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RPPR Final Report
as of 12-Jun-2018

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STEM Degrees: 4 **STEM Participants:** 0

Major Goals: The main objectives of our project is to experimentally understand the hitherto poorly characterized underlying reaction mechanisms involved in the explosive decomposition of model compounds of energetic materials such as of nitrohydrocarbons in the condensed phase. This is aimed to change our understanding of their long-term stability and explosion efficiency and may also lead to the development of novel insensitive energetic materials.

We trigger the decomposition of the model compounds by ionizing radiation in form of energetic electrons and (vacuum) ultraviolet (VUV) photons with energies below the ionization energy of the target molecules in a contamination free ultra high vacuum setup at low temperatures. The decomposition processes are monitored on line and in situ via an array of complementary spectroscopic tools (FTIR, Ra, UVVIS) and most recently electron paramagnetic resonance (EPR). Based on the kinetic fits of the temporal evolution of newly formed species along with data from the decomposition of (partially) deuterated reactants, we extract general concepts on the reaction mechanisms, products, intermediates, and branching ratios. Molecules subliming during the warm up phase are photoionized analyzed exploiting tunable VUV light and then mass analyzed in a reflectron time of flight mass spectrometer (ReTOF-PI) thus gaining a systematic understanding of the decomposition products.

Accomplishments: Please see uploaded pdf file.

Training Opportunities: We trained 9 scientists (P. Maksyutenko, S. Góbi, L. G. Muzangwa, B. M. Jones, M. Förstel, P. Crandall, B. J. Sun, M. H. Wu, Y. A. Tsegaw) in the fields of energetic materials, condensed phase physical chemistry, ultra-high vacuum technology, laser technology, and physical organic chemistry. Names denoted in italics represent graduate students; names in bold indicate group members having accepted faculty/staff positions. Our collaborative training involved well-reputed theoreticians (Chang, National Dong Hwa University, Taiwan; Mebel, Florida International University) and experimentalists (Sander, University of Bochum, Germany) demonstrating our commitment to train scientists across the disciplines capable of assuming leading roles in sciences in the future.

RPPR Final Report
as of 12-Jun-2018

Results Dissemination: P1 P. Maksyutenko, L.G Muzangwa, B.M. Jones, R.I. Kaiser, Lyman a Photolysis of Solid Nitromethane (CH3NO2) and D3-Nitromethane (CD3NO2) - Untangling the Reaction Mechanisms Involved in the Decomposition of Model Compounds of Energetic Materials. Phys. Chem. Chem. Phys. 17, 7514–7527 (2015).

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P8 S. Góbi, Parker B. Crandall, P. Maksyutenko, M. Förstel, and R.I. Kaiser, Accessing the Nitromethane (CH3NO2) Potential Energy Surface in Methanol (CH3OH)–Nitrogen Monoxide (NO) Ices Exposed to Ionizing Radiation: An FTIR and PI-ReTOF-MS Investigation, J. Phys. Chem. A 122, 2329-2343 (2018).

Honors and Awards: Ralf I Kaiser was elected American Chemical Society (ACS) (2017)

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Participant Type: PD/PI
Participant: Ralf I Kaiser
Person Months Worked: 12.00
Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Funding Support:

Participant Type: PD/PI
Participant: Ralf I Kaiser
Person Months Worked: 12.00
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Other Collaborators:

Funding Support:

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Project Contribution:
International Collaboration:
International Travel:
National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Sandor Gobi
Person Months Worked: 15.00 **Funding Support:**
Project Contribution:
International Collaboration:
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National Academy Member: N
Other Collaborators:

Participant Type: Postdoctoral (scholar, fellow or other postdoctoral position)
Participant: Brant M Jones
Person Months Worked: 12.00 **Funding Support:**
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International Travel:
National Academy Member: N
Other Collaborators:

Untangling the Reaction Mechanisms Involved in the Decomposition of Model Compounds of Energetic Materials in the Condensed Phase

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Final Report

ABSTRACT

The main objectives of our project is to experimentally understand the hitherto poorly characterized underlying reaction mechanisms involved in the explosive decomposition of model compounds of energetic materials such as of nitrohydrocarbons in the condensed phase. This is aimed to change our understanding of their long-term stability and explosion efficiency and may also lead to the development of novel insensitive energetic materials.

We trigger the decomposition of the model compounds by ionizing radiation in form of energetic electrons and (vacuum) ultraviolet (VUV) photons with energies below the ionization energy of the target molecules in a contamination free ultra high vacuum setup at low temperatures. The decomposition processes are monitored *on line* and *in situ* via an array of complementary spectroscopic tools (FTIR, Ra, UVVIS) and most recently electron paramagnetic resonance (EPR). Based on the kinetic fits of the temporal evolution of newly formed species along with data from the decomposition of (partially) deuterated reactants, we extract general concepts on the reaction mechanisms, products, intermediates, and branching ratios. Molecules subliming during the warm up phase are photoionized analyzed exploiting tunable VUV light and then mass analyzed in a reflectron time of flight mass spectrometer (ReTOF-PI) thus gaining a systematic understanding of the decomposition products.

1. RESULTS

Our research program *Untangling the Reaction Mechanisms Involved in the Decomposition of Model Compounds of Energetic Materials in the Condensed Phase* has been extremely productive not only in terms of exciting scientific results disseminated via publications **P1–P8,** [**Error! Reference source not found.**–**Error! Reference source not found.**] but also from the standpoint of human resource development.

1.1. SCIENTIFIC RESULTS

The main objectives of our project have been to experimentally unravel the hitherto poorly characterized reaction mechanisms involved in the decomposition of nitromethane (CH_3NO_2) as the simplest representative of a model compound of nitrohydrocarbon-based energetic materials in the condensed phase (**P1–P5**). The experiments were conducted in a novel ultrahigh-vacuum surface science machine within thin films of nitromethane ices triggering their decomposition via energetic electrons and monochromatic vacuum ultraviolet photons with energies up to 10.49 eV. The experiments established a comprehensive protocol to monitor the fragmentation and successive higher-order reaction products of nitromethane (CH_3NO_2) in the condensed phase on line and *in situ* via an array of complementary spectroscopic tools such as Fourier Transform Infrared (FTIR) spectroscopy and electron paramagnetic resonance (EPR). After the radiation exposure, molecules subliming during the warm-up phase were photoionized exploiting tunable vacuum ultraviolet (VUV) light and then mass analyzed in a reflectron time of flight mass spectrometer (PI-ReTOF-MS) thus gaining a comprehensive inventory of the *isomer selective* decomposition and reaction products. These data provided compelling evidence of multiple non-equilibrium reaction mechanisms, products, and intermediates, which were found to be quite distinct from those observed in the decomposition of nitromethane in the gas phase under collision less conditions. The following five key mechanisms (**M1**–**M5**) shall be highlighted.

M1: Isomerization – Decomposition: The infrared data suggest (pseudo) first order kinetics and the initial formation of cis methyl nitrite (CH_3ONO) via isomerization of nitromethane (CH_3NO_2) (reaction (1)) (**P1–P2**) (Fig. 1). Methyl nitrite (CH_3ONO) decomposed via two competing pathways involving a radical route and a molecular fragmentation mechanism into the methoxy radical (CH_3O) plus nitrogen monoxide (NO) (reaction (2a)) and into formaldehyde (H_2CO) plus nitrosyl hydride (HNO) (reaction (2b)), respectively. The decomposition of nitromethane into methyl radicals (CH_3) plus nitrogen dioxide (NO_2) (reaction (3)) was traced via EPR spectroscopy (**P5**). These mechanisms were also observed in gas-phase studies [**Error! Reference source not found.**, **Error! Reference source not found.**]. It shall be highlighted that the branching ratios strongly depend on the source of ionizing radiation (elec-trons versus photons) and also the photolysis wavelength.

M2: Mass Growth Processes: With the help of isotopically labeled reactants, the PI-ReTOF-MS analysis exposed three classes of higher molecular weight products, which are uniquely formed in the condensed phase: i) nitroso compounds, ii) nitrite compounds, and iii) higher molecular weight molecules (**P1–P2**). A key molecular mass growth process was attributed to insertion of carbene (CH_2) into carbon–hydrogen bonds forming from nitrosomethane (CH_3NO) ***nitrosoalkanes***: nitrosoethane (C_2H_5NO) and nitrosopropane (C_3H_7NO). Starting with methylnitrite (CH_3ONO), carbene insertion leads to ***nitritoalkanes***: ethylnitrite (C_2H_5ONO) and propylnitrite (C_3H_7ONO). We also identified molecules, which necessitate the reaction of (fragments of) two nitromethane building blocks; further, the formation of $CH_3NONOCH_3$ and

$CH_3NONO_2CH_3$ requires two neighboring nitrosomethane and nitrosomethane/nitromethane molecules to react.

M3: Non-Equilibrium Mechanisms: The reactions in the condensed phase expose exotic non-equilibrium decomposition pathways, which have not been observed in previous gas-phase experiments. These are the decomposition of nitromethane (CH_3NO_2) and methyl nitrite (CH_3ONO) via atomic hydrogen loss to CH_2NO_2 and CH_2ONO radicals via reactions (4a) and (4b), respectively, fragmentation to nitrosomethane (CH_3NO) plus atomic oxygen (O) (reaction (5)), and decomposition to carbene (CH_2) plus nitrous acid (HONO) (reaction (6)). These pathways were confirmed in nitromethane (CH_3NO_2) – D3-nitromethane (CD_3NO_2) ices (**P3**), are highly endoergic by up to 440 $kJmol^{-1}$, and could be opened up through the interaction of ionizing radiation with nitromethane in the condensed phase.

M4: Exotic Structural Isomers: An isomer specific study of the products formed in the exposed nitromethane ices was performed via photoionization – reflectron time of flight mass spectrometry (PI-ReTOF-MS) of the subliming products employing tunable vacuum ultraviolet photons for ionization (Figs. 1 & 2). Supported by electronic structure calculations, nitromethane (CH_3NO_2) was found to isomerize to methyl nitrite (CH_3ONO) (reaction (1)), but also via hydrogen migration to the hitherto elusive aci-nitromethane isomer ($H_2CNO(OH)$) (reaction (7)). The latter rearranged to nitrosomethanol ($HOCH_2NO$) through hydroxyl group (OH) migration. The importance of hydrogen migrations in the condensed phase was also verified via the nitrosomethane (CH_3NO) – formaldehyde oxime isomer (H_2NCOH) pair. These studies revealed the involvement of two exotic isomers in the decomposition of nitromethane: aci-nitromethane ($H_2CNO(OH)$) and nitrosomethanol ($HOCH_2NO$).

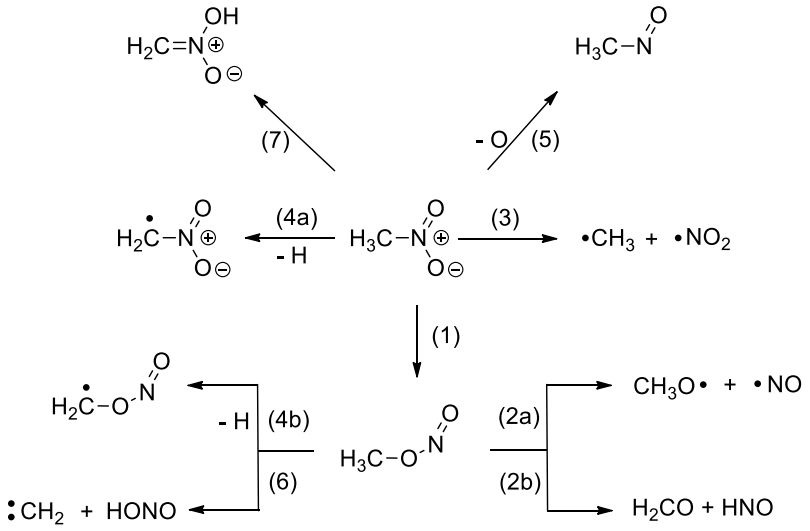
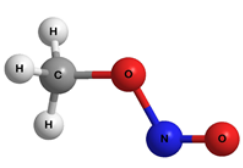
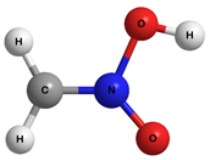


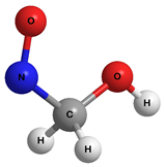
Fig. 1: Key isomerization and decomposition pathways of nitromethane in the condensed phase.



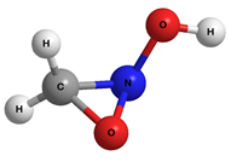
methyl nitrite



aci-nitromethane



nitrosomethanol



2-hydroxy-oxaziridine

Fig. 2: Structural isomers of nitromethane involved in the decomposition of nitromethane in the condensed phase under non-equilibrium conditions (**P1–P5**, **P8**). Attempts to identify the chiral cyclic 2-hydroxy-oxaziridine isomer (c-$H_2CON(OH)$) are in progress.

M5: Hitherto elusive high energy density hydrides of nitrogen – triazane (H_2NNHNH_2; N_3H_5) along with triazene (H_2NNNH; N_3H_3) and/or triimide (HNHNNH; N_3H_3) –were synthesized in low-temperature ammonia matrices (**P6–P7**) (Fig. 3). These species are higher-order nitrogen hydrides of ammonia (NH_3) and hydrazine (N_2H_4) and are of fundamental importance for the understanding of the stability of single-bonded chains of nitrogen atoms and a potential key intermediate in the hydrogen – nitrogen chemistry. Triazane and triazene were formed through irradiation of ammonia ices with energetic electrons and detected in the gas phase after sublimation of the irradiated samples via tunable, soft vacuum ultraviolet (VUV) photoionization coupled with a reflectron-time-of-flight mass spectroscopy. Isotopic substitution experiments exploiting irradiation of D3-ammonia ices confirmed the identification through the detection of fully deuterated counterparts D5-triazane (N_3D_5) and D3-triazene (N_3D_3). These molecules represent surprisingly stable species with nitrogen–nitrogen bond length shorter by a few picometers than in hydrazine and lifetimes exceeding 6 ± 2 μs at 170 K.

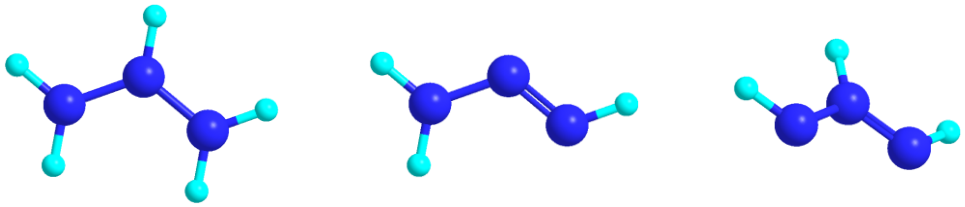


Fig. 3: Hydrides of nitrogen involved in non-equilibrium chemistry in ammonia ices (**P6–P7**).

1.2. HUMAN RESOURCE DEVELOPMENT

We trained 9 scientists (P. Maksyutenko, S. Góbi, L. G. Muzangwa, **B. M. Jones, M. Förstel**, *P. Crandall*, *B. J. Sun*, *M. H. Wu*, *Y. A. Tsegaw*) in the fields of energetic materials, condensed phase physical chemistry, ultra-high vacuum technology, laser technology, and physical organic chemistry. Names denoted in italics represent graduate students; names in bold indicate group members having accepted faculty/staff positions. Our collaborative training involved well-reputed theoreticians (Chang, National Dong Hwa University, Taiwan; Mebel, Florida International University) and experimentalists (Sander, University of Bochum, Germany) demonstrating our commitment to train scientists across the disciplines capable of assuming leading roles in sciences in the future.

2. Publications

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