transition state theory (TST) using the formula

$$k_{TST} = \frac{k_B T}{h} \frac{Q_{TS}}{\prod Q_{reac}} \exp\left(\frac{-\Delta E_0}{RT}\right) \tag{1}$$

where k_B is the Boltzmann constant, T is the temperature, h is the Planck constant, Q_i is the partition function of the reactant and transition state (TS), DE is the energy barrier to activation, and R is the universal gas constant. Variational transition state theory (VTST) was applied to analysis of the dissociation reactions without activation energy barriers. These calculations were performed using the GPOP software package developed by Miyoshi [31]. The pressure dependence of rate for a monomolecular reaction in the gas phase must generally be considered. However, in the liquid phase, a species is surrounded by many species; i.e., the liquid state can be considered as a high-pressure condition. Thus, the rate at the high-pressure limit was used for monomolecular reaction in the liquid phase. In our previous work, liquid-phase calculations were performed at the CBS-QB3 [29]//ωB97X-D [30]/6-311++G(d,p)/SCRF = (solvent = water) level of theory, and the associated potential energy diagrams and TS structures were identified and investigated [24,25,27]. Radical recombination and proton transfer with no barriers were simply modeled as diffusion-limited reactions with the rate coefficient set at 10^{12} $cm^3\,mol^{-1}\,s^{-1}$. This assumption is supported by data from the aqueous kinetics database of the Notre Dame Radiation Laboratory, which generally shows rate coefficients between 10^{12} and 10^{13} $cm^3\,mol^{-1}\,s^{-1}$ for radical recombination reactions. The diffusivity-dependent encounter rate of two species and the Stokes-Einstein diffusion within the solvent were used to estimate these rate coefficients [12,32].

The important reactions associated with the decomposition of liquid phase ADN and the associated kinetic parameters for the modified Arrhenius equation are provided in Table 1.

This work investigated and modeled the thermal chemistry associated with the isomerization, conformational changes, and dissociation of ADN. Previous studies show that liquid ADN and HDN also have both an isomer and four conformers. In the present study, two liquid ADN isomers ($ADN_I = NH_4$–$N(NO_2)_2$ and $ADN_{II} = NH_4$–$ON(O)NNO_2$, Fig. 1), two HDN isomers ($HDN_I = HN(NO_2)_2$ and $HDN_{II} = HON(O)NNO_2$, Fig. 1), and the dinitraminic anion ($DN^- = N(NO_2)_2^-$) were also considered. It is noted that an ion in molten salt is surrounded by many counter ions. DN^- can be surrounded by several NH_4^+ ions and larger clusters including several ADN units can exist in molten ADN. Rahm and Brinck [33] investigated the thermal decomposition of solid-state ADN by the quantum chemical modeling of molecular clusters. In the present paper, only a minimal unit of ADN clusters (ADN_I and ADN_{II}) is of concern as the first step toward a deep understanding of the thermal decomposition of liquid-state ADN.

2.2. Thermodynamic data

Thermodynamic data were developed based on quantum chemistry calculations using the Gaussian 09 program package [34]. Optimization and frequency analysis were conducted using the G4 [35] and the G4/SCRF = (solvent = water) level of theory. Solvent effects were included by application of the self-consistent reaction field (SCRF) and polarizable continuum model (PCM) options within the program when investigating the liquid species in molten ADN. However, no solvent parameters of molten ADN were available; therefore, water solvation was used to determine the solvent effect when examining reactions in molten ADN. The dielectric constant (the e value of water is 78.3553) is one of the important parameters involved in the solvation effect. The dielectric constants (e) of ammonium-based protic ionic-liquids are substantially higher than those of aprotic ionic-liquids. The dielectric constants of ethylammonium nitrate and methylammonium formate are 26.2 and 41.0, respectively [36]. Dielectric constants tend to increase with increasing length of the alkyl chain. Thus, we have believed that molten ammonium salts including ADN have a large value of e. Yamashita and Asai [37] measured e for ammonium nitrate (AN), which is typical ammonium-based protic salt that is analogous with ADN. AN is also a major product from the decomposition of ADN. The dielectric constant for AN has been reported to be approximately 40 at 383 K, and it is also reported that the dielectric constant tends to increase with the temperature [37]. In addition to this, novel ADN-based monopropellants LMP-103S and FLP-106, which are novel ADN-based monopropellants invented and tested within a co-operative project between the Swedish Space Corporation and the Swedish Defense Research Agency, are a blend of ADN, water, methanol, and ammonia [1]. Water solvation effects can provide some insights into chemical reactions in such ADN-based propellants. Although we have used the water solvation effect as a substitute for liquid ADN in this study, the water solvation effect should be replaced with a more adequate solvation effect in future work.

Thermal correction, entropy (S_{liq}), and heat capacity (C_P) values were calculated from the partition function using statistical mechanics, employing the GPOP software [31]. The heats of formation for gas-phase molecules ($\Delta_f H^\circ_{gas}$) were calculated by the traditional atomization method (ARM-1) [38]. The standard heat of formation for a compound in solution is obtained from the gas-phase heat of formation and the enthalpy of solvation at 298.15 K, as in the following two equations.

$$\Delta_f H^\circ_{liq} = \Delta_f H^\circ_{gas} + \Delta_{solv} H^\circ \tag{2}$$

$$\Delta_{solv} H^\circ = H_{liq,\,calc} - H_{gas,\,calc} \tag{3}$$

Here, $\Delta_{solv}H^\circ$ is the solvation enthalpy, and $H_{liq,calc}$ and $H_{gas,calc}$ are the heats of formation at 298.15 K calculated directly using the G4 methods. Tables 2 and 3 list the heats of formation for gas and liquid phase compounds obtained from the G4 level of theory and thermodynamic data.

In Table 2, the enthalpy of formation of 5 conformers of ADN in the liquid phase varies from −43.6 to −47.6 kJ/mol. At the same time, the enthalpy of formation of ADN in solid phase is −134.8 $kJ\,mol^{-1}$ [39]. Considering the heat of solution (142 $J\,mol^{-1}$ [1]), the enthalpy of formation of ADN in the liquid phase can