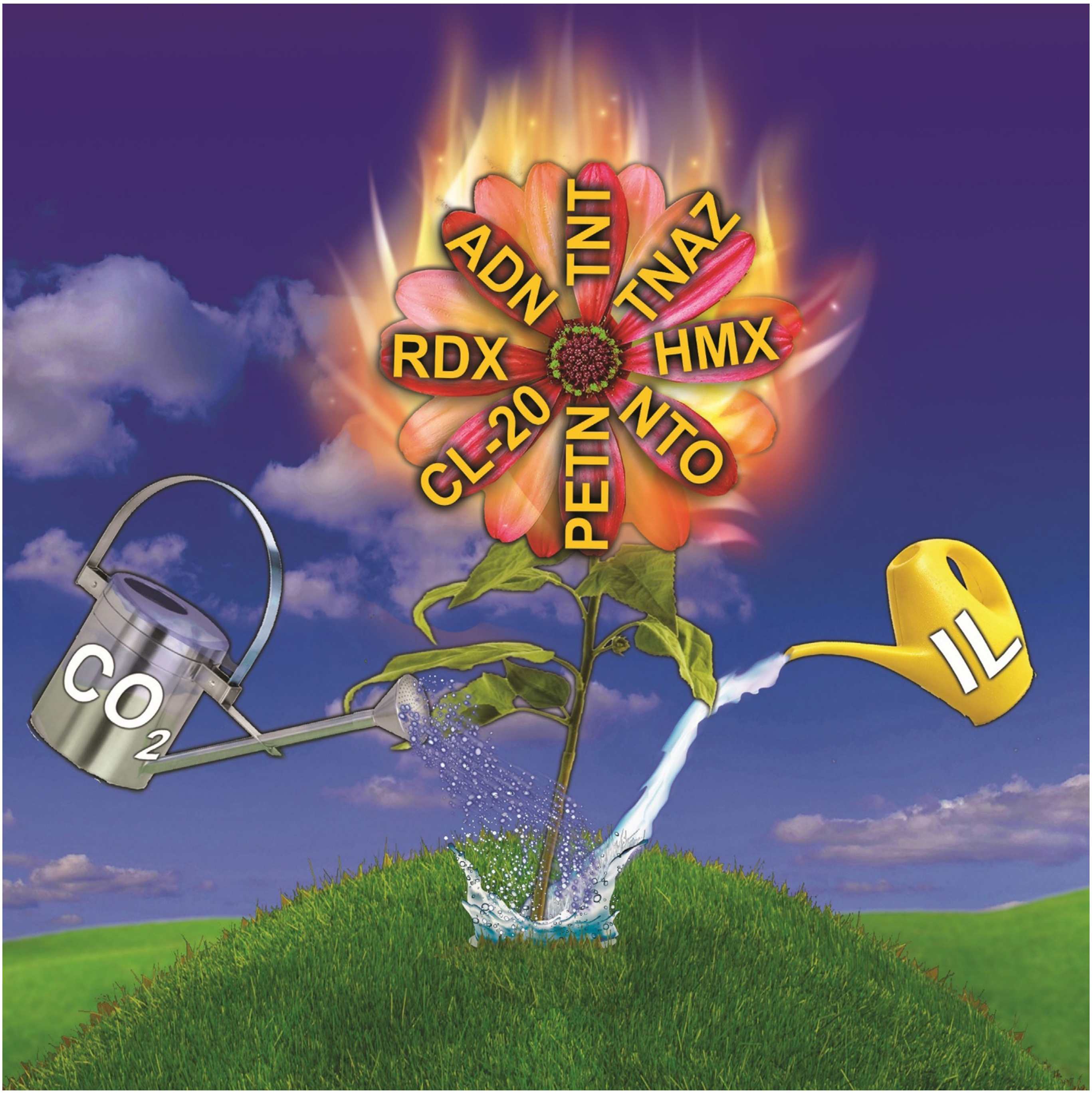
ChemPubSoc Europe

DOI: 10.1002/cssc.201701053

CHEMSUSCHEM
Reviews

Prospective Symbiosis of Green Chemistry and Energetic Materials

Ilya V. Kuchurov, Mikhail N. Zharkov, Leonid L. Fershtat, Nina N. Makhova,* and Sergey G. Zlotin*[a]



A global increase in environmental pollution demands the development of new "cleaner" chemical processes. Among urgent improvements, the replacement of traditional hydrocarbon-derived toxic organic solvents with neoteric solvents less harmful for the environment is one of the most vital issues. As a result of the favorable combination of their unique properties, ionic liquids (ILs), dense gases, and supercritical fluids (SCFs) have gained considerable attention as suitable green chemistry media for the preparation and modification of important chemical compounds and materials. In particular, they have a significant potential in a specific and very important area of research associated with the manufacture and processing of high-energy materials (HEMs). These large-scale manufacturing processes, in which hazardous chemicals and extreme conditions are used, produce a huge amount of hard-to-dispose-of waste. Furthermore, they are risky to staff, and any improvements that would reduce the fire and explosion risks of the corresponding processes are highly desirable. In this Review, useful applications of almost nonflammable ILs, dense gases, and SCFs (first of all, CO_2) for nitration and other reactions used for manufacturing HEMs are considered. Recent advances in the field of energetic (oxygen-balanced and hypergolic) ILs are summarized. Significant attention is paid to the SCF-based micronization techniques, which improve the energetic performance of HEMs through an efficient control of the morphology and particle size distribution of the HEM fine particles, and to useful applications of SCFs in HEM processing that makes them less hazardous.

1. Introduction

A global increase in environmental pollution has led to an ever-increasing control over the use and disposal of hazardous materials by the chemical industry. This means that the chemical industry is continually searching for new "cleaner" alternatives to current processes. This research area is called green or sustainable chemistry and focuses on basic and technological improvements that allow the prevention of local and global pollution and reduce the huge consumption of nonrenewable resources.[1,2] Among these improvements, careful management of environmentally friendly solvents for the chemical industry is one of the most vital issues because traditional hydrocarbon-derived organic solvents are now consumed in inadmissible quantities in many chemical and purification processes. Furthermore, organic solvents are often toxic and contribute significantly to environmental pollution. Over the past decades, ionic liquids (ILs),[3,4] sub- or supercritical fluids (SCFs),[5] and some other neoteric solvents[6,7] have gained considerable attention as suitable alternatives for liquid-phase chemical processes.

ILs are low-melting salts (m.p. $\leq 100\,^{\circ}C$) that commonly consist of a voluminous organic cation and an organic or inorganic (often fluorinated) anion. They have considerable advantages over traditional organic solvents, in particular, a negligible vapor pressure, an ability to be in the liquid state over a wide temperature range, high thermal stability, significant ionic conductivity, structural tunability, powerful solvating properties, and recyclability. Furthermore, a number of ILs contain Lewis and/or Brønsted acid or base fragments and, therefore, can act as efficient catalysts for a variety of chemical reactions.[8–12] A significant acceleration effect of the IL media on these reactions may be attributed to a decrease in the activation energy of the rate-determining step. On the other hand, highly polar or charged intermediates and activated complexes could become more stable in the IL media because of Coulombic interactions with the IL cations and/or anions; this may have a favorable impact on process efficiency and selectivity.[13,14]

The physical properties of SCFs are also different from those of ordinary gases and liquids and partially have the features of both.[5] They have a diffusivity and viscosity close to a gas and can diffuse through solids. The densities of SCFs are similar to the corresponding liquids so they can dissolve some chemical compounds and materials. The properties of SCFs are strongly influenced by changes in the pressure and temperature. Near the critical point, even small changes of these parameters may result in large changes in density, which allows many properties of sub- and supercritical fluid to be "fine-tuned" to better suit corresponding industrial and laboratory processes.[15,16] CO_2, a commonly used SCF, is particularly attractive as reaction and process medium because of its low cost, nontoxicity, nonflammability, and thermal stability. The critical point of CO_2 is easily accessible at the critical temperature (T_C) 31.1 °C and critical pressure (P_C) 7.38 MPa. Industrially available, nonflammable, and chemically resistant freons, in particular 1,1,1,2-tetrafluoroethane ($T_C = 101.06\,^{\circ}C$, $P_C = 4.06$ MPa)[17] that do not fall into the category of ozone-depleting substances[18] may also have useful applications in chemistry and chemical engineering.

Because of the useful combination of unique properties, both ILs and SCFs are extensively studied nowadays as green chemistry media for the preparation and modification of important chemical compounds and materials. The pronounced acceleration effect of ILs has been observed in Diels–Alder,[19] Michael addition,[20] Knoevenagel,[21] Baylis–Hillman,[22] cross-coupling,[23] and cyclocondensation reactions.[24,25] Task-specific ILs are useful recyclable organocatalysts of chemical (particularly asymmetric) reactions.[26–29] Supercritical CO_2 ($scCO_2$) has been often used in chemistry and chemical engineering as a green extracting agent of useful substances from plant and animal raw materials,[30] as an inexpensive and efficient eluent

---

[a] Dr. I. V. Kuchurov, M. N. Zharkov, Dr. L. L. Fershtat, Prof. N. N. Makhova, Prof. S. G. Zlotin
N. D. Zelinsky Institute of Organic Chemistry
Russian Academy of Sciences
Leninsky Prospect, 47, Moscow (Russia)
E-mail: mnn@ioc.ac.ru
zlotin@ioc.ac.ru

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/cssc.201701053.

for chromatography,[31] and as a convenient medium for the environmentally friendly preparation of chemical compounds and materials. Homogeneous[32] and heterogeneous[33] catalytic or biocatalytic (enzymatic) reactions,[34–36] green polymerization processes,[15,16,37] and some other chemical reactions[38–40] were performed efficiently in sub- and supercritical CO_2.

The global concern with regard to environmental safety in different industrial areas also affected the production of high-energy materials (HEMs). The application of green chemistry methods in the preparation and processing of HEMs is a specific and very important area of research.[41–47] Of particular importance is the fact that dangerous HEMs are often produced on extremely large scales. In the corresponding manufacturing processes, hazardous chemicals, chemically resistant solvents, and extreme reaction conditions are commonly needed to deliver the required level of accumulated energy to products. These requirements make the HEM manufacturing processes risky to staff and environment. Furthermore, they significantly complicate recycling and appropriate waste disposal, particularly for nitration reactions in which a large amount of hard-to-dispose-of mixed-acid waste is produced.[48] This Review summarizes prospective approaches to address these concerns based on applications of ILs and sub- or supercritical fluids (CO_2 and freons) in the preparation and processing of HEMs. In particular, useful application of these almost nonflammable neoteric media in nitration and some other reactions used for the manufacturing of HEMs that make these reactions less fire and explosion risky[49,50] are considered. Recent advances

Ilya V. Kuchurov graduated from Volgograd State Technical University with a Master's degree in 2007. After three years research work in 2010 he obtained his Ph.D. from N. D. Zelinsky Institute of Organic Chemistry and stayed for in the Laboratory of Fine Organic Synthesis at this Institute as a Senior Researcher. His principle areas of interest are the synthesis bioactive and high-energy nitrogen-containing compounds using the approaches of Green Chemistry.

Mikhail N. Zharkov obtained his Bachelor's degree in 2011 and Master's degree in 2013 from Volgograd State Technical University. He is currently a Ph.D. student in the Laboratory of Fine Organic Synthesis at N. D. Zelinsky Institute of Organic Chemistry under the supervision of Dr. Kuchurov. His research interests are in the development of new methods of the synthesis of *N*-nitro compounds in compressed fluid media.

Leonid L. Fershtat graduated from the D. I. Mendeleev University of Chemical Technology in 2012 (faculty Higher Chemical College of the Russian Academy of Sciences). He received his Ph.D. degree from the N. D. Zelinsky Institute of Organic Chemistry in 2015 under the supervision of Professor N. N. Makhova. Currently, he is a researcher in the same institute. His scientific interests include the development of novel methodologies in the field of nitrogen-containing heterocycles and the search for pharmacologically active and high-energy heterocyclic derivatives.

Nina N. Makhova received a Ph.D. degree in organic chemistry at Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences (ZIOC RAS), in 1971, Dr. Sc. in organic chemistry at ZIOC RAS in 1989 and became a full professor in 1995. From 1995 until now she is the head of the Laboratory of Nitrogen-Containing Compounds at ZIOC RAS. Her scientific interests have been focused on the chemistry of nitrogen-oxygen heterocycles and their use in the synthesis of pharmacologically active and high-energy structures. She was awarded by the Russian Academy of Sciences with the Zelinsky prize for achievements in organic chemistry and catalysis (2014).

Sergey Zlotin received a Ph.D. (1978) and Doctor of Science degrees (1992) in Organic Chemistry from Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences. He has been a full professor since 2003 and the head of N. D. Nazarov Laboratory of Fine Organic Synthesis since 2001. His major research interests include bioactive and energy-rich nitrogen-oxygen systems, asymmetric organocatalysis, and Green Chemistry. He was awarded by the Russian Academy of Sciences with the Zelinsky prize for the achievements in organic chemistry and catalysis (2014).

(published after the excellent review by Zhang and Shreeve[51]) in the field of energetic ionic liquids (EILs),[52–54] (in particular oxygen-balanced EILs[55–57] and hypergolic EILs capable of fast ignition upon contact with oxidizers[13,52]) are thoroughly analyzed. Significant attention is paid to SCF-based micronization techniques that improve the energetic performance of HEMs significantly through the efficient control of the morphology and particle size distribution of the HEM fine particles without degradation or contamination of products.[58]

Application of ILs in aromatic nitration[59] and the use of $scCO_2$ in the processing of energetic materials[60] are partly reviewed. However, to the best of our knowledge, no comprehensive interdisciplinary review covering all these aspects of the synthesis and modification (micronization) of HEMs using ILs and sub- or supercritical fluids has been published so far. Herein, we attempted to fill this gap with a focus on recent advances in these important areas of research.

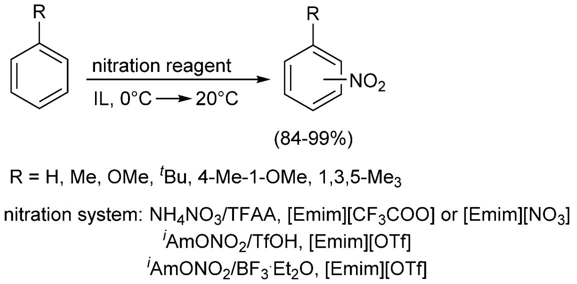
2. IL-Based Green Approaches to the Synthesis and Transformation of HEMs

ILs are considered as safe and environmentally friendly reaction media in the dangerous preparation of HEMs (green chemistry). They accelerate reactions and allow them to be performed under mild conditions, thus reducing the hazard of HEM handling. Over the past decades, a number of HEMs were successfully synthesized in IL media. Aromatic nitration was tested in classical room-temperature ILs and/or in the presence of task-specific acidic ILs (Brønsted-acid catalysis) using various nitrating reagents. As a result, the required amount of mixed acids (nitric and sulfuric) subject to disposal was reduced noticeably. Significant attention was paid to target-oriented synthesis and transformations of known and prospective HEMs in the presence of ILs as solvents and catalysts. In some cases, ILs themselves act as nitrating/nitrosating agents or HEMs. EILs, in particular oxygen-balanced EILs bearing polynitrogen cations and oxygen-rich anions and hypergolic EILs that ignite upon contact with oxidizers because of an exothermic redox reaction, are considered as promising HEMs and green substitutes for the toxic hydrazine-derived components of liquid propellants.[13,52] In this section, IL-mediated nitration reactions and other syntheses of HEMs, useful applications of ILs as reagents, and recent advances in the synthesis and characterization of EILs are presented.

2.1. IL-mediated aromatic nitration

The nitration of aromatic compounds is a classic chemical reaction of great industrial importance. Mononitroarenes are key precursors for aniline derivatives, which are used in the manufacturing of dyes[61] and polymers;[62] in contrast, polynitroarenes, especially 2,4,6-trinitrotoluene (TNT), were used in a broad range of industrial and military application as HEMs for decades.[63] The development of environmentally benign nitration processes is a challenge as the traditional nitration with a huge excess of mixed nitric and sulfuric acids leads to the superfluous production of acidic waste, which requires environmentally dangerous and energy-consuming disposal. The use of ILs as solvents for the electrophilic nitration of arenes could address this challenge.

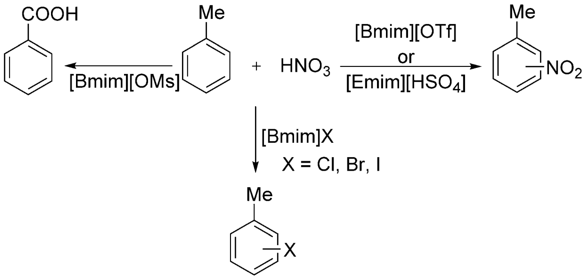
The nitration of arenes in an IL medium was first published in 2001.[64] The reactions were performed in 1-ethyl-3-methylimidazolium-based ILs ([Emim][X]; X = triflate (OTf), CF_3COO, NO_3) or protonated Hünig's base (*N*,*N*-diisopropylethylamine, [HNEt*i*Pr_2][CF_3COO]) using a wide range of nitrating agents (NH_4NO_3/TFAA (TFAA = trifluoroacetic anhydride), *i*$C_5H_{11}ONO_2$/$BF_3{\cdot}Et_2O$, *i*$C_5H_{11}ONO_2$/TfOH, $Cu(NO_3)_2$/TFAA, and $AgNO_3/Tf_2O$ (Tf_2O = triflic anhydride). Among these, NH_4NO_3/TFAA (in combination with [Emim][CF_3COO] or [Emim][NO_3]) and *i*$C_5H_{11}ONO_2/BF_3{\cdot}Et_2O$ or *i*$C_5H_{11}ONO_2$/TfOH nitration systems (in combination with [Emim][OTf]) provided the best nitration efficiency and a convenient recycling/reuse of ILs. The active nitronium salt NO_2BF_4 appeared to be unsuitable as a nitrating agent as it nitrated the imidazolium ring of the IL solvent. Under optimal conditions, benzene and its derivatives (toluene, anisole, 4-methylanisole, *tert*-butylbenzene, mesitylene, fluorobenzene, etc.) afforded the corresponding mononitration products with the preferred formation of *ortho* and *para* isomers (the *ortho*/*para* ratio varied from 70:30 for anisole to 8:92 for fluorobenzene) in good-to-excellent yields (Scheme 1). In the case of trifluoromethylbenzene, the yield of the nitration product was lower whereas nitrobenzene could not be further nitrated. The nitration of 4-fluorotoluene afforded (apart from the major *ortho* and *para* isomers) the minor *meta* isomer, the content of which increased with the increase of the reaction time.



Scheme 1. Electrophilic mononitration of aromatics in IL media. Adapted from Ref. [64]. ^{i}AmONO2 = isoamyl nitrite.

Similar results were reported for the aromatic nitration of both activated and deactivated substrates with acetyl nitrate (HNO_3/Ac_2O) in imidazolium ([Bmim][BF_4], [Bmim][PF_6], [Bdmim][BF_4]; Bmim = 1-butyl-3-methylimidazolium, Bdmim = 1-butyl-2,3-dimethylimidazolium) and pyrrolidinium ([Bmpyrr][OTf], [Bmpyrr][NTf_2]; Bmpyrr = 1-butyl-1-methylpyrrolidinium) ILs.[65–67] The nitronium ion was evidently generated from the acetyl nitrate and acted as the true nitrating agent in the IL media. The best yields of mononitration products (70–96%) were attained in [Bmpyrr][NTf_2]. However, attempts to convert nitrobenzene into dinitrobenzene in [Bmpyrr][NTf_2] failed. Importantly, the association of acetyl nitrate with ILs improved the *para* selectivity (*ortho*/*para* ratio varied from 22:78 to

18:82) for halobenzene nitration compared to that in molecular solvents (CH_2Cl_2 or CCl_4). Unexpectedly, the nitration of toluene with nitric acid in various ILs afforded different products depending on the IL used (nitrotoluene in [Bmim][OTf] or [Emim][HSO_4]; halogenated toluene in [Bmim]Hal (Hal = Cl, Br, I); and benzoic acid in [Bmim][OMs] (OMs = mesylate), evidently as a result of *ipso* substitution or oxidation reactions (Scheme 2).[68]



Scheme 2. Nitration of toluene with HNO_3 in different ILs. Adapted from Ref. [68].

Readily available ethylammonium nitrate (EAN)-based systems (EAN/Tf_2O and EAN/TFAA) proved to be convenient in situ sources for triflyl nitrate ($TfONO_2$) and trifluoroacetyl nitrate (CF_3COONO_2), respectively. These nitration systems were used for the facile nitration of various, in particular deactivated, arenes and heteroarenes (furan, thiophene) under very mild conditions, with the recovery and reuse of the IL.[69] Metal nitrates were also suitable nitrating agents or catalysts for aromatic nitration reactions. Indeed, the nitration of phenol derivatives with ferric nitrate proceeded with excellent *para* selectivity (76–86 %) in [Bmim][BF_4].[70] Similar reactions with the $Fe(NO_3)_3$/EAN system (either neat or supported on K-10 montmorillonite) were significantly accelerated under ultrasound irradiation to afford *para*-nitration products as major isomers.[71] A suspension of $Bi(NO_3)_3\cdot 5H_2O$ (BN) in imidazolium-based ILs ([Bmim][PF_6] or [Bmim][BF_4]) effectively nitrated activated arenes under mild conditions without external promoters.[72] The BN/[Hmim][ClO_4]–HNO_3/Ac_2O nitrating system proved to be suitable for the green polynitration of activated arenes (phenol, anisole, toluene, phloroglucinol, and trimethoxybenzene) to produce the corresponding trinitro compounds in moderate-to-excellent yields. Furthermore, the IL catalyst could be reused three times without a loss of activity. This sulfuric acid free system has the advantages of strong nitrating ability, environmental friendliness, low cost, and high potential for industrial application.[73] An inorganic IL (Ag–K–Na nitrate eutectic mixture; Ag/K/Na = 0.51:0.42:0.07) served as an effective reagent and medium for the nitration of naphthalene and hydroquinone dimethyl ether. The reaction proceeded with unusual regioselectivity, which indicated a radical process.[74] Highly effective systems for the nitration of arenes with acetyl nitrate include quaternary ammonium ILs ([N_{4446}][NTf_2], N_{4446} = tributylhexylammonium) and copper or indium bis[(perfluoroalkyl)sulfonyl]imide ($Cu[N(C_4F_9SO_2)_2]_2$ or $In(NTf_2)_3$) catalysts (Figure 1).

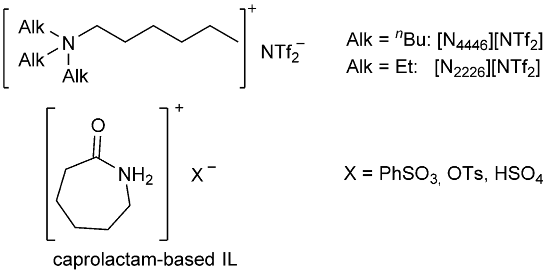


Figure 1. Quaternary ammonium and caprolactam-based ILs.

The nitration of chlorobenzene in the presence of each catalyst (2 mol %) proceeded at room temperature with 87–90 % conversion to afford isomeric nitration products with an approximately 4.5:1 *para/ortho* ratio. Importantly, the catalytic systems could be easily recovered and reused over five times in the reaction.[75] Similar results were attained for the nitration of benzene derivatives with HNO_3 in the presence of the IL-lanthanide (Ln)-based [N_{4446}][NTf_2]/$Ln(N(C_4F_9SO_2)_2)_2$ catalytic system (5 mol %).[76] New acidic caprolactam-based ILs (X = OTs, $PhSO_3$, HSO_4) efficiently catalyzed aromatic nitration in the presence of NO_2/air[77] or HNO_3/acetic anhydride (Ac_2O) as nitrating agents.[78] At the optimal chlorobenzene/IL molar ratio of 10:1.5, isomeric chloronitrobenzenes were produced in 71 % total yield with a 7.7:1 *para/ortho* ratio, which is superior to that obtained with a nitric/sulfuric acid nitrating system. In addition, the ILs could be reused several times without a loss of efficiency.

The obtained results confirm the significant benefits of ILs as green media for aromatic nitration. The IL-based nitration systems do not require large quantities of strong acids and offer a simple nonaqueous workup. The yield and isomer distribution of the corresponding nitration products in the IL media are comparable or better than those in conventional nitration procedures. Furthermore, relatively simple operations allow convenient recovery and recycling of the ILs.

In some cases, ILs may serve as efficient green catalysts of aromatic nitration reactions. Over the past decade, a series of Brønsted-acidic task-specific ionic liquids (TSILs) was synthesized as an alternative to traditional sulfuric or hydrochloric acids and used as acidic catalysts in various acid-catalyzed chemical processes, including aromatic nitration reactions (Figure 2).

The nitration of arenes (benzene, toluene, chlorobenzene) with a NO_2/air mixture in the presence of TSILs [Bspy][X] (Bspy = 1-(4-sulfonylbutyl)pyridinium, X = HSO_4, OTf, OTs) with *N*-(sulfoalkyl)pyridinium cation and RSO_3^- anions (15 mol %) proceeded with promising *para* selectivity to afford mononitration products in moderate yields. The fivefold recycling of TSILs resulted in only a 9 % decrease in the yield. This methodology offers significant improvements with regard to the product yield, operational simplicity, mild reaction conditions, and the “green” aspect of avoiding toxic catalysts and solvents.[79] The regioselective mononitration of aromatic compounds also occurred when HNO_3 was used as the nitrating reagent and acyclic tetraalkylammonium salts bearing alkyl sulfonyl groups

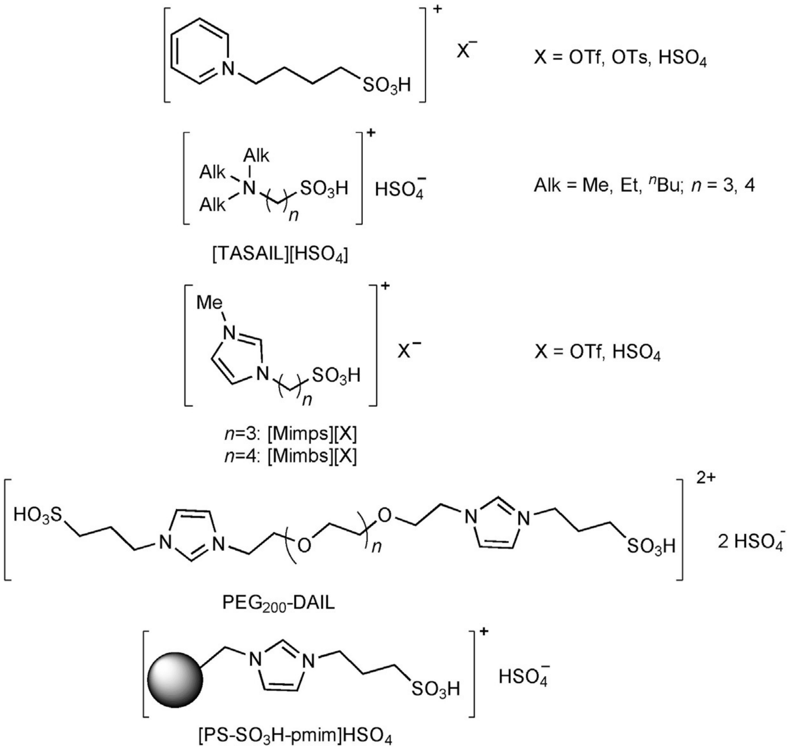


Figure 2. Selected examples of TSILs.

and the HSO_4 anion ([TASAIL][HSO_4], TASAIL = trialkylsulfonylalkyl ionic liquid) served as recyclable acidic catalysts (20 mol %).[80] New Brønsted acids consisting of SO_3H-functionalized 1,3-dialkylimidazolium cations and RSO_3^- anions were effective catalysts for the aromatic nitration. Various arenes reacted with a 62 % nitric-acid–TSIL ([Mimbs][OTf] or [Mimps][OTf]; Figure 2) nitrating systems under solvent-free conditions to produce the corresponding nitroarenes and water as the only byproduct. The reactions were performed in a biphasic mode; as a result, the nitroarene could be easily separated by decantation and the remaining TSIL could be reused without any purification.[81] Thus, the nitration of toluene with 68 % HNO_3 in the presence of [Mimps][HSO_4] (2 mol %) as the catalyst proceeded with 100 % conversion to yield a mixture of *ortho*/*para* nitrotoluenes in a 0.7:1.0 ratio.[82] A combination of polyethyleneglycol-based dicationic TSIL (PEG_{200}-DAIL) bearing the NTf_2 anion as the catalyst and N_2O_5 as the nitrating agent improved the *para* selectivity for alkylbenzene and the *ortho* selectivity for halogenated benzene nitration reactions significantly. PEG_{200}-DAIL could be recycled five times without a significant loss of catalytic activity and with only 5 % loss of weight.[83] To further simplify catalyst recycling, a series of heterogeneous polystyrene-supported TSILs ([PS-SO_3H-pmim][HSO_4]; Figure 2) was prepared and tested in reactions of arenes with nitric acid. The catalytic performance of [PS-SO_3H-pmim][HSO_4] improved with the increase in the amount of the supported TSIL. However, the *para* selectivity depended mainly on the arene structure rather than the TSIL content. The heterogeneous catalyst was recycled multiple times in the nitrotoluene synthesis with only a slight decrease of activity after the fifth run.[84]

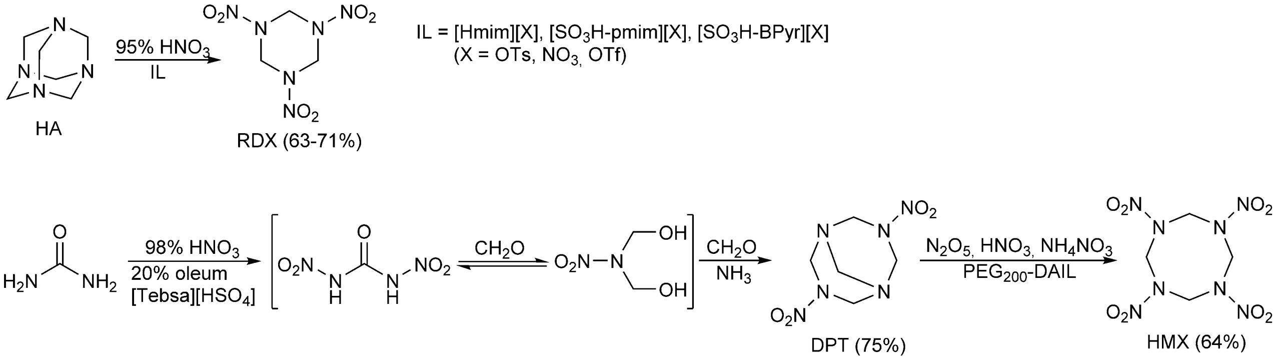
The synthesis and application of Brønsted-acidic TSILs as catalysts for aromatic nitration presented a considerable breakthrough in this field of green chemistry by the elimination of environmentally harmful and hard-to-dispose-of strong acids from these important reactions. In addition, the TSILs are an excellent green alternative to traditional catalysts for a number of other acid-promoted chemical reactions.[85,86]

2.2. IL-mediated synthesis of polynitro compounds

ILs are effective reaction media and catalysts for the preparation of both known and new high-energy polynitro compounds. In the presence of ILs, these compounds (sensitive to heating, shock, and friction) may be produced under milder conditions (at lower temperature) and with higher rates and/or yields than when using conventional methods.

The direct nitrolysis of hexamethylenetetramine (HA) with 95 % nitric acid catalyzed by Brønsted-acidic ILs resulted in the formation of hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX). ILs based on both imidazolium ([Hmim]X [SO_3H-pmim][X]) and pyridinium ([SO_3H-bpyr][X]; SO_3H-bpyr = butylpyridiniumsulfonic acid, in all cases X = OTs, OTf, NO_3) exhibited noticeable catalytic activities, with [SO_3H-bpyr][NO_3] being the best catalyst. In the presence of this catalyst (3 mol %), the yield of RDX was 10 % higher than that from a conventional system that did not contain an IL (Scheme 3).[87]

The dicationic TSIL PEG_{200}-DAIL (Figure 2) was effective in the synthesis of industrially important explosive cyclotetramethylene tetranitramine [octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX)] by the nitrolysis of 3,7-dinitro-1,3,5,7-tetra-



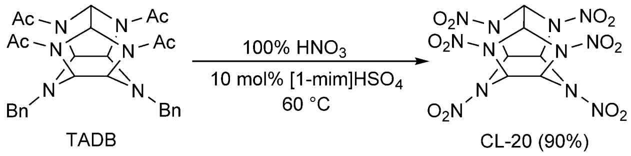
Scheme 3. Synthesis of RDX and HMX in ILs. Adapted from Refs. [87,89].

azabicyclo[3,3,1]nonane (DPT) using the $N_2O_5/HNO_3/NH_4NO_3$ nitrating system. The cooperative use of PEG$_{200}$-DAIL and N_2O_5 increased the yield of HMX up to 64%.[88] Furthermore, the starting DPT could be in turn prepared by the nitration of urea using a 98% HNO_3/20% oleum mixture in the presence of another TSIL (triethylbutylsulfonic acid hydrogen sulfate, [Tebsa][HSO_4]; Scheme 3).[89]

Nano-HMX particles were produced by spraying a raw HMX solution in [Hmim]Br into purified ice water. XRD measurements indicated that nanocrystals of the thus prepared HMX had the same energetically favorable β form as the raw HMX. Compared with raw HMX, the nano-HMX particles had a much lower impact sensitivity. However, they are easier to explode than raw HMX under thermal stimulus because of the lower values of peak temperature and activation energy.[90]

A one-pot methodology for the synthesis of an even more powerful explosive [2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane (CL-20)] through the nitration of 2,4,6,8-tetraacetyl-10,12-dibenzyl-2,4,6,8,10,12-hexaazaisowurtzitane (TADB) with fuming nitric acid in the presence of Brønsted-acidic ILs was recently developed.[91] Several ILs were tested in this reaction: 1-methylimidazolium hydrogen sulfate ([1-mim][HSO_4]), 3-methyl-1-sulfonic acid imidazolium chloride ([Msim][Cl]), and 1-methylimidazolium hydrogen formate ([1-mim]HCO_2). Under optimal conditions, which included the heating of a solvent-free TADB/HNO_3 mixture in 1:150 molar ratio at 60 °C in the presence of [1-mim][HSO_4] (10 mol%), CL-20 was produced in 90% yield. As it was stable under the proposed conditions, the IL could be reused several times and exhibited the same catalytic performance (Scheme 4).

SO_3H-functionalized Brønsted-acidic ILs appear to be promising promoters for the green synthesis of fused nitrogen heterocycles containing several energy-rich N–nitro groups. In combination with N_2O_5, they form a useful nitrating system for the efficient conversion of 1,4,5,8-tetraazabicyclo[4.4.0]decane (TAD) to 1,4,5,8-tetranitro-1,4,5,8-tetraazabicyclo[4.4.0]decane (TNAD).[92] Among the several tested ILs (e.g., [Hmim][X]; X = HSO_4, NO_3, OTs), the TSIL [SO_3H-bmim][HSO_4] (3 mol%) showed the best catalytic performance, with nitration proceeding under mild conditions, and the yield of TNAD was improved by 3–6% (Scheme 5).



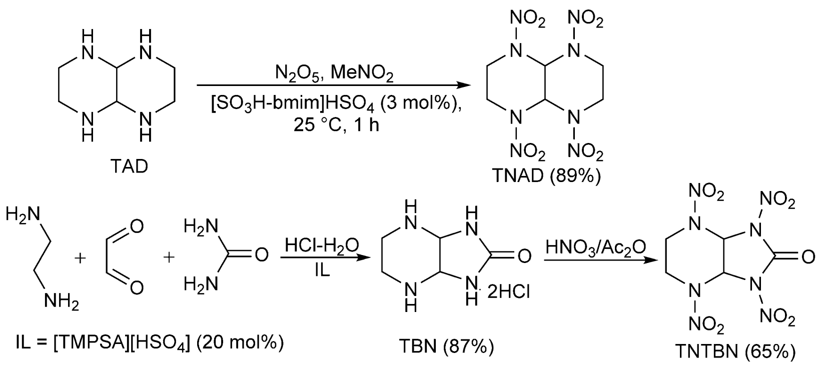
Scheme 4. IL-catalyzed synthesis of CL-20. Adapted from Ref. [91].

2,5,7,9-Tetrahydro-2,5,7,9-tetraazabicyclo[4.3.0]nonan-8-one dihydrochloride (TBN), which is a key precursor for another explosive, 2,5,7,9-tetranitro-2,5,7,9-tetraazabicyclo[4.3.0]nonan-8-one (TNTBN), was efficiently prepared by a three-component condensation of ethylenediamine, glyoxal, and urea catalyzed by a SO_3H-functionalized Brønsted-acidic IL [TMPSA][HSO_4] (Figure 2). Subsequent nitration of the TBN gave rise to the target compound TNTBN in good yield. The catalysts could be reused without a significant loss of the catalytic activity.[93]

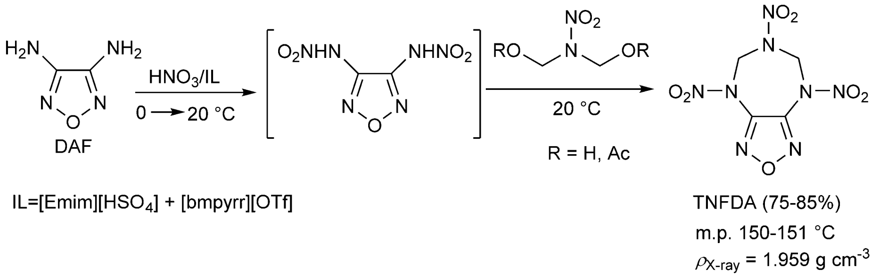
A high-energy bicyclic furazan derivative [4,6,8-trinitro-5,6,7,8-tetrahydro-4*H*-furazano[3,4-*f*][1,3,5]triazepine (TNFDA)], fused with an exhaustively nitrated triazepine ring was efficiently synthesized from available 3,4-diaminofurazan (DAF) in an acidic IL medium. The developed one-pot two-step procedure included the nitration of DAF with HNO_3 to afford intermediate 3,4-di(nitramino)furazan followed by the gradual addition of 2-nitroazapropane-1,3-diol or its acetate to the reaction mixture. The best overall TNFDA yield was obtained in the mixed-IL system consisting of [Emim][HSO_4] and [Bmpyrr][OTf] in a 1:2 ratio (Scheme 6).[94]

A convenient, environment-friendly synthesis of nitrobenzofuroxan (BF) from 2,4-dinitrochlorobenzene and sodium azide was developed in IL media. The reaction proceeded through the formation of the intermediate azidodinitrobenzene. Under optimal conditions, [Empyrr][BF_4] or [Empyrr][OTf] (Empyrr = 1-ethyl-1-methylpyrrolidinium)/Bu_4NBr (TBAB) (10 mol%) two-component IL system at 60 °C, excellent yields of BF (93–95%) were obtained. Benzodifuroxan (BDF) and the powerful hydrogen-free explosive benzotrifuroxan (BTF) were similarly prepared in high yields (Scheme 7).[95]

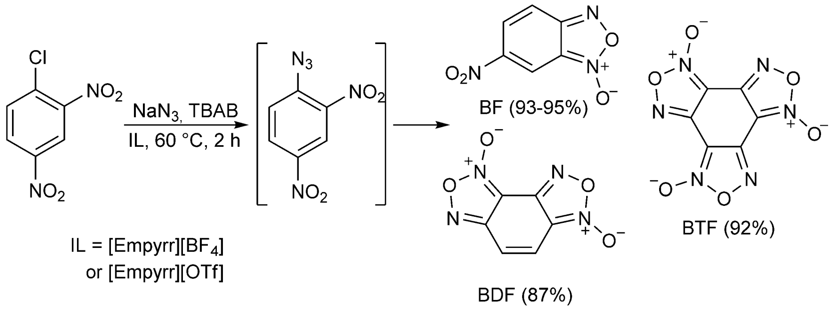
The high-energy oxidizer 3,4-dinitrofurazan (DNF) was synthesized from 3,4-diaminofurazan using a concentrated H_2SO_4/



Scheme 5. TSIL-assisted syntheses of TNAD and TNTBN. Adapted from Ref. [92,93].



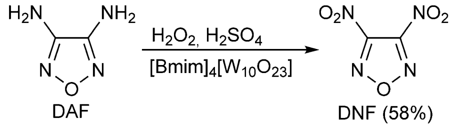
Scheme 6. One-pot synthesis of TNFDA in the IL medium (ρ: density; values in parentheses, also in the following schemes, correspond to yields). Adapted from Ref. [94].



Scheme 7. Synthesis of benzofuroxans in ILs (values in parentheses correspond to yields). Adapted from Ref. [95].

50% H_2O_2 mixture (1.0:1.5 molar ratio) in the presence of the 1-methyl-3-butylimidazolium decatungstate ($[Bmim]_4[W_{10}O_{23}]$) catalyst (0.2 mol%; Scheme 8).[96] The use of the IL metal salt instead of the conventional $Na_2WO_4 \cdot 2H_2O$ catalyst increased the DNF yield in the oxidation reaction significantly (from 39 to 58%).[97]

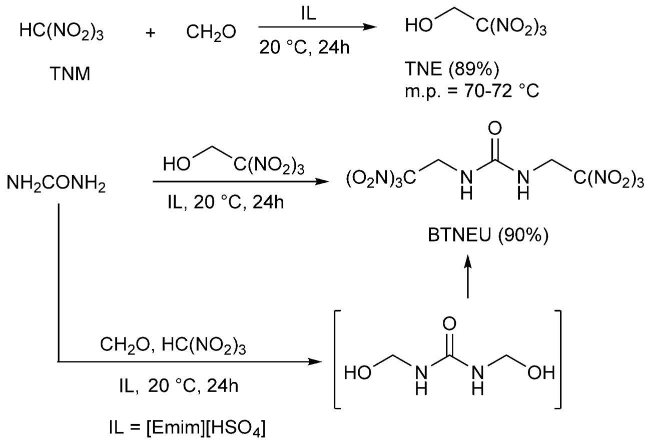
Trinitroethanol (TNE) is a useful building block for the preparation of a number of energetic compounds containing the trinitromethyl group. It is commonly synthesized by the Henry reaction of trinitromethane (TNM) with paraformaldehyde in CCl_4 at 60–65 °C followed by careful crystallization of the raw product. Imidazolium ILs accelerate and improve the selectivity of this reaction, yielding analytically pure TNE, which made the dangerous crystallization step unnecessary. The best TNE yield (89%) was reached in the acidic IL [Emim][HSO_4]. Furthermore, this readily recyclable IL could be reused four times without a noticeable decrease of the process efficiency (83–84% yield).[98] A similar protocol was applied successfully to the synthesis of 2,2-dinitropropane-1,3-diol from paraformaldehyde and dinitromethane (1:1); the latter was generated in situ through the acidic treatment of dinitromethane sodium salt. The IL [Emim]



Scheme 8. $[Bmim]_4[W_{10}O_{23}]$-catalyzed oxidation of diaminofurazan to dinitrofurazan. Adapted from Refs. [96,97].

[HSO$_4$] was an appropriate reaction medium and catalyst for the Mannich reaction of TNE with less-nucleophilic amines, such as urea and 4-aminofuroxans. The synthesis of 1,3-bis(2,2,2-trinitroethyl)urea (BTNEU) from urea and TNE was performed safely in [Emim][HSO$_4$] to afford the raw product in a high purity (further purification was not needed) in 90% yield. Here, a three-fold recyclability of the IL was also demonstrated (Scheme 9).

Although aminofuroxans are even weaker nucleophiles than urea, they could be efficiently converted to 4-(2,2,2-trinitroethylamino)furoxans (TNEAFO) by treatment with TNE in IL media. Imidazolium and pyrrolidinium ILs appeared suitable media for this transformation, among which [Bmpyrr][OTf] exhibited the best performance. A three-component version of the Mannich reaction, in which aminofuroxans, formaldehyde, and TNM were used as starting compounds and the [Bmpyrr][OTf] served as the solvent, afforded the same condensation products in acceptable yields. Thus prepared TNEAFO were converted to (2,2,2-trinitroethylnitroamino)furoxans (TNENAFO) under the action of the HNO$_3$/TFAA nitrating system in [Bmpyrr][OTf].[99] (2,2,2-Trinitroethylnitroamino)furazans (TNENAF) were obtained from the corresponding aminofurazans by a similar condensation/nitration reaction sequence in the IL medium and their physicochemical and energetic characteristics were determined (Scheme 10).[100]

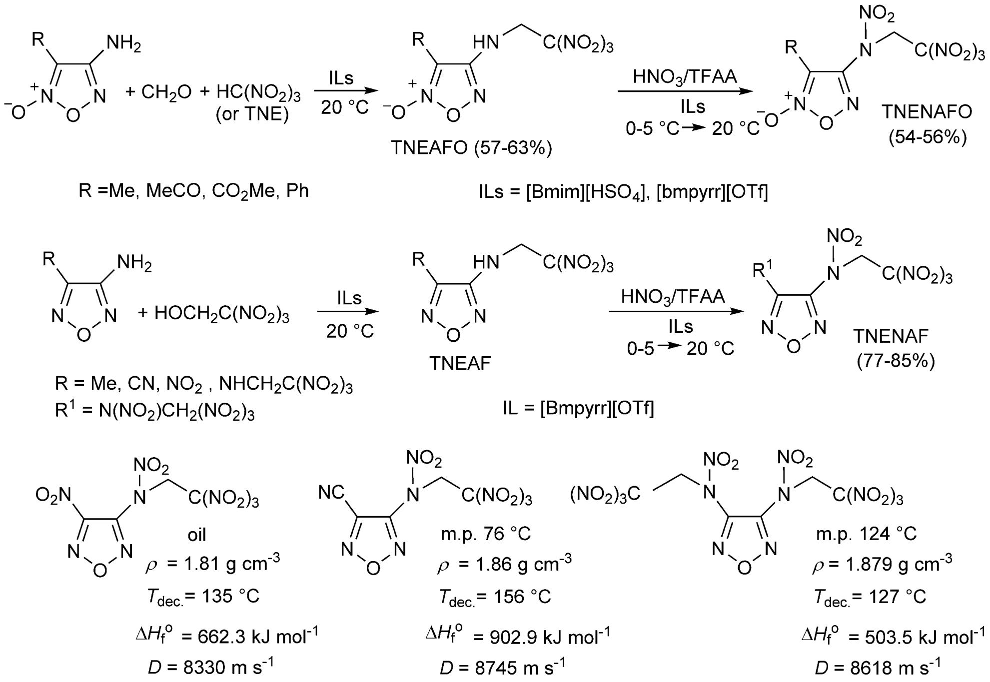


Scheme 9. Synthesis of trinitroethanol and bis(trinitroethyl)urea in [Emim][HSO$_4$]. Adapted from Ref. [98].

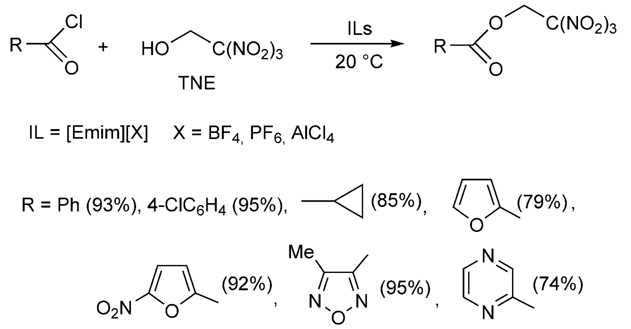
Acyl chlorides reacted smoothly with TNE in the imidazolium ILs with perhaloborate, phosphate, or aluminate anions to afford the corresponding trinitroethyl esters in 74–95% yield at ambient temperature, which is a significant improvement to known methods in which hazardous heating is needed. Although the esterification reactions proceeded faster in [Emim][AlCl$_4$] than in [Emim][BF$_4$] or [Emim][PF$_6$] media, high HEM yields were obtained in all mentioned ILs (Scheme 11).[101]

The catalytic system [Emim][AlCl$_4$]/FeCl$_3$ (5 mol%) promoted the reactions of CHCl$_3$ or CCl$_4$ with TNE or 2-fluoro-2,2-dinitroethanol (FDNE) efficiently, affording the corresponding orthoformates (TNEOF or TFDNEOF) and orthocarbonates (TNEOC or TFDNEOC) in high yields (Scheme 12). The esterification reactions proceeded faster under the proposed conditions than in organic solvents.[102]

These results clearly show that the application of ILs as reaction media and/or catalysts may significantly reduce undesirable explosion risks associated with the syntheses of energy-



Scheme 10. Synthesis of (trinitroethylamino)- and (trinitroethylnitramino)furazans and furoxans in ILs. Adapted from Refs. [99,100]. T_d = decomposition temperature; D = detonation velocity.



Scheme 11. Synthesis of trinitroethyl esters in the IL media. Adapted from Ref. [101].

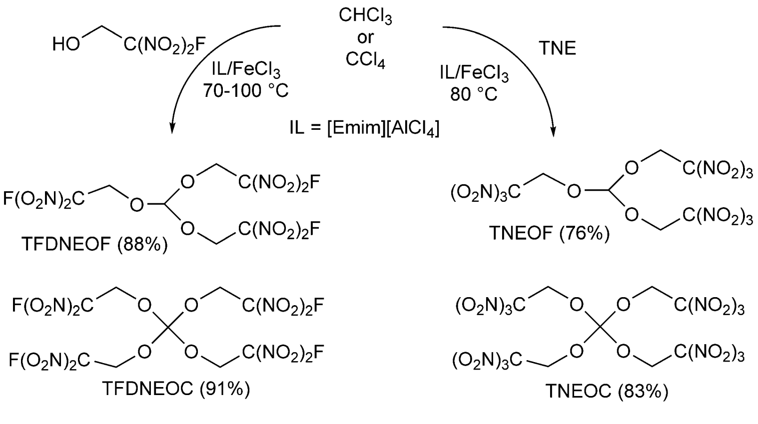
rich polynitro compounds (RDX, HMX, CL-20, etc.). The corresponding chemical reactions could be performed in this case under milder and/or safer conditions than in organic solvents, in particular, as one-pot processes, to afford target explosives in high yields. Therefore, the useful application of ILs to this specific area of organic chemistry may be considered as an important and prospective contribution to energetic material science.

2.3. IL-mediated preparation of other energetic compounds

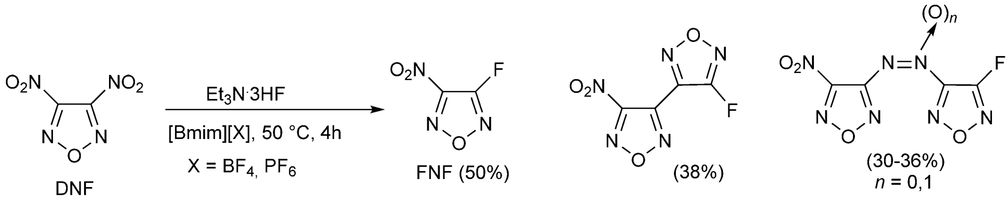
ILs may serve as useful ionic media and/or catalysts for the preparation of energetic compounds that contain high-energy structural moieties other than the nitro group (high-enthalpy heterocycles, carbocycles, azides, etc.).

A convenient synthesis of fluorofurazans based on nucleophilic substitution of the nitro group in nitrofurazan derivatives, particularly in dinitrofurazan (DNF), with the fluoride ion in the IL media ([Bmim][BF_4] or [Bmim][PF_6]) was developed. The hydrofluoric acid triethylammonium salt appeared a suitable source of the fluoride ion in the proposed conditions. As a result, several new liquid or low-melting high-energy fluoronitrofurazan derivatives became readily accessible via the developed procedure (Scheme 13).[103] It should be noted that $Et_3N{\cdot}3HF$ cannot convert DNF to fluoronitrofurazan (FNF) in conventional organic solvents (CH_3CN, $CHCl_3$).

High-enthalpy polynitrogen heterocycles, tetrazoles, are applied in materials science and medicinal chemistry as prospective explosives, components of information recording systems, and carboxylic acid surrogates.[104,105] They are commonly synthesized by the [3+2] cycloaddition of metal or organic azides to nitriles in organic solvents. These reactions that involve explosive and toxic azide substrates and intermediates require high temperatures (>100 °C), which makes them dangerous. The replacement of organic solvents with ILs capable of keeping volatile hazardous byproducts (especially, HN_3) in the ionic media by Coulombic interactions, accelerated the reactions and reduced the explosion and poisoning risks significantly. The acidic IL [Emim][HSO_4] was a substrate-specific reaction medium and catalyst for the synthesis of 5-substituted 1*H*-tetrazoles, and [Bmim][BF_4] or [Bmim][PF_6] were suitable for the preparation of 1,5-disubstituted tetrazoles (Scheme 14).[106] 5-Substituted 1*H*-tetrazoles were prepared in moderate-to-high yields (42–98 %) by the 4-(*N*,*N*-dimethylamino)pyridinium acetate catalyzed [3+2] cycloaddition of NaN_3 to cyanoarenes



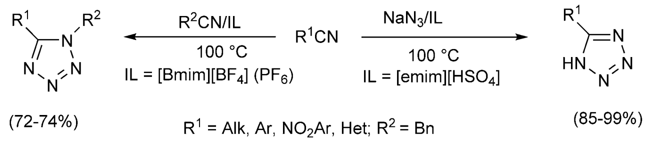
Scheme 12. Synthesis of TNE- or FDNE-based orthoformates and orthocarbonates in the IL/$FeCl_3$ system. Adapted from Ref. [102].



Scheme 13. Synthesis of fluoronitrofurazans in ILs. Adapted from Ref. [103].

(heteroarenes) under solvent-free conditions. This method is also suitable for the selective conversion of dinitriles to cyanotetrazoles.[107]

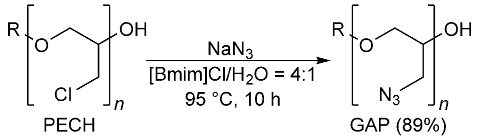
Glycidyl azide polymers (GAP), important components of high-energy binders,[108] were efficiently prepared by the reaction of polyepichlorohydrin (PECH) prepolymer with sodium azide in a [Bmim]Cl/water (4:1) mixture without a catalyst (Scheme 15).[109] The method eliminates solvent pollution and simplifies the reaction postprocessing.



Scheme 14. IL-promoted syntheses of tetrazoles. Adapted from Ref. [106].

3,4-Dinitrofuroxan (DNFO) tends to generate nitroformonitrile oxide (NFNO) at room temperature through the cycloreversion reaction.[110] This reactivity pattern opens a convenient synthetic route to 3-nitroisoxazoles and 3-nitroisoxazolines, which can be employed to synthesize libraries of these valuable compounds. The method is based on the [3+2] cycloaddition of in situ-generated NFNO to acetylenes or olefins in the presence of [Bmim][BF_4] (40 mol%). It is also applicable to the synthesis of 1,2,4-oxadiazole and 1,2,4-dioxazole nitro derivatives through cycloaddition reactions of NFNO with trichloroacetonitrile or hexafluoroacetone, correspondingly (Scheme 16).[111,112]

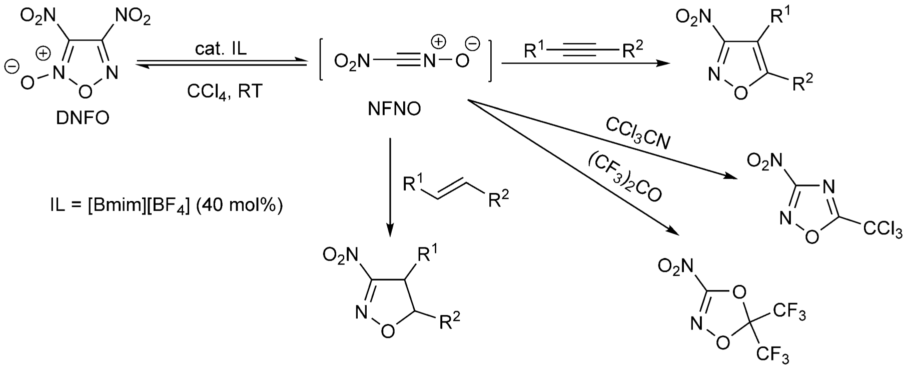
A promising green alternative to the practically important $AlCl_3$-promoted isomerization of *endo*-tetrahydrodicyclopentadiene (THDCPD) to the corresponding *exo* isomer and, finally, to adamantane is based on the use of a dialkylimidazolium chloride/$AlCl_3$ catalytic system. *exo*-THDCPD constitutes the standard high-energy-density Jet Propellant-10 fuel (JP-10)[113,114] with an approximately 20% higher volumetric energy (39.6 MJ L^{-1}) than conventional petroleum distillates. The lower freezing point (−79 °C) and higher flash point (54 °C) of *exo*-THDCPD meet the requirements of both land and air applications. The IL/$AlCl_3$-promoted catalytic *endo*/*exo* isomerization occurs efficiently under mild conditions (Scheme 17) with conversion and selectivity values beyond 98%. Further isomerization of *exo*-THDCPD to adamantane requires a higher temperature and longer exposure time. The IL-based procedure is superior to conventional methods in terms of low energy consumption and environmental friendliness.[115]



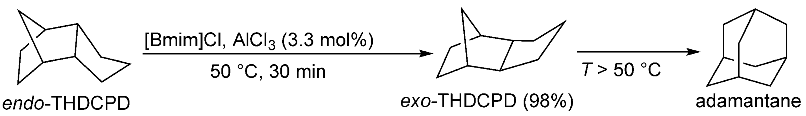
Scheme 15. Synthesis of glycidyl azide polymers in aqueous IL. Adapted from Ref. [109].

2.4. Nitrosation and nitration reactions with IL-based reagents

The TSILs containing active nitrite or nitrate anions may act not only as solvents or catalysts but sometimes as reagents for the nitrosation and nitration reactions. In particular, the new dicationic IL 1-methyl-3-{2-[2-(1-methyl-1*H*-imidazol-3-ium-3-yl)ethyloxy]ethyl}-1*H*-imidazol-3-ium dinitrite (DNIL) was synthesized and used in combination with HCl as a convenient ni-



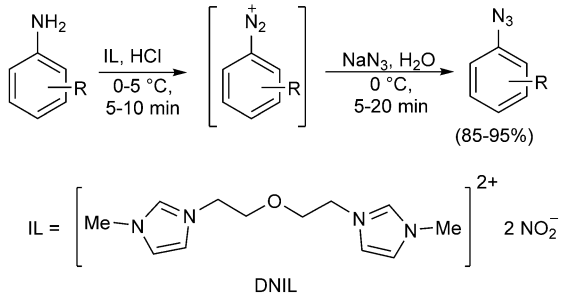
Scheme 16. IL-promoted syntheses of *N*,*O*-heterocycles nitro derivatives from DNFO by [3+2] cycloaddition reactions. Adapted from Refs. [111,112].



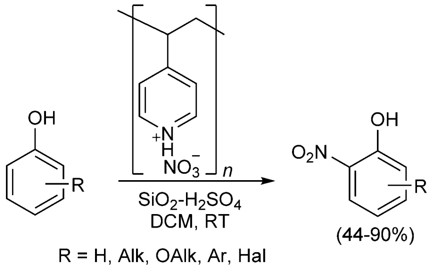
Scheme 17. IL-promoted *endo*/*exo* isomerization of THDCPD and the adamantane synthesis. Adapted from Ref. [115].

trosonium source in the diazotization of aryl amines to the corresponding diazonium salts. The latter were converted to aryl azides in nearly quantitative yields by the Sandmeyer reaction with sodium azide in water (Scheme 18).[116] DNIL is an easier-to-handle nitrosating agent than conventional HNO_2 and it can be stored for several months without a significant loss of activity. Important advantages of this methodology are the high efficiency and selectivity and mild reaction conditions, which avoid the need for toxic reagents and solvents.

A mixture of an IL-like poly(4-vinylpyridinium) nitrate and silica sulfuric acid in dichloromethane was used to perform regioselective *ortho*-nitration of phenol derivatives. The reaction proceeded under heterogeneous conditions and afforded the corresponding *o*-nitrophenols in moderate-to-high yields (Scheme 19).[117]



Scheme 18. DNIL-assisted conversion of anilines to arylazides. Adapted from Ref. [116].



Scheme 19. Regioselective nitration of phenols with poly(4-vinylpyridinium) nitrate. Adapted from Ref. [117]. DCM = dichloromethane.

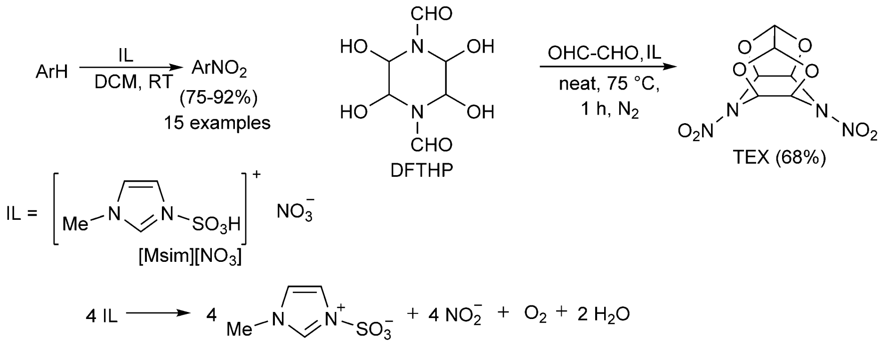
Another TSIL-based nitrating agent, 1-methyl-3-hydroxysulfonyl imidazolium nitrate ([Msim][NO_3]), was recently synthesized by the treatment of 1-methylimidazole with chlorosulfonic acid followed by the anion metathesis reaction. [Msim][NO_3] was useful for the nitration of arenes (in particular, aniline derivatives)[118] and 1,4-diformyl-2,3,5,6-tetrahydroxypiperazine (DFTHP), a precursor to the highly energetic 4,10-dinitro-2,6,8,12-tetraoxa-4,10-diazatetracyclo[5.5.0.$0^{5,9}0^{3,11}$]dodecane (TEX) scaffold (Scheme 20).[119] The authors believe that the true nitrating reagent in both reactions is the nitrite radical generated in situ from [Msim][NO_3] under the reaction conditions. The radical was trapped by iodine and butylated hydroxytoluene.

2.5. EILs

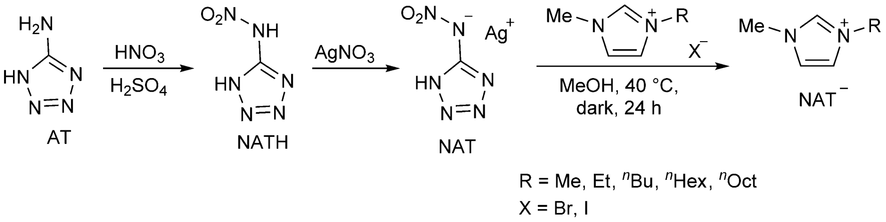
Low-melting energetic salts (m.p. ≤ 100 °C) have all the advantages of ILs: low vapor pressure, high thermal stability, high density, safe handling (e.g., low sensitivity to impact, friction, and electric discharge), low toxicity, and simple production routes, which make them ideal candidates to minimize the hazardous conditions associated with handling, processing, and transportation of explosive materials. Therefore, EILs are currently considered to be promising components for green propellants.[13,54,120–123] There are two types of EILs. The first type includes "oxygen-balanced" EILs, which contain a high-enthalpy polynitrogen organic cation (e.g., guanidinium, imidazolium, triazolium, or tetrazolium) along with an oxygen-rich anion (e.g., ClO_4, NO_3, $N(NO_2)_2$, or $C(NO_2)_3$). The second type includes hypergolic ILs, which ignite instantly upon contact with an appropriate oxidizer. The former can be used as components of various high-energy formulations, including monopropellants, whereas the latter are considered as useful components for bipropellants.

2.5.1. Oxygen-balanced EILs

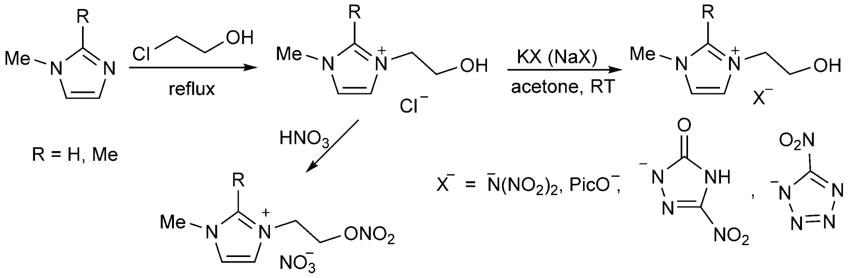
The concept of EILs was first proposed in 2003 for 1,2,3- and 1,2,4-triazolium salts bearing the NO_3, ClO_4, or $N(NO_2)_2$ anions.[124] The authors defined these compounds as new, highly energetic members of the intensively advancing class of materials identified as ILs. Since then, a large number of other



Scheme 20. Nitration of arenes and DFTHP with [Msim][NO_3]. Adapted from Ref. [119].



Scheme 21. Synthesis of imidazolium nitraminotetrazolate EILs. Adapted from Ref. [125].



Scheme 22. Imidazolium-based EILs with O-rich anions. Adapted from Ref. [127]. PicO = picrate.

oxygen-balanced (mainly CO-balanced) EILs were synthesized and discussed in several review articles.[13,41,51] Herein, we consider only recent results published, that is, from the past two years.

1-Methyl-3-alkylimidazolium-based EILs with 5-nitroaminotetrazolate anion (NAT^-) were prepared in high yields by a three-step procedure that included the acidic nitration of 5-aminotetrazole (AT), transformation of resulting nitraminotetrazole (NATH) to its Ag salt, and replacement of the Ag^+ cation with an imidazolium cation in the presence of the corresponding imidazolium halide (Scheme 21).[125] The synthesized EILs contain modest accumulated energy. However, they are thermally stable, have a low sensitivity to impact and friction, and do not generate environmentally harmful gases upon decomposition.

A complex theoretical study of EILs containing the Emim cation and nitrotetrazolate, dinitramide, or dicyanamide anion was performed using the high-accuracy G3MP2 (MP2 = Møller–Plesset perturbation theory second order) method and the M06L, M05-2X, M06-2X, and B3LYP DFT methods.[126] The nitrogen-enriched EILs had thermochemical, fluid, and specific impulse (I_{sp}) properties comparable with or superior to those of conventional ILs. The binding energies were in the range of 336–400 kJ mol^{-1} at DFT levels, and the atomization procedure used to compute their heats of formation (ΔH_f^0) at the G3MP2 level produced results in very close agreement with available experimental data (maximum deviation < 5 %). The highly positive enthalpy of formation ($\Delta H_f^0 = 167$–559 kJ mol^{-1}) confirmed the high-energy state of the prepared ILs.

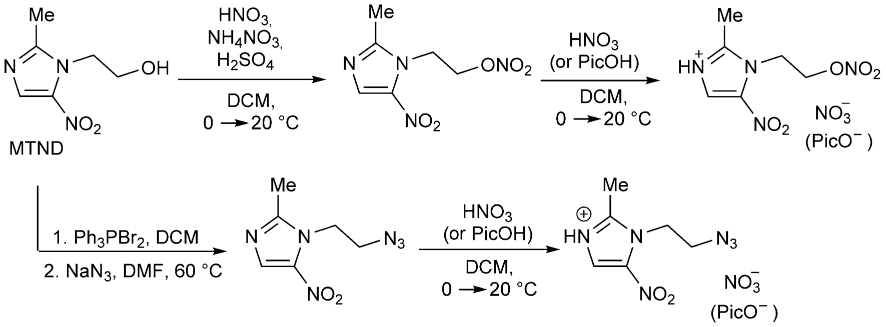
1-Methyl-3-hydroxyethyl- and 1-methyl-3-nitroxyethylimidazolium salts with oxygen-rich anions were synthesized by a sequence of quaternization, nitration, and anion metathesis reactions (Scheme 22).[127] According to thermogravimetric analysis and differential scanning calorimetry data, these EILs exhibited promising thermal stabilities (the decomposition points were ≈160 °C for *N*-nitroxyethylimidazolium nitrate and > 190 °C for *N*-(hydroxyethyl)imidazolium). The calculated densities, standard enthalpies of formation, and detonation parameters rank them as promising high-energy materials.

A known antimicrobial agent, metronidazole (MTND), was transformed into the corresponding nitroxyethyl and azidoethyl derivatives by nitration or azidation reactions. Subsequent treatment of the latter with nitric or picric acids under mild conditions afforded the corresponding EILs bearing protonated imidazolium cations and the nitrate or picrate anions. Unfortunately, the prepared energetic materials had moderate decomposition temperatures (Scheme 23).[128]

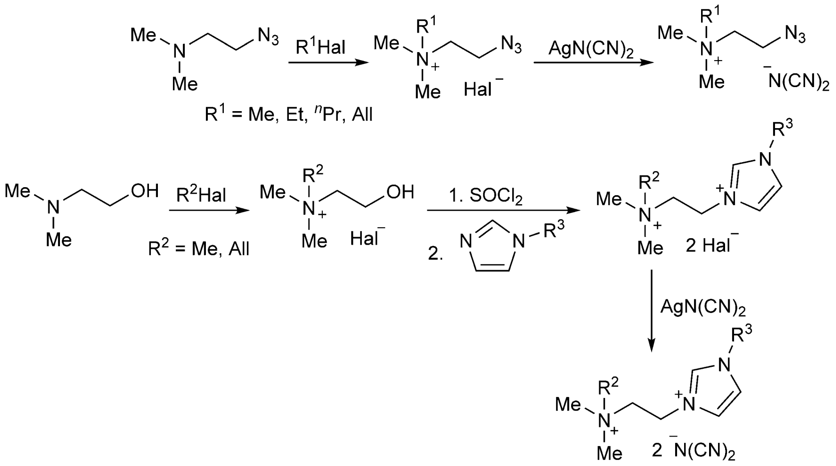
Two simple models were proposed to correlate the thermal stability with the elemental composition and structural features of imidazolium-based EILs. The first takes into account the number of selected atoms in cation and anion units. Another suitable correction term was added to the second model to adjust the predicted results with specific cation/anion moieties. Experimental data for 164 imidazolium-based EILs were used to create new correlations in this model. Both models were tested and compared with the available group contribution method for 17 imidazolium-based EILs with complex molecular structures.[129] The obtained theoretical results were in agreement with those predicted by the group contribution method.

2.5.2. Hypergolic ILs

Commonly, carcinogenic, highly volatile, and toxic hydrazine derivatives are used as principal components of bipropellant rocket fuels in combination with powerful oxidants such as di-



Scheme 23. Synthesis of MTND-based EILs. Adapted from Ref. [128].



Scheme 24. Hypergolic ILs that bear propan-2-ylidene methanetriamium cations and dicyanamide anion. Adapted from Ref. [131]. All = allyl.

nitrogen tetroxide (N_2O_4) and white fuming nitric acid (WFNA). Such mixtures are referred to as hypergolic bipropellants and ignite upon the contact of hydrazine fuel with a suitable oxidizer because of the highly exothermic redox reaction.[13] Some EILs that have an appropriate composition and low toxicity appear to be promising alternatives to hydrazine derivatives.

The breakthrough idea to replace hydrazine with hypergolic dicyanamide-based ILs in bipropellant formulations, which was proposed in 2008,[120] opened an important and promising research area and encouraged chemists to search for more environmentally benign hypergolic EILs and to explore their potential as nontoxic aerospace propellants. Nowadays, high-performance hypergolic ILs have become a hotspot in the field of IL chemistry and have been surveyed in excellent recent reviews.[51,52,129,130] The ideal IL substituents for hypergolic hydrazine derivatives must meet a number of important criteria, including short ignition delay (ID) time, low viscosity, sufficient conductivity, high density, and thermal stability. The search for promising IL candidates is based on a wide choice of IL anions and a broad variation of the cation structure. The shortest ID times were obtained for hypergolic ILs with polynitrogen heterocyclic cations and B-based anions (e.g., $BH_2(CN)_2$). Significant attention has also been paid to the synthesis of new dicyanamide-based hypergolic ILs.[131]

Three new hypergolic ILs containing propan-2-ylidene methanetriamium cations and dicyanamide anions were synthesized from the corresponding mono-, di-, and triaminoguanidine hydrochlorides by anion metathesis and characterized by using microanalysis, spectroscopy, and thermogravimetry-differential thermal analysis (TG-DTA) (Scheme 24).[131] The synthesized ILs showed prominent hypergolic properties with WFNA and exhibited potential as bipropellants; however, their ID times were inferior (56–138 ms) to that of unsymmetrical dimethylhydrazine (UDMH; 4.8 ms).[132]

ILs (m.p. $< 100\,^{\circ}C$) that contained imidazolium, 1,2,4-triazolium, pyrrolidinium, or pyridinium-derived cations and dicyanamide, azide, or nitrocyanamide anions (Figure 3) were synthesized by treatment of corresponding halide-based ILs (Cl, Br, I) with Ag salts of the respective N–H acids. Key physical, thermal, and ignition properties of the prepared ILs were determined to evaluate their potential as hypergolic fuels.[54] The best ID time (19 ms) with WFNA was found for 3-methyl-1-propargylimidazolium dicyanamide.

Interesting dicyanamide-based ILs containing (azidoethyl)-trialkylammonium cations or tetraalkylammonium/dialkylimidazolium doubly charged counterparts were recently reported (Scheme 25).[133] The thermal stability of ILs bearing doubly charged cations was higher than that of their singly charged

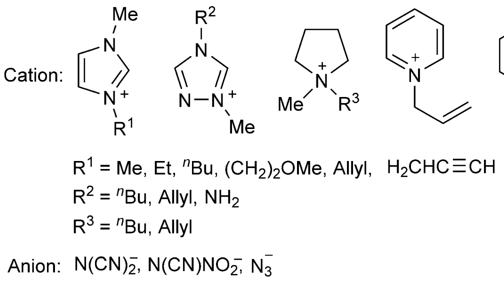


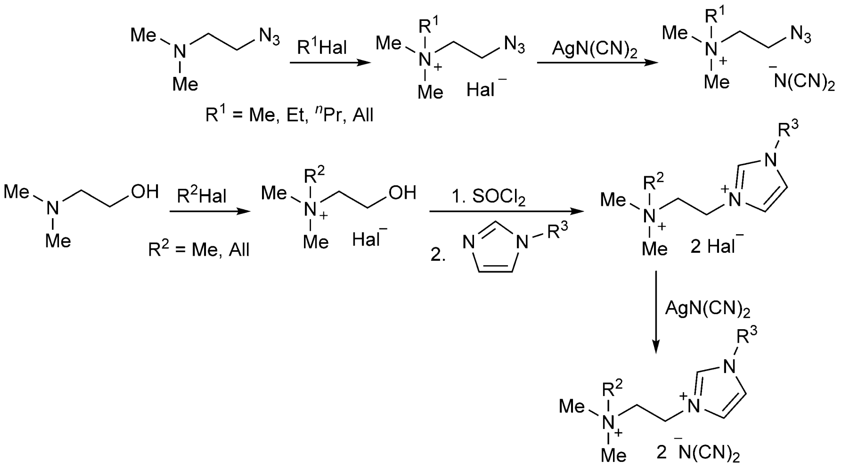
Figure 3. Potential hypergolic ILs.

analogs. All synthesized compounds exhibited moderate-to-high hypergolic activity (ID times were 13–63 ms according to droplet tests with WFNA). The obtained results attested the potential applicability of several candidates as bipropellant components or monopropellant energetic additives.

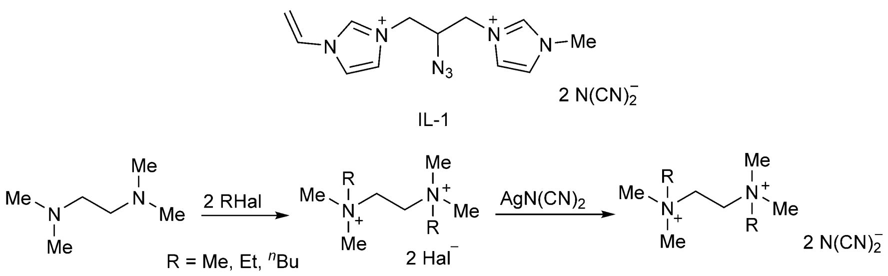
ILs that contain doubly charged bisimidazolium cations with incorporated azido groups (e.g., IL-1) and two dicyanamide anions were prepared recently by using a similar synthetic route (Scheme 26).[134] More bistetraalkylammonium-based analogs were also synthesized from tetramethylethylenediamine in two steps, which included double N-alkylation with the corresponding alkyl halide followed by replacement of the halide anions by dicyanamide anions.[135] These C_2-symmetrical doubly charged cationic ILs had a high thermal stability (T_d up to 200 °C) and promising density (1.02–1.22 g cm^{-3}) and heat of formation values (85.1–154.4 kJ mol^{-1}). These data, along with their reasonable ID times (84 ms with WFNA), make this class of hypergolic ILs a promising platform for the design of efficient and green bipropellant fuels.

Two series of superbase-derived hypergolic ILs containing 1,5-diazabicyclo[4.3.0]non-5-ene (DBN) or 1,8-diazabicyclo-[5.4.0]undec-7-ene (DBU) cations and dicyanamide or cyanoborohydride anions were produced by means of standard synthetic routes (Scheme 27).[136] Among these new energetic ionic materials, 11 salts were liquid at ambient temperature. Some of them exhibited promising hypergolic properties (ID time <50 ms with WFNA). The densities of these ionic compounds ranged from 1.00 to 1.22 g cm^{-3}, and their heats of formation varied between 38.0 and 478.6 kJ mol^{-1}. Surprisingly, the new ILs possessed unexpectedly high thermal stabilities (T_d > 280 °C), and the allylated DBN/dicyanamide derivative had the highest T_d value (310 °C) of known hypergolic ILs. The EILs with a pyridinium cation and dicyanamide or cyanoborohydride anions had similar characteristics, which are attractive for liquid bipropellant formulations.[137]

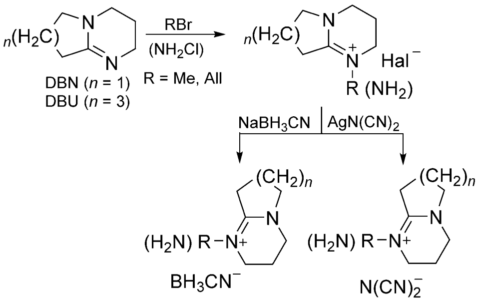
Another promising type of hypergolic ILs developed recently consisted of N-rich salts with (2-methyltetrazol-5-yl)diazotate anions and ammonia-, hydrazine-, or guanidine(aminoguanidine)-derived cations.[138] The key (2-methyltetrazol-5-yl)diazotic



Scheme 25. Preparation of dicyanamide-based hypergolic ILs that bear singly or doubly cations. Adapted from Ref. [133].



Scheme 26. Synthesis of symmetrical doubly charged cationic EILs with dicyanamide anions. Adapted from Refs. [134,135].



Scheme 27. DBN and DBU-based hypergolic ILs with dicyanamide or cyanoborohydride anions. Adapted from Ref. [136].

acid (MTDA) was produced in high yield by the diazotization of 5-amino-2-methyltetrazole with isoamyl nitrite. MTDA readily gave rise to ammonium or hydrazinium salts with aqueous ammonia or hydrazine-hydrate, respectively. The corresponding guanidinium, aminoguanidinium, diaminoguanidinium, or triaminoguanidinium salts were prepared in 65–92% overall yields by a two-step procedure that included the treatment of MTDA with barium hydroxide followed by the anion metathesis reactions of barium MTDA with the respective guanidinium-derived sulfates. The special properties of these N-rich salts revealed their high potential as hypergolic ILs (Scheme 28).

Interesting ILs with 5-cyanotetrazolide anion ($C_2N_5^-$) and different cations (Emim, Bmim, Bmpyr], and Me_4Gu (tetramethylguanidine) were prepared by the [3+2] cycloaddition of Cat^+ N_3^- to cyanogen.[139] According to the TGA, cyclic voltammetry, viscosimetry, and impedance spectroscopy data, the prepared 1-butyl-1-methylpyrrolidinium 5-cyanotetrazolide [Bmpyrr] [C_2N_5] had a high thermal stability (up to 230 °C), wide electrochemical window (4.5 V), moderate viscosity (25 mPa s^{-1} at 20 °C), reasonable ionic conductivity (5.4 mS cm^{-1} at 20 °C), and could be recommended as a promising electrolyte for lithium-ion batteries.

Gao and Shreeve contributed significantly to the area of high-performance hypergolic ILs[140] by designing new types of ILs with the 2,2-dimethyltriazanium (DMTA)[141] and bis(1-allyl-1*H*-imidazole-3-yl)dihydroboronium[129] cations. The recent research activity of this group mainly focused on exploring hypergolic ILs with H-rich anions, in particular, borohydride (BH_4^-)[132] and dicyanoborate ($BH_2(CN)_2^-$) anions (Figure 4).[142] These ILs possess improved physicochemical and hypergolic properties and meet nearly all of the important criteria of an ideal propellant fuel including low melting point, low viscosity, high thermal stability, and extremely short ID time (<5 ms with WFNA).[129]

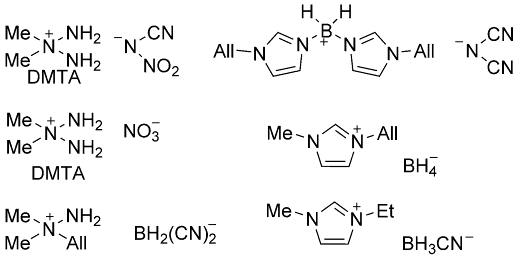
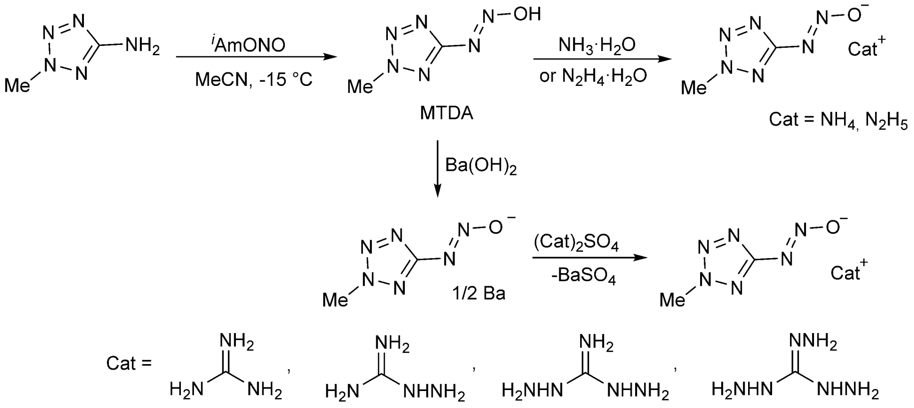


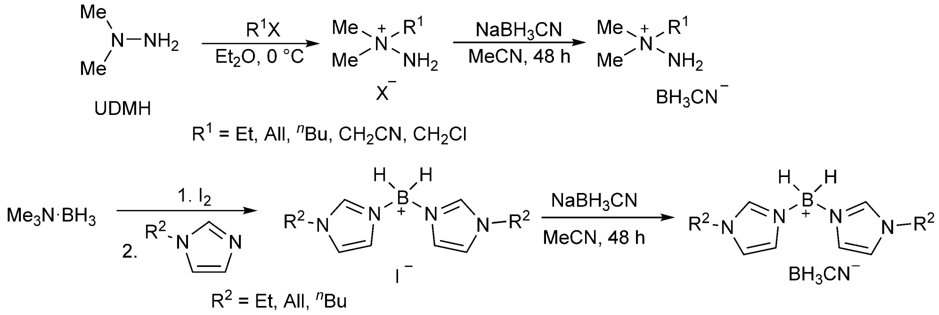
Figure 4. Promising types of hypergolic ILs developed by Gao and Shreeve. Adapted from Refs. [140–142].

Potentially useful ILs with 1,1,1-trialkylhydrazinium or bis(1-alkyl-1*H*-imidazol-3-yl)dihydroboronium cations and the cyanoborohydride anion were synthesized by Schreeve et al. (Scheme 29).[143] These ILs, comparable with UDMH in terms of their hypergolic performance, have some unique advantages, in particular, negligible vapor pressure and very short ID time (<10 ms with WFNA). Furthermore, they can be readily synthesized and stored over a long period of time, which is an important requirement for bipropellant components.

Promising imidazolium- and pyrrolidinium-based hypergolic ILs with the borohydride anion were also prepared using an efficient synthetic pathway that did not require toxic UDMH, ammonia, or halide precursors (Scheme 30).[144] Some of them had unique properties, in particular, a high density (0.85–0.93 vs. 0.78 g cm^{-1} for UDMH), prominent specific impulse value (I_{sp} up to 213 vs. 198 s for UDMH), positive heat of formation, and ultrafast ID time (≤3 ms with WFNA). Unfortunately, the borohydride-derived ILs are moisture sensitive and need to be protected from water by, for example, hydrophobic encapsulation.

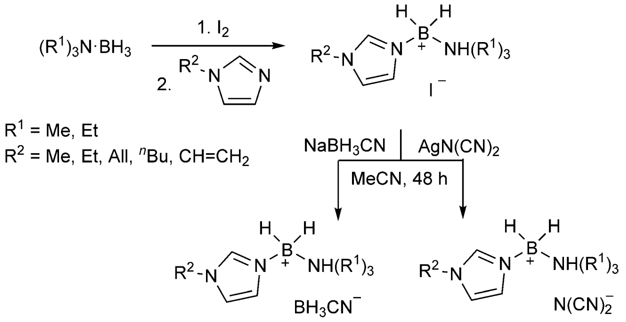


Scheme 28. MTDA-based hypergolic ILs with polynitrogen cations. Adapted from Ref. [138].



Scheme 29. Synthesis of cyanoborohydride-based hypergolic ILs that contain 1,1,1-trialkylhydrazinium or bis(1-alkyl-1*H*-imidazole-3-yl)dihydroboronium cations. Adapted from Ref. [143].

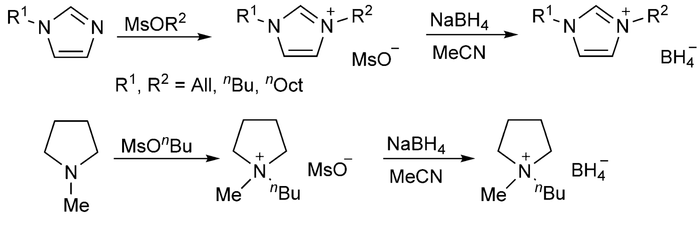
The same synthetic approach was utilized for the preparation of unsymmetrical hypergolic ILs with imidazolyl–amine–BH_2 cations and dicyanamide or cyanoborohydride anions.[145] The complexation of amines with the borane unit endowed the complexes with hypergolic behavior (ID time of 20–40 ms with WFNA). Among the synthesized ILs, moisture-stable structures were identified. Recently, similar hypergolic ILs bearing extended alkyl groups were synthesized from trialkylaminoboranes and alkylimidazole (1:1 ratio) in the presence of iodine (0.5 equiv.) followed by the anion metathesis reaction with $NaBH_3CN$ or $AgN(CN)_2$ (Scheme 31).[146] Promising characteristics of the cyanoborohydride salt leader (R^1 = Me, R^2 = All; I_{sp} = 204 s, ID time 14 ms, good thermal stability) confirm the potential of such ILs as prospective green propellant components.



Scheme 31. Synthesis of dihydroboronium ILs that consist of dicyanamide or cyanoborohydride anions. Adapted from Refs. [145,146].

Several attempts have been made to predict the physicochemical properties of hypergolic ILs by using quantum chemical calculations. In particular, the quantitative structure–property relationship method (QSPR)[147] was used to predict their ID times based on linear correlations using a set of descriptors, which define electrostatics, hydrogen bonding, and other structural features of ILs. Despite the satisfactory correlation of the theoretical descriptors determined from the QSPR calculations with experimental data for four dozen ILs, the authors had to admit that further efforts should be made to enlarge the size of the experimental training set.

Hypergolic reactions of ILs with oxidizers (e.g., WFNA) start with the protonation of the IL anion. To estimate the cation impact, an ab initio study of cation proton affinity and proton transfer energy was performed for a set of cations at the MP2 level of theory.[148] Specifically, guanidinium, dimethyltriazanium, triethylammonium, *N*-ethyl-*N*-methylpyrrolidinium, *N*-ethylpyridinium, 1,4-dimethyl-1,2,4-triazolium, 1-ethyl-4-methyl-1,2,4-triazolium, and 1-butyl-4-methyl-1,2,4-triazolium cations were studied. The proton-transfer energies from the cations to a set of anions studied previously were calculated; an inverse correlation between the latter and the likelihood that the cation/anion combination will react hypergolically with WFNA was found. It was suggested that this correlation is attributable to a balance between the energy released by the proton transfer and the rate of proton transfer determined by the ionicity of the IL.



Scheme 30. Synthesis of imidazolium- and pyrrolidinium-based hypergolic ILs with the borohydride anion. Adapted from Ref. [144].

In summary, the obtained data show that the utilization of ILs as solvents, catalysts, reagents, or products reduce the environment pollution and explosion risks significantly for diverse dangerous processes associated with HEM synthesis and handling. ILs offer considerable advantages over conventional organic solvents because of their lower vapor pressure, liquidity over a wide temperature range, high thermal stability, ionic conductivity, and variability of the chemical and physicochemical properties. Furthermore, they accelerate the dangerous syntheses of HEMs, which permits them to be conducted at lower temperature and makes them safer. Energetic ILs developed recently possessing useful physicochemical properties may find application in various high-energy formulations, including mono- and bipropellant compositions.

3. Preparation and Processing of Energetic Materials in Sub- or Supercritical Fluids

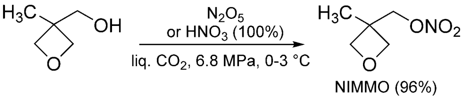
Along with ILs, available dense gases of natural or synthetic origin in the liquid or supercritical state have attracted considerable attention over the past decades as cheap and environmentally friendly media and tools for the green synthesis and processing of HEMs. As a result of their specific physicochemical properties, in particular nonflammability, high heat capacity (for CO_2, $C_p = 6.35\,J\,g^{-1}\,K^{-1}$ at 25 °C and a pressure of 6.4 MPa[149] cf. for dichloromethane, $C_p = 1.70\,J\,g^{-1}\,K^{-1}$ at 20 °C[150]), and resistance to strong oxidants (nitrating agents), the dense gases, first of all CO_2 and lower fluorinated hydrocarbons (freons), are particularly attractive as green media for nitration reactions, an important class of chemical reactions used widely to manufacture HEMs.[49,50] Another promising HEM-oriented application area for SCFs includes supercritical micronization techniques.[58] The latter are considered as promising alternatives to conventional precipitation methods as they allow the significant reduction of particle size and strict control over their morphology and size distribution by varying the SCF process parameters. Furthermore, SCFs may serve as promising substitutes of organic solvents in HEM processing, which makes them less harmful for the environment and applicable for the production of unique types of energetic compositions. Notably, the use of industrially available CO_2 derived from manmade sources could be considered as a form of sequestration, although the sequestered volumes are still not high.

3.1. Nitration reactions in liquefied gases or supercritical fluids

The key energetic components of explosives, powders, and solid propellants contain nitro groups. Therefore, it is not surprising that their production is usually based on nitration reactions. In industry, nitration reactions are commonly performed using a large excess of mixed acids (e.g., HNO_3/H_2SO_4), which act as both the nitrating agent and reaction medium.[151,152] These processes are harmful for the environment as huge amounts of acidic wastes are produced, which require expensive and energy-consuming disposal.[153,154] A promising approach to address these environmental issues is based on the use of H_2SO_4-free N_2O_5/liquefied gases or a SCF nitrating system. The N_2O_5 is an active and versatile nitrating agent, which can be prepared easily in a laboratory and in industry by the oxidation of available N_2O_4 with O_3.[155] Other important advantages of N_2O_5 over conventional nitrating agents are the higher regioselectivity for the nitration of polyfunctional substrates, simplicity of product isolation, and ease of temperature control.[49] However, some industrially available gases (CO_2 or freons) in either the liquid or supercritical state are advantageous with regard to being a safe and inert solvent that can be easily separated from the reaction products by simple decompression. Importantly, N_2O_5 is highly soluble in dense CO_2 and freons, which allows the corresponding nitration reactions to be performed under homogeneous conditions. In some cases, a 100 % nitric acid/liquid CO_2 mixture may also be suitable as a green reagent/solvent system for the nitration of active substrates.

3.1.1. O-Nitration reactions

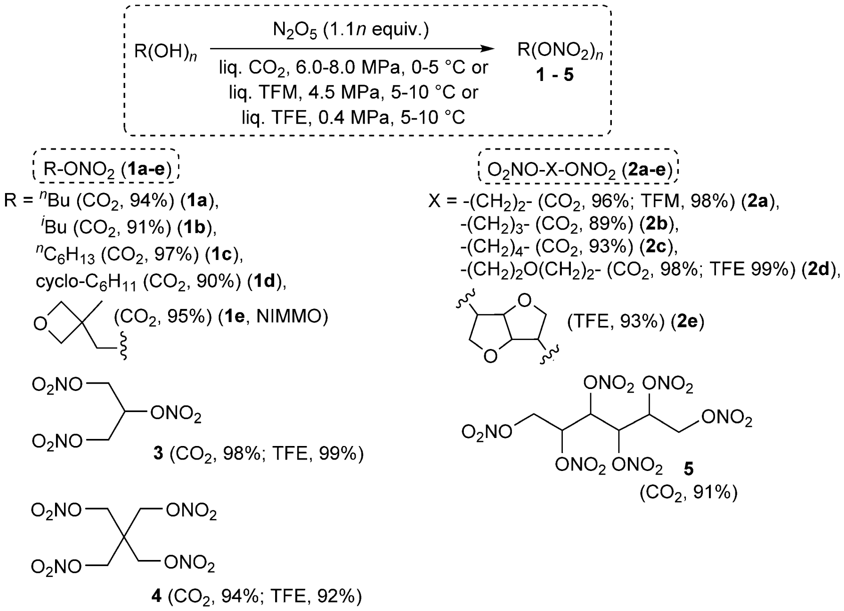
Nitroesters represent one of the most important types of HEMs. Nitroglycerin (NG) and nitrocellulose (NC) have found a large-scale industrial application as key components of powders and propellants.[156] Furthermore, NG has been used widely for decades as an efficient remedy for the treatment of cardiovascular diseases.[157,158] The first nitration in CO_2 medium was the synthesis of an energetic polymer precursor, 3-nitroxymethyl-3-methyloxetane (NIMMO; Scheme 32).[159,160] The reaction was performed by the addition of 3-methyl-3-oxetanemethanol to a solution of nitrating agent (N_2O_5 or 100 % nitric acid) in liquid CO_2 at −5 °C and 6.8 MPa to afford the corresponding nitrate NIMMO in 96 % yield. For comparison, the corresponding reaction performed in dichloromethane was complicated by the partial (≈10 %) oligomerization of the produced NIMMO under the reaction conditions.



Scheme 32. Nitration of 3-methyl-3-oxetanemethanol in liquid CO_2. Adapted from Ref. [159].

Later, to reduce explosion risks associated with the presence of a significant excess of nitrating agent at the initial reaction stage, which could be dangerous for a large-scale production of HEMs, an alternative fluid nitration protocol was developed. It is based on the inverse reagent mixing order (dosing of N_2O_5 solution in liquid CO_2 to a solution or suspension of an alcohol in the same media; Scheme 33).[161] The protocol proved to be applicable to green nitration of various alcohols and polyols. In the presence of just 10 mol % excess of N_2O_5, the corresponding nitroesters **1**–**5** bearing up to six nitrate groups were obtained in one step with excellent yields. Furthermore, the technique appeared suitable for processing solid alcohols to polynitrate compounds, to produce active pharmaceutical ingredients for treating of cardiovascular diseases (e.g. pentaerythritol tetranitrate (**4**) and D-mannitol hexanitrate (**5**)), inaccessible by the original dosing mode.

Low-molecular-weight fluorocarbons, or freons, in particular trifluoromethane (TFM) and 1,1,1,2-tetrafluoroethane (TFE), appeared to be even more attractive nitration media. Retaining all engineering advantages of CO_2 (nonflammability, nontoxicity, resistance to nitrating agents, high diffusion coefficient, and heat capacity), the fluorinated hydrocarbons have a remarkably lower equilibrium vapor pressure (4.16 MPa for CHF_3 and 0.57 MPa for CF_3CH_2F at 20 °C) than CO_2 (5.73 MPa at 20 °C)[162] and could be, therefore, liquefied more easily. In practice, this means that although they have the same efficiency (high yields of the products **2a**, **2d**, **3**, and **4**; Scheme 33), the nitration reactions in freon media can be performed at a signifi-

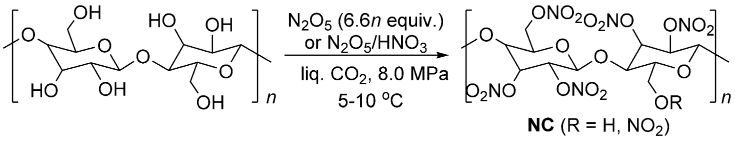


Scheme 33. Nitration of alcohols and polyols in liquid CO_2 or freon media. Adapted from Refs. [161, 163].

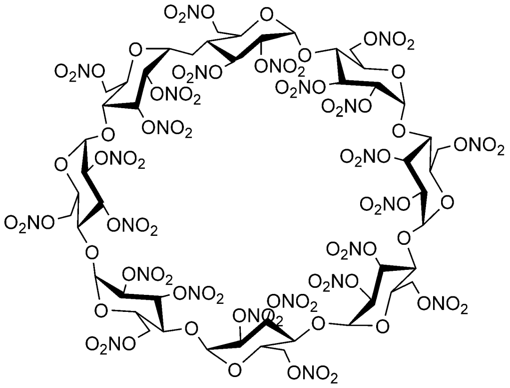
cantly lower pressure attainable with simpler and, therefore, less expensive equipment.[163]

The nitration of γ-cyclodextrin containing eight glucopyranose units with 24 hydroxyl groups in a liquid CO_2 medium yielded γ-cyclodextrin polynitrate (**6**) with a near-maximum N content (13.5%; Figure 5).[164] At the first step, HNO_3 was pumped into a pressure vessel with a cooling jacket that contained P_2O_5 or oleum ($H_2SO_4{\cdot}SO_3$) at −25 °C and approximately 10.0 MPa. The generated N_2O_5 was transported through a valve to the second vessel containing solid γ-cyclodextrin, and nitration was performed at −10 °C and 6.8 MPa. The best yield of **6** (91%) was achieved with a small excess (10%) of N_2O_5 in the presence of NaF as additive to bind the HNO_3 formed during the reaction. Product **6** is used as a substitute for nitrocellulose in smokeless powders, propellants, and other HEMs.[165–167]

The nitration of cellulose with N_2O_5 or its mixtures with 100% HNO_3 (nitrooleum) also proceeded efficiently in liquid CO_2 at 10 °C and 8.0 MPa. Depending on the composition and amount of the nitrating agent, reaction time (60–180 min), and the type of cellulose (cotton, linen, etc.), NC was formed with a N content of 11.0–13.8 wt% (Scheme 34).[164,168,169] Other nitration agents, for example, an HNO_3/Ac_2O (1:1 to 1:5) mixture, can also be used in liquid or $scCO_2$ media for cellulose nitration.[170] Nevertheless, the dense CO_2/N_2O_5 or dense $CO_2/N_2O_5/100\%\ HNO_3$ systems are preferable from an environmental point of view as the only byproduct in this case is an easy-to-recover HNO_3. The obtained results are of practical importance if we take into account that the NC is a large-capacity product used in industrial and military powders,[156] some types of membranes,[171] paints, lacquers, varnishes, and celluloid.



Scheme 34. Nitration of cellulose in liquid CO_2. Adapted from Ref. [169].



6

Figure 5. γ-Cyclodextrin nitrate.

3.1.2. N-Nitration reactions

The nitramine group ($N{-}NO_2$) is a prominent energy-rich and active oxygen-containing "explosophore" that is incorporated into a series of industrially manufactured HEMs, including powerful explosives and the key ingredients of propellants and

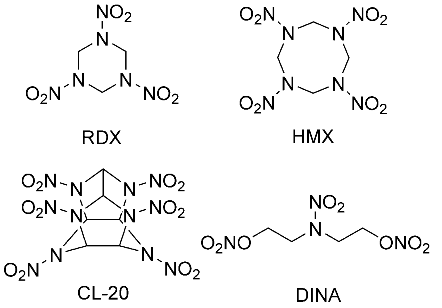
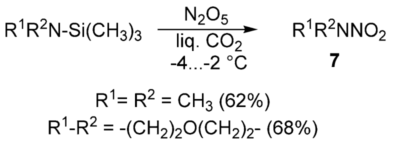


Figure 6. Practically important HEMs containing nitramine groups.

powders. Most important of these are RDX and HMX (Figure 6). RDX exhibits both a high brisance [velocity of detonation (VOD) ≈8440 $m\,s^{-1}$, $d = 1.70\ g\,cm^{-3}$] and stability and finds extensive use as a military explosive in the form of compressed or cast mixtures with other explosives or in the form of plastic-bonded explosives (PBXs) in which it is incorporated into a polymer matrix with added plasticizer.[172] HMX (VOD ≈9110 $m\,s^{-1}$, $d = 1.90\ g\,cm^{-3}$) is a more powerful explosive than RDX because of its higher density. However, it is characterized by a higher production cost than RDX and is currently applied in unique propellants and explosive formulations.[156,173] The most powerful explosive that has nitramine groups is 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane, known as CL-20.[174,175] The compact cage structure of the isowurtzitane skeleton results in an extremely high crystal density ($d = 2.04\ g\,cm^{-3}$) and VOD values (≈9380 $m\,s^{-1}$) of CL-20. It is already applied in crucial high-performance propellants and is considered as the most promising ingredient for advanced future weapon systems. Some HEMs containing the nitramino functionality in conjunction with nitrate ester or C–nitro functionalities have useful properties. In particular, *N*-nitrodiethanolamine dinitrate (DINA), which is a low-melting (m.p. = 51 °C) powerful explosive (VOD ≈ 7580 $m\,s^{-1}$), can be melt-cast readily into charges.[176]

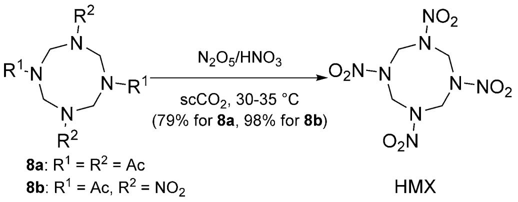
Environmentally benign green processes for the manufacturing of these energetic ingredients and materials are highly desirable to reduce the huge amount of toxic wastes which are treated, disposed of, or otherwise released into the environment in existing HEM production processes.

The first N-nitration reaction (nitration of silylamines with N_2O_5) in a CO_2 medium was developed in 1999 (Scheme 35).[177] However, this fluid nitrodesilylation reaction afforded the corresponding *N*-nitroamines **7** in lower yields than conventional methods.[178] Furthermore, the undesirable silyl nitrate byproduct was generated in this reaction along with target *N*-nitroamines **7**.



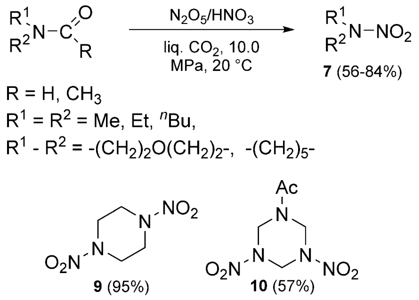
Scheme 35. Nitrodesilylation of silylamines in liquid CO_2. Adapted from Ref. [177].

Afterwards, the nitrolysis of acylamides with N_2O_5 or nitrooleum in dense CO_2 medium gave rise to the corresponding nitramines.[164] In particular, it was claimed that the treatment of 1,3,5,7-tetraacetyl-1,3,5,7-tetraazacyclooctane (**8a**) or 1,5-dinitro-3,7-diacetyl-1,3,5,7-tetraazacyclooctane (**8b**) with N_2O_5 or nitrooleum in $scCO_2$ at 30–35 °C produced the powerful explosive HMX in 79 and 98 % yield, respectively (Scheme 36). However, specific experimental details needed to reproduce these results were not mentioned by the authors.



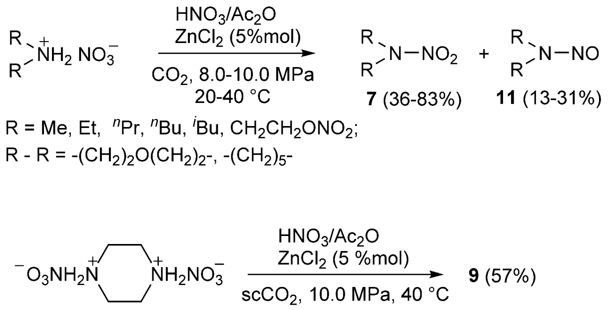
Scheme 36. Patented syntheses of HMX in $scCO_2$. Adapted from Ref. [164].

The nitrolysis of linear and cyclic acylamides with the N_2O_5 or nitrooleum nitrating systems in dense CO_2 medium was studied carefully to identify the reaction scope and optimal conditions (Scheme 37).[179] The best yield of the corresponding nitramines **7** was obtained in liquid CO_2 in the presence of concentrated HNO_3 (3 equiv.). Under fluid conditions, *N*,*N*′-diacetylpiperazine afforded *N*,*N*′-dinitropiperazine (**9**), a component of solid propellants with a reduced burning rate and increased transparency of combustion products,[180] in 95 % yield. Notably, if a similar reaction was performed under neat conditions with N_2O_5 generated in situ from HNO_3 and $(CF_3CO)_2O$, the yield of **9** was only 45 %,[181] which underlines the advantage of the fluid nitration procedure. However, the reaction of 1,3,5-triacetylhexahydro-1,3,5-triazine with nitrooleum in a CO_2 medium produced the dinitro compound **10** (57 % yield) rather than RDX. This result contradicts the data presented in the patent,[164] and further studies are clearly needed to confirm the applicability of the fluid nitrolysis method for the preparation of RDX and HMX.



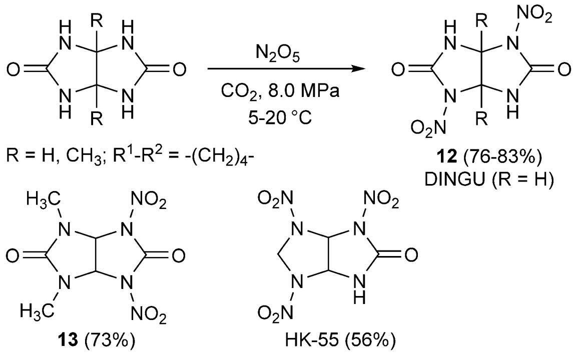
Scheme 37. Nitrolysis of linear and cyclic *N*,*N*-dialkylamides in liquid CO_2. Adapted from Ref. [179].

An alternative green approach to secondary N-nitramines **7** is based on the treatment of dialkylammonium nitrates with the 100% HNO_3/Ac_2O nitrating system in a dense CO_2 medium in the presence of $ZnCl_2$ as the catalyst.[182,183] The method provided an efficient synthesis of various nitramines, in particular, compounds **9** and DINA. However, the reaction selectivity was lower than that in N_2O_5-promoted nitrolisys reactions and depended on the molecular structure of parent nitrate salts. Dimethylamine and dialkylamines containing incorporated functional groups produced nitramines **7** selectively, whereas a majority of simple dialkylamine salts afforded nitrosoamines **11** as byproducts along with nitramines **7** (Scheme 38). The formation of **11** may be attributed to the byproduction of a nitrosating agent (N_2O_3) from $ZnCl_2$, HNO_3, and Ac_2O at the redox step of the catalytic nitration reaction (for the mechanism, see Ref. [184]).



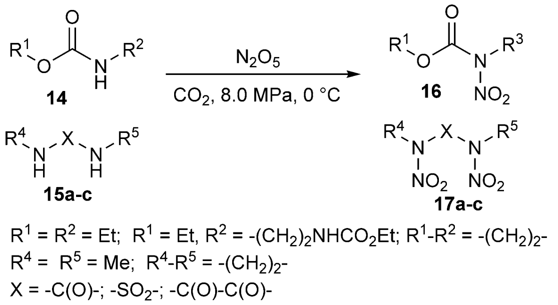
Scheme 38. Catalytic synthesis of N-nitramines in liquid or $scCO_2$. Adapted from Ref. [183].

The N-nitration of glycoluril and its 7,8-disubstituted analogs with N_2O_5 (4.0 equiv.) in liquid CO_2 (8.0 MPa, 5–20 °C) resulted in the synthesis of the bicyclic urea dinitro derivatives **12** (Scheme 39).[185] A similar nitration of 1,3-dimethylglycoluril led to compound **13** with both nitro groups attached to the same urea fragment. The method is also applicable to the fluid nitration of hexahydroimidazo[4,5-*d*]imidazol-2(1*H*)-one to produce 2,4,6-trinitro-2,4,6,8-tetraazabicyclo[3.3.0]octan-3-one (HK-55). 1,4-Dinitroglycouril (DINGU) is considered an insensitive high explosive (VOD ≈ 7580 $m\,s^{-1}$, $d = 1.99\,g\,cm^{-3}$), and an advantage of the high-energy compound HK-55 ($d = 1.905\,g\,cm^{-3}$) is its low shock sensitivity.[186]



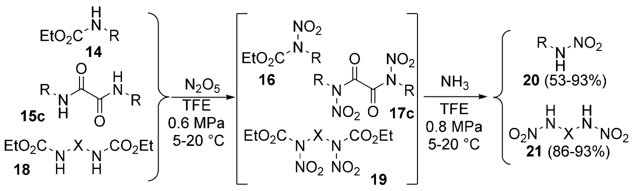
Scheme 39. N-nitration of bicyclic urea derivatives in liquid CO_2. Adapted from Ref. [185].

N-Alkylcarbamates **14** and N-alkylamides **15 a–c** of carbonic, sulfuric, and oxalic acids were nitrated readily with N_2O_5 in a liquid CO_2 medium to yield the corresponding N-nitro compounds **16** and **17 a–c** in high yields (Scheme 40).[187] The products **16** and **17** are key precursors of primary N-nitramines (in particular, methylnitramine and ethylenedinitramine), which are produced on a commercial scale and are used for the synthesis of useful HEMs through condensation reactions.[188–190] The successful application of the N_2O_5/liquid CO_2 nitrating system made it possible to achieve high yields of energetic products and avoid the use of environmentally harmful nitrating agents (e.g., mixed acids HNO_3/H_2SO_4[191] or $NH_4NO_3/(CF_3CO)_2$[192]) and toxic chlorinated solvents.[178]



Scheme 40. N-nitration of N-alkylcarbamates and N-alkylamides in liquid CO_2. Adapted from Ref. [187].

Shock- and/or friction-sensitive N-nitrourethanes and N-nitramides are commonly converted to primary N-nitramines by basic hydrolysis[188] or ammonolysis reactions.[193–196] Recently,[163,197,198] a safer and more efficient one-pot synthesis of primary N-nitramines through a sequence of nitration/ammonolysis reactions in liquid TFE was developed. N-Alkylcarbamate **14**, **18**, or N,N′-dialkyloxalamide **15 c** was nitrated with a 10% molar excess of N_2O_5 in TFE (Scheme 41). The resulting suspension of nitro compounds **16**, **19**, or **17 c** in TFE was treated with liquid ammonia in the same vessel to afford, after decompression and protonation with Brønsted acid, nitramines **20** or **21** in excellent overall yields. The procedure is environ-

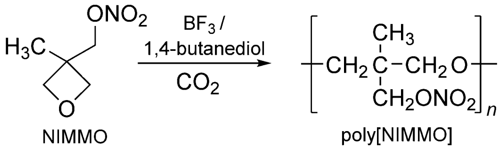


Scheme 41. One-pot synthesis of primary N-nitramines from N-alkylcarbamates or N,N′-dialkyloxalamides in liquid TFE. Adapted from Ref. [198].

mentally friendly as the only byproducts are ammonium nitrate and ethyl carbamate or oxamide, which may have further chemical or agricultural application (e.g., as fertilizers). The TFE can be recompressed readily (as it is in freezing units) and recycled into the reaction.

3.2. Synthesis of energetic polymers in liquid or supercritical CO_2

A few reports on the preparation of energetic polymers in SCFs were published.[159,199] Energetic poly[NIMMO] was obtained in the CO_2 medium by the cationic polymerization of NIMMO in the presence of BF_3/1,4-butanediol initiator (Scheme 42).[159] The product had a low impact sensitivity and was well suited for industrial application as an energetic binder for rocket propellants and plastic-bonded explosives.[200] Remarkably, both the formation of the BF_3/1,4-butanediol complex and the polymerization in the CO_2 medium had smooth temperature profiles without strong exothermic effects (≤1.3 °C increase), whereas a 15 °C temperature increase was reported in CH_2Cl_2.[201] Poly[NIMMO] obtained in this way was fractionated with $scCO_2$ at 60 °C and pressures up to 230 atm.



Scheme 42. Preparation of poly[NIMMO] by the polymerization of NIMMO in liquid CO_2. Adapted from Ref. [159].

Energetic poly(glycidyl nitrate) (poly[GLYN]), poly(2-azidomethyl-2′-methyloxetane) (poly[AMMO]), and 2,2′-bis-azidomethyloxetane (poly[BAMO]) were also prepared successfully by the cationic polymerization of the corresponding glycidol- and oxetane-derived monomers in $scCO_2$ in the presence of the BF_3·THF complex as a catalyst (Figure 7).[199] The special properties of the polymers produced in the SCF were close to those of traditionally prepared polymers. However, the use of $scCO_2$ as a suitable medium for polymerization reactions provides clear safety (accurate temperature control) and environmental benefits over organic solvents because of its high heat capacity, the absence of toxicity, and nonflammability.

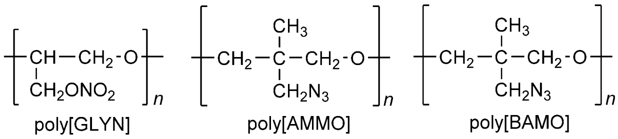


Figure 7. Energetic polymers prepared by cationic polymerization of glicidol- and oxetane-derived monomers in $scCO_2$ medium.

3.3. Micronization of energetic compounds in sub- or supercritical fluids

The energetic and exploitable properties of HEMs strongly depend on the size and geometry of their particles. However, such substances are quite difficult (and dangerous) in physical and mechanical processing because of their instability and high sensitivity to shock and friction. A search for new safe methods to obtain energetically favorable fine particles that are safer to handle, more reliable in operation, and less expensive is a key topic of the modern chemistry of HEMs. Significant advances in this important area of research are associated with the successful application of dense gases in the liquid or supercritical state as safe and green solvents and tools for the processing of HEMs.

The useful pressure-dependent solvent properties of gases and liquids above their critical points were first demonstrated in 1879 by Hannay and Hogarth.[202] This was exploited used lately in various separation (extraction),[203,204] purification,[205] and fractionation techniques.[206] Furthermore, this concept underlies a very promising, “nonextractive”, supercritical fluid nucleation method, which allows the precipitation of a solid from its solution in a supercritical fluid when it is expanded to a lower pressure.[207,208]

In 1989, Gallagher et al. pioneered the micronization of nitroguanidine (NIGU) using $scCO_2$.[209] The main idea of the method is based on the addition of compressed CO_2 to a solution of a nitro compound in an organic solvent under flow-rate control until the pressure reaches its final level. In this case, CO_2 acts as an antisolvent for the substrate because it is readily miscible with organic solvents, whereas the nitro compound is insoluble in liquid CO_2 and, commonly, in its mixtures with organic solvents. Solvent substitution occurs gradually, and particles of the nitro compound precipitate (Figure 8). This method, which is currently known as gas antisolvent (GAS), has some advantages over common recrystallization processes as it af-

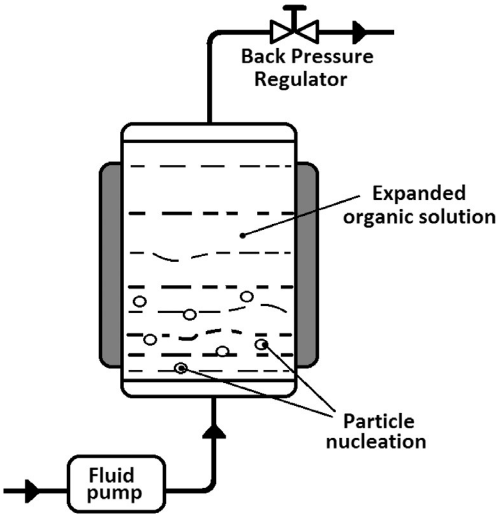


Figure 8. General scheme of the GAS micronization process. Adapted from Ref. [210].

fords “cleaner” particles without any solvent residues because of the volatility of CO_2.

Solutions of NIGU in dimethylformamide (DMF) or *N*-methylpyrrolidone (NMP) were subjected to such micronization. Fluids miscible with DMF and NMP, including CO_2, $CHClF_2$, and CCl_2F_2, were applicable as antisolvents and CO_2 was preferable because of its environmentally friendly character. The concentration, temperature, and pressure values were not the crucial parameters determining the particle size, whereas the antisolvent addition time was most important. With a very rapid expansion path (over a few seconds), the formed NIGU particles were just a few micrometers in size and regularly shaped. If the addition time was several minutes, the particles became irregular with a wider particle size distribution, which was unfavorable for most applications. Later, the same research group[211] applied CO_2 to the micronization of an important HEM (RDX) from an acetone or cyclohexanone (CHN) solution by the CO_2-initiated GAS process. The use of CHN produced RDX particles without cavities and with an improved size distribution and morphology. The authors found that the pressure level at which the nucleation started (so-called “threshold pressure” or THP) was the key point in the particle size formation. For small regular particles, it is necessary to “walk through” this point as quickly as possible to the final pressure (Figure 9, case A). If the system is held at the threshold point for a longer time, for example, 60 min, with slow CO_2 addition (case B), the nuclei grow into large monodispersed crystals. Steady addition through the THP with increasing expansion (case C) gave rise to variable-sized particles and a continuous size distribution. The final pressure and the concentration of the RDX solution (10–15 wt %) do not correlate with the size distribution or morphology of the generated particles. A high temperature (up to 90 °C) increased the THP and made it broader; this was regarded as unfavorable for small and regular particles. Therefore, in most cases, the recommended temperature was 20–30 °C for slow-CO_2-injection and 50 °C for rapid-injection processes.

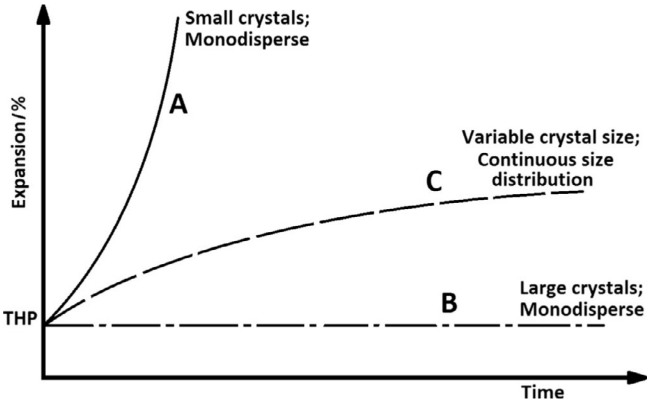


Figure 9. GAS micronization of RDX under various conditions. Adapted from Ref. [211].

Another “hard-to-dissolve” compound, HMX, was micronized by Cai et al. using a similar GAS process.[212] The authors reported the recrystallization of HMX from acetone or γ-butyrolactone (GBL) at 33 °C and 12 MPa giving fine (2–5 μm) particles. The crystal size increased with the increase in solution concentration.

A remarkable advantage of the antisolvent method for HMX micronization is the opportunity to change the crystalline form of the substrate. The β form of HMX, which is preferred in terms of density and sensitivity, was prepared by Teipel et al. by the precipitation of the substrate from its acetone or GBL solutions with CO_2.[213,214] At 60 °C and a final pressure of 8 MPa reached in 60 s, particles with mean sizes of 65 or 90 μm, respectively, formed. The diversity in particle size was attributed to different solvent capacities of acetone and GBL towards HMX. A higher concentration (acetone solution) demanded a lower pressure to form the initial supersaturation.

An important contribution to micronization of HMX by the GAS process was made by Kim et al.[215] The experiments were performed using different solvents and various operating parameters (temperature, CO_2 addition rate, initial solute concentration, and agitation rate). It was observed that the crystal structure and crystal phase of precipitated ultrafine HMX particles mainly depended on the solvent used in the GAS process. Among the tested solvents (DMF, dimethylsulfoxide (DMSO), acetonitrile (ACN), CHN, and GBL), GBL yielded the stable β phase of HMX particles with a truncated octahedron morphology. Smaller HMX particles [the median value of the particle size distribution $(D_{50}) \approx 15\ \mu m$] were obtained at 25 °C, 50 mL min^{-1} CO_2 flow rate, a low HMX concentration (30 % of maximum solubility), and 900 rpm agitation rate.

Lee et al.[216] went further and, by using a batchwise nonlinear model predictive approach to the GAS process, obtained predesigned HMX microparticles from corresponding GBL solutions. It was highlighted that the higher expansion rate–smaller particles correlation typical of GAS[211] grew weaker with the increase of the temperature. The proposed dynamic control of GAS processing[217] may be considered as the first step towards the development of automated industrial-scale micronization facilities, which would make manufacturing of micronized HEM particles safer and more reliable.

Another important type of micronization process is based on the rapid expansion of supercritical solutions (RESS). The method presupposes the dissolution of the material in $scCO_2$ and its recrystallization by a rapid expansion of the solution into a large vessel that occurs at a lower pressure (Figure 10).

Despite the experimental simplicity, this method has a significant limitation: the substrate must be soluble in $scCO_2$, at least partially. Therefore, any information on the solubility of HEMs is very important in the design of the large-scale production processes based on SCFs. The solubility of RDX in compressed CO_2 was measured over temperature and pressure ranges of 303–353 K (30–80 °C) and 6.9–48.3 MPa by using a dynamic flow apparatus.[218] RDX is poorly soluble in CO_2 with a maximum solubility of 0.25 mg g^{-1} CO_2 at the highest temperatures and pressures studied (80 °C and 48.3 MPa). Niehaus et al.[219] studied the solubility of RDX, 3-nitro-1,2,4-triazole (NTO), pentaerythritol tetranitrate (PETN), and NIGU in pure $scCO_2$ and its 1–4 wt % mixtures with organic solvents (acetone, alcohols, ACN, CHN, and CH_2Cl_2). The authors used an ex-

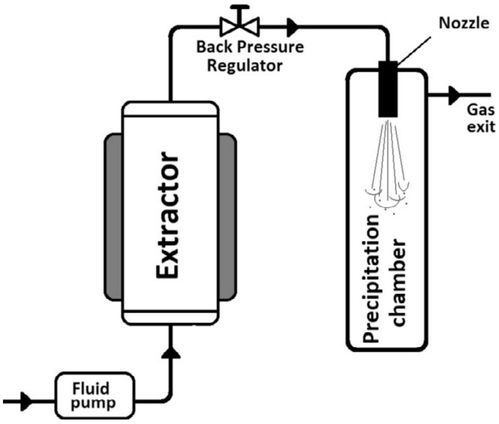


Figure 10. General scheme of the RESS micronization process. Adapted from Ref. [210].

traction-type apparatus to show that only PETN is moderately soluble in scCO$_2$ (≈18 wt% of PETN migrated to the scCO$_2$ phase at 30 MPa, 50 °C over 30 min at a CO$_2$ flow rate of 0.81 mL min^{-1}) and could be micronized by the RESS process. RDX and NTO are poorly soluble in scCO$_2$ (<1 wt% under the same conditions) and only mixtures of CO$_2$ with *i*PrOH, ACN, or acetone (4 wt% of each) could, in some cases, be used for the RESS micronization of these two substrates. As a rule, antisolvent processes, for example, GAS, are better suited for the micronization of HEMs poorly soluble in CO$_2$.

RESS micronization of TNT and NTO with the use of scCO$_2$ was reported by Teipel et al.[220]. TNT, which is 2–3 orders of magnitude more soluble in scCO$_2$ than RDX,[221] could be easily recrystallized by the RESS process. A solution of TNT in scCO$_2$ was passed under pre-expansion conditions (22 MPa, 185 °C) through nozzles ($\varnothing = 50$ or 100 μm) to afford needle-like particles with mean sizes of 14 or 10 μm, respectively. Similarly, NTO was precipitated by RESS using an acetone/CO$_2$ solvent system (1:2000 ratio of flow rates). In this case, needle-like particles (mean size 540 nm) were obtained at 20 MPa/60 °C pre-expansion conditions and 150 μm nozzle diameter.

Although RDX had been considered as an inappropriate substrate for RESS because of its low solubility,[219] Stepanov et al. obtained RDX nanoparticles by the rapid expansion of its solution in scCO$_2$.[222] Evidently, high pressures and temperatures improve the solvency of scCO$_2$ that gives rise to a higher RDX concentration in solution. As a result, supersaturation is attained faster upon expansion to give the desired particles of RDX. A further increase of the pre-expansion pressure (up to 23 MPa) resulted in smaller crystals. Most likely, the supersaturated state forces intensive nucleation but not the crystal growth. Under optimal pre-expansion conditions (90 °C, 15 MPa, 100 μm nozzle diameter or 65 °C, 23 MPa, 100 μm), regular RDX nanoparticles with a mean size of 110±35 nm were generated. However, this correlation became weaker at higher pressures (23–30 MPa).

Afterwards, the same research group[223] proposed and experimentally confirmed a ″spray-drying″ model for the RESS process in which a liquid solvent was replaced with a supercritical one. According to this model, the lower solubility of the substrate (in particular, RDX) in scCO$_2$ should lead to smaller particles. Hence, the higher the pre-expansion pressure is, the bigger the generated particles grow.

Stepanov and co-workers[224] designed a cycled RESS process for the RDX micronization. The unit comprised the extraction part, RESS vessels, and CO$_2$-regeneration part for low (0.1 MPa) and high (5 MPa) discharge pressure cases. The authors claimed that the discharge pressure dramatically influences the particles size. At constant pre-expansion conditions (85 °C or 35 MPa), particles with 200 or 500 nm mean size, were obtained. A comparison of the RDX particles with coarse samples (Class-1 and Class-5 RDX from BAE Systems) showed that the least sensitive crystals are those with 500 nm size (Table 1). In the case of smaller particles, resensitization occurred to both shock and impact stimuli.

Table 1. Impact sensitivity and shock sensitivity tests results for RDX samples. Adapted from Ref. [224].

Material	Impact sensitivity, H_{50} [cm]	Shock sensitivity [GPa]
200 nm RDX (RESS)	57	2.1
500 nm RDX (RESS)	73	2.6
4 mm RDX	32	2.0
Class 1 RDX	–	–
Class 5 RDX	23	1.1

The CHF$_3$ fluid was tested for the processing of CL-20, one of the most powerful industrial explosives.[225] With a quite a low critical point (26.1 °C, 4.8 MPa), low toxicity for humans,[226] and higher polarity (dipole moment 1.649 D)[162] than CO$_2$, this fluid is more suitable for industrial uses. CL-20 was micronized successfully (pre-expansion conditions: 15 MPa and 80 °C) to particles 1–10 μm in size. Unfortunately, no data on RESS micronization of CL-20 in CO$_2$ are available to compare these two promising fluids.

Lee et al. studied RDX micronization by RESS[227] using dimethyl ether (DME) as a potential supercritical solvent, which exhibits suitable critical parameters (128 °C, 5.4 MPa) and a higher solvent capacity than CO$_2$. The authors found a correlation between the RESS process conditions and the properties of generated particles. The solution density was the crucial feature. A higher density (because of the increasing pressure) led to a higher substrate concentration (solvent capacity growth), which in turn resulted in more rapid supersaturation during the expansion and smaller particles. However, a further temperature increase resulted in agglomerated particles. Fine particles with 0.36–2.48 μm mean size were obtained under optimal pre-expansion conditions (12–18 MPa, 20 °C, 100 μm nozzle diameter).

Another type of antisolvent process, so-called “supercritical antisolvent” (SAS), is based on the injection of an organic solution of the substrate into a vessel filled in which scCO$_2$ is pumped through (Figure 11). SAS, as well as the GAS, is suitable for the micronization of CO$_2$-insoluble substrates, in partic-

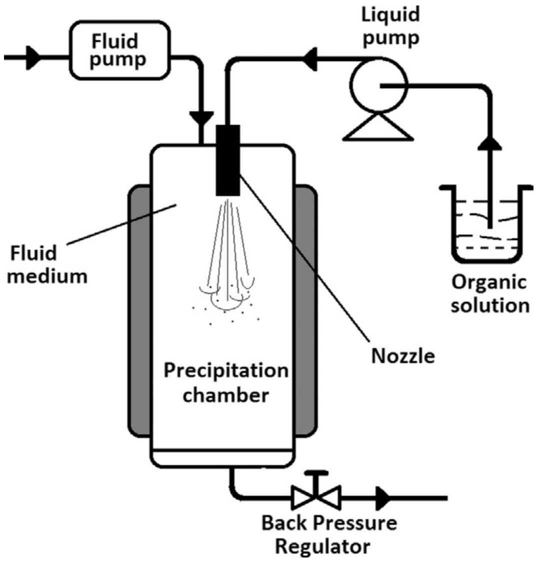


Figure 11. General scheme of the SAS micronization process. Adapted from Ref. [210].

ular, RDX, HMX, and hexanitrostilbene.[220] A solution of RDX in acetone (5 wt %) was injected at 480 mL h^{-1} through a 100 μm nozzle into $scCO_2$, which was pumped at 6 kg h^{-1} (15 MPa, 50 °C), to afford particles 32 μm in size. The use of a coaxial two-flow nozzle resulted in 16 μm particles of RDX under the same conditions. Similarly, solutions of HMX in CHN (4 wt %) and hexanitrostilbene in DMF (1 wt %) were processed into 2.3 and 3.5 μm particles of corresponding HEMs by SAS micronization.

Teipel et al. presented results of Reverchon's research group on NTO micronization through the SAS process in their outstanding book.[228] The researchers tested DMSO and methanol as organic solvents at different solvent/antisolvent ($scCO_2$) ratios. In DMSO-based systems, the substrate was partially lost because of the cosolvent effect and generated NTO particles (mean diameter <100 nm) were strongly networked. However, in the $CH_3OH/scCO_2$ system, regular 120 nm-sized NTO particles were obtained by SAS micronization. The authors compared NTO particles precipitated with SAS and GAS methods and noticed that SAS produced an amorphous roundish product whereas GAS produced crystalline NTO. The difference in the particle morphology was attributed to the particular effects of the supercritical antisolvent: the SAS system makes nuclei precipitate rapidly from microdroplets and the GAS system allows them to grow to the crystal structure.

Kim et al.[229] investigated the aforementioned solvent effect on HMX particle morphology in the SAS process. DMSO, DMF, NMP, acetone, and CHN were used as solvents. According to FTIR spectroscopy, only the last two solvents gave rise to the desirable β-phase crystals. Under optimal conditions (40 °C, 15 MPa, 15 mL min^{-1} CO_2 flow rate, and 2 mL min^{-1} flow rate of 2 wt % HMX solution in acetone or CHN), the desired ultrafine particles (9.5 or 6.1 μm, respectively) were produced.

As RDX faces no problem with its crystal phase, Lee et al. searched for a better solvent for the SAS micronization of this explosive.[230] The experiments were performed at 15 MPa, 50 °C, and a CO_2 flow rate of 40 g min^{-1}. The RDX particles of 11.4–17.7 μm average size precipitated from acetone, DMSO, or NMP. In the case of other tested solvents (ACN, DMF, or CHN), smaller (2.6–6.6 μm) RDX particles were obtained under similar conditions (Table 2). According to thermal analysis, smaller crystals had a higher decomposition enthalpy, which is strong evidence for the importance of micronization.

The efficiency of the GAS and SAS micronization techniques was compared thoroughly by recording the FTIR spectra of HMX crystals obtained by both methods.[231] Unexpectedly, the authors discovered that no desired HMX β phase was produced by SAS precipitation, regardless of the solvent used (these results are at variance with the work by Kim et al.[229]). Only GAS processes with acetone solution afforded energetically favorable prismlike crystals of the β phase. β-HMX crystals with a smaller mean size (12.9 μm) and narrower particle size distribution were generated from acetone solution (2.17 wt %) at 50 mL min^{-1} CO_2 addition rate, moderate agitation (400 rpm), 40 °C, and a final pressure of 8 MPa. The temperature and pressure had no significant effect in this case.

The abundance of variables in antisolvent processes has pushed scientists to develop adequate models to describe them. Bayat et al.[232] proposed the statistical optimization of the SAS processing of HMX. By varying the solvent type, solute concentration, feed rates, and temperature and pressure at the precipitation chamber and using Taguchi robust design method with several allowances, they predicted theoretically the optimal micronization conditions. Under these conditions (CHN, HMX concentration 3.5 mol L^{-1}, solution rate 3 mL min^{-1}, and CO_2 rate 70 mL min^{-1}), the authors managed to obtain spherical particles of HMX with 56 nm diameter, which was impossible before the optimization.

Table 2. Effect of SAS process conditions on RDX particles parameters. Adapted from Ref. [230].

Solvent	Solution concentration [wt %]	Solution injection rate [g min^{-1}]	Particle mean size [μm]	Particle shape	Decomposition enthalpy [J g^{-1}]
Acetone	5.0	3.2	17.7	rod-shaped granular	583.4 ± 7.3
DMSO	20.0	0.3	12.8	granular	847.7 ± 1.3
NMP	9.1	0.7	11.4	irregular	967.1 ± 7.3
ACN	4.8	0.7	6.6	granular	823.9 ± 12.1
DMF	11.1	0.7	5.1	granular	1131 ± 30.5
CHN	5.0	1.2	2.6	rod-shaped granular	1620 ± 24.3

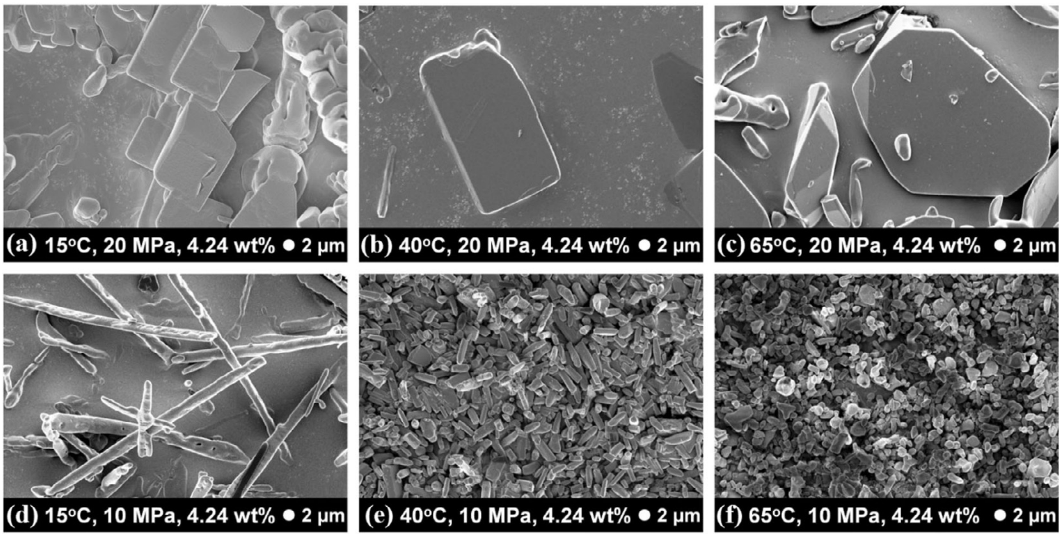


Figure 12. Size and morphology of RDX particles precipitated in SAS experiments at different pressures and temperatures. Reproduced with permission from Ref. [236].

Dou et al.[233] added a new parameter, the pressure drop (PressD) on the nozzle, to describe the SAS processing of RDX adequately. In their experiments, a 20% solution of RDX in DMF was injected into a vessel at a 25 mL min^{-1} flow rate, 10 MPa, and 40 °C with a CO_2 feed rate of 25 mL min^{-1}. The variation of PressD (0, 4.5, and 11 MPa) by changing the nozzle length afforded RDX particles with mean sizes of 13.1, 11.6, and 8.7 μm, respectively. Moreover, the authors managed to obtain even 5.9 μm particles of the same HEM using PressD of 15 MPa.[234] SEM and optical microscopy images were used to show that a higher PressD led to rounder and regular crystals, a shape that is always preferable for HEMs.[235]

Seo et al.[236] performed a complex study on the CO_2-mediated SAS micronization of RDX from its acetone solution using the Hansen solubility parameter concept. They found that the particles could demonstrate either agglomeration or crystallization behavior depending on the temperature or pressure. A lower pressure (10 MPa) led to smaller particles, whereas at a higher pressure (20 MPa), much larger platelike structures (10 to >100 μm) were obtained (Figure 12 a, b, and c vs. d, e, and f). The temperature also had a significant impact on the particle size and morphology in experiments at 10 MPa. Strongly agglomerated rodlike products were produced at 15 °C (Figure 11 d), whereas much smaller particles were generated at 40–65 °C, and their form changed from cylindrical to spherical (Figure 12 e vs. f).

Porous and faceted particles were produced in SAS experiments from a 8.48 wt% RDX/acetone solution, whereas regular crystals precipitated at a lower RDX concentration (2–4 wt%). Visualization of the SAS micronization at 65 °C and a RDX concentration of 2.17 wt% shows clearly that close to the system critical point, every 1 MPa matters for efficient jet breaking (Figure 13) and the optimal pressure was slightly above critical (>11 MPa, Figure 13 c and d). The obtained results prove that CO_2-based micronization processes are green and quite tunable methods for manufacturing of HEM particles. Every parameter of these processes is an important key to obtain the most energetically efficient and safe-to-handle ultradispersed fine HEM particles with a narrow size distribution. The predictive approach may be considered as a promising tool to solve the important multiparametric optimization tasks associated with HEM micronization processing.

However, a serious problem arose unexpectedly with $scCO_2$-assisted HEM micronization. Even if HEM particles of the desired morphology were produced, they were inclined to gather into large loose agglomerates, which did not have the required properties. An original solution was offered by Essel et al.,[237] who suggested spraying the $scCO_2$ substrate solution into a vessel filled with water to prevent agglomeration. However, in practice, H_2O absorbed CO_2 quickly to afford an acidic medium, which induced particle coarsening and agglomeration because of the Ostwald ripening effect. To overcome this problem, the authors added a base (dilute NH_4OH) to the system, which suppressed the agglomeration and restored a suspension of 30 nm-sized free particles. Furthermore, the authors enhanced the thermodynamic stability of the aqueous suspension by adding a small amount of a water-soluble polymer, polyvinylpyrrolidone (PVP) or polyethylenimine (PEI). The latter appeared to be preferable because of its stronger affinity with the RDX surface. Coated RDX particles demonstrated a weaker propensity to agglomeration and were less sensitive to shock and friction. Furthermore, they had a better adhesion to other components of industrial compositions.

Along with modern recrystallization methods, a classic approach to obtain HEM microparticles, based on milling in aqueous media, is still in use. However, a weak point of this approach is that it requires an extra drying stage. This is where CO_2 could be useful again. Liu et al.[238] compared several drying methods, in particular, simple and vacuum drying, washing with ethyl acetate, ethanol, and isopropanol, and CO_2-based supercritical drying (SCD) or supercritical freeze drying (SCFD), to obtain milled water-free HMX nanoparticles

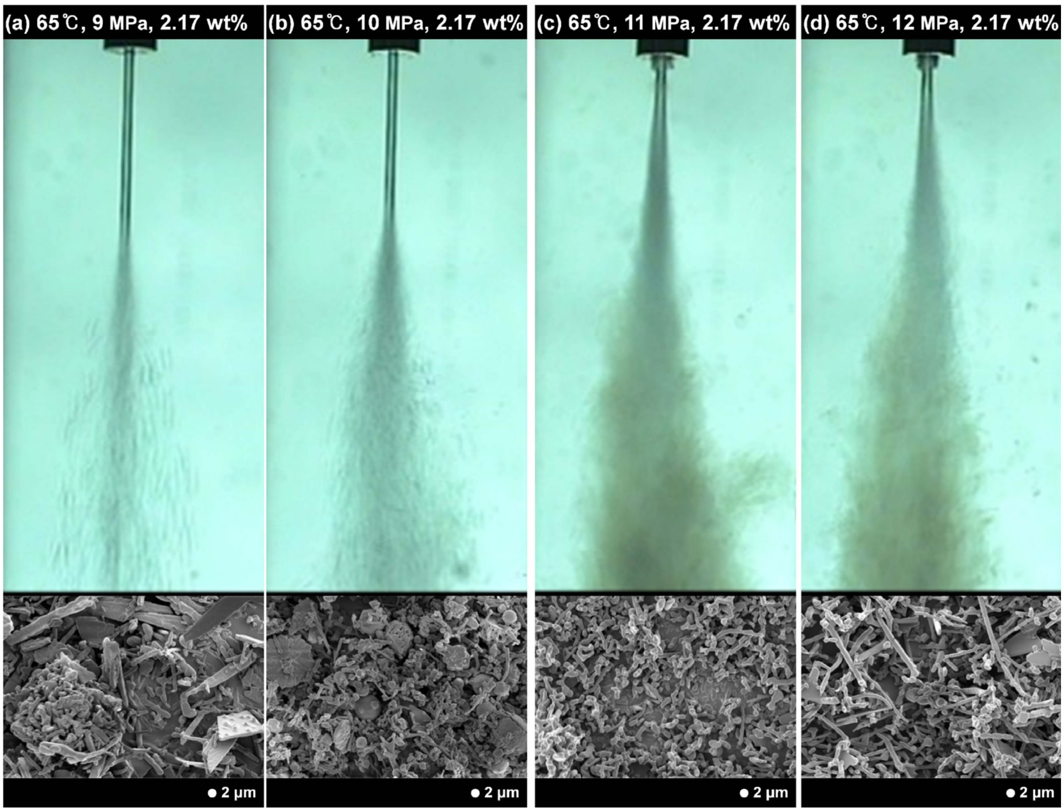


Figure 13. Jet behavior and the morphology of RDX particles precipitated at 65 °C and different pressures. Reproduced with permission from Ref. [236].

(≈80 nm). The SCD and SCFD methods appeared preferable as they prevent the agglomeration of crystals. Of these, the SCFD method, which produced nanoparticles of a smaller mean size (160 vs. 190 nm for the SCD), is better suited for the large-scale manufacturing of nano-HMX.

3.4. HEM processing with supercritical fluids

Energetic substances are rarely used in their pure form but rather in combination with polymeric or wax binders such as PBXs. These materials require some form of processing, which often involves organic solvents.[173,239] The development of processes that eliminate or reduce the need for the use of organic solvents in formulation steps is highly desirable to decrease the amount of waste created by the production of HEMs.[240] Supercritical fluids, primarily $scCO_2$, are considered as promising tools to address the environmental issue associated with HEM manufacture.

HEM binder polymers such as polyethylene (PE), oxidized PE, poly(urethane) (Estane), cellulose acetate/butyrate (CAB), poly(vinylidene fluoride-*co*-hexafluoropropylene) (Fluorel and Viton), and poly(chlorotrifluoroethylene-*co*-vinylidene fluoride) (Kel-F 800 and Kel-F 3700) were studied in $scCO_2$ at up to 300 °C and 300 MPa to evaluate their solubility and phase behavior (Table 3).[241]

Table 3. Selected plastic-bonded explosives.[156,241]

Name	Components
PBXN-5	HMX/Viton-A
PBXN-6	RDX/Viton-A
PBXN-201	RDX/Viton-A/Teflon
PBXN-9502	TATB/Kel-F 800
LX-17	TATB/Kel-F 800
MTV igniter	Mg/Teflon/Viton-A (or Flourel)
IR flare	Mg/Teflon/Viton
LOVA propellant	RDX/CAB/NC
COMP A-3	RDX/polyethylene (or Oxidized PE or WAX)
LX-14	HMX/Estane

Hydrocarbon waxes of a molecular weight ≤ 1000 Da are soluble in $scCO_2$. However, high-molecular-weight PE and polymers with polar groups such as oxidized PE, polyurethane, Kel-F 3700, and CAB are nearly insoluble in $scCO_2$ even at 290 °C and 247.5 MPa. The addition of acetone (22 wt %) or ethanol (29 wt %) as modifier improves the solubility significantly. The fluorinated polymers Fluorel, Viton, and Kel-F 800 are highly soluble in $scCO_2$ because of the contribution of the vinylidene fluoride units, and their solubility is further improved in an acetone/$scCO_2$ (1:9) mixture. The structure of the polymer backbone plays an important role: Fluorel dissolves in pure $scCO_2$ (284 °C and 220.0 MPa), whereas Viton A does not. Supercritical CO_2 has a significant potential in the manufacture of PBX molding powders and extrusion feedstock using Fluorel or Kel-F 800 binder and for the precise control of the coating of sensitive explosive powders with a specific polymer binder. Furthermore, it is useful to recycle and recover valuable ingredients from existing Fluorel-based MTV (Mg/Teflon/Viton) and PBX or Kel-F 800-based PBX formulations.

An environmentally friendly method, the so-called super-shock process, was designated for the preparation of MTV pyrotechnics.[159,242] In this process, Viton was precipitated from an acetone/magnesium/Teflon/Viton paste with $scCO_2$, which coated the magnesium and Teflon. After that, acetone was removed using a $scCO_2$ flow (60 °C, 14.2 MPa). Virtually no hazardous waste was generated in this process because the processing fluids, acetone and CO_2, were separately recovered and recycled. However, in the traditional shock-gel process, in which hexane is used as the precipitant, over 10 kg of hazardous waste was produced per kg of MTV.[243,244] Moreover, the simplicity of gaseous CO_2 separation from products (decompression) eliminates the energy-consuming step of MTV crumb drying. Furthermore, a portion of the starting materials, which remained intact during the processing, could be used in the next batch.

The coating of HEM particles with polymer films protects them from the adverse effect of moisture and light, improves chemical compatibility of energetic particles (e.g., ammonium dinitramide (ADN) with other components of high-energy compositions, and makes their molding safer. A fluidized-bed encapsulation process, in which $scCO_2$ was used as a solvent for the coating material and as a carrier fluid for fluidized-bed formation, was developed by Teipel and co-workers.[245,246] This process allowed the safe encapsulation of thermally labile and moisture-sensitive 30–100 μm sized particles of important HEMs (ADN and PETN) at ambient temperature.

Another patented method[247] for the coating of solid energetic particles in supercritical fluids includes one-pot nucleation and deposition steps followed by thermal conditioning (e.g., polymerization) of the coated particles. The method was claimed to be applicable for the coating of various solid propellant components (CL-20, HMX, RDX, 1,3,3-trinitroazetidine, NH_4NO_3, NH_4ClO_4, ADN, carbohydrazide, metal, polymeric azides, etc.). Later, the SAS method was used to coat CL-20 crystals with hydroxyl-terminated polybutadiene.[248] The polymer was dissolved in CH_2Cl_2, and particles of CL-20 were added to the solution. Pressurizing of the suspension with $scCO_2$ antisolvent at 60 °C and 12 MPa caused polymer precipitation on the CL-20 surface as a thin film. The subsequent removal of CH_2Cl_2 with the $scCO_2$ flow left coated CL-20 particles with excellent safety characteristics (Table 4).

Table 4. Shock (SS), friction (FS) and electric spark (ES) sensitivities of naked and coated CL-20 particles. Adapted from Ref. [248].

Material	SS [J]	FS [N]	ES [mJ]
uncoated CL-20	1.4	73	116
coated CL-20	2.7 ± 0.3	157 ± 17	> 712

Nanoparticles of RDX were coated with polystyrene or poly(vinylidene fluoride-*co*-hexafluoropropylene) ($VDF\text{-}HFP_{22}$) polymer films by RESS-type coprecipitation.[249] Supercritical CO_2 was pumped at a constant mass flow rate through the extraction vessel at 13.0–20.5 MPa and 48–53 °C. The poorly soluble RDX precipitated first, and then the polymer deposited on the surface of the RDX nanoparticles. The core–shell structure of the coated particles (≈100 nm) was confirmed by using SEM and TEM. MS (GC–MS) and X-ray powder diffraction (XRPD) were used to demonstrate that the produced powders contained 70–73 % of RDX.

Microcellular combustible materials based on polymer-bonded nitramines possess several advantages such as an adjustable energy content, high burn rate, and low vulnerability.[250] They burn out in a reduced time at a giant internal surface area to leave no burn residue. These materials have immense potential for application in propellants, combustible cartridge cases,[251,252] and caseless ammunition.[253]

A microcellular combustible ordnance material composed of RDX and poly(methyl methacrylate) (PMMA) was fabricated using the solvent method and foamed by using $scCO_2$.[254–257] The samples were processed in designed foaming molds with expansion ratios of 1.1, 1.2, and 1.35 (the molds with a certain expansion ratio determine the foaming space of the saturated preform). The foaming temperature, saturation pressure, sorption/desorption time, and RDX content (50–70 %) were the key factors that exerted a significant impact on the density, porosity, and homogeneity of the RDX/PMMA porous samples according to the SEM data (Figure 14). The obtained microcellular combustible objects are superior to traditional ones with regard to heat and moisture resistance.[254] The method was successfully applied to an RDX-based propellant. It is also applicable to traditional single-, double-, and triple-based propellants as well as to the low vulnerability ammunition (LOVA) propellant.

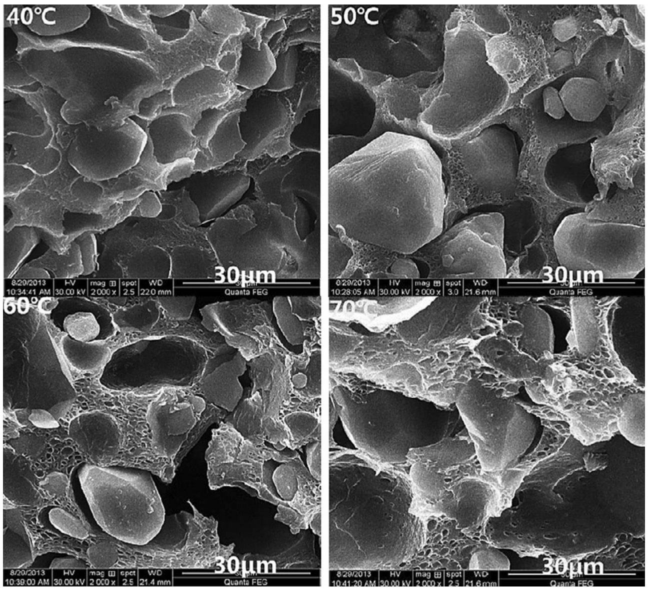


Figure 14. SEM images of foamed samples with different foaming temperatures (saturation pressure = 15 MPa, expansion ratio = 1.35). Reproduced with permission from Ref. [254].

Promising porous HEMs with a large specific surface area are energetic polymer-based aerogels. Nitrocellulose aerogel was prepared from an acetone solution of NC, toluene diisocyanate, and ditinbutyl dilaurate using a $scCO_2$ drying method (12 MPa, 45 °C).[258] The produced microstructured aerogel can be used as a gel matrix for NC/RDX, NC/HMX, NC/Al, and NC/AP/RDX nanocomposite energetic materials. The NC/HMX nanocomposites were prepared by an improved sol–gel supercritical method. The NC particles of approximately 30 nm in size were cross-linked to form a network structure, and HMX nanoparticles were embedded into this matrix.[259] Different cosolvents should be used for each component (e.g., ethyl acetate for NC and δ-butyrolactone for HMX). A transparent gel with strong elasticity, which comprised NC, HMX, and the corresponding solvents, was subjected to supercritical extraction with CO_2 to afford the nanocomposite. Nitrate glycerol ether cellulose (NGEC)-based aerogels of up to 183 $m^2 g^{-1}$ surface area were prepared by drying the corresponding alcogels with $scCO_2$ (50 °C, 16 MPa) followed by slow decompression to avoid cracking.[260] The obtained NGEC aerogels with tunable pore structures could have a potential application as a inexpensive moderate-surface-area HEM in explosives and propellants.

4. Conclusions

This Review shows that ionic liquids (ILs) and sub- or supercritical fluids, which are considered as green-chemistry tools, have a great potential in the field of energetic materials science. The application of thermally stable ILs having negligible vapor pressure as the reaction medium and (or) promoters make dangerous processes, which are used for high-energy material (HEM) synthesis and handling, safer. Nitration in ILs does not require large quantities of strong acids and offers a simple nonaqueous workup. A series of industrially important (hexahydro-1,3,5-trinitro-1,3,5-triazine; RDX, cyclotetramethylene tetranitramine; HMX, 2,4,6,8,10,12-hexanitro-2,4,6,8,10,12-hexaazaisowurtzitane; CL-20) and prospective HEMs was produced in the IL media under milder conditions than that in conventional solvents. A considerable breakthrough in efficient HEM synthesis was achieved by the catalytic application of Brønsted-acidic ILs. Nitrate or nitrite salts could be used as mild reagents for nitration or nitrosation reactions.

Important achievements have been made in the area of so-called energetic ILs, in particular oxygen-balanced and hypergolic ILs, which has become a hotspot in energetic materials science. However, the special properties of the synthesized energetic ILs have not yet fully met the strict requirements of rocket propellants. Therefore, a search for new, more efficient energetic and hypergolic ILs is expected to be a challenge in the near future.

Very promising results were afforded by the extensive application of CO_2 and lower fluorinated hydrocarbons (freons), which are readily available in the liquid or supercritical state, in HEM synthesis and processing. The combined use of these inexpensive, nontoxic, and nonflammable dense gases as reaction media and dinitrogen pentoxide as an efficient nitrating agent reduces fire and explosion risks significantly (nitration in fire extinguishers) and eliminates the use of environmentally harmful H_2SO_4 in nitration reactions. Furthermore, CO_2 and freons are attractive for industrial use because they can be separated readily from the reaction products by simple decompression. Both O- and N-nitration reactions were efficiently performed in these neoteric solvents to afford industrially manufactured HEMs; however, their applicability to the production of RDX and HMX is still under question.

Efficient supercritical fluid (SCF)-based gas antisolvent, supercritical antisolvent, and rapid expansion of supercritical solutions micronization techniques have been elaborated for the efficient control over the morphology and particle size distribution to provide the most energy-rich fine particles of HEMs, including RDX, HMX, CL-20, 3-nitro-1,2,4-triazole, pentaerythritol tetranitrate, and nitroguanidine. SCFs are useful to coat HEM particles with polymer films and for the preparation of microcellular combustible materials. Further evolution of these promising lines of research may result in the development of HEMs that would be safer to handle, more reliable in processing, and less expensive.

Acknowledgements

This work was supported by the Russian Science Foundation (grant no. 14-50-00126).

Conflict of interest

The authors declare no conflict of interest.

Keywords: green chemistry · ionic liquids · solvent effects · supercritical fluids · synthesis design

[1] *Handbook of Green Chemistry and Technology* (Eds.: J. Clark, D. Macquarrie), Blackwell Science Ltd., Oxford, **2002**, 562 pp.
[2] M. Lancaster, *Green Chemistry: An Introductory Text, 3nd ed.*, RSC, Cambridge, **2016**, 374 pp.
[3] *Ionic liquids in Synthesis, 2nd ed.* (Eds.: P. Wasserscheid, T. Welton), Wiley-VCH, **2008**, 776 pp.
[4] T. Welton, *Chem. Rev.* **1999**, *99*, 2071–2084.
[5] *Chemical Synthesis using Supercritical Fluids* (Eds.: P. G. Jessop, W. Leitner), Wiley-VCH, Weinheim, **1999**, 480 pp.
[6] I. T. Horváth, *Acc. Chem. Res.* **1998**, *31*, 641–650.
[7] *Organic Reactions in Water: Principles, Strategies and Applications* (Ed.: U. M. Lindstrom), Wiley-Blackwell, **2007**, 424 pp.
[8] R. D. Rogers, K. R. Seddon, S. Volkov, *Green Industrial Applications of Ionic Liquids*, Springer, New York, **2003**, 553 pp.
[9] F. Jutz, J. M. Andanson, A. Baiker, *Chem. Rev.* **2011**, *111*, 322–353.
[10] J. P. Hallett, T. Welton, *Chem. Rev.* **2011**, *111*, 3508–3576.
[11] H. Wang, G. Gurau, R. D. Rogers, *Chem. Soc. Rev.* **2012**, *41*, 1519–1537.
[12] P. Prediger, Y. Genisson, C. R. D. Correia, *Curr. Org. Chem.* **2013**, *17*, 238–256.
[13] E. Sebastiao, C. Cook, A. Hub, M. Murugesu, *J. Mater. Chem. A* **2014**, *2*, 8153–8173.
[14] H. Olivier-Bourbigou, L. Magna, *J. Mol. Catal. A* **2002**, *182–183*, 419–437.
[15] E. J. Beckman, *J. Supercrit. Fluids* **2004**, *28*, 121–191.
[16] *Supercritical Fluid Nanotechnology: Advances and Applications in Composites and Hybrid Nanomaterials* (Eds.: C. Domingo Pascual, P. Subra-Paternault), CRC Press, **2015**, 566 pp.
[17] R. Tillner-Roth, H. D. Baehr, *J. Phys. Chem. Ref. Data* **1994**, *23*, 657–729.

[18] “Refrigerants—Environmental Properties”. The Engineering ToolBox. Available from http://www.engineeringtoolbox.com/Refrigerants-Environment-Properties-d 1220.html (accessed September 2017).

[19] A. Aggarwal, N. L. Lancaster, A. R. Sethi, T. Welton, *Green Chem.* **2002**, *4*, 517–520.

[20] M. M. D’Anna, V. Gallo, P. Mastrorilli, C. F. Nobile, G. Romanazzi, G. P. Suranna, *Chem. Commun.* **2002**, 434–435.

[21] D. Imao, S. Fujihara, T. Yamamoto, T. Ohta, Y. Ito, *Tetrahedron* **2005**, *61*, 6988–6992.

[22] D. Basavaiah, A. J. Rao, T. Satyanarayana, *Chem. Rev.* **2003**, *103*, 811–892.

[23] X.-F. Yang, M. Wang, R. S. Varma, C.-J. Li, *J. Mol. Catal. A* **2004**, *214*, 147–154.

[24] M. A. P. Martins, C. P. Frizzo, A. Z. Tier, D. N. Moreira, N. Zanatta, H. G. Bonacorso, *Chem. Rev.* **2014**, *114*, PR1–PR70.

[25] N. N. Makhova, M. I. Pleshchev, M. A. Epishina, A. S. Kulikov, *Chem. Heterocycl. Compd.* **2014**, *50*, 634–646.

[26] J.-H. Qin, B. Ma, X.-F. Liu, H.-L. Lu, X.-Y. Dong, S.-Q. Zang, H. Hou, *Dalton Trans.* **2015**, *44*, 14594–14603.

[27] S. G. Zlotin, N. N. Makhova, *Russ. Chem. Rev.* **2010**, *79*, 543–583.

[28] “Ionic Liquid Organocatalysts”: D. E. Siyutkin, A. S. Kucherenko, S. G. Zlotin in *Comprehensive Enantioselective Organocatalysis: Catalysts, Reactions, and Applications, Vol. 2* (Ed.: P. I. Dalko), Wiley-VCH, **2013**, p. 617–650.

[29] R. S. Tukhvatshin, A. S. Kucherenko, Y. V. Nelyubina, S. G. Zlotin, *ACS Catal.* **2017**, *7*, 2981–2989.

[30] M. McHugh, V. Krukonis, *Supercritical Fluid Extraction: Principles and Practice*, Elsevier, Amsterdam, **2013**, 608 pp.

[31] C. F. Poole, *Supercritical Fluid Chromatography*, Elsevier, Amsterdam, **2017**, 572 pp.

[32] P. G. Jessop, *J. Supercrit. Fluids* **2006**, *38*, 211–231.

[33] A. Kruse, H. Vogel, *Chem. Eng. Technol.* **2008**, *31*, 23–32.

[34] T. Matsuda, T. Harada, K. Nakamura, *Green Chem.* **2004**, *6*, 440–444.

[35] I. V. Kuchurov, A. G. Nigmatov, E. V. Kryuchkova, A. A. Kostenko, A. S. Kucherenko, S. G. Zlotin, *Green Chem.* **2014**, *16*, 1521–1526.

[36] E. V. Filatova, O. V. Turova, I. V. Kuchurov, A. A. Kostenko, A. G. Nigmatov, S. G. Zlotin, *J. Supercrit. Fluids* **2016**, *109*, 35–42.

[37] L. Du, J. Y. Kelly, G. W. Roberts, J. M. DeSimone, *J. Supercrit. Fluids* **2009**, *47*, 447–457.

[38] M. Chatterjee, T. Ishizaka, A. Chatterjee, H. Kawanami, *Green Chem.* **2017**, *19*, 1315–1326.

[39] A. C. Benages, O. Boutureira, S. Castillon, Y. Diaz, M. I. Matheu, *Green Chem.* **2017**, *19*, 2687–2694.

[40] A. Caballero, E. Despagnet-Ayoub, M. M. Díaz-Requejo, A. Díaz-Rodríguez, M. E. González-Núñez, R. Mello, B. K. Muñoz, W.-S. Ojo, G. Asensio, M. Etienne, P. J. Pérez, *Science* **2011**, *332*, 835–838.

[41] R. P. Singh, R. D. Verma, D. T. Meshri, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2006**, *45*, 3584–3601; *Angew. Chem.* **2006**, *118*, 3664–3682.

[42] G. Steinhauser, T. M. Klapötke, *Angew. Chem. Int. Ed.* **2008**, *47*, 3330–3347; *Angew. Chem.* **2008**, *120*, 3376–3394.

[43] H. Gao, J. M. Shreeve, *Chem. Rev.* **2011**, *111*, 7377–7436.

[44] D. E. Chavez, M. A. Hiskey, *J. Energ. Mater.* **1999**, *17*, 357–377.

[45] *Defense Industries: Science and Technology Related to Security: Impact of Conventional Munitions on Environment and Population* (Eds.: P. C. Branco, H. Schubert, J. Campos), Kluwer Academic Publishers, Dordrecht, Netherlands, **2007**, 386 pp..

[46] M. B. Talawar, R. Sivabalan, T. Mukundan, H. Muthurajan, A. K. Sikder, B. R. Gandhe, A. Subhananda Rao, *J. Hazard. Mater.* **2009**, *161*, 589–607.

[47] S. G. Zlotin, A. M. Churakov, O. A. Luk’yanov, N. N. Makhova, A. Yu. Sukhorukov, V. A. Tartakovsky, *Mendeleev Commun.* **2015**, *25*, 399–409.

[48] *Green Energetic Materials* (Ed.: T. Brinck), Wiley, England, **2014**, 304 pp.

[49] J. P. Agrawal, R. D. Hodgson, *Organic Chemistry of Explosives*, Wiley, England, **2007**, 414 pp.

[50] Th. M. Klapötke, *Chemistry of High-Energy Materials, 3rd ed.*, Walter de Gruyter, Berlin, **2015**, 350 pp.

[51] Q. Zhang, J. M. Shreeve, *Chem. Rev.* **2014**, *114*, 10527–10574.

[52] J. Le Bideau, L. Viau, A. Vioux, *Chem. Soc. Rev.* **2011**, *40*, 907–925.

[53] S. Huang, X. Qi, T. Liu, K. Wang, W. Zhang, J. Li, Q. Zhang, *Chem. Eur. J.* **2016**, *22*, 10187–10193.

[54] P. D. McCrary, G. Chatel, S. A. Alaniz, O. A. Cojocaru, P. A. Beasley, L. A. Flores, S. P. Kelley, P. S. Barber, R. D. Rogers, *Energy Fuels* **2014**, *28*, 3460–3473.

[55] Y.-H. Joo, J. M. Shreeve, *J. Am. Chem. Soc.* **2010**, *132*, 15081–15090.

[56] R. Wang, H. Xu, Y. Guo, R. Sa, J. M. Shreeve, *J. Am. Chem. Soc.* **2010**, *132*, 11904–11905.

[57] T. M. Klapötke, J. Stierstorfer, *J. Am. Chem. Soc.* **2009**, *131*, 1122–1134.

[58] M. Türk, *Particle Formation with Supercritical Fluids: Challenges and Limitations, Vol. 6*, Elsevier, Amsterdam, **2014**, 152 pp.

[59] D. M. Badgujar, M. B. Talawar, P. P. Mahulikar, *Propellants Explos. Pyrotech.* **2016**, *41*, 24–34.

[60] S. M. Pourmortazavi, S. S. Hajimirsadeghi, *Ind. Eng. Chem. Res.* **2005**, *44*, 6523–6533.

[61] K. Jurek, J. Kabatc, K. Kostrzewska, *Dyes Pigm.* **2016**, *133*, 273–279.

[62] T. E. Milja, V. S. Krupa, T. P. Rao, *RSC Adv.* **2014**, *4*, 30718–30724.

[63] M. E. Germain, M. J. Knapp, *Chem. Soc. Rev.* **2009**, *38*, 2543–2555.

[64] K. K. Laali, V. J. Gettwert, *J. Org. Chem.* **2001**, *66*, 35–40.

[65] N. L. Lancaster, V. Llopis-Mestre, *Chem. Commun.* **2003**, 2812.

[66] K. Smith, S. Liu, G. A. El-Hiti, *Ind. Eng. Chem. Res.* **2005**, *44*, 8611–8615.

[67] E. Dal, N. L. Lancaster, *Org. Biomol. Chem.* **2005**, *3*, 682–686.

[68] M. J. Earle, S. P. Katdare, K. R. Seddon, *Org. Lett.* **2004**, *6*, 707–710.

[69] G. Aridoss, K. K. Laali, *J. Org. Chem.* **2011**, *76*, 8088–8094.

[70] R. Rajagopal, K. V. Srinivasan, *Synth. Commun.* **2003**, *33*, 961–966.

[71] R. Rajagopal, K. V. Srinivasan, *Ultrason. Sonochem.* **2003**, *10*, 41–43.

[72] J. Jacoway, G. G. K. S. N. Kumar, K. K. Laali, *Tetrahedron Lett.* **2012**, *53*, 6782–6785.

[73] S. Weizhi, Y. U. Shitao, X. Mo, *Chem. Res. Chin. Univ.* **2015**, *31*, 761–765.

[74] M. Mascal, L. Yin, R. Edwards, M. Jarosh, *J. Org. Chem.* **2008**, *73*, 6148–6151.

[75] S.-J. Wang, Z.-Y. Sun, J. Nie, *Chin. J. Chem.* **2008**, *26*, 2256–2260.

[76] S. Wang, S. Jiang, J. Nie, *Adv. Synth. Catal.* **2009**, *351*, 1939–1945.

[77] X. Qi, G. Cheng, C. Lu, D. Qian, *Synth. Commun.* **2008**, *38*, 537–545.

[78] C. Zhang, M.-J. Yu, X.-Yu. Pan, G. Wu, L. Jin, W.-D. Gao, M. Du, J.-C. Zhang, *J. Mol. Catal. A* **2014**, *383–384*, 101–105.

[79] G. Cheng, X. Duan, X. Qi, C. Lu, *Catal. Commun.* **2008**, *10*, 201–204.

[80] D. Fang, Q.-R. Shi, J. Cheng, K. Gong, Z.-L. Liu, *Appl. Catal. A* **2008**, *345*, 158–163.

[81] K. Qiao, C. Yokoyama, *Chem. Lett.* **2004**, *33*, 808–809.

[82] D. Fang, Q.-R. Shi, K. Gong, Z.-L. Liu, C.-X. Lu, *Chin. J. Energ. Mater.* **2007**, *15*, 122–124.

[83] P.-C. Wang, M. Lu, *Tetrahedron Lett.* **2011**, *52*, 1452–1455.

[84] L. X. Li, Q. L. Ling, Z. L. Liu, X. D. Xing, X. Q. Zhu, X. Meng, *Bull. Korean Chem. Soc.* **2012**, *33*, 3373–3377.

[85] M. Vafaeezadeh, H. Alinezhad, *J. Mol. Liq.* **2016**, *218*, 95–105.

[86] T. L. Greaves, C. J. Drummond, *Chem. Rev.* **2015**, *115*, 11379–11448.

[87] G. Cheng, X. Li, X. Qi, C. Lu, *J. Energ. Mater.* **2010**, *28*, 35–44.

[88] H. Z. Zhi, J. Luo, G. A. Feng, C. X. Lv, *Chin. Chem. Lett.* **2009**, *20*, 379–382.

[89] X.-B. Liu, M. Lu, *E-J. Chem.* **2011**, *8*, 97–100.

[90] C. An, H. Li, W. Guo, X. Geng, J. Wang, *Propellants Explos. Pyrotech.* **2014**, *39*, 701–706.

[91] Y. Bayat, M. Mahdi, Ahari-Mostafavi, N. Hasani, *Propellants Explos. Pyrotech.* **2014**, *39*, 649–652.

[92] X.-F. Cao, B.-D. Li, M. Wang, *Chin. Chem. Lett.* **2014**, *25*, 423–426.

[93] X. Liu, M. Lu, *J. Energ. Mater.* **2012**, *30*, 30–39.

[94] A. B. Sheremetev, N. S. Alexandrova, K. Yu. Suponitsky, M. Yu. Antipin, V. A. Tartakovsky, *Mendeleev Commun.* **2010**, *20*, 249–252.

[95] A. B. Sheremetev, N. S. Aleksandrova, N. V. Ignat’ev, M. Schulte, *Mendeleev Commun.* **2012**, *22*, 95–97.

[96] A. B. Sheremetev, N. S. Alexandrova, I. L. Yudin, *Mendeleev Commun.* **2003**, *13*, 31–34.

[97] H.-P. Ren, Z.-W. Liu, J. Lu, Z.-T. Liu, *Ind. Eng. Chem. Res.* **2011**, *50*, 6615–6619.

[98] M. A. Epishina, I. V. Ovchinnikov, A. S. Kulikov, N. N. Makhova, V. A. Tartakovsky, *Mendeleev Commun.* **2011**, *21*, 21–23.

[99] A. O. Finogenov, M. A. Epishina, A. S. Kulikov, N. N. Makhova, I. V. Anan’ev, V. A. Tartakovsky, *Russ. Chem. Bull. Int. Ed.* **2010**, *59*, 2108–2113.

[100] A. B. Sheremetev, N. S. Aleksandrova, N. V. Palysaeva, M. I. Struchkova, V. A. Tartakovsky, K. Yu. Suponitsky, *Chem. Eur. J.* **2013**, *19*, 12446–12457.

[101] A. B. Sheremetev, I. L. Yudin, K. Yu. Suponitsky, *Mendeleev Commun.* **2006**, *16*, 264–266.
[102] A. B. Sheremetev, I. L. Yudin, *Mendeleev Commun.* **2005**, *15*, 204–206.
[103] A. B. Sheremetev, N. S. Alexandrova, D. E. Dmitriev, *Mendeleev Commun.* **2006**, *16*, 163–165.
[104] T. M. Klapötke, T. G. Witkowski, *Propellants Explos. Pyrotech.* **2015**, *40*, 366–373.
[105] P. He, J.-G. Zhang, X. Yin, J.-T. Wu, L. Wu, Z.-N. Zhou, T.-L. Zhang, *Chem. Eur. J.* **2016**, *22*, 7670–7685.
[106] M. A. Epishina, A. S. Kulikov, N. V. Ignat'ev, M. Schulte, N. N. Makhova, *Mendeleev Commun.* **2011**, *21*, 334–336.
[107] N. Nowrouzi, S. Farahi, M. Irajzadeh, *Tetrahedron Lett.* **2015**, *56*, 739–742.
[108] J. G. Wang, D. liu, G. Y. Gao, J. X. Li, *Chem. Propellants Polym. Mater.* **2007**, *5*, 16.
[109] X. Xu, M. Liu, Yu. Yin, C. Zheng, P. Denga, D. Xue, *Green Chem.* **2016**, *18*, 1364–1367.
[110] I. V. Ovchinnikov, N. A. Popov, N. N. Makhova, L. I. Khmelinitskii, V. A. Shlyapochnikov, *Mendeleev Commun.* **1995**, *5*, 231–233.
[111] L. L. Fershtat, I. V. Ovchinnikov, N. N. Makhova, *Tetrahedron Lett.* **2014**, *55*, 2398–2400.
[112] L. L. Fershtat, D. V. Khakimov, N. N. Makhova, *Russ. Chem. Bull. Int. Ed.* **2015**, *64*, 415–422.
[113] T. J. Bruno, M. L. Huber, A. Laesecke, E. W. Lemmon, R. A. Perkins, Thermophysical properties of JP-10, NISTIR 6640. National Institute of Standards and Technology, Boulder, CO, **2006**.
[114] J.-J. Zou, X. Zhang, J. Kong, L. Wang, *Fuel* **2008**, *87*, 3655–3659.
[115] L. Wang, J.-J. Zou, X. Zhang, L. Wang, *Fuel* **2012**, *91*, 164–169.
[116] H. Eshghi, M. Bakavoli, M. Ghasemzadeh, *Res. Chem. Intermed.* **2015**, *41*, 3999–4007.
[117] H. Goudarziafshar, *Chin. Chem. Lett.* **2012**, *23*, 458–461.
[118] M. A. Zolfigol, A. Khazaei, A. R. Moosavi-Zare, A. Zare, H. G. Kruger, Z. Asgari, V. Khakyzadeh, M. Kazem-Rostami, *J. Org. Chem.* **2012**, *77*, 3640–3645.
[119] H. Ghaderia, M. A. Zolfigol, Ya. Bayat, M. Zareia, E. Noroozizadeha, *Synlett* **2016**, *27*, 2246–2250.
[120] S. Schneider, T. Hawkins, M. Rosander, G. Vaghjiani, S. Chambreau, G. W. Drake, *Energy Fuels* **2008**, *22*, 2871–2872.
[121] Y. Zhang, H. Gao, Y. H. Joo, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2011**, *50*, 9554–9562; *Angew. Chem.* **2011**, *123*, 9726–9734.
[122] Q. Zhang, J. M. Shreeve, *Chem. Eur. J.* **2013**, *19*, 15446–15451.
[123] C. B. Jones, R. Haiges, T. Schroer, K. O. Christe, *Angew. Chem. Int. Ed.* **2006**, *45*, 4981–4984; *Angew. Chem.* **2006**, *118*, 5103–5106.
[124] T. Hawkins, A. Brand, L. Hall, M. Mckay, *Propellants Explos. Pyrotech.* **2003**, *28*, 174–180.
[125] Y.-F. Gao, L. Zhang, L. He, Y. Zhao, N. Tang, W.-L. Yuan, G.-H. Tao, *RSC Adv.* **2015**, *5*, 54527–54534.
[126] E. Thomas, K. P. Vijayalakshmi, B. K. George, *RSC Adv.* **2015**, *5*, 71896–71902.
[127] Y. Liu, X. Zhang, H. Ning, H. Yang, *Chin. J. Org. Chem.* **2016**, *36*, 1133–1142.
[128] M. A. Romero, *Org. Chem. Int.* **2016**, https://doi.org/10.1155/2016/4705809.
[129] Y. Zhang, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2011**, *50*, 935–937; *Angew. Chem.* **2011**, *123*, 965–967.
[130] S. Huang, X. Qi, W. Zhang, T. Liu, Q. Zhang, *Chem. Asian J.* **2015**, *10*, 2725–2732.
[131] T. Zhang, L. Liu, C. Li, Y. Zhang, Z. Li, S. Zhang, *J. Mol. Struct.* **2014**, *1067*, 195–204.
[132] S. Li, H. Gao, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2014**, *53*, 2969–2972; *Angew. Chem.* **2014**, *126*, 3013–3016.
[133] R. Fareghi-Alamdari, F. Ghorbani-Zamani, N. Zekri, *RSC Adv.* **2016**, *6*, 26386–26391.
[134] R. Fareghi-Alamdari, R. Hatefipour, *Thermochim. Acta* **2015**, *617*, 172–178.
[135] T. Fei, H. Cai, *J. Energ. Mater.* **2016**, *34*, 138–151.
[136] W. Zhang, X. Qi, S. Huang, J. Li, Q. Zhang, *J. Mater. Chem. A* **2015**, *3*, 20664–20672.
[137] V. K. Bhosale, P. S. Kulkarni, *Propellants Explos. Pyrotech.* **2016**, *41*, 1013–1019.
[138] Q. Wang, H. Lu, F. Pang, J. Huang, F. Nieb, F.-X. Chen, *RSC Adv.* **2016**, *6*, 56827–56830.
[139] T. Bergholz, B. Oelkers, B. Huber, B. Roling, J. Sundermeyer, *Chem. Eur. J.* **2015**, *21*, 2613–2620.
[140] H. Gao, J. M. Shreeve, *J. Mater. Chem.* **2012**, *22*, 11022–11024.
[141] H. Gao, Y. H. Joo, B. Twamley, Z. Zhuo, J. M. Shreeve, *Angew. Chem. Int. Ed.* **2009**, *48*, 2792–2795; *Angew. Chem.* **2009**, *121*, 2830–2833.
[142] K. Wang, Y. Zhang, D. Chand, D. A. Parrish, J. M. Shreeve, *Chem. Eur. J.* **2012**, *18*, 16931–16937.
[143] Q. Zhang, P. Yin, J. Zhang, J. M. Shreeve, *Chem. Eur. J.* **2014**, *20*, 6909–6914.
[144] D. Chand, J. Zhang, J. M. Shreeve, *Chem. Eur. J.* **2015**, *21*, 13297–13301.
[145] P. V. Ramachandran, A. S. Kulkarni, M. A. Pfeil, J. D. Dennis, J. D. Willits, S. D. Heister, S. F. Son, T. L. Pourpoint, *Chem. Eur. J.* **2014**, *20*, 16869–16872.
[146] X. Li, H. Lu, Q. Wang, J. Huang, F. Nie, H. Li, F.-X. Chen, *Chin. J. Chem.* **2016**, 1–6.
[147] D. A. Newsome, G. L. Vaghjiani, D. Sengupta, *Propellants Explos. Pyrotech.* **2015**, *40*, 759–764.
[148] C. M. Carlin, M. S. Gordon, *J. Phys. Chem. A* **2016**, *120*, 6059–6063.
[149] R. Span, W. Wagner, *J. Phys. Chem. Ref. Data* **1996**, *25*, 1509.
[150] J. A. Riddick, W. B. Bunger, *Organic Solvents, 3rd ed.*, Wiley, New York, **1970**, 1041 pp.
[151] L. Li, Ch. Yao, F. Jiao, M. Han, G. Chen, *Chem. Eng. Process.* **2017**, *117*, 179–185.
[152] Y. Zhang, D. Zhang, K. Dong, P. Lv, S. Pang, Ch. Sun, *Org. Process Res. Dev.* **2016**, *20*, 1911–1916.
[153] J. G. Speight, *Environmental Organic Chemistry for Engineers*, Butterworth-Heinemann, UK, **2016**, 538 pp.
[154] S. Gong, L. Liu, J. Zhang, Q. Cui, *Process Saf. Environ. Prot.* **2014**, *92*, 577–582.
[155] M. B. Talawar, R. Sivabalan, B. G. Polke, U. R. Nair, G. M. Gore, S. N. Asthana, *J. Hazard. Mater.* **2005**, *124*, 153.
[156] R. Mayer, J. Kohler, A. Homburg, *Explosives, 7th ed.*, Wiley-VCH, Weinheim, **2016**, 442 pp.
[157] A. Koenig, C. Roegler, K. Lange, A. Daiber, E. Glusa, J. Lehmann, *Bioorg. Med. Chem. Lett.* **2007**, *17*, 5881.
[158] A. Koenig, K. Lange, J. Konter, A. Daiber, D. Stalleicken, E. Glusa, J. Lehmann, *J. Cardiovasc. Pharmacol.* **2007**, *50*, 68.
[159] R. E. Farncomb, G. W. Nauflett, *Waste Manage.* **1998**, *17*, 123–127.
[160] G. W. Nauflett, R. E. Farncomb, *Proceedings of JANNAF Propellant Development & Characterization Subcommittee and Safety & Environmental Protection Subcommittee Joint Meeting (USA)*, **1998**, 1.
[161] I. V. Kuchurov, I. V. Fomenkov, S. G. Zlotin, V. A. Tartakovsky, *Mendeleev Commun.* **2012**, *22*, 67–69.
[162] "Thermophysical Properties of Fluid Systems". Available from http://webbook.nist.gov/chemistry/fluid/ (accessed May 2017).
[163] M. N. Zharkov, I. V. Kuchurov, I. V. Fomenkov, S. G. Zlotin (ZIOC RAS), RU2611009, **2017**.
[164] G. W. Nauflett, R. E. Farncomb (US Navy), US6177033B1, **2001**.
[165] J. P. Consaga, S. L. Collignon (US Navy), US5114506 A, **1992**.
[166] A. Ruebner, G. L. Statton, J. P. Consaga (Mach I, Inc.), US6527887 B1, **2003**.
[167] J. P. Consaga, R. C. Gill, *Proc. 29th International Annual Conf. of ICT* (Karlsruhe, Germany) **1998**, V5-1.
[168] I. V. Kuchurov, S. G. Zlotin, I. V. Fomenkov, A. A. Guskov (ZIOC RAS), RU2523472, **2014**.
[169] A. A. Guskov, I. V. Kuchurov, S. G. Zlotin, *Russ. J. Phys. Chem. B* **2015**, *9*, 1130.
[170] A. D. Ivakhnov, T E. Skrebets, K. G. Bogolitsyn (NArFU, Russia), RU2572419, **2016**.
[171] L. Kreplak, H. Wang, U. Aebi, X.-P. Kong, *J. Mol. Biol.* **2007**, *374*, 365.
[172] M. Reardon, E. Bender, *J. Forensic Sci.* **2005**, *50*, 1–7.
[173] P. W. Cooper, *Explosives Engineering*, Wiley-VCH, New York, **1996**, 460 pp.
[174] A. T. Nielsen (US Navy), US5693794 A, **1988**.
[175] A. T. Nielsen, A. P. Chafin, S. L. Christian, D. W. Moore, M. P. Nadler, R. A. Nissan, D. J. Vanderah, R. D. Gilardi, C. F. George, J. L. Flippen-Anderson, *Tetrahedron* **1998**, *54*, 11793.

[176] K. G. Herring, L. E. Toombs, G. F. Wright, W. J. Chute, *Can. J. Res.* **1948**, *26B*, 89.
[177] N. Chanhan, M. E. Colclough, J. Hamid, *Proceedings of the 6th Meeting on Supercritical Fluids*, Nottingham, UK, **1999**, 115.
[178] R. W. Millar, S. P. Philbin, *Tetrahedron* **1997**, *53*, 4371.
[179] I. V. Kuchurov, I. V. Fomenkov, S. G. Zlotin, *Russ. Chem. Bull.* **2010**, *59*, 2147.
[180] B. P. Zhukov, Energeticheskie kondensirovanny esistemy. Kratkiy ehntsiklopedicheskiy slovar [Energy condensed systems. Concise encyclopedic dictionary], Yanus-K Publ., Moscow, **2000**—in Russian.
[181] J. H. Robson, J. Reinhart, *J. Am. Chem. Soc.* **1955**, *77*, 2453.
[182] I. V. Kuchurov, S. G. Zlotin (ZIOC RAS), RU2378251, **2010**.
[183] I. V. Kuchurov, I. V. Fomenkov, S. G. Zlotin, *Russ. Chem. Bull.* **2009**, *58*, 2058.
[184] Th. Connor, G. F. Wright, G. N. R. Smart, *Can. J. Res.* **1948**, *26B*, 294.
[185] M. N. Zharkov, I. V. Kuchurov, I. V. Fomenkov, S. G. Zlotin, V. A. Tartakovsky, *Mendeleev Commun.* **2015**, *25*, 15–16.
[186] P. F. Pagoria, A. R. Mitchell, E. S. Jessop, *Propellants Explos. Pyrotech.* **1996**, *21*, 14.
[187] I. V. Kuchurov, I. V. Fomenkov, S. G. Zlotin, V. A. Tartakovsky, *Mendeleev Commun.* **2013**, *23*, 81–83.
[188] W. E. Bachmann, W. J. Horton, E. L. Jenner, N. W. MacNaughton, C. E. Maxwell, *J. Am. Chem. Soc.* **1950**, *72*, 3132.
[189] G. W. Nauflett (US Navy), US4513148 A, **1985**.
[190] M. S. Chang, R. R. Orndoff (US Navy), US4476322 A, **1983**.
[191] O. C. W. Allenby, G. F. Wright, *Can. J. Res.* **1947**, *25B*, 295.
[192] S. C. Suri, R. D. Chapman, *Synthesis* **1988**, 743.
[193] Y. H. Joo, M. S. Jean'ne, *Chem. Commun.* **2010**, *46*, 142.
[194] G. F. Wright, G. N. R. Smart, *Can. J. Res.* **1948**, *26*, 284.
[195] L. J. Winters, D. B. Learn, S. C. Desai, *J. Org. Chem.* **1965**, *30*, 2471.
[196] J. P. Freeman, W. D. Emmons, R. M. Ross, *J. Am. Chem. Soc.* **1955**, *77*, 6062.
[197] M. N. Zharkov, I. V. Kuchurov, I. V. Fomenkov, S. G. Zlotin (ZIOC RAS), RU2610282, **2017**.
[198] M. N. Zharkov, I. V. Kuchurov, I. V. Fomenkov, V. A. Tartakovsky, I. V. Fedyanin, S. G. Zlotin, *Synthesis* **2017**, *49*, 1103–1108.
[199] A. G. Stern, J. A. Kenar, N. J. Trivedi, W. M. Koppes, R. E. Farncomb, S. Turner, *Green Energetics at The Naval Surface Warfare Center, Indian-Head Division in Defense Industries: Science and Technology Related to Security* (Eds.: P. C. Branco, H. Schubert, J. Campos), Kluwer Academic Publishers, Dordrecht, Netherlands, **2004**, pp 141–207.
[200] H. J. Desai, A. V. Cunliffe, J. Hamid, P. J. Honey, M. J. Stewart, *Polymer* **1996**, *37*, 3461.
[201] R. L. Willer, R. S. Day, A. G. Stern (Thiokol Corporation), US5120827 A, **1992**.
[202] J. B. Hannay, J. Hogarth, *Proc. R. Soc. London* **1879**, *29*, 324.
[203] M. A. McHugh, V. J. Krukonis, *Supercritical Fluid Extraction: Principles and Practice*, Butterworth Publishing, Boston, **1986**, 507 pp.
[204] E. Stahl, K. W. Quirin, D. Gerard, *Dense Gases for Extraction and Refining*, Springer Verlag, Berlin, **1987**, 237 pp.
[205] V. J. Krukonis, *Polym. News* **1985**, *11*, 7–16.
[206] I. Yilgör, J. E. McGrath, V. J. Krukonis, *Polym. Bull.* **1984**, *12*, 499–506.
[207] M. E. Paulaltis, V. J. Krukonis, R. T. Kurnik, R. C. Reid, *Rev. Chem. Eng.* **1983**, *1*, 179–250.
[208] R. C. Petersen, D. W. Matson, R. D. Smith, *J. Am. Chem. Soc.* **1986**, *108*, 2100–2102.
[209] P. M. Gallagher, M. P. Coffey, V. J. Krukonis, N. Klasutis in *ACS symposium series, Vol. 406* (Eds.: K. P. Johnston, J. M. L. Penninger), American Chemical Society, Washington, DC, **1989**, pp. 334–354.
[210] J. Jung, M. Perrut, *J. Supercrit. Fluids* **2001**, *20*, 179–219.
[211] P. M. Gallagher, M. P. Coffey, V. J. Krukonis, *J. Supercrit. Fluids* **1992**, *5*, 130–142.
[212] J.-G. Cai, X.-C. Liao, Z.-Y. Zhou, *Proceedings of 4th International Symposium Supercritical Fluids* (Sendai, Japan) **1997**, pp. 23–27.
[213] U. Teipel, U. Förter-Barth, H. Kröber, H. Krause, *Proceedings of 3rd World Congress on Particle Technology*, Brighton, GB, **1998**, p. 189.
[214] U. Teipel, U. Förter-Barth, H. Krause, *Propellants Explos. Pyrotech.* **1999**, *24*, 195–198.
[215] S.-J. Kim, B.-M. Lee, B.-C. Lee, H.-S. Kim, H. Kim, Y.-W. Lee, *J. Supercrit. Fluids* **2011**, *59*, 108–116.
[216] S. J. Lee, S. Kim, B. Seo, Y.-W. Lee, J. M. Lee, *Ind. Eng. Chem. Res.* **2015**, *54*, 11894–11902.
[217] S. Kim, S. J. Lee, B. Seo, Y.-W. Lee, J. M. Lee, *Ind. Eng. Chem. Res.* **2015**, *54*, 11087–11096.
[218] J. B. Morris, *J. Chem. Eng. Data* **1998**, *43*, 269–273.
[219] M. Niehaus, U. Teipel, G. Bunte, H. H. Krause, *Propellants Explos. Pyrotech.* **1997**, *22*, 176–179.
[220] U. Teipel, H. Kröber, H. H. Krause, *Propellants Explos. Pyrotech.* **2001**, *26*, 168–173.
[221] M. Ashraf-Khorassani, L. T. Taylor, *J. Chem. Eng. Data* **1999**, *44*, 1254–1258.
[222] V. Stepanov, I. B. Elkina, T. Matsunaga, A. V. Chernyshev, E. N. Chesnokov, X. Zhang, N. L. Lavrik, L. N. Krasnoperov, *Propellants Explos. Pyrotech.* **2005**, *30*, 178–183.
[223] T. Matsunaga, A. V. Chernyshev, E. N. Chesnokov, L. N. Krasnoperov, *Phys. Chem. Chem. Phys.* **2007**, *9*, 5249–5259.
[224] V. Stepanov, V. Anglade, W. A. Balas Hummers, A. V. Bezmelnitsyn, L. N. Krasnoperov, *Propellants Explos. Pyrotech.* **2011**, *36*, 240–246.
[225] E. Marioth, S. Löbbecke, H. Krause *Proceedings of 31st International Annual Conference of ICT*, Karlsruhe, Germany, **2000**, p. 119.
[226] S. C. Fagan, A. A. Rahill, G. Balakrishnan, J. R. Ewing, C. A. Branch, G. G. Brown, *J. Toxicol. Environ. Health Part A* **1995**, *45*, 221.
[227] B.-M. Lee, D. S. Kim, Y.-H. Lee, B.-C. Lee, H.-S. Kim, H. Kim, Y.-W. Lee, *J. Supercrit. Fluids* **2011**, *57*, 251.
[228] E. Reverchon, H. Kröber, U. Teipel in *Energetic Materials: Particle Processing and Characterization* (Ed.: U. Teipel), Wiley-VCH, Weinheim, Germany, **2005**, pp. 159–182.
[229] C. K. Kim, B. C. Lee, Y. W. Lee, H. S. Kim, *Korean J. Chem. Eng.* **2009**, *26*, 1125–1129.
[230] B.-M. Lee, J.-S. Jeong, Y.-H. Lee, B.-Ch. Lee, H.-S. Kim, H. Kim, Y.-W. Lee, *Ind. Eng. Chem. Res.* **2009**, *48*, 11162–11167.
[231] B.-M. Lee, S.-J. Kim, B.-Ch. Lee, H.-S. Kim, H. Kim, Y.-W. Lee, *Ind. Eng. Chem. Res.* **2011**, *50*, 9107–9115.
[232] Y. Bayat, S. M. Pourmortazavi, H. Iravani, H. Ahadi, *J. Supercrit. Fluids* **2012**, *72*, 248–254.
[233] H. Dou, K.-H. Kim, S. T. Kim, B.-Ch. Lee, H.-S. Kim, E. Ch. Jung, S. Lee, *Chromatographia* **2012**, *75*, 903–911.
[234] H. Dou, K.-H. Kim, B.-Ch. Lee, J. Choe, H.-S. Kim, S. Lee, *Powder Technol.* **2013**, *235*, 814–822.
[235] X. Song, Y. Wang, Ch. An, X. Guo, F. Li, *J. Hazard. Mater.* **2008**, *159*, 222–229.
[236] B. Seo, T. Kim, H. J. Park, J.-Y. Kim, K. D. Lee, J. M. Lee, Y.-W. Lee, *J. Supercrit. Fluids* **2016**, *111*, 112–120.
[237] J. T. Essel, A. C. Cortopassi, K. K. Kuo, Ch. G. Leh, J. H. Adair, *Propellants Explos. Pyrotech.* **2012**, *37*, 699–706.
[238] J. Liu, W. Jiang, F. Li, L. Wang, J. Zeng, Q. Li, Y. Wang, Q. Yang, *Propellants Explos. Pyrotech.* **2014**, *39*, 30–39.
[239] J. P. Agrawal, *High Energy Materials: Propellants, Explosives and Pyrotechnics*, Wiley-VCH, Weinheim, **2015**, 498 pp.
[240] D. E. Chavez in *Green Energetic Materials* (Ed.: T. Brinck), Wiley, UK, **2014**, pp. 235–258.
[241] T. P. DiNoia, M. A. McHugh, J. E. Cocchiaro, J. B. Morris, *Waste Manage.* **1998**, *17*, 151–158.
[242] G. W. Nauflett, R. E. Farncomb, L. Chordia (US Navy), US5886293 A, **1999**.
[243] R. L Dow, G. B. Rice (US Navy), US3420695 A, **1969**.
[244] E.-Ch. Koch, *Metal-Fluorocarbon Based Energetic Materials*, Wiley-VCH, **2012**, 342 pp.
[245] E. Schmidt, R. Nastke, T. Heintz, M. Niehaus, U. Teipel in *Energetic Materials: Particle Processing and Characterization* (Ed.: U. Teipel), Wiley-VCH, Weinheim, Germany, **2005**, pp. 183–223.
[246] H. Kröber, U. Teipel, *Chem. Eng. Process.* **2005**, *44*, 215–219.
[247] A. K. Sunol (University Of South Florida), US6426116 B1, **2002**.
[248] Ch. Marraud, S. Marre, F. Cansell, C. Aymonier (Snpe Materiaux Energetiques), WO2009081048 A3, **2010**.
[249] B. He, V. Stepanov, H. Qiu, L. N. Krasnoperov, *Propellants Explos. Pyrotech.* **2015**, *40*, 659–664.
[250] A. Messmer, A. Pfatteicher, K. Schmid, W. Kuglstatter, *Proceedings of 31st International Annual Conf. of ICT*, Karlsruhe, Germany, **2000**, pp. 111/1–13.
[251] G. R. Kurulkar, R. K. Syal, H. Singh, *J. Energ. Mater.* **1996**, *14*, 127–149.

[252] M. T. Shedge, C. H. Patel, S. K. Tadkod, G. D. Murthy, *Def. Sci. J.* **2008**, *58*, 390–397.
[253] J. Böhnlein-Mauß, H. Kröber, *Propellants Explos. Pyrotech.* **2009**, *34*, 239–244.
[254] W. Yang, Y. Li, S. Ying, *Propellants Explos. Pyrotech.* **2014**, *39*, 568–573.
[255] W. Yang, Y. Li, S. Ying, *J. Energ. Mater.* **2015**, *33*, 91–101.
[256] W. Yang, S. Ying, *Propellants Explos. Pyrotech.* **2016**, *41*, 136–141.
[257] W. Yang, Y. Li, S. Ying, *Cent. Eur. J. Energ. Mater.* **2014**, *11*, 257–269.
[258] M. Jin, N. Luo, G. Li, Y. Luo, *J. Therm. Anal. Calorim.* **2015**, *121*, 901–908.
[259] Y. Wang, X. Song, D. Song, L. Liang, C. An, J. Wang, *J. Hazard. Mater.* **2016**, *312*, 73–83.
[260] Y. Zhang, Z. Shao, J. Li, K. Gao, Y. Liu, *J. Appl. Polym. Sci.* **2015**, *132*, 41405.

Manuscript received: June 13, 2017
Accepted manuscript online: July 6, 2017
Version of record online: September 18, 2017