Retraction

Retraction: Detailed kinetic modeling of nitroglycerin low-temperature decomposition (J. Phys.: Conf. Ser. 1721 012002)

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Published 03 March 2021

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Retraction published: 03 March 2020
Detailed kinetic modeling of nitroglycerin low-temperature decomposition

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Abstract. Nitroglycerin (NG) is mostly used as an ingredient in double-base propellant formulations. In this study, a first automatically generated detailed kinetic model of NG decomposition has been developed. The construction of this model was made possible by performing computations with the open source software package Reaction Mechanism Generator (RMG). To enable a faster convergence, significant intermediate species of NG decomposition and optimized operating conditions were indicated in the RMG input parameters. Thermochemical data related to the significant NG decomposition species were derived from ab initio calculations at the B3LYP 6-31G(d,p) level of theory. To validate the RMG-built mechanism, simulations were performed with CHEMKIN-Pro. Computed species profiles from simulations were compared with flash pyrolysis measurements from the literature. Sensitivity analysis were performed and the most important elementary reactions were identified. Some rate constants were slightly adjusted to improve the predictivity of the model. The model is able to predict the species concentration profile of the main pyrolysis products. Although experimental data are scarce, this automated kinetic generation approach, applied to energetic materials, seems to be highly promising.

1. Introduction
Nitroglycerin (NG), also known as glyceryl or glycerol trinitrate, is one of the common ingredients used in energetic materials (EM) formulations since the late 1800s [1]. Despite the fact that NG has been for a long time incorporated in gun propellant, the understanding of its ignition and burning behavior still needs to be explored. The combustion of EM can be investigated by applying different strategies and detailed kinetic modeling is one of them [2].

Bowden et al. [3] studied, in 1947, pure NG combustion and observed that the initiation was occurring in the gas-phase. The same observation was reported by Robertson in 1948 [4]. Later in 1970, Waring and Krastins [5] investigated the thermal decomposition of NG. They identified intermediate species and postulated gas-phase decomposition paths. When they studied the NG volatilization and thermal decomposition in double-based propellant, Sadasivan and Bhaumik [6] reported O-NO$_2$ cleavage (also called homolysis) to be the initial decomposition elementary reaction. Miller and Anderson [2] presented a first NG kinetic model based on a global condensed-phase decomposition path and a detailed kinetic gas-phase mechanism (35 species and 178 reversible reactions). The authors validated their model on burning rates measurements. Major NG species products measurements were conducted by Roos and Brill in 2002 [7]. The same year, Hiyoshi and Brill measured the time dependence of NG pyrolysis products in argon and air atmospheres [8]. The
arising of quantum chemical investigations also contributed to expand the knowledge concerning NG decomposition. Yan et al. [9] performed DFT (Density Functional Theory) calculations to determine the main channels of unimolecular decomposition of NG. The authors targeted and calculated rate constants and activation energies for two main initial mechanisms: O-NO\(_2\) cleavage and HONO elimination. According to their results, O-NO\(_2\) homolysis pathway is more likely to occur than HONO elimination. In 2017, Pei et al. [10] described the O-NO\(_2\) cleavage as the first stage of NG decomposition and focused on the second stage: autocatalytic NG decomposition. The authors performed the DFT B3LYP 6-31G(d,p) method to provide rate constants and activation energies for five important NG decomposition pathways. Hydrogen abstraction from NG by NO\(_2\) is mentioned to be the preferred elementary step for autocatalytic NG decomposition.

The detailed kinetic approach is mostly applied to hydrocarbon fuels used for the automotive and aviation domains [11] [12] [13]. However some detailed kinetic schemes able to model the combustion of an EM can be found in the literature. RDX and HMX are probably the most studied EMs for which there are kinetic models available [14] [15] [16] [17] [18] [19] [20] [21]. Recently, initial gas-phase decomposition steps of RDX were investigated by Chen and Goldsmith using DFT calculations. Kinetic models were also developed in the frame of space propulsion for ammonium perchlorate/hydroxyl-terminated-polybutadiene (AP/HTPB) [22] and hypergolic mixtures [23]. The list of EMs that could be investigated by kinetic modeling is still exhaustive, it might due to the complexity in obtaining such large mechanisms and validating it. The open-source software RMG (Reaction Mechanism Generator) [24] recently (approximately in 2016) added to its database an exhaustive description nitrogen chemistry. It already contained carbon, hydrogen and oxygen. RMG is able to generate elementary chemical reactions to build detailed kinetics models based on an implemented general understanding of chemical reactivity. Fuller et al. [25] obtained and evaluated a RMG generated promising kinetic model for a liquid monopropellant named Otto Fuel II (OF). OF is mainly composed (76% by mass) of propylene-glycol-dinitrate (PGDN) which is structurally similar to NG.

The aim of the present work is to develop a detailed kinetic model for NG decomposition. Findings from the published prior investigations concerning the first steps of NG decomposition were taken into account and if possible included in RMG calculations. The automatic reaction mechanism generation, through RMG, was applied to NG in the conditions of Hiyoshi and Brill [8]. The model was reduced, evaluated by closed vessel simulations and compared with Hiyoshi and Brill experimental species profile from NG pyrolysis. Thermochemical data (enthalpy, entropy and heat capacity) related to the significant NG decomposition species were derived from ab initio calculations.

2. Methods

2.1. Mechanism development

NG decomposition has been investigated and elementary reactions were obtained from the open-source software RMG (version 2.1.9). The theory behind how RMG operates was recently described by Gao et al. [24]. Nevertheless, the appropriate functioning of RMG clearly depends on the input data that the user provides. In order to guide the software in elucidating important pathways of the investigated system, a seed mechanism called NOx2018, containing updated NO/NO\(_2\) chemistry, has been addressed. Moreover, thermodynamic and reaction libraries related to NO/NO\(_2\) database (e. g. NitrogenCurran, Klippenstein_Glarborg2016…), were also specified. Main intermediates of NG decomposition were indicated in the input file in order to obtain a faster convergence. Since the first stages of NG decomposition, such as O-NO\(_2\) cleavage and HONO elimination, were well investigated [9] [10], the effort in targeting significant intermediate species have been intuitively achieved. A total of 62 of key species and intermediates have been specified. Since the generated mechanism was aimed to be confronted to Hiyoshi and Brill measurements, the conditions of the RMG computation were taken similar to their experimental efforts. The “TerminationTime » parameter, which represents a time at which the simulation should be terminated, was set to 16 s. Since RMG requires pressure and
temperature conditions: 623 K and 0.5 MPa were specified. Palopoli and Brill provided key informations concerning the experimental work conducted by Hiyoshi and Brill [26]. In their experiment, 1 mg of sample was placed in a 25 cm$^3$ vessel which is equivalent to a molar fraction of NG of 0.003 that was specified to RMG. Many “terminationConversion” parameters, which represent a conversion at which the simulation should be terminated, were investigated: 0.3, 0.5, 0.7 and 0.9. Finally, to reduce the complexity of the mechanism, it has been chosen not to allow the growth of heavy molecular compounds so the size of the products have been restricted.

2.2. Closed vessel simulation
Simulations were performed with the closed homogeneous reactor model which is included in ANSYS CHEMKIN-PRO [27]. The simulated reactor was taken to be zero-dimensional time-dependent adiabatic and isobaric similarly to Hiyoshi and Brill conditions. In their experiment, a very small sample quantity was placed close to a heater filament which had a high heating rate (20000 C.s$^{-1}$), which might rapidly vaporizes NG in the reactor. Consequently, the mixture sample/surrounding atmosphere can be assumed homogeneous. The temperature and pressure were set to be respectively 623 K and 0.5 MPa of argon. As it has been deduced from Palopoli and Brill experiment description, the vessel volume was set to 25 cm$^3$ and contained initially 0.003 of NG (molar fraction).

2.3. Computational chemistry
The generated mechanism includes mostly common combustion intermediates for which accurate thermochemical data are tabulated. RMG also provides less common species that are crucial for the mechanism since they are derived specifically from NG decomposition. For these novel species, RMG estimates thermodynamic properties via Benson’s group additivity rules [28], which is convenient but can be improved. DFT calculations were performed, using Gaussian 16 [29], to obtain more accurate thermodynamic data for significant NG combustion intermediates. The DFT B3LYP 6-31G(d,p), following the protocol from Osmont et al. [30], has been applied for novel species to obtain standard enthalpies of formation at 298.15 K, heat capacities and entropies. Calculations were performed in the temperature range of 300-5000 K. Calculated properties were finally converted, using FITDAT (utility from CHEMKIN-Pro), into the polynomial fitting coefficients which is the CHEMKIN-compatible format. The thermodynamic database for significant NG combustion intermediates obtained from RMG was replaced, in the mechanism, by the DFT calculated one.

3. Results and discussion
RMG calculations were performed at four different conversion parameters in order to evaluate the impact on the generated mechanism. Differences have been observed and first test simulations revealed that when the conversion parameter is set to 0.5, 0.7 and 0.9, the generated mechanisms contains limiting steps with inconsistent generated radical species. It can be explained by the fact that a high conversion parameter might force the software to take reaction paths through inconsistent intermediate species. The mechanism generated with a conversion parameter of 0.3 did not include inconsistent limiting steps and was selected to continue this investigation. It contained 209 species and 14425 elementary reactions (also called the master mechanism), which provides an exhaustive description of the NG decomposition but is also inconvenient since it would lead to a tremendous computation time. A reduction of the mechanism seemed essential.

ANSYS CHEMKIN-Pro includes implemented methods for kinetic mechanism reduction. Directed Relation Graph with Error Propagation (DRGEP) method [31] has been applied with CO, CO$_2$, H$_2$O, NO and NO$_2$ calculated profiles specified as target parameters for mechanism reduction. Absolute tolerance, defined as the absolute error enabled to the target parameter after reduction, and relative tolerance, which defines how large the relative difference between skeletal mechanism and master mechanism can be, were set respectively to $10^{-6}$ and 10%. The resulting skeletal mechanism contained 74 species and 1011 elementary reactions. Polynomial coefficients were calculated for 23 specific NG decomposition intermediates and implemented in the skeletal mechanism. Fuller et al. [25] performed
transition state calculations to O-NO$_2$ cleavage and HONO elimination for PGDN first decomposition steps. Since PGDN is structurally similar to NG, calculated rate constants were associated to NG O-NO$_2$ cleavage and HONO elimination (Table 1). NG, such as PGDN, has two types of O-NO$_2$ homolysis and HONO elimination due to its molecular structure. Both types were taken into account in the skeletal mechanism.

**Table 1.** Rate constants initially calculated for PGDN and associated to NG first decomposition elementary reactions [25]. Units are cm$^3$. mol$^{-1}$ and kcal.

| Reaction                     | A          | n   | Ea   |
|------------------------------|------------|-----|------|
| 1. NG = C$_3$H$_5$N$_2$O$_7$-1 + NO$_2$ | 4.3 x 10$^{81}$ | -20.2 | 60.4 |
| 2. NG = C$_3$H$_5$N$_2$O$_7$-2 + NO$_2$ | 8.1 x 10$^{83}$ | -20.9 | 62.2 |
| 3. NG = C$_3$H$_4$N$_2$O$_7$-1 + HONO | 3.3 x 10$^{77}$ | -20.8 | 64.0 |
| 4. NG = C$_3$H$_4$N$_2$O$_7$-2 + HONO | 1.1 x 10$^{76}$ | -20.6 | 63.5 |

The modified skeletal mechanism has been investigated with the closed homogeneous reactor from ANSYS CHEMKIN-Pro under Hiyoshi and Brill conditions. The simulation integrates sensitivity analysis on the species concentration of CO, CO$_2$, H$_2$O, NO and NO$_2$. Calculated first-order sensitivity coefficients of the most sensitive reactions were plotted in Figure 1.
Figure 1. First-order sensitivity coefficients as a function of time on CO (a), CO$_2$ (b), H$_2$O (c), NO (d) and NO$_2$ (e) species concentration for the most sensitive reactions.

It can be observed in Figure 1 that sensitive reactions are mostly composed of small species. Reaction 319 has the highest sensitivity coefficients for the mole fractions analysis of CO, CO$_2$, H$_2$O and NO, especially before $10^{-6}$ s. For the same mole fractions, reactions 189 and 565, at $4 \times 10^{-4}$ s, show an opposite behavior. Both reactions share HCO as a reactant and CO as product. Sensitivity analysis applied on NO$_2$ is quite different from the other profiles. Sensitivity coefficients peaks at 0.78 sec, notably for reactions 187 and 189. At this time the NO$_2$ mole fraction strongly decreases (Figure 2). Since the reactions presented in Figure 1 are highly sensitive, the sensitivity analysis helped in improving the kinetic model. Presented reactions rate constants have been slightly modified for a better fitting of experimental profiles. Modifications of the rate constants did not exceed one order of magnitude, which can be, especially for reactions involving small species, assimilated in the range of calculation and/or experimental error.

Figure 2 presents simulated normalized mole fraction profiles of CO, CO$_2$, H$_2$O, NO and NO$_2$ obtained with the optimized skeletal mechanism and Hiyoshi and Brill experimental conditions. The investigated species represents the major combustion products. CO$_2$, NO$_2$ and NO fairly adjust well
with Hiyoshi and Brill experimental results. The model poorly estimates the CO and H$_2$O profiles. Since the CO$_2$ profile correlates well with the experiment and CO and CO$_2$ are the only carbon containing products, it seems difficult to find a better adjustment for CO. The model clearly overestimates the H$_2$O profile and no better adjustments were found. Hiyoshi and Brill mentioned that H$_2$ concentration profile could not be measured which can have an impact on the H$_2$O concentration profile. Furthermore, it can be assumed, in their case, that condensation phenomena could have occurred and might decrease the H$_2$O measured concentration profile.

Figure 2. Experimental and normalized mole fraction profile of CO (a), CO$_2$ (b), H$_2$O (c), NO (d) and NO$_2$ (e).

4. Conclusion
The aim of this study was to evaluate the potential of an automatically generated mechanism for EM combustion. A detailed kinetic mechanism of NG decomposition has been obtained, at precise temperature and pressure conditions, through RMG calculations. The generated detailed mechanism has been reduced to optimize the computation time when simulation is performed. Thermochemical data of specific NG combustion intermediates were optimized thanks to DFT calculation. Sensitivity
analysis was conducted and rate constants of the most sensitive reactions were adjusted to improve the predictive capacity of the model. First simulation results are encouraging and the lack of available experimental data for validation is regretted. The application of automatic mechanism generation for EM would require more investigations but seems to be, for a first attempt, highly promising.

Acknowledgments
The authors want to acknowledge Dr. Yann Fenard for the useful advices concerning detailed kinetic modeling.

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