

Review

Organic and Inorganic Biocidal Energetic Materials for Agent Defeat Weapons: An Overview and Research Perspectives

Andrea Pietro Reverberi ^{1,*}, Valery Pavlovic Meshalkin ^{2,3} , Oleg B. Butusov ², Tamara B. Chistyakova ³, Maurizio Ferretti ¹ , Anna Maria Cardinale ¹ and Bruno Fabiano ⁴ 

¹ DCCI, Department of Chemistry and Industrial Chemistry, Università degli Studi di Genova, Via Dodecaneso 31, 16146 Genova, Italy

² Mendeleev University of Chemical Technology of Russia, 127047 Moscow, Russia

³ Saint-Petersburg State Institute of Technology, Technical University, 190013 St. Petersburg, Russia

⁴ DICCA, Department of Civil, Chemical and Environmental Engineering, Polytechnic School, Università degli Studi di Genova, Via Opera Pia 15, 16145 Genova, Italy

* Correspondence: reverb@dichep.unige.it

Abstract: A critical survey concerning biocidal energetics is proposed according to a classification depending on their chemical structure. The need of optimizing the performances of such compounds is an important target for the inertization of biological weapons, requiring a synergy between the thermal effects of combustion/detonation with the biocidal effects of reaction products released into the environment. The main physicochemical aspects related to the synthesis technique, the thermodynamic variables and the antimicrobial activity have been discussed and compared. In particular, different kinds of biocides have been taken into account, with particular attention to the role of iodine as one of the most promising and eco-friendly chemical species to this purpose, in line with the paradigms of environmental protection and the rational utilization of chemicals. Furthermore, the protocols adopted to assess the effectiveness of biocidal agents have been thoroughly examined according to the recent studies proposed by some of the most reputable research groups in the field. Finally, some insights for future investigations are proposed.

Keywords: energetic material; biocide; agent defeat weapon; thermite; antimicrobial; waste



Citation: Reverberi, A.P.; Meshalkin, V.P.; Butusov, O.B.; Chistyakova, T.B.; Ferretti, M.; Cardinale, A.M.; Fabiano, B. Organic and Inorganic Biocidal Energetic Materials for Agent Defeat Weapons: An Overview and Research Perspectives. *Energies* **2023**, *16*, 675. <https://doi.org/10.3390/en16020675>

Academic Editor: Antonio Zuorro

Received: 27 November 2022

Revised: 27 December 2022

Accepted: 4 January 2023

Published: 6 January 2023



Copyright: © 2023 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<https://creativecommons.org/licenses/by/4.0/>).

1. Introduction

The use of biological weapons (BW) represents one of the major threats for today's communities and the research on this field is dramatically active though still generally encrypted [1,2]. BWs have had a long and continuous use over time [3], with different levels of refinement according to the progression of technology and information on the biochemistry of pathogens. Up to now, there has not been a univocally accepted classification concerning weapons of mass destruction (WMD). As a general scheme, WMD typically includes nuclear, chemical and biological armies [4] and it should be remarked that, while the former destroys both animated and inanimate targets, the latter two only injure living forms. Additionally, BWs differ from chemical weapons (CWs) for many aspects, of which the most important are the time of symptoms' appearance, the contagiousity (absent in CWs) and the difficulty of detection in the environment, owing to a considerable difference of mass required by a CW with respect to a BW [5,6]. However, the boundary line between CW and BW is, in some cases, somewhat subtle and questionable [7]. The conjunction ring is represented by toxins, which differ from true BW-like microorganisms in that they do not reproduce themselves, apart from prion proteins [8,9]. From the other side, toxins are not classifiable as CWs for three basic reasons. In fact, toxins suitable for military uses are of a natural origin, being biologically produced [10]; they have a low volatility and they are not active by dermal poisoning, in contrast with most man-made chemical warfare agents. In some cases, their difficulty of extraction and concentration may pose serious limits to a

practical use in the field [11] Nowadays, a wide variety of toxins as possible candidates for weaponization have been studied in detail, such as botulinum neurotoxin [12], clostridial neurotoxins [13], conotoxin [14] and plant toxins [15,16]. There is a great variability in the lethality of toxins, whose poisonous properties are usually measured in LD₅₀, namely the lethal dose expressed in mass per kg of the victim's body in 50% of cases. From the data gathered by Colonel David R. Franz [17] in a manual of the U.S. Army Medical Research Institute, one can observe that the most poisonous toxins of bacterial origin have an LD₅₀ in the range of 0.001–0.002 µg/kg, a value smaller by several magnitude orders in comparison to the one of the mostly toxic CWs, cholinesterase inhibitors (nerve agents), such as VX, Sarin and Soman [18,19], whose LD₅₀ lies in the range of 15–100 µg/kg.

The paper of Seth W. Carus [20] is probably the best in-depth historical analysis of BWs, including both toxins and pathogen-induced diseases, where he pointed out a generalized disinformation characterizing past surveys about this topic. From a methodological point of view, he divided the evolution of BWs into three consecutive stages. In the last one, starting at the end of World War II and leading to the present time, unsettling scenarios are looming [21,22]. In fact, the tests carried out in the Large Area Coverage of the United States led to the conclusion that the consequences of BWs on living species could be comparable to or even more catastrophic than those related to the use of thermonuclear weapons.

In a context pertaining to BWs more closely restricted to microorganisms, Eneh [23] analyzed the role of several parameters characterizing the practical use of a biological agent in war or in bioterroristic attacks and he ruled out advantages and drawbacks related to the use of BWs. The identification/choice of the best pathogen is subject to a multiobjective optimization of several factors, such as virulence, pathogenicity, incubation period and transmissibility. Of course, these aspects must be matched with a resistance of the microorganism to drying, conservation and storage in vessels preceding the phase of delivery, usually relying upon aerosolization. Afterwards, the pathogen is subject to other causes of inactivation, related to temperature, UV light and other environmental conditions. For these reasons, several investigations have been carried out about microorganisms of different species as possible candidates for BWs [24–28], with a particular attention focused on *Bacillus anthracis*, as it proved to be particularly suitable for real application, even as a foodborne bioterroristic agent, owing to its ease of production, lethality and the stability of spores before and after dispersion [29]. Another serious concern related to this etiologic agent stems from its capability of developing resistance towards antibiotics [30,31].

At this point, the reader could ask himself two basic questions, namely:

1. What could be a possible strategy to counter the proliferation of BWs?
2. Are there some techniques, processes and/or materials capable of the inertization of the stockpiles of biowarfare agents already produced and what is the role of mass/energy transfer in this context?

Giving an answer to question 1 was the main task of multilateral negotiations starting in the years 1969–1972 and leading to the well-known Biological Weapon Convention, a treaty aiming at banning all BWs explicitly defining them as “repugnant to the conscience of mankind”. A discussion on the compliance with its provisions in the following times refers to the issue of international cooperation and therefore it is beyond the scope of this paper [32].

Instead, the present survey is intended to give a collection of multiple responses, offered by the scientific community on the subject, to the research questions raised at point 2. On that note, the use of biocidal energetic materials (BEMs) represents a challenging strategy that has a twofold purpose: the inertization of stockpiles of biological agents together with the disinfection of an area subject to contamination by pathogens, thus optimizing the utilization of chemicals in compliance with the environmental equilibrium. For what has been said, BEMs are commonly classified as Agent Defeat Weapons (ADWs). This compendium is meant to fill the theoretical gap concerning surveys about BEMs, which are generally focused on organic [33] or inorganic compounds, but do not include an overview and a critical analysis on both aspects. This paper is organized as follows. In Section 2,

the physicochemical parameters characterizing BEMs are discussed and compared with ones typical of generic energetic materials. In Section 3, the BEMs are classified according to their composition and biocidal activity, whose estimation is carried out according to the protocols described in Section 4. Finally, Section 5 contains the final considerations, together with some possible hints for inspiring future research.

2. Basic Variables and Properties of EMs and BEMs

BEMs are a subset of a much larger ensemble represented by energetic materials (EMs), mainly comprising explosives [34,35], pyrotechnics [36] and propellants [37,38] with several applications in the real world, including micromechanical systems [39] and safety devices typically adopted in automotive technology [40].

The action mechanism of BEMs relies upon two different processes, triggered by a chemical reaction carried out by the combustion, deflagration or detonation of the energetic material. The relevant thermal effect, together with the chemical species released in the surrounding environment after the reaction, exert a biocidal action on the microorganisms and inertize the biological weapon.

Most of the physicochemical variables characterizing EMs are the same describing BEMs, as the latter require the use of energy-releasing materials mechanically and thermally acting for the inactivation of bioaerosols and the destruction of bioweapon stockpiles and warheads. Seminal texts for EMs are the books of Keshavarz and Klapötke [41,42] and we refer the reader to the references quoted therein. However, BEMs need additional describing variables, taking into account the type and concentration of the biocidal species contained in the decomposition products of the BEM itself. Those last aspects may be relevant in the case of industrial production and the connected need of preventing accidents for human health and the environment, according to the framework of the Seveso-III-Directive (2012/18/EU) [43]. A list of variables generally used to characterize and to estimate the performances of a BEM can be found in Figure 1. A concise yet informative survey about key metrics for the performances of EMs can be found in the paper of O'Sullivan and Dzilla [44]. For some of them, such as density, heat of reaction, oxygen balance, impact and friction sensitivity, thermal stability and the mass fraction of biocidal molecules in reaction products, there is a commonly shared opinion among researchers about their role in the maximization of BEM performances. For example, a great effort of research is devoted to maximize the density, as BEMs of high densities allow the confinement of high chemical energy in small volumes, thus increasing the overall mechanical and thermal yield. The same consideration is valid for the enthalpy of reaction as far as thermal effects are concerned. However, the discussion about the role of detonation pressure and reaction speed is more puzzling and controversial, being often case-dependent.

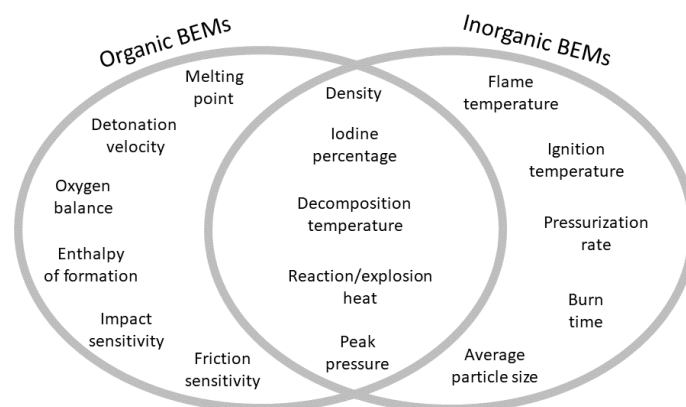


Figure 1. Scheme of the most important variables characterizing BEMs according to their basic chemical composition/formulation.

Some variables, such as the detonation velocity, may be measured with standard experimental apparatuses, even though test improvement is necessary, as discrepancies of results from different laboratories are still too large to be reliable [45]. Some others, such as the specific impulse [46,47], are generally calculated using theoretical or semi-empirical models that have been proposed in the last decades and have been progressively updated in the recent years in order to make increasingly accurate forecasts [48]. Analogously, sensitivity is strongly correlated to crystal packing and intermolecular interactions, whose estimation is often entrusted to specific packages, such as CrystalExplorer, based on Hirschfeld surface analysis [49].

Muravyev et al. [50] collected the experimental data of 260 different EMs from specialized publications on the topic and observed that the detonation velocity is a generally known parameter for all species, while experimental data on other parameters are less available. Interestingly, these authors focused on tuning the characteristics of energetic molecules, whose performances can be improved by acting essentially on four main parameters, such as density, heat of formation, cage strain and the balance between functional groups that have combustible and comburent properties in the same molecule.

Many thermodynamical software tools such as EMDB [51], CHEETAH [52], EXPLO5 [53], Gaussian 09 [54] and others have been adopted to theoretically determine the combustion and/or detonation parameters of single molecules and mixtures. As pointed out by Grys and Trzciński [55], most of them are subject to proprietary uses and they cannot be generally updated, owing to commercial constraints actually hindering the modification of the source codes. A group of Russian scientists [56] proposed theoretical approaches to calculate several physicochemical properties of EMs, including the enthalpy of formation [57], by a method (MAC) based on the additivity of atomic contributions [58]. This technique proved to be useful in the estimation of the overall performances of organic EMs that have the general expression $C_aH_bN_cO_dFe$.

As previously stated, BEMs have many points in common with EMs in terms of the thermodynamic variables describing their detonation properties, but new parameters related to their biocidal performances become equally important. While the selection of the best chemicals or chemical mixtures for BEM composition spans over a wide range of choices, the situation is different as far as the tuning and prediction of the best biocidal compounds in the reaction products is concerned. In fact, the non-thermal biocidal effect is entrusted to some specific elements or compounds, such as halogens, hydrogen fluoride (HF), sulphur halides, silver compounds, metal oxides nanoparticles and a few other inorganic species with a likely lethal effect on the pathogens. However, if a low toxicity on man and on the environment is required, the choice narrows dramatically. In this context, elemental iodine plays a leading role, in that it satisfies both of the aforementioned conditions. Nowadays, in line with the paradigms of sustainability, inherent safety and eco-compatibility, applied in a number of emerging material process developments [59], green biocidal energetics are attracting growing attention, but this line of research is only just beginning.

3. Types and Classification of BEMs

A classification taking into account the chemical nature and composition of BEMs resorts to essentially two main cornerstones, namely organic and inorganic compounds. Of course, many further subsets can be envisaged, according to inner compositional details related to the specific energetic and biocidal carriers.

3.1. Organic BEMs

In this subsection, halogenated derivatives of heterocyclic compounds represent the most important category of molecules where iodine, fluorine and chlorine are the most suitable candidates in order of decreasing importance in terms of both relevant research publications and possible real applications.

3.1.1. Single-Block Structures

By this term, a structure is meant where halogens and energetic functional groups are bound to a single basic scaffold, generally but not necessarily represented by a heterocyclic or polyheterocyclic carbon ring.

Fluorinated and Chlorinated Molecules

The reasons explaining a lower overall success of fluorinated and chlorinated BEMs compared to their iodinated counterparts are essentially due to several motivations, which can be summarized in the following points [60], namely:

- Fluorinated/chlorinated energetics generally release hydrofluoric/hydrochloric acid (HF/HCl) or Cl_2 in the decomposition products following a deflagration/detonation, and HF or Cl_2 are disadvantageous compared to iodine for two different reasons. HF and Cl_2 are typically highly active though non-persistent biocidals, owing to their high vapor pressure at room temperature, with boiling points at $19.5\text{ }^\circ\text{C}$ and $-34.6\text{ }^\circ\text{C}$, respectively. Both of them are gaseous at room temperature and they have a very irritating action on the mucous membranes of humans, explaining why one of them was used as a chemical agent in World War I [61,62]. Conversely, HCl has a very weak biocidal activity with respect to HF [63].
- In some cases, fluorinated hydrocarbons of low-molecular weight that have non-biocidal properties such as CF_4 are present in the detonation products in place of HF, thus decreasing the sporicidal performances of the corresponding BEM.
- Being the most electronegative element among all atoms, fluorine tends to form stable C-F bonds, thus reducing the heat of the decomposition of the organic BEM where it is contained. Moreover, when hydrogen is replaced by fluorine in energetic molecules, the extent of intermolecular hydrogen bonding tends to decrease, thus leading to a decrease in the melting point of the corresponding compound. As an example, fluorinated aromatic nitrocompounds generally have a melting point considerably smaller than the corresponding non-fluorinated molecules. This fact poses a serious technical limitation, as a biocidal explosive is much better employed in solid than in liquid state.

Difluoramines, namely molecules containing the functional group $-\text{NF}_2$ [64], have been studied both experimentally and theoretically [65], owing to their beneficial effect in improving the energetic performances of BEMs. However, poly-difluoramines often proved to be exceedingly sensitive to mechanical impact, with properties even resembling those of primary explosives. Chapman [60] concluded claiming a limited viability of such compounds for a possible use as ADWs. Dichloramines showed considerably lower performances with respect to the corresponding difluoramines, both for energetic and biocidal properties. Some of them did not even detonate [63].

Energetic molecules containing the pentafluorosulfanyl group ($-\text{SF}_5$) have been objects of attention for their thermal stability, high density and low sensitivity. Energetic ionic salts made of SF_5 -substituted triazolium, imidazolium and pyridinium were synthesized by Gao et al. [66]. In this case, again, the relevant compounds showed a marked lowering of the melting point.

Iodinated Molecules

It has been proven that I_2 , which is released after the deflagration/detonation of iodinated BEMs, has a very intense action on cell membranes and it kills viruses and bacteria at concentrations generally smaller than 15 ppm [67]. This explains why iodine-based energetic biocides are in the hotspot of ADW research [68]. Among the simplest structures belonging to this category, it is worth mentioning the iodo-nitro-derivatives of benzene, which have been produced by two- or three-step synthesis according to the study of Zhao et al. [69], where the energetic carriers are represented by nitro- ($-\text{NO}_2$) or azido- ($-\text{N}_3$) groups, as reported in Figure 2. Their synthesis process relies upon an initial

iodization of the C-H bonds [70], followed by an addition of a $-\text{NO}_2$ group and finally by a nucleophilic substitution between two different energetic groups.

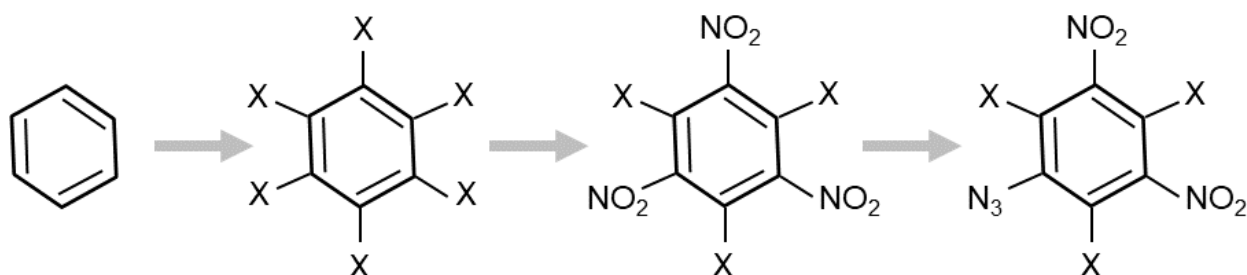


Figure 2. Scheme of the synthesis of a single-block halogenated nitro-azido biocidal energetic material, where X is a halogen atom. The figure has been adapted and modified from Ref. [69], where X = I.

The two compounds thereby formed, namely 1,3,5-triiodo-2,4,6-trinitrobenzene (TITNB) and 1-azido-2,4,6-triiodo-3,5-dinitrobenzene, have been theoretically investigated in their thermodynamic properties, whose main strengths stem from the high density (>2.9) and their surprisingly high values for the enthalpy of formation, detonation velocity and iodine percent composition. Trinitrotoluene (TNT) is routinely taken as a benchmark when assessing the energetic performances of organic BEMs.

Other basic structures that have been used as starting points for the synthesis of such polyiodide compounds are heterocyclic five-member or six-member carbon rings containing from one to four nitrogen atoms, linked to energetic functional groups such as $-\text{NO}_2$, $-\text{IO}_2$, $-\text{N}_3$ and others [71,72]. The heterocyclic skeletons usually adopted in the literature rely upon iodinated polyiodazoles, iodinated furan and more rarely upon iodinated thiophene.

In N-eterocyclic compounds, all other conditions being equal, their enthalpy of formation grows for increasing values of their nitrogen-carbon ratio, thus shifting towards more endothermic structures, thus giving more appealing detonating performances [73]. However, as previously observed, this fact does not necessarily imply that a molecule that has a negative heat of formation may have poor detonating performances: TNT is a classic example.

Many of the aforementioned single-block iodinated BEMs, named as “first generation ADWs” suffer from a structural constraint about how to realize an optimal trade-off between iodine and energy-carrier bonds [74]. This amounts to saying that, owing to a limited number of bonding sites in a single-block structure, the higher the number of $-\text{I}$ bonds, the fewer are the sites available for energy-carrier groups, such as, for example, $-\text{NO}_2$. As a consequence, maximally iodinated blocks may decompose giving a high biocidal yield, but they have poor or even null detonation performances [73]. Conversely, maximally nitro-substituted single-blocks have good detonation performances but scarce biocidal properties and a dramatic drop in density. These statements are consistent with the physical properties of the compounds obtained by Chand and Shreeve [75], who synthesized a dinitro-substituted iodopyrazole by a sequence of steps analogous to the ones previously described.

To overcome these drawbacks, He et al. [76] proposed the use of the oxygen-carrier $-\text{IO}_2$ in place of the customarily used $-\text{NO}_2$, so as to merge together the energetic and biocidal properties in a single functional group. They synthesized several iodyl- and polyiodyl-pirazoles and imidazoles with very satisfactory values of thermal stability, density, detonation velocity, detonation pressure and iodine content. Intriguingly, four out of five of these compounds have a negative enthalpy of formation, but the high sensitivity to mechanical impact may represent a serious aspect to be taken into account for real applications of $-\text{IO}_2$ -containing BEMs.

The aforementioned target of simultaneously improving biocidal and detonation performances is framed in a problem of multiobjective optimization, leading to the production of the “second-generation” BEMs that will be dealt with in the following subsections.

3.1.2. Multiblock Structures

As previously said, such “second-generation” structures represent the natural evolution of the formerly simple-block molecules. Again, most of them are iodinated molecules, where energetic and biocidal building blocks are linked together by aliphatic bridges [77]. Usually, but not necessarily, the biocidal blocks are poly-iodine-substituted non-explosive structures, while the energy-carrier blocks are aromatic molecules usually containing multiple $-\text{NO}_2$ groups or N-heterocyclic molecules that have the highest N/C ratio, namely cationated nitrogen structures [44], possibly themselves containing $-\text{NO}_2$ groups. In Figure 3, an example of molecules belonging to single- and multiblock structures has been proposed.

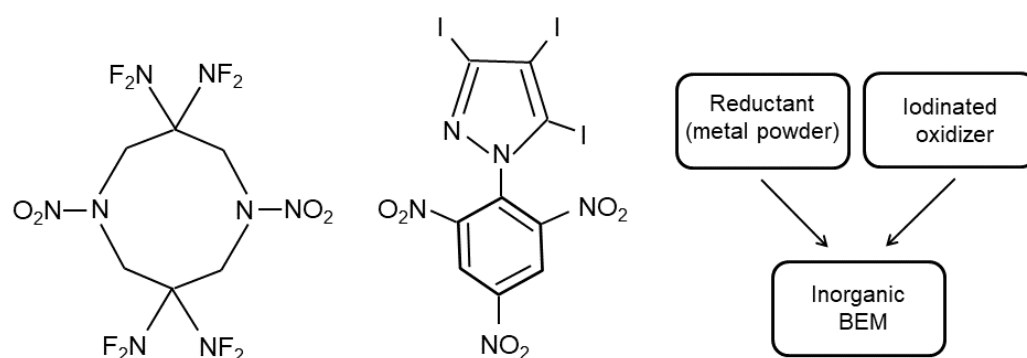


Figure 3. Left image: example of a single-block organic BEM containing haloamine groups (HNFX; 3,3,7,7-tetrakis (difluoramino) octahydro-1,5-dinitro-1,5-diazocine). Central image: example of a multiblock organic BEM (3,4,5-triiodo-1-(2,4,6-trinitrophenyl)-1H-pyrazole). Right image: simplified scheme of a process where an iodinated inorganic BEM is obtained by mixing, where iodine is contained in the oxidizer.

Zhao et al. [78] investigated the properties of three different BEMs, made of aminotriazoles linked to iodinated pyrazoles and imidazoles by methylene bridges. Interestingly, all compounds showed high detonation velocities in the range of 4496–5555 m/s, with an iodine percent composition never below 48.7%. The relevant antibacterial performances proved to be superior to those typical of iodinated test molecules such as 3,4,5 triiodopyrazole (TIPy).

The bridges between biocidal and energy-carrier blocks may be themselves enriched with energetic functional groups or “explosophores” [79]. He et al. [80] synthesized energetic-bridged polyiodopyrazoles linked together by poly-nitro poly-aza-alkanes characterized by the presence of energetic $=\text{N}-\text{NO}_2$ groups with iodine percent composition greater than 66.73% and satisfactory global performances as BEMs.

Examples of multiblock fluorinated compounds are less common. However, Garg et al. [81] succeeded in linking $-\text{CF}_3$ and pentafluorosulfanyl ($-\text{SF}_5$) groups to energetic blocks, such as polytriazoles produced by click chemistry techniques, where triazoles are synthesized starting from alkynes and azides. Within certain limits, it is possible to tune the formation of biocidal HF in the detonation products, avoiding the presence of other noxious or unwanted compounds such as fluorophosgene (COF_2). To this purpose, the presence of the group $-\text{SF}_5$ has proven to be beneficial [82].

3.1.3. Ionic Organic Compounds and Energetic Biocidal Cocrystals

Ionic salts of ammonium (NH_4^+) and guanidinium ($\text{C}(\text{NH}_2)_3^+$) with difluoriodate anion (IF_2O_2^-) had some interesting biocidal properties, owing to a release of both HF and I_2 in their decomposition products, with a synergistic effect in their disinfectant activity [83]. However, they proved to be corrosive towards steel during sensitivity tests, where no

explosion was detected, thus showing poor energetic properties. Similar drawbacks affect other alkyl ammonium iodides and polyiodides, whose energetic properties are tuned by the presence of N-NH₂ functional groups in the cation, while the iodide/polyiodide anion impacts on the density of the material [84]. To improve the energetic performances, other authors synthesized several different ionic BEMs where the cationic skeleton is made by an azolinium ion or by azoles linked to a guanidinium ion. The anionic moiety is represented by iodate (-IO₃) or periodate (-IO₄) oxidizing groups [85]. Their surprising detonation velocity, even greater than 7200 m/s, exceeded the one typical of TNT, but the iodine content was rarely exceeding 50%. As an exception, He et al. [86] synthesized poly-iodoimidazolium iodates and periodates with acceptable detonation properties and iodine content never below 70%.

Non-covalent interactions between the atoms of functional groups belonging to different molecules have been exploited to realize engineered cocrystals [87]. Intriguingly, such bonds may be established between electronegative atoms, owing to the presence of locally positive regions in their electrostatic potential distribution, defined as σ -holes, whose formation is favored as the electronegativity of the halogen decreases [88]. On that note, some researchers have synthesized cocrystals made of single-block polynitro aromatic compounds, acting only as energetics/explosophores, with other single-block poly-iodinated aromatics, such as the previously mentioned TITNB, acting as energetic biocidal iodine carriers. The electrostatic interactions are established between the iodine of a molecule and the oxygen of the nitro-group of the other one. The great advantage offered by these new challenging materials stems from a synergistic effect of properties, such as the shock sensitivity of the cocrystals, which may be less sensitive to the impact than each of the components, with important safety implications [89].

3.2. Inorganic BEMs

While the previously discussed organic BEMs generally comprise a single molecular species where biocidal and energetic functions are devolved to specific functional groups, inorganic BEMs are usually made of two or more solid phases in intimate contact. In some conditions, these solid phases undergo a combustible-comburent exothermic chemical reaction, while in other cases they are simply a mix of a biocidal precursor and a combustible reacting with air oxygen. Irrespective of these mechanisms, the final target is the production of a heat wave and release of reaction products, both having biocidal activity in the surroundings. Therefore, new physico-chemical phenomena, not present when discussing organic BEMs, gain an important role in this context, owing to the importance of interphase heat transfer. As a consequence, in addition to the chemical nature of solid reactants, their granulometry and mixing degree are basic parameters conditioning the global performances of this kind of energetic materials. A satisfactory modeling of energy transfer between granular reacting materials may require a specific formalism, differing from the one adopted in the case of a standard continuum approach [90].

The chemicals released into the environment consist of elemental iodine or other inorganic molecules capable of destroying microbial colonies. For this reason, inorganic BEMs have been classified here according to the presence or absence of iodine in their composition, as other halogens in place of it are not usually adopted in inorganic BEMs and the motivation is essentially of a thermodynamic nature. In fact, being the least electronegative of all halogens (of course, astatine is not considered), it is more likely to be found free in the reaction products than other halogens.

3.2.1. Biocidal Thermites

Historically, thermites represented a mixture of metal oxides with powdered aluminium, capable of triggering a strongly exothermic reaction after being ignited by a proper device. Here, the definition is generalized to reacting solid phases made of an oxidizer (comburent) and a reductant, releasing heat and biocidal reaction products.

The combustion performances of biocidal thermites are mainly defined in terms of ignition temperature, flame temperature, burning time, peak pressure and pressure rise rate, which is directly proportional to the burn rate. The ignition temperature is usually determined by T-jump mass spectrometry [91], where a platinum wire covered by a layer of powdered material is heated by a current flowing through it in an inert atmosphere or in air [92]. A high-speed camera collects images monitoring the combustion start and its progression [93]. All the other aforementioned variables can be measured by a constant-volume cell, connected with a suitable spectrometer, by which an estimation of the flame temperature can be carried out [94]. The burning process of a single particle is preferentially analyzed by a specific apparatus, based on a low-energy laser scattering diagnostic system, to determine particle diameters and a high-energy laser beam to trigger combustion [95].

Biocidal Thermites with Salts of Iodine Oxyacids

Metal iodates and periodates of generic formula $\text{Me}^{n+}(\text{IO}_3)_n^-$ and $\text{Me}^{n+}(\text{IO}_4)_n^-$, where Me is an alkaline earth metal, a transition metal or Bi, have been proposed and tested as oxidizers, which are mixed with combustible compounds or with zerovalent powdered elements acting as a reductant. Alkali metal salts of iodine-containing oxidizers are usually discarded, as they form alkali iodides in their combustion/deflagration products in place of free I_2 , with a dramatic drop in biocidal performances, but there are exceptions. Kotter and Groven [96] used boron carbide (B_4C) as a fuel mixed with sodium periodate (NaIO_4) as a comburent, and they succeeded in obtaining a high yield of I_2 in the combustion products. This fact can be understood taking into account that, despite B_2O_3 being a weakly acid anhydride, it is capable of driving out other anions such as I^- at high temperature, setting free I_2 . Among the latter, powdered Al is an almost ubiquitous presence in most mixtures of this kind and it is advantaged by its highly electropositive character and by the high formation enthalpy of its oxide Al_2O_3 . For these reasons, its thermites have a particularly high temperature flame, an aspect often desired as it promotes a likely thermal shock on the microbial colonies. However, irrespective of oxidizer composition, Al-thermites have some disadvantages that may assume a dramatic role. In fact, a sintering process of fuel particles, particularly typical of powdered Al, may often act as a rate limiting step of reaction kinetics. In some conditions, typically occurring in thermites not producing gaseous products of reaction, Al-thermites may suffer from an incomplete combustion [97].

It has been observed that the reactivity of metastable interstitial composites (MICs) is greatly enhanced when the reactants are confined to a nanosized scale [98]. This property, initially observed for non-biocidal thermites [99], has been successfully extended to BEMs. On that note, Wang et al. [100] prepared several metal iodates in fine powders by mechanochemistry, using metal nitrates and KIO_3 as a starting reagent. This technique proved to be a valid alternative to standard wet chemical methods for the production of metal iodate microparticles, except for $\text{Bi}(\text{IO}_3)_3$ and $\text{Fe}(\text{IO}_3)_3$. These last two oxidizers were more advantageously produced following more traditional protocols, based on precipitation and crystallization schemes, respectively [101]. It was observed that these metal iodate thermites outperform the analogous non-biocidal metal-oxide-based thermites in several energetic parameters. An interesting recent protocol for the synthesis of Cu, Fe and Bi iodates in situ consists of mixing two solid phases, made of an energetic salt such as aluminium iodate hexahydrate ($\text{Al}(\text{H}_2\text{O})_6(\text{IO}_3)_3$ (HIO_3)₂) [102], together with the oxide of a metal whose iodate is to be obtained [103]. In this way, the relevant metal iodates are formed by solid–solid exothermic reaction at conveniently low temperatures (<450 °C). This technique may represent a versatile method to tune a thermite reaction starting with a ternary mixture comprising aluminium iodate, a metal oxide and a powdered metal as a reductant.

As previously mentioned, the mixing of oxidizer and reductant solid phases is a fundamental aspect that can be realized in different ways, as amply discussed in the excellent review paper by Dreizin [104]. A standard technique, typically adopted for biocidal nanothermites, consists of dispersing the solid phases in an organic solvent, where

they are not soluble, following by sonication and the further evaporation of the solvent, leaving the phases very homogeneously mixed. More recent and appealing methods rely upon additive manufacturing techniques, including printing, extrusion, templating and electrospraying technologies [105]. However, these techniques still require a careful understanding of the heat transfer processes to damp flame stand-off effects [106]. Arrested reactive milling is an atypical top-down method for the preparation of BEM mixtures, currently object of growing attention [107]. According to this technique, solid phases susceptible of chemical reaction are milled together, stopping the comminution at the threshold corresponding to the onset of the mechanically activated chemical reaction. In this way, the interfacial contact between reacting phases is maximized with respect to other physical methods, with obvious advantages in the thermochemistry of combustion. However, this method poses some safety problems as it requires an accurate control of the process time. Additionally, a small amount of reaction products often contaminates the mixture, despite stopping before the threshold time.

Among iodates, $\text{Ca}(\text{IO}_3)_2$ is in the hotspot for its peculiarity of releasing the highest amount of molecular iodine with respect to many other inorganic salts [108] and for its relative stability towards heat and moisture. It can be easily synthesized by standard wet chemical routes and it has intrinsic antibacterial activity by itself against certain resistant pathogens [109]. Wang et al. [110] studied the combustion dynamics of Al and B with $\text{Ca}(\text{IO}_3)_2$ in powdered mixtures, produced by arrested reactive milling [111]. The process consisted of comminuting the premixed components under argon atmosphere by means of shaker and planetary millers, in the presence of hexane as a process control agent. The authors focused in particular on the starting ignition steps and observed that a B/ $\text{Ca}(\text{IO}_3)_2$ mixture had an ignition temperature 450 K lower than in the case with Al. This parameter is important as it corresponds to the minimum temperature for I_2 release. Interestingly, taking in to account that the ignition temperature of the B/ $\text{Ca}(\text{IO}_3)_2$ mixture was lower than the melting temperature of all solid reactants and products, the authors concluded that this process was based on a pure heterogeneous reaction between solid phases.

In another study [112], the performances of Al and B were compared with those obtained using Ti in place of them. The ignition temperatures of Ti/ $\text{Ca}(\text{IO}_3)_2$ thermites were considerably lower than Al/ $\text{Ca}(\text{IO}_3)_2$ or B/ $\text{Ca}(\text{IO}_3)_2$ ones and it was speculated that this difference was ascribable to the melting point of Al and to the diffusive resistance to interphase contact due to molten B_2O_3 on B surface. In this case again, a reduction in the particle diameters of reactants was beneficial to enhance the reactivity of these pirolants. In order to optimize the I_2 produced by combustion, a binary B- I_2 composite powder was tested in place of B alone [113]. Despite a limited affinity between B and elemental I_2 , a prolonged milling of both elements' powders allowed the obtainment of a relatively stable composite, probably owing to the formation of a metastable boron-iodine compound. The as-prepared composite was ultimately mixed with $\text{Ca}(\text{IO}_3)_2$ by arrested reactive milling, giving a thermite with lower ignition temperature than B/ $\text{Ca}(\text{IO}_3)_2$ thermites.

Several variants of $\text{Ca}(\text{IO}_3)_2$ -based thermites have been tested, according to the choice of the combustible phase composition. For example, Ghildiyal et al. [114] faced the problem of energy density limitations imposed by the interstitial porosity of the fuel-oxidant mixture. To this purpose, they mixed Al and Si nanoparticles with respective diameters of 80 nm and 5 nm, together with a fluorinated binder and the comburent $\text{Ca}(\text{IO}_3)_2$ in a proper organic solvent, which was further electrosprayed giving homogenized mesoparticles after the evaporation of the solvent. The thermite was then ignited in a constant-volume cell, to study the relevant burn time and pressure. It was observed that some combustion parameters improved up to 8% Si, due to an increase in the energy density of the composite. After this threshold, the thermite reactivity worsened dramatically, due to sintering effects and to the intrinsic slow burning kinetics of Si.

The preparation of a Mg- $\text{Ca}(\text{IO}_3)_2$ nanocomposite BEM [115,116] is another successful example of the arrested reactive milling technique. The thermite combustion was tested both in air-acetylene flame and by laser ignition in air. The release of I_2 occurred according

to multiple steps for growing temperatures, depending on the progressive decomposition of the comburent phase. Despite the presence of powdered Mg, the thermite produced by shaker milling was surprisingly stable in air, thus ensuring a good possibility of real technical applications.

Iodates of other cations give variable performances. For example, silver iodate (AgIO_3) has been proposed using Al as fuel [117], but it has been observed that AgI is the chemical species mostly present in combustion products in place of I_2 . Of course, AgI also has an antibacterial activity, but not so intense towards cell membranes as I_2 .

Biocidal Thermites with Iodine Pentoxide and Iodic Acids

Iodic acid exists in different hydrated forms, which have been observed by thermogravimetric (TG) analysis during the heating of HIO_3 , which loses water giving firstly HI_3O_8 and finally I_2O_5 [118]. All these compounds are very powerful oxidizers and for this fact they enter into the composition of several biocide thermite mixtures [119]. Like other gas-producing oxidizers enhancing the inner advective heat transfer, I_2O_5 offers the advantage of damping the effect of reactive sintering of the combustible phase, which may lead to a significant slowing down of combustion kinetics, even to the point of stopping the reaction [120,121]. As for metal-iodate-based compositions, the performances of this kind of thermite may depend greatly on the mixing techniques between components. In fact, when Al and I_2O_5 are mixed by ultrasonication dispersion in different apolar and polar carrier solvents such as hexane or organic alcohols, the flame speed can vary up to three times by changing the solvent [122].

When mixed with powdered Al, nanosized I_2O_5 outperforms standard thermites, based on metal oxides, in terms of burn time and pressurization rate, giving a combustion velocity up to 2000 m/s [123]. Wu et al. [124] proposed a scalable and versatile method to prepare iodine oxides and iodic acid microparticles by aerosol spray pyrolysis, starting from HIO_3 . The main drawback of I_2O_5 stems from its high hygroscopicity, which seriously endangers the stability and the combustion performances of the thermites containing it. To overcome this limitation, Feng et al. [125] proposed an aerosol process where I_2O_5 particles are passivated by a Fe_2O_3 coating layer produced by dissociation of a $\text{Fe}(\text{CO})_5$ precursor in air. Changing the shell thickness served to vary the combustion parameters of such a passivated comburent when mixed with powdered Al.

The combustion dynamics of Al/iodine oxide-iodic acids have been investigated in detail [126,127]. In particular, it was experimentally observed that the ignition temperature of these thermites is strictly related to the melting point of Al (660 °C), irrespective of the temperature corresponding to the oxygen release from the pure oxidizer [128]. An analogous phenomenon was observed in non-biocidal Al-thermites of different composition [129]. This finding led to the conclusion that, when Al is the fuel, its interphase mobility/diffusion is the rate-limiting step of the combustion process. This trend changed radically when Ti was adopted in place of Al as a fuel, giving an ignition temperature lower than that corresponding to the oxygen release from the comburent. In this situation, Wu et al. [128] hypothesized the onset of a condensed phase reaction mechanism.

From these results, one can deduce that the different physicochemical characteristics of a specific fuel in this kind of thermite offered a valid instrument aiming at tuning their combustion and biocidal performances. On that note, Xu et al. [130] investigated the effect of adding Ti and Si nanopowders on the reactivity and flame temperature of Al/ I_2O_5 thermites. A change in the reaction regime was observed, which offered the possibility of shifting the combustion start from a gas phase control to a condensed phase control. Importantly, these authors found that the energy release is dependent on burn time instead on flame temperature. Analogously, the positive role of nano-Ti was investigated in another study [131], where Ti proved to be beneficial for many different combustion variables, including burn times, the peak pressure and the pressurization rate, compared with Al/ I_2O_5 thermites not containing Ti. In particular, the last two variables increased

by even three orders of magnitude and the ignition temperature decreased by more than 300 °C by mixing Al with Ti, with appealing practical applications in the real world.

Hobosian and Martirosyan [132] enlightened on the synergistic effects of combined bismuth and iodine oxidizers fueled by Al powders, owing to the well-known bactericidal effects of free iodine and Bi compounds [133]. In particular, when Bi(OH)₃ enters the composition of BEMs, it enhances the normalized gas generation, thus contributing to a larger diffusion of biocidal agents in the surroundings. For this peculiarity, it may be considered one of the most performant nanoenergetic gas generators (NGGs).

3.2.2. Biocidal Energetic Mixtures with Iodine or Other Halogens in Non-Oxidized Form

This subsection is essentially focused on binary or ternary energetic composite or nanocomposite powders, where Al and I₂ are the main ingredients. These blends contain preferentially iodine in elemental form or iodides of other elements, hence with iodine that has an oxidation number equal to 0 or −1. The mix is generally realized by mechanical alloying based upon milling or cryomilling processes [134,135], with a careful control of the operating conditions to avoid the onset of a chemical reaction between the solid phases, owing to the intrinsic chemical affinity between Al and I₂. This subset of BEMs represents a somewhat uncommon example where top-down physical methods are the first choice among the synthesis techniques. Very often, the milling vessels are equipped with liquid-nitrogen-cooled jackets to ensure the maintenance of sufficiently low temperatures in order to damp the formation of halogenated reaction products, such as AlI₃. By the way, Zhang et al. [136] used a technique based on the cryogenic milling of zerovalent Al and I₂, adopting experimental conditions differing from one another according to the duration of the milling process, the presence of liquid N₂ inside the vessel and the mass fraction of I₂, rising up to 30 wt. %. The latter parameter had the strongest influence on the stability and ignition temperature of the as-prepared mixtures. The best trade-off between I₂ release, thermal stability, total combustion pressure and pressure rise was offered by a powder containing 20% I₂.

Ternary mixtures of type Al·B·I₂ have been tested to assess the role of boron for a possible improvement of performances [137]. Analogously, Abraham et al. [138] reported a tendency of boron to fix elemental iodine in several samples with different Al/B mass ratios. TG analysis allowed the authors to conclude that the temperature of iodine release is higher than that corresponding to the boiling point of I₂, confirming the positive effect of boron in enhancing the stability of these BEMs. Other authors compared the performances of boron–iodine mixtures in the presence of different powdered metals, such as Al or Mg. All composites were sufficiently stable, with a mass loss of less than 3% of the I₂ present in the composite [139]. The burning characteristics of single particles were studied by injecting the powdered BEM into an air-acetylene flame. Both the temperature of ignition and the combustion pressure were found to be directly and inversely proportional to the boron concentration of the sample. When Mg replaces Al in the composition of the powder, there is a lowering of the ignition temperature and in the burn time of a single particle. This finding seems to be consistent with the greater electropositive character of Mg with respect to Al. More atypical compositions, based on Al·TiI₄ and Al·NbCl₅, have been experienced and compared in another work, but the efficacy of chlorinated BEMs did not reach the satisfactory levels of iodinated ones [140].

3.2.3. Non-Halogenated Biocidal Thermites

In this category, sulphur-based BEMs have been objects of attention, owing to a biocidal activity that is based on a supposed synergy between gaseous SO₂ and solid particles, both formed by combustion. Persulfate salts as oxidizers have been tested in place of iodine-containing comburent for the preparation of Al-based thermites [141]. It has been observed that an Al/K₂S₂O₈ thermite may theoretically produce biocidal SO₂ up to 31% of the initial comburent mass. Other authors, however, express some skepticism about the real biocidal effectiveness of SO₂ in the field.

Mg-S composites have been prepared by two different mechanical milling techniques, operated at room temperature and under liquid nitrogen to avoid a mechanochemical synthesis of the corresponding sulphide MgS [142]. Whatever the experimental conditions, a chemical reaction between the solid phases was unavoidable for milling times greater than 20 min. The composites were tested for ignition by heated filament and electrostatic discharge experiments, while combustion was studied by powder injection into air-acetylene flame and by the constant volume explosion of aerosols. The combustion products showed biocidal action against spores of *Bacillus thuringiensis* giving an inactivation factor close to that obtained by typical iodinated composites such as Al·I₂ and Al·B·I₂. In another analogous study relying upon similar preparation techniques, the biocidal properties of an elemental Mg and Mg-S composite were measured and compared [143]. The authors observed the existence of a biocidal effect of MgO, produced by the combustion of elemental Mg powder, which did not differ significantly from that typical of burnt Mg-S composite particles, likewise forming MgO. For these reasons, the authors concluded that sulphur oxides alone do not give a significant contribution to the biocidal performances. The inner mechanisms of the combustion of Mg and Mg-S powders were investigated in detail by Liu et al. [144], who concluded that powdered Mg undergoes a combustion process mainly confined to the metal particle surface. On the other side, Mg-S composite particles burn according to a two-step process, firstly dominated by a sulphur evaporation, followed by a metal Mg combustion. It is worth reminding that MgO has the unusual property of chemisorbing halogens and this phenomenon is particularly intense for smaller particle diameters, even reaching 43% of the total MgO nanoparticle mass [145]. For this reason, excellent bactericidal properties were detected for MgO nanoparticles with adsorbed mixed halogens or a combination between them, as in the case of MgO/ICl₃.

In the field of low-gas-producing BEMs, silver compounds as a main ingredient for biocidal mixtures have been objects of attention. As well known by wet chemistry synthesis methods [146], zerovalent Ag dispersions have a strong disinfectant power, which increases for lowering particle diameters. This property is persistent both in wet and in dry states, making Ag an interesting component for BEMs. Owing to the high adiabatic temperature of combustion, the biocidal effect relied upon the formation of Ag vapors, which suddenly condensed forming solid Ag particles dispersed in the environment. Namely, energetic blends of variable composition have been proposed, whose main components are Ag₂O and Al [147]. CuO was added in order to increase the reaction kinetics, with beneficial effects on the pressurization rate. However, the biocidal performances of Ag₂O-based blends were impaired by a sintering process between Ag particles and by the formation of a shell layer of reaction products, such as alumina, reducing the active surface of zerovalent Ag and finally endangering a biocidal action.

As an alternative to pure Ag₂O, a silver-iron oxide AgFeO₂ was adopted as comburent for powdered Al [148]. Experimental tests on combustion performances revealed that this mixture gives a pressurization rate 100 times greater than that typical of other traditional thermites based on single-metal oxides. Additionally, post-combustion products contained bioavailable elemental Ag in nanosized particles of 80 nm average diameter, probably formed by its vaporization and further condensation.

3.3. Organic–Inorganic BEMs and Composites

In some cases, organic–inorganic mixtures allowed for the overcoming some drawbacks related to the physico-chemical properties of elemental iodine. In fact, zerovalent I₂ has a remarkable sublimation pressure at room temperature and it has corrosive properties on metal containers, thus posing some concerns in terms of long storage stability. In this context, tetraiodoethylene (C₂I₄) [149] and iodoform (CHI₃) have been proposed as valid iodine carriers, thanks to their high iodine content and lower volatility with respect to elemental iodine. CHI₃ is synthesized with a relatively more ease with respect to C₂I₄ and hence the former may be preferable for practical applications. This compound has been mixed with Al powder by means of two different mechanical processes, namely by a liquid

N₂-cooled attritor mill and an air-cooled shaker mill operated at room temperature [150]. As usual, the mixtures have been tested for thermal stability by TG analysis in argon to determine the sequence of thermal steps corresponding to I₂ release, while ignition and combustion tests have been carried out in air. This study revealed the importance of the operating variables during milling, as the cryomilled samples proved to be more stable than those prepared at room temperature at the same iodine concentration. In addition, the ignition temperature of CHI₃/Al mixtures was lower than the one of Al/I₂ composites.

The recent development of additive manufacturing techniques promoted new challenging studies in composite organic–inorganic BEMs [151]. However, real applications of this technology to ADWs are only just beginning [152]. Kline et al. [153] set up a technique for the production of biocidal burn sticks of 2 mm width, fabricated by means of a 3D printer, where hydroxypropyl methylcellulose (HPMC) and a polymer binder (polyvinylidene fluoride, PVDF) were mixed with a ternary termite made of an Al–I₂O₅–CuO mixture in various proportions. They investigated the heat transfer mechanisms in an open-environment combustion and concluded that, in these specific operating conditions, the presence of a component such as CuO transferring heat by vapor condensation may enable a stable fire propagation [154].

Other techniques where iodinated or fluorinated polymers are used as a binder for biocidal substrates containing thermites of various compositions have been experienced [155]. Unlike Teflon (PTFE), PVDF has a greater solubility in many organic solvents and this property makes it particularly versatile for making engineered energetic materials, as it lends itself to be mixed with Al-based energetic blends and further electrospayed on suitable substrates [156,157]. On this subject, Hu et al. [158] electrospayed a Bi(IO₃)₃–Al–PVDF mixture and obtained crack-free and flexible films, which were tested for thermal stability and combustion properties. They postulated that Al reacts both with the binder and with Bi(IO₃)₃, releasing AlF₃ and I₂ from the respective compounds. Interestingly, the former reaction gave a thermal contribution higher than the latter and this fact explained an increase in propagation velocity with respect to thermites of analogous composition not containing a binder. Thus, the binder was proven to have a multipurpose mechanical and chemical action. In fact, in the absence of an intrinsic oxidizer such as Bi(IO₃)₃, other authors observed that the burning rate of Al–PVDF mixtures may dramatically decrease for growing iodine content, up to a lack of propagation when I₂ was greater than 40% [159]. The problem was circumvented by realizing a laminated structure, where the iodine-containing layers were alternate to those iodine-free.

Among other organics suitable for spray deposition, nitrocellulose (NC) has been employed in formulations containing Al nanopowder and manganous iodate (Mn(IO₃)₂) [160], blended by physical mixing and electrospaying. The processes of the ignition and combustion of such BEMs have been investigated by standard methods, by which it was ascertained that the electrospayed composite had an ignition temperature more than 200 °C lower than that prepared by physical mixing. As an alternative to NC-based formulations, polyurethane-based blends have been experienced in the realization of biocidal sprayable pyrotechnics, producing a rigid, flammable foam [161].

The use of carbon as a reductant, in the form of carbon black, carbon nanotubes, nanofibers [162] or functionalized graphene [163], can be a valid ploy to circumvent the limits imposed by the sintering and/or surface passivation typical of a fuel such as Al. In fact, Wu et al. [164] observed that carbon, irrespective of its allotropic state and in concentrations as low as 3%, may reduce the temperature of I₂ release from the comburents containing it, both in the case of Al–I₂O₅ and Ta–I₂O₅ thermites.

A recent challenging strategy to obtain highly energetic biocides is based on the preparation of organic–inorganic cocrystals, in analogy to what has been previously discussed in Section 3.1.3. This technique requires the combination of weak bases with weak acids, thus promoting the formation of cocrystals. In this context, iodic acids do not represent excessively strong protonators and hence they have been used as valid iodine-carrier candidates to form cocrystals with weak organic bases such as triazoles, azotriazoles and other

heterocyclic molecules [165]. In a way, the weakness of these bounds does not allow them to be classified as ionic organic compounds. The detonation velocity of these materials may even exceed 7500 m/s, with an iodine content in the range of 32–51%.

The paper of Kumar Chinnam et al. [166] is one of the rare investigations where biocidal energetic coordination polymers have been studied and synthesized, with a monomeric structure comprising a transition metal, an energetic block and four iodine atoms. This unusual BEM has the peculiarity of forming, by combustion, a gaseous phase of free I₂, together with a solid phase of I₂-coated ZnO particles enhancing the overall biocidal effects. In a parallel context, the current research is focused on the synthesis of energetic 2D or 3D metal–organic frameworks (MOFs) containing a transition metal cation forming a coordination backbone with a proper polydentate ligand, usually bis-triazole, azotriazole, hydrazine or hydrazine-derivatives, where the anion is an energetic carrier such as NO₃[−] or ClO₄[−] [167,168]. When the latter anions are replaced by IO₃[−], the MOF acquires biocidal properties, as free iodine is released by detonation. The advantage offered by these structures consists mainly of a high density, with superior detonation performances [169]. Chattopadhyay et al. [170] realized an interesting mini-review on these smart biotechnological tools.

4. Methods and Protocols for Biocidal Tests

A key problem in assessing the validity of a BEM stems from measuring the bioactivity of the temperature and reaction products in killing a microorganism used as a military weapon. Of course, experimental tests using extremely hazardous pathogens such as bacillus anthracis could not be performed, for obvious reasons related to safety. As an alternative, many different affine microorganisms of similar biochemical properties have been adopted as target cells. However, the selection of the most suitable surrogate microorganism is not a simple task [171].

The biocidal efficiency of a BEM can be quantitatively assessed by measuring the inertization of the microorganisms present in an airborne aerosol or immobilized on a suitable surface.

During the last decade, a research group of the Department of Environmental Health in the University of Cincinnati developed a laboratory facility that can be considered a benchmark in the realization of reliable biocidal tests, aiming at quantifying the separated effects of the thermal and chemical inactivation of airborne microorganisms [172,173]. The sequence of operations starts with a collision nebulizer where the colonies are vehiculated in a properly filtered air stream, followed by an electrical charge equilibrator and a test chamber, where the airborne colonies are mixed with the combustion products of a burned BEM. Afterwards, the gas stream is adequately cooled and it finally enters a sampling collector, where the microorganisms are captured for a final count of the population surviving at the inactivation. The inactivation factor (IF) is calculated as a ratio between the concentration of culturable pathogens C_c collected downstream from the apparatus, in the absence and in the presence of exposure to biocidal effects, that is:

$$IF = \frac{C_c(\text{without exposure})}{C_c(\text{with exposure})} \quad (1)$$

In the case of spores as pathogens, the concentrations are expressed in terms of colony forming units (CFUs). It is worth reminding that this approach is based on the technique of culturable spores after exposure, but other methods exist [174]. The exposure chamber can operate according to several construction variants. It can be equipped by a nozzle burner, where BEM particles are premixed with the gaseous fuel and burned in a flame, or by a strand burner, where a BEM powder is mixed with a wax forming a compact burning strand. In a different realization, the burner can be replaced by a heating element, if only a thermal biocidal effect is to be assessed [175]. The bioaerosol stream flows through the chamber in a direction parallel to the flame geometry in an axial scheme, while it flows through the chamber in a direction normal to the flame geometry

in a tangential scheme [140]. In the latter setup, the flame distance from the bioaerosol stream can be properly adjusted in order to modulate the thermochemical shock on the microorganisms [176,177]. A simplified representation of different types of exposure chambers is reported in Figure 4. These technical variants make it possible to study the biocidal properties of energetic powders by acting on different tuning variables, including temperature and exposure time, notwithstanding the fact that an accurate bioaerosol temperature and humidity monitoring is not an easy task [178]. In this context, simulation studies are somewhat uncommon, but there are exceptions. By the way, Wang et al. [179] used a standard CFD software to model the biocidal effects of an Al·B·I₂ ternary composite combustion, under the assumption of a steady I₂ release from the burner. Interestingly, a good validation of experimental data was performed for different values of the burner distance from the bioaerosol stream.

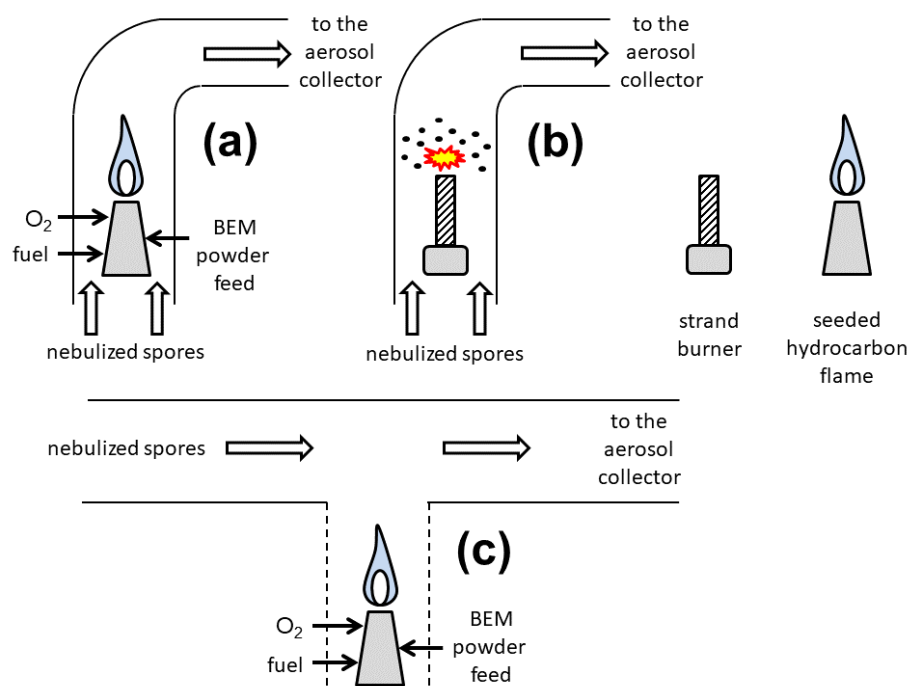


Figure 4. Schemes of the exposure chamber, adapted and modified from Refs. [173,177], according to three different technical solutions: (a) axial exposure chamber with a gas burner for BEM combustion; (b) axial exposure chamber with a solid strand burner; (c) tangential gas burner with adjustable distance (dashed lines) between the flame and the aerosolized stream.

In place of airborne bioaerosols, other protocols rely upon the use of immobilized spores on a temperature-controlled heated wire or surface, located in a proper chamber where combustion products from BEMs or biocidal gases are fed. According to this approach, Zhou et al. [180] studied the effects of moist Cl₂ and temperature on the neutralization of *Bacillus thuringiensis* as a surrogate of anthrax spores. The immobilization of microorganisms on a substrate allows an accurate management of temperature and its derivative, leading to a deeper understanding of the mechanisms of spore inertization. For example, it was observed that both the value of the temperature peak and an ultrafast heating exceeding 10⁵ °C/s contributed significantly to spore inertization, while repetitive heating had no appreciable effect [181]. More simplified arrangements have been conceived by other investigators, who used two superposed glass vials where the upper one contains the immobilized spores and the lower one the energetic material releasing biocide vapors [182].

Different experimental facilities have been proposed for more specific cases where a biocidal agent is released after a detonation. A typical setting is made by an explosion chamber connected with an exhaust chamber to expand the shock wave [183]. The former

contains a vessel where the energetic material is burst in an atmosphere containing the spores of a pathogen previously dispersed by nebulization [184]. The biocidal efficiency is determined by counting the CFU before and after the combustion/detonation. Detonation experiments can also be carried out in barometric calorimeters, containing a detonation charge and a sample-holder, equipped with a prefixed number of spores and located at the lid of the calorimeter [185].

As a general consideration, it is worth reminding that a satisfactory simulation of pathogen inertization at laboratory scale may be highly affected by the variants of equipment used [186,187]. A first cause of uncertainty in the estimation of bioaerosol inertization efficiency lies in the broad size distribution of the droplet diameter. Additionally, an intrinsic difficulty in the estimation of droplet loss fraction affecting a bioaerosol stream is an important aspect to be considered carefully in biocidal tests. The causes of this phenomenon can be mainly ascribed to gravity settling and droplet capture by wall effect. For this reason, an accurate modeling of fluid dynamic variables in the relevant laboratory equipment can play a significant role [188].

5. Concluding Remarks and Research Perspectives

In this brief survey, it appears that many technical possibilities can be adopted to realize a BEM. From a compositional point of view, the first question to ask is whether to choose an organic or inorganic BEM. Each one has strengths and weaknesses that can be summarized in the following points:

- Organic BEM strengths:
 - Being made of single molecules or composites where the intramolecular distances between explosophores and comburentes are of a subnanometric scale, they offer the advantage of being free from interphase heat and mass transfer limitations during the process of energy and biocidal agent release.
 - Their dissociation energy and iodine content can be modulated over a wide range of values, depending on the number of explosophore groups and halogen bonds.
 - Except for some fluorinated compounds, they generally have hydrophobic properties, low hygroscopicity and low/moderate corrosive action against storage containers.
- Organic BEM weaknesses:
 - The production costs tend to rise when the structural complexity of the synthesized molecule and its percentage of halogen content increase. For example, when attempting to produce a polyiodide substituted aromatic compound containing a high percentage of iodine, the progressive electrophilic substitution with iodine atoms may deactivate the molecule towards the further addition of electrophilic groups. This implies adopting cumbersome chemical routes, often requiring drastic and costly operating conditions in order to ensure a high reaction yield. Some multiblock structures can be considered as niche products or even just scientific curiosities.
 - High positive values of formation enthalpy are generally associated with a high detonation risk by friction and mechanical impact, to the point of compromising a practical use owing to serious safety issues.
- Inorganic BEM strengths:
 - Oxidizer and reductant, entering their composition, can be produced by cost-effective standard wet chemical processes by physical unit operations, respectively. However, the cost tends to increase when reactants at a nanosized scale are required to optimize the combustion performances.
 - The volumetric energy density of thermite mixtures is, on average, more than two times higher than the one typical of standard organic explosives, with high biocidal yield by thermal shock.
- Inorganic BEM weaknesses:

- The energetic and biocidal performances are strongly conditioned by interphase heat and mass transfer limitations. As a consequence, reagent comminution has a basic role in this context, with a great influence on the chemical kinetics of combustion. In some cases, an insufficient reagent comminution can lead to a reaction stop.
- Despite the low cost of raw reagents, their mixing may require expensive and hazardous processes, particularly when nanosized mixtures are to be produced. Arrested reactive milling, typically adopted at the laboratory scale, needs a very accurate control of the operating conditions and its scalability can give rise to serious plant safety issues.
- Solid oxidizers are often hydrophilic ionic compounds, sometimes soluble in water, with a high hygroscopicity. This is a serious drawback, typically affecting iodates and I_2O_5 , which may endanger stability in long-term storage. Being electrolytes, they may trigger corrosion phenomena in metallic vessels.

The topic explored in this review provides significant challenges for developing novel processes and production technologies enhancing the sustainability and quality of the products, but equally has risks that require a deep understanding and management. The modeling aspects of research are generally focused on foreseeing the values of the thermodynamic variables describing combustion, explosion or detonation characteristics [55], similar to process design in industrial oxidation processes involving flame propagation phenomena [189], together with the composition of the reaction products, which is basically important for the prevision of the biocidal effectiveness. To achieve this task, many authors have presented studies relying upon software packages emphasizing thermodynamic aspects over kinetic ones. As a consequence, discrepancies between the predicted and actually observed BEM reaction variables were found in some cases. As examples, the detonation velocities of some low-energy organic BEMs have been calculated, but the experiments revealed that these compounds may not detonate at all. In the case of inorganic BEMs made of powdered solid mixtures, a prevision about the effect of interphase energy transfer may be affected by significant uncertainties.

With the above consideration in mind, one may conclude that a correct assessment of BEM properties must inevitably be based on experimental tests, thus opening new issues on how to carry out a reliable biocidal test. An analysis of the studies reported in Section 4 reveals that many different experimental approaches have been proposed and hence a unifying protocol is actually lacking, thus suggesting the organization of round robin test trials by different laboratories and institutions, in line with the approach proposed by Pisman et al. [45]. Currently, also considering the significant scatter in the experimental data obtained by different protocols, it is difficult to make a quantitative comparison between the biocidal performances that will actually be found in the field.

A Forward-Looking Perspective

Finally, it seems reasonable to say that the future range of choices still leaves plenty of room for scientific creativity, both for organic and inorganic BEM formulations. As possible insights for future research lines in organic BEM recipes, it is worth observing that very few investigations have been proposed about polyiodinated polymers (excluding MOFs) as comburent fillers, taking into account the high capability of some polymers in retaining I_2 at high concentrations [190]. To this purpose, Makhayeva et al. [191] have recently reviewed many cases where iodine forms complexes with polymers of natural or artificial origin. Despite the fact that their paper is mainly focused on biomedical applications, owing to the well-known antibacterial, fungicidal and virucidal properties of iodine, it may offer important insights for possible applications of new iodine carriers for BEMs.

Furthermore, while the $-NF_2$ group is amply recognized as an energy carrier in the field of haloamines [64], little is known about the possibility of using iodamines as likely candidates for BEMs. Jander [192] is one of the very few authors who investigated the synthesis of iodamines in non-aqueous solvents.

Nitrogen triiodide (NI₃), the simplest compound containing only N–I bonds, is a well-known energetic material with a highly positive heat of formation. Its extremely high iodine content, up to 96.4%, together with its unusual dissociation energy (−290 kJ/mol) for such a simple molecule, would make it an appealing candidate to the purpose, but its extreme sensitivity to mechanical impact in the dry state actually prevents any practical application of it. To the best of our knowledge, only two studies considered the problem of how to stabilize this seemingly unmanageable molecule. Marinho and De Farias [193] observed that a NI₃ incorporation in a suitable polymeric matrix and the presence of NH₃ as a molecular adduct in its structure may increase its stability, thus opening new challenging scenarios and possibilities. Analogously, Jander [194] studied the adducts of NI₃ with O, S, P and tertiary N bases and he remarked that only urotropine was efficient in providing a greater stability to NI₃ at room temperature.

To conclude, despite these promising findings both in older and recent scientific publications, it is intriguing to observe that no studies about iodamine-group-containing organic BEMs have been proposed in literature. Of course, these are only research hints and scientific curiosities in a myriad of other compounds and formulations yet to be investigated.

Author Contributions: All authors contributed significantly and equivalently to all aspects pertaining to the realization of the present paper. All authors have read and agreed to the published version of the manuscript.

Funding: The research was carried out at the expense of a grant from the Russian Science Foundation—Project No. 21-79-30029 “Development of a complex of technologies for processing waste of hazard classes 3–5 with the production of useful products”.

Data Availability Statement: Not applicable.

Acknowledgments: One of us (A.P.R.) is particularly grateful to Andrea Basso for enlightening discussions and valuable suggestions.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Carus, W.S. A century of biological-weapons programs (1915–2015): Reviewing the evidence. *Nonprolif. Rev.* **2017**, *24*, 129–153. [CrossRef]
2. Hosseini-Shokouh, S.J.; Sheikhi, R.; Hosseini, S.; Moradimajd, P. The biological weapons threats and coping strategies for health promotion. *J. Educ. Health Promot.* **2021**, *10*, 127. [PubMed]
3. Michalski, A.; Knap, J.; Bielawska-Drózd, A.; Bartoszcze, M. Lessons learned from 2001–2021—from the bioterrorism to the pandemic era. *Ann. Agric. Environ. Med.* **2022**, *29*, 1–11. [CrossRef] [PubMed]
4. Novosiolova, T.; Whitby, S.; Dando, M.; Shang, L. Strengthening biological security after COVID-19: Using cartoons for engaging life science stakeholders with the Biological and Toxin Weapons Convention (BTWC). *J. Biosaf. Bio Secur.* **2022**, *4*, 68–74. [CrossRef]
5. Chemical and Biological Warfare Overview, United States Air Force, Center for Unconventional Weapons Studies. Available online: <https://www.airuniversity.af.edu> (accessed on 9 October 2022).
6. Caves, J.P., Jr.; Carus, W.S. *The Future of Weapons of Mass Destruction: Their Nature and Role in 2030*; Occasional Paper 10; National Defense University Press: Washington, DC, USA, 2014. Available online: <https://www.researchgate.net> (accessed on 9 October 2022).
7. Wheelis, M.L. Biological warfare before 1914. In *Biological and Toxin Weapons: Research, Development, and Use from the Middle Ages to 1945*; Geissler, E., van Courtland Moon, J.E., Eds.; Oxford University Press: New York, NY, USA, 1999; pp. 8–34.
8. Xavier, E.A. Prions: The danger of biochemical weapons. *Food Sci. Technol.* **2014**, *34*, 433–440. [CrossRef]
9. Xavier, E.A. Prion/virus the danger of biological weapons. *World J. Biol. Pharm. Health Sci.* **2022**, *10*, 031–035. [CrossRef]
10. Pitschmann, V.; Hon, Z. Military importance of natural toxins and their analogs. *Molecules* **2016**, *21*, 556. [CrossRef]
11. Pita, R.; Romero, A. Toxins as weapons: A historical review. *Forensic Sci. Rev.* **2014**, *26*, 86–95.
12. Ambrose, E.A. Botulinum neurotoxin, tetanus toxin, and anthrax lethal factor countermeasures. *Top. Med. Chem.* **2017**, *22*, 47–67.
13. Chen, S. Clostridial neurotoxins: Mode of substrate recognition and novel therapy development. *Curr. Protein Pept. Sci.* **2014**, *15*, 490–503. [CrossRef]
14. Bjørn-Yoshimoto, W.E.; Ramiro, I.B.L.; Yandell, M.; McIntosh, J.M.; Olivera, B.M.; Ellgaard, L.; Safavi-Hemami, H. Curses of cures: A review of numerous benefits versus the biosecurity concerns of conotoxin research. *Biomedicines* **2020**, *8*, 235. [CrossRef]
15. Ludovici, G.M.; Arduini, D.; Gaudio, P.; Chierici, A.; Manenti, G.; Malizia, A. The threat of plant toxins and bioterrorism: A review. *Def. S T Tech. Bull.* **2022**, *15*, 57–67.

16. Słomińska-Wojewódzka, M.; Sandvig, K. Ricin and ricin-containing immunotoxins: Insights into intracellular transport and mechanism of action in Vitro. *Antibodies* **2013**, *2*, 236–269. [CrossRef]
17. Franz, D.R. *Defense against Toxin Weapons*; University Press of the Pacific: Stockton, CA, USA, 2005.
18. Belvís, R.; Morollón, N.; Cortés-Vicente, E.; Morán, I. Tabun, sarin, soman, VX and novichoks: Organophosphate nerve agents for military or criminal purposes. *Kranion* **2022**, *17*, 65–77.
19. Aroniadou-Anderjaska, V.; Apland, J.P.; Figueiredo, T.H.; De Araujo Furtado, M.; Braga, M.F. Acetylcholinesterase inhibitors (nerve agents) as weapons of mass destruction: History, mechanisms of action, and medical countermeasures. *Neuropharmacology* **2020**, *181*, 108298. [CrossRef]
20. Carus, W.S. The history of biological weapons use: What we know and what we don't. *Health Secur.* **2015**, *13*, 219–255. [CrossRef]
21. Kirby, R. The Evolving Role of Biological Weapons. Available online: <https://www.thefreelibrary.com/Theevolvingroleofbiologicalweapons-a0169309540> (accessed on 9 November 2022).
22. Vijithra, N.; Ravichandran, R. Biowarfare—A peril gaining ground. *J. Crit. Rev.* **2020**, *7*, 774–781.
23. Eneh, O.C. Biological weapons-agents for life and environmental destruction. *Res. J. Environ. Toxicol.* **2012**, *6*, 65–87.
24. Pohanka, M. Bacillus anthracis as a biological warfare agent: Infection, diagnosis and countermeasures. *Bratisl. Med. J.* **2020**, *121*, 175–181. [CrossRef]
25. Watson, A.K.; Ellington, S.; Nelson, C.; Treadwell, T.; Jamieson, D.J.; Meaney-Delman, D.M. Preparing for biological threats: Addressing the needs of pregnant women. *Birth Defects Res.* **2017**, *109*, 391–398. [CrossRef]
26. Pechous, R.D.; Sivaraman, V.; Stasulli, N.M.; Goldman, W.E. Pneumonic plague: The darker side of Yersinia pestis. *Trends Microbiol.* **2016**, *24*, 190–197. [CrossRef]
27. Hartzell, J.D.; Wilson, K.; Lutwick, L.I. The biowarfare aspects of Q fever. *Encycl. Bacteriol. Res. Dev.* **2021**, *11*, 1965–1974.
28. D'Souza, M.H.; Patel, T.R. Biodefense implications of new-world hantaviruses. *Front. Bioeng. Biotechnol.* **2020**, *8*, 925. [CrossRef] [PubMed]
29. Sathua, K.; Flora, S.J.S. Bacterial biological warfare agents. In *Handbook on Biological Warfare Preparedness*, 1st ed.; Flora, S.J.S., Pachauri, V., Eds.; Academic Press: Cambridge, MA, USA; Elsevier: Cambridge, UK, 2019; pp. 13–31.
30. Leonard, T.H.; Siratan, E.; Hartiadi, L.Y.; Crystalia, A.A. Insight into antimicrobial peptides in fighting anthrax: A review. *Drug Dev. Res.* **2021**, *82*, 754–766. [CrossRef] [PubMed]
31. Pérez, J.; Contreras-Moreno, F.J.; Marcos-Torres, F.J.; Moraleta-Muñoz, A.; Muñoz-Dorado, J. The antibiotic crisis: How bacterial predators can help. *Comput. Struct. Biotechnol. J.* **2020**, *18*, 2547–2555. [CrossRef]
32. Feakes, D. The Biological Weapon Convention. *Rev. Sci. Et Tech.* **2017**, *36*, 621–628. [CrossRef] [PubMed]
33. Chang, J.; Zhao, G.; Zhao, X.; He, C.; Pang, S.; Shreeve, J.M. New promises from an old friend: Iodine-rich compounds as prospective energetic biocidal agents. *Acc. Chem. Res.* **2021**, *54*, 332–343. [CrossRef] [PubMed]
34. Thangadurai, S.; Kartha, K.P.S.; Shsrma, D.R.; Shukla, S.K. Review of some newly synthesized high energetic materials. *Sci. Technol. Energ. Mater.* **2004**, *6*, 215–226.
35. Kramarczyk, B.; Suda, K.; Kowalik, P.; Swiatek, K.; Jaszcz, K.; Jarosz, T. Emulsion Explosives: A tutorial review and highlight of recent progress. *Materials* **2022**, *15*, 4952. [CrossRef]
36. Klapotke, T.M. *Energetic Materials Encyclopedia*; De Gruyter: Berlin, Germany; Boston, MA, USA, 2021; Volume 1–3.
37. Agrawal, J.P. *High Energy Materials: Propellants, Explosives and Pyrotechnics*; Wiley-VCH: Weinheim, Germany, 2010.
38. Agrawal, J.P.; Dodke, V.S. Some novel high energy materials for improved performance. *Z. Für Anorg. Und Allg. Chem.* **2021**, *647*, 1856–1882. [CrossRef]
39. Rossi, C.; Zhang, K.; Estève, D.; Alphonse, P.; Tailhades, P.; Vahlas, C. Nanoenergetic materials for MEMs: A review. *J. Micromech. Syst.* **2007**, *14*, 919–931. [CrossRef]
40. Wu, T.; Sevely, F.; Julien, B.; Sodre, F.; Cure, J.; Tenailleau, C.; Esteve, A.; Rossi, C. New coordination complexes-based gas-generating energetic composites. *Combust. Flame* **2020**, *219*, 478–487. [CrossRef]
41. Keshavarz, M.H.; Klapotke, T.M. *The Properties of Energ. Materials*; De Gruyter: Berlin, Germany; Boston, MA, USA, 2018.
42. Klapotke, T.M. *Chemistry of High Energy Materials*; De Gruyter: Berlin, Germany; Boston, MA, USA, 2022.
43. Laurent, A.; Pey, A.; Gurtel, P.; Fabiano, B. A critical perspective on the implementation of the EU Council Seveso Directives in France, Germany, Italy and Spain. *Process Saf. Environ. Prot.* **2021**, *148*, 47–74. [CrossRef]
44. O'Sullivan, O.T.; Dzilla, M.J. Properties and promise of catenated nitrogen systems as high-energy-density materials. *Chem. Rev.* **2020**, *120*, 5682–5744. [CrossRef] [PubMed]
45. Pisman, H.J.; Fabiano, B. The Delft 1974 and 2019 European Loss Prevention Symposia: Highlights and an impression of process safety evolutionary changes from the 1st to the 16th LPS. *Process Saf. Environ. Prot.* **2021**, *147*, 80–91. [CrossRef]
46. Frem, D. The specific impulse as an important parameter for predicting chemical high explosives performance. *Z. Für Anorg. Und Allg. Chem.* **2018**, *644*, 235–240. [CrossRef]
47. Frem, D. A reliable method for predicting the specific impulse of chemical propellants. *J. Aerosp. Technol. Manag.* **2018**, *10*, 3318. [CrossRef]
48. Pannell, J.J.; Panoutsos, G.; Cooke, S.B.; Pope, D.J.; Rigby, S.E. Predicting specific impulse distributions for spherical explosives in the extreme near-field using a Gaussian function. *Int. J. Prot. Struct.* **2021**, *12*, 437–459. [CrossRef]

49. Spackman, P.R.; Turner, M.J.; McKinnon, J.J.; Wolff, S.K.; Grimwood, D.J.; Jayatilaka, D.; Spackman, M.A. CrystalExplorer: A program for Hirshfeld surface analysis, visualization and quantitative analysis of molecular crystals. *J. Appl. Crystallogr.* **2021**, *54*, 1006–1011. [[CrossRef](#)]
50. Muravyev, N.V.; Wozniak, D.R.; Piercey, D.G. Progress and performance of energetic materials: Open dataset, tool, and implications for synthesis. *J. Mater. Chem. A* **2022**, *10*, 11054–11073. [[CrossRef](#)]
51. Keshavarz, M.H.; Klapötke, T.M.; Sućeska, M. Energetic Materials Designing Bench (EMDB), Version 1.0. *Propellants Explos. Pyrotech.* **2017**, *42*, 854–856. [[CrossRef](#)]
52. Bondarchuk, S.V.; Yefimenko, N.A. An algorithm for evaluation of potential hazards in research and development of new energetic materials in terms of their detonation and ballistic profiles. *Propellants Explos. Pyrotech.* **2018**, *43*, 818–824. [[CrossRef](#)]
53. Sućeska, M. *EXPLO5, Version 6.03*; Brodarski Institute: Zagreb, Croatia, 2015.
54. Frisch, M.; Trucks, G.; Schlegel, H.; Scuseria, G.; Robb, M.; Cheeseman, J.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. *Gaussian 09 Package*; Gaussian Inc.: Pittsburgh, PA, USA, 2009.
55. Grys, S.; Trzciński, W.A. Calculation of combustion, explosion and detonation characteristics of energetic materials. *Cent. Eur. J. Energ. Mater.* **2010**, *7*, 97–113.
56. Smolenskii, E.A.; Pivina, T.S.; Ryzhov, A.N.; Maslova, L.K.; Zefirov, N.S. Computer aided modeling of physicochemical characteristics of various energy sources. *Russ. Chem. Bull. Int. Ed.* **2016**, *65*, 1395–1405. [[CrossRef](#)]
57. Smirnov, A.S.; Smirnov, S.P.; Pivina, T.S.; Lempert, D.B.; Maslova, L.K. Comprehensive assessment of physicochemical properties of new energetic materials. *Russ. Chem. Bull. Int. Ed.* **2016**, *65*, 2315–2332. [[CrossRef](#)]
58. Smirnov, S.P.; Smirnov, A.S. Forecasting the characteristics of explosives. *Russ. J. Appl. Chem.* **2009**, *82*, 1807–1815. [[CrossRef](#)]
59. Fabiano, B.; Reverberi, A.P.; Varbanov, P.S. Safety opportunities for the synthesis of metal nanoparticles and short-cut approach to workplace risk evaluation. *J. Clean. Prod.* **2019**, *209*, 297–308. [[CrossRef](#)]
60. Chapman, R.D. *Halogenated Explosives to Defeat Biological Agents*; Technical Report of the Naval Air Warfare Center Weapons Division (NAWCWD); China Lake: Kern County, CA, USA, 2015.
61. Milanez, S. Chlorine. In *Handbook of Toxicology of Chemical Warfare Agents*, 3rd ed.; Gupta, R.C., Ed.; Academic Press: Cambridge, MA, USA; Elsevier: London, UK, 2020; pp. 321–340.
62. Achanta, S.; Jordt, S.E. Toxic effects of chlorine gas and potential treatments: A literature review. *Toxicol. Mech. Methods* **2021**, *31*, 244–256. [[CrossRef](#)]
63. Chapman, R.D. *N,N-dihaloamine Explosives as Harmful Agent Defeat Materials*; Technical Report of the Naval Air Warfare Center Weapons Division Chemistry Branch; China Lake: Kern County, CA, USA, 2014.
64. Chen, J.; Yu, Y.; Li, Y.; Pang, S. Reagents leading to difluoramino (NF₂) products. *J. Fluor. Chem.* **2018**, *205*, 35–42. [[CrossRef](#)]
65. Khan, R.U.; Zhu, W. Computational insight into polynitromethyl and polydifluoroaminomethyl-substituted energetic derivatives of 2,3-dihydro pyrazino [2, 3-e] [1, 2, 3, 4] tetrazine. *J. Mol. Model.* **2020**, *26*, 78. [[CrossRef](#)]
66. Gao, H.; Ye, C.; Winter, R.F.; Gard, G.L.; Sitzmann, M.E.; Shreeve, J.M. Pentafluorosulfanyl (SF₅) containing energetic salts. *Eur. J. Inorg. Chem.* **2006**, *16*, 3221–3226. [[CrossRef](#)]
67. Kaiho, T. *Iodine Chemistry and Applications*; John Wiley and Sons: New York, NY, USA, 2015.
68. Chen, P.; Dou, H.; Fei, T.; He, C.-L.; Pang, S.-P. Research progress in iodine-based energetic biocidal agents. *Chin. J. Energ. Mater.* **2018**, *26*, 958–966.
69. Zhao, G.; He, C.; Kumar, D.; Hooper, J.P.; Imler, G.H.; Parrish, D.A.; Shreeve, J.M. 1,3,5-Triiodo-2,4,6-trinitrobenzene (TITNB) from benzene: Balancing performance and high thermal stability of functional energetic materials. *Chem. Eng. J.* **2019**, *378*, 122119. [[CrossRef](#)]
70. Yu, H.-T.; Zhao, C.; Chen, N.-H.; Yin, P.; He, C.-L.; Pang, S.-P. Review on iodization of C-H bonds in nitrogen heterocycles. *Chin. J. Energ. Mater.* **2022**, *30*, 70–77.
71. Chand, D.; He, C.; Mitchell, L.A.; Parrish, D.A.; Shreeve, J.M. Electrophilic iodination: A gateway to high iodine compounds and energetic materials. *Dalton Trans.* **2016**, *45*, 13827–13833. [[CrossRef](#)]
72. Chand, D.; He, C.; Hooper, J.P.; Mitchell, L.A.; Parrish, D.A.; Shreeve, J.M. Mono- and diiodo-1,2,3-triazoles and their mono nitro derivatives. *Dalton Trans.* **2016**, *45*, 9684–9688. [[CrossRef](#)]
73. Zhao, G.; He, C.; Zhou, W.; Hooper, J.P.; Imler, G.H.; Parrish, D.A.; Shreeve, J.M. Control of biohazards: A high performance energetic polycyclized iodine –containing biocide. *Inorg. Chem.* **2018**, *57*, 8673–8680. [[CrossRef](#)]
74. Lian, P.; Chen, L.; Chen, J.; Wang, J.; Wang, J.; Chen, J. The nitration of 1-methyl-2,4,5-triiodoimidazole and its oxidation by product under nitration conditions. *J. Energ. Mater.* **2022**, *40*, 46–60. [[CrossRef](#)]
75. Chand, D.; Shreeve, J.M. Versatile polyiodopyrazoles: Synthesis and biocidal promise. *Chem. Commun.* **2015**, *51*, 3438–3441. [[CrossRef](#)]
76. He, C.; Zhang, J.; Shreeve, J.M. Dense iodine-rich compounds with low detonation pressures as biocidal agents. *Chem.—Eur. J.* **2013**, *19*, 7503–7509. [[CrossRef](#)]
77. Zhao, G.; He, C.; Kumar, D.; Hooper, J.P.; Imler, G.H.; Parrish, D.A.; Shreeve, J.M. Functional energetic biocides by coupling of energetic and biocidal polyiodo building blocks. *Chem. Eng. J.* **2019**, *368*, 244–251. [[CrossRef](#)]
78. Zhao, G.; Kumar, D.; He, C.; Hooper, J.P.; Imler, G.H.; Parrish, D.A.; Shreeve, J.M. New generation agent defeat weapons: Energetic N,N'-ethylene-bridged polyiodoazoles. *Chem.—Eur. J.* **2017**, *23*, 16753–16757. [[CrossRef](#)]

79. Zhang, J.; He, C.; Parrish, D.A.; Shreeve, J.M. nitramines with varying sensitivities: Functionalized dipyrazolyl-N-nitromethanamines as energetic materials. *Chem.—Eur. J.* **2013**, *19*, 8929–8936. [[CrossRef](#)] [[PubMed](#)]
80. He, C.; Zhao, G.; Hooper, J.P.; Shreeve, J.M. Energy and biocides storage compounds: Synthesis and characterization of energetic bridged bis(triiodoazoles). *Inorg. Chem.* **2017**, *56*, 13547–13552. [[CrossRef](#)] [[PubMed](#)]
81. Garg, S.; Shreeve, J.M. Trifluoromethyl- or pentafluorosulfanyl-substituted poly-1,2,3-triazole compounds as dense stable energetic materials. *J. Mater. Chem.* **2011**, *21*, 4787–4795. [[CrossRef](#)]
82. Martinez, H.; Zheng, Z.; Dolbier, W.R., Jr. Energetic materials containing fluorine. Design, synthesis and testing of furazan-containing energetic materials bearing a pentafluorosulfanyl group. *J. Fluor. Chem.* **2012**, *143*, 112–122. [[CrossRef](#)]
83. Fischer, D.; Klapötke, T.M.; Stierstorfer, J. Synthesis and characterization of guanidinium difluoroiodate, $[\text{C}(\text{NH}_2)_3]^+[\text{IF}_2\text{O}_2]^-$ and its evaluation as an ingredient in agent defeat weapons. *Z. Für Anorg. Und Allg. Chem.* **2011**, *637*, 660–665. [[CrossRef](#)]
84. He, C.; Parrish, D.A.; Shreeve, J.M. Alkyl ammonium cation stabilized biocidal polyiodides with adaptable high density and low pressure. *Chem.—Eur. J.* **2014**, *20*, 6699–6706. [[CrossRef](#)]
85. Li, Y.; Cao, Y.; Song, S.; Chen, S.; Wang, Y.; Wang, K.; Zhang, Q. Self-assembly of iodine-containing oxidants with nitrogen-rich heterocyclic compounds for novel energetic biocidal agents. *Chem. Eng. J.* **2022**, *442*, 136326. [[CrossRef](#)]
86. He, C.; Hooper, J.P.; Shreeve, J.M. Iodine-rich imidazolium iodate and periodate salts: En route to single-based biocidal agents. *Inorg. Chem.* **2016**, *55*, 12844–12850. [[CrossRef](#)]
87. Şen, N. Crystal engineering with energetic picric acid and halogen-based salts: Promising properties of a new family of insensitive materials. *J. Mol. Struct.* **2022**, *1254*, 132381. [[CrossRef](#)]
88. Politzer, P.; Murray, J.S.; Clark, T. Halogen bonding and other σ -hole interactions: A perspective. *Phys. Chem. Chem. Phys.* **2013**, *15*, 11178–11189. [[CrossRef](#)] [[PubMed](#)]
89. Bennion, J.C.; Vogt, L.; Tuckerman, M.E.; Matzger, A.J. Isostructural cocrystals of 1,3,5-trinitrobenzene assembled by halogen bonding. *Cryst. Growth Des.* **2016**, *16*, 4688–4693. [[CrossRef](#)]
90. Reverberi, A.P.; Fabiano, B.; Dovì, V.G. Use of inverse modelling techniques for the estimation of heat transfer coefficients to fluids in cylindrical conduits. *Int. Commun. Heat Mass Transf.* **2013**, *42*, 25–31. [[CrossRef](#)]
91. Zhou, L.; Piekielek, N.; Chowdhury, S.; Zachariah, M.R. Time-resolved mass spectrometry of the exothermic reaction between nanoaluminum and metal oxides: The role of oxygen release. *J. Phys. Chem. C* **2010**, *114*, 14269–14275. [[CrossRef](#)]
92. Shoshin, Y.L.; Trunov, M.A.; Zhu, X.; Schoenitz, M.; Dreizin, E.L. Ignition of aluminum-rich Al-Ti mechanical alloys in air. *Combust. Flame* **2006**, *144*, 688–697. [[CrossRef](#)]
93. Zhou, L.; Piekielek, N.; Chowdhury, S.; Zachariah, M.R. T-jump/time-of-flight mass spectrometry for time-resolved analysis of energetic materials. *Rapid Commun. Mass Spectrom.* **2009**, *1*, 194–202. [[CrossRef](#)] [[PubMed](#)]
94. Wang, H.; Jian, G.; Egan, C.G.; Zachariah, M.R. Assembly and reactive properties of Al/CuO based nanothermite microparticles. *Combust. Flame* **2014**, *161*, 2203–2208. [[CrossRef](#)]
95. Gill, R.J.; Mohan, S.; Dreizin, E.L. Sizing and burn time measurements of micron-sized metal powders. *Rev. Sci. Instrum.* **2009**, *80*, 064101. [[CrossRef](#)]
96. Kotter, L.N.; Groven, L.J. Boron carbide based biocide compositions: A study of iodated particle size on combustion and iodine output. *Propellants Explos. Pyrotech.* **2020**, *45*, 509–517. [[CrossRef](#)]
97. Jacob, R.J.; Ortiz-Moncalvo, D.L.; Overdeep, K.R.; Weihs, T.P.; Zachariah, M.R. Incomplete reactions in nanothermite composites. *J. Appl. Phys.* **2017**, *121*, 054307. [[CrossRef](#)]
98. Qiao, Z.; Shen, J.; Wang, J.; Huang, B.; Yang, Z.; Yang, G.; Zhang, K. Fast deflagration to detonation transition of energetic material based on a quasi-core/shell structured nanothermite composite. *Compos. Sci. Technol.* **2015**, *107*, 113–119. [[CrossRef](#)]
99. Rossi, C. Two decades of research on nano-energetic materials. *Propellants Explos. Pyrotech.* **2014**, *39*, 323–327. [[CrossRef](#)]
100. Wang, H.; DeLisio, J.B.; Wu, T.; Wang, X.; Zachariah, M.R. One-step solvent-free mechanochemical synthesis of metal iodate fine powders. *Powder Technol.* **2018**, *324*, 62–68. [[CrossRef](#)]
101. Wang, H.; Jian, G.; Zhou, W.; DeLisio, J.B.; Lee, V.T.; Zachariah, M.R. Metal iodate-based energetic composites and their combustion and biocidal performance. *ACS Appl. Mater. Interfaces* **2015**, *7*, 17363–17370. [[CrossRef](#)] [[PubMed](#)]
102. Smith, D.K.; Bello, M.N.; Unruh, D.K.; Pantoya, M.L. Synthesis and reactive characterization of aluminum iodate hexahydrate crystals $[\text{Al}(\text{H}_2\text{O})_6](\text{IO}_3)_3(\text{HIO}_3)_2$. *Combust. Flame* **2017**, *179*, 154–156. [[CrossRef](#)]
103. Shancita, I.; Miller, K.K.; Silverstein, P.D.; Kalman, J.; Pantoya, M.L. Synthesis of metal iodates from an energetic salt. *RSC Adv.* **2020**, *10*, 14403–14409. [[CrossRef](#)] [[PubMed](#)]
104. Dreizin, E.L. Metal-based reactive nanomaterials. *Prog. Energy Combust. Sci.* **2009**, *35*, 141–167. [[CrossRef](#)]
105. Chen, N.; He, C.; Pang, S. Additive manufacturing of energetic materials: Tailoring energetic performance via printing. *J. Mater. Sci. Technol.* **2022**, *127*, 29–47. [[CrossRef](#)]
106. Wang, H.; Biswas, P.; Kline, D.J.; Zachariah, M.R. Flame stand-off effects on propagation of 3D printed 94 wt% nanosized pyrolants loading composites. *Chem. Eng. J.* **2022**, *434*, 134487. [[CrossRef](#)]
107. Dreizin, E.L.; Schoenitz, M. Mechanochemically prepared reactive and energetic materials: A review. *J. Mater. Sci.* **2017**, *52*, 11789–11809. [[CrossRef](#)]
108. Oxley, J.C.; Smith, J.L.; Porter, M.M.; Yekel, M.J.; Canaria, J.A. Potential biocides: Iodine-producing pyrotechnics. *Propellants Explos. Pyrotech.* **2017**, *42*, 960–973. [[CrossRef](#)]

109. Jasmin, M.; Sugathan, S.; Manoj, P.K. Growth and characterization of gel-grown single crystals of calcium iodate. *AIP Conf. Proc.* **2021**, *2369*, 020137.
110. Wang, S.; Liu, X.; Schoenitz, M.; Dreizin, E.L. Nanocomposite thermites with calcium iodate oxidizer. *Propellants Explos. Pyrotech.* **2017**, *42*, 284–292. [[CrossRef](#)]
111. Stamatis, D.; Dreizin, E.L. Thermal initiation of consolidated nanocomposite thermites. *Combust. Flame* **2011**, *158*, 1631–1637. [[CrossRef](#)]
112. Wang, H.; Kline, D.J.; Rehwoldt, M.; Zachariah, M.R. Ignition and combustion characterization of $\text{Ca}(\text{IO}_3)_2$ -based pyrotechnic composites with B, Al, and Ti. *Propellants Explos. Pyrotech.* **2018**, *43*, 977–985. [[CrossRef](#)]
113. Liu, X.; Schoenitz, M.; Dreizin, E.L. Boron-based reactive materials with high concentrations of iodine as a biocidal additive. *Chem. Eng. J.* **2017**, *325*, 495–501. [[CrossRef](#)]
114. Ghildiyal, P.; Ke, X.; Biswas, P.; Nava, G.; Schwan, J.; Xu, F.; Kline, D.J.; Wang, H.; Mangolini, L.; Zachariah, M.R. Silicon nanoparticles for the reactivity and energetic density enhancement of energetic-biocidal mesoparticle composites. *ACS Appl. Mater. Interfaces* **2021**, *13*, 458–467. [[CrossRef](#)]
115. Liu, X.; Sims, A.; Murzyn, C.; Glumac, N.G.; Dreizin, E.L. Iodine release by combustion of composite $\text{Mg-Ca}(\text{IO}_3)_2$ powder. *Combust. Sci. Technol.* **2021**, *193*, 1042–1054. [[CrossRef](#)]
116. Liu, X.; Schoenitz, M.; Dreizin, E.L. Preparation, ignition, and combustion of magnesium-calcium iodate reactive nano-composite powders. *Chem. Eng. J.* **2019**, *359*, 955–962. [[CrossRef](#)]
117. Sullivan, K.T.; Piekol, N.W.; Chowdhury, S.; Wu, C.; Zachariah, M.R.; Johnson, C.E. Ignition and combustion characteristics of nanoscale Al/AgIO₃: A potential energetic biocidal system. *Combust. Sci. Technol.* **2011**, *183*, 285–302. [[CrossRef](#)]
118. Little, B.K.; Emery, S.B.; Nittinger, J.C.; Fantasia, R.C.; Lindsay, M.C. Physicochemical characterization of iodine (V) oxide, part 1: Hydration rates. *Propellants Explos. Pyrotech.* **2015**, *40*, 595–603. [[CrossRef](#)]
119. Clark, B.R.; Pantoya, M.L. The aluminium and iodine pentoxide reaction for the destruction of spore forming bacteria. *Phys. Chem. Chem. Phys.* **2010**, *12*, 12653–12657. [[CrossRef](#)] [[PubMed](#)]
120. Sullivan, K.T.; Piekol, N.W.; Wu, C.; Chowdhury, S.; Kelly, S.T.; Hufnagel, T.C.; Fezzaa, K.; Zachariah, M.R. Reactive sintering: An important component in the combustion of nanocomposites thermites. *Combust. Flame* **2012**, *159*, 2–15. [[CrossRef](#)]
121. Chakraborty, P.; Zachariah, M.R. Do nanoenergetic particles remain nano-sized during combustion? *Combust. Flame* **2014**, *161*, 1408–1416. [[CrossRef](#)]
122. Smith, D.K.; McCollum, J.; Pantoya, M.L. Effect of environment on iodine oxidation state and reactivity with aluminium. *Phys. Chem. Chem. Phys.* **2016**, *18*, 11243–11250. [[CrossRef](#)]
123. Martirosyan, K.S.; Wang, L.; Luss, D. Development of nanoenergetic materials based on Al/I₂O₅ system. In Proceedings of the Technical 2010 NSTI Nanotechnology Conference and Expo, Anaheim, CA, USA, 21–24 June 2010; Volume 2, pp. 137–140.
124. Wu, T.; SyBing, A.; Wang, X.; Zachariah, M.R. Aerosol synthesis of phase pure iodine/iodic biocide microparticles. *J. Mater. Res.* **2017**, *32*, 890–896. [[CrossRef](#)]
125. Feng, J.; Jian, G.; Liu, Q.; Zachariah, M.R. Passivated iodine pentoxide oxidizer for potential biocidal nanoenergetic applications. *ACS Appl. Mater. Interfaces* **2013**, *5*, 8875–8880. [[CrossRef](#)]
126. Hobosyan, M.A.; Kazansky, A.; Martirosyan, K.S. Nanoenergetic composites based on I₂O₅/Al for biological agent defeat. In Proceedings of the Technical 2012 NSTI Nanotechnology Conference and Expo, NSTI-Nanotech 2012, Santa Clara, CA, USA, 18–21 June 2012; pp. 599–602.
127. Jian, G.; Chowdhury, S.; Feng, J.; Zachariah, M.R. The ignition and combustion study of nano-Al and iodine pentoxide thermite. In Proceedings of the 8th US National Combustion Meeting 2013, Park City, UT, USA, 19–22 May 2013; pp. 1287–1299.
128. Wu, T.; Wang, X.; Zavaliy, P.Y.; DeLisio, J.B.; Wang, H.; Zachariah, M.R. Performance of iodine oxides/iodic acids as oxidizers in thermite systems. *Combust. Flame* **2018**, *191*, 335–342. [[CrossRef](#)]
129. Jian, G.; Chowdhury, S.; Sullivan, K.; Zachariah, M.R. Nanothermite reactions: Is gas phase oxygen generation from the oxygen carrier an essential prerequisite to ignition? *Combust. Flame* **2013**, *160*, 432–437. [[CrossRef](#)]
130. Xu, F.; Biswas, P.; Nava, G.; Schwan, J.; Kline, D.K.; Rehwoldt, M.C.; Mangolini, L.; Zachariah, M.R. Tuning the reactivity and energy release rate of I₂O₅ based ternary thermite systems. *Combust. Flame* **2021**, *228*, 210–217. [[CrossRef](#)]
131. Zhao, W.; Wang, X.; Wang, H.; Wu, T.; Kline, D.J.; Rehwoldt, H.R.; Zachariah, M.R. Titanium enhanced ignition and combustion of Al/I₂O₅ mesoparticles composites. *Combust. Flame* **2020**, *212*, 245–251. [[CrossRef](#)]
132. Hobosyan, M.A.; Martirosyan, K.S. Tuning the reactivity of nano-energetic gas generators based on bismuth and iodine oxidizers. In *Nano-Energetic Materials*; Bhattacharya, S., Agarwal, A.K., Rajagopalan, T., Patel, V.K., Eds.; Springer Nature: Singapore, 2019; pp. 191–212.
133. Reverberi, A.P.; Varbanov, P.S.; Lauciello, S.; Salerno, M.; Fabiano, B. An eco-friendly process for zerovalent bismuth nanoparticles synthesis. *J. Clean. Prod.* **2018**, *198*, 37–45. [[CrossRef](#)]
134. Guerrero, S.E.; Dreizin, E.L.; Shafirovich, E. Combustion of thermite mixtures based on mechanically alloyed aluminium-iodine material. *Combust. Flame* **2016**, *164*, 164–166. [[CrossRef](#)]
135. Zhang, S.; Schoenitz, M.; Dreizin, E.L. Mechanically alloyed Al-I composite materials. *J. Phys. Chem. Solids* **2010**, *71*, 1213–1220. [[CrossRef](#)]
136. Zhang, S.; Badiola, C.; Schoenitz, M.; Dreizin, E. Oxidation, ignition, and combustion of Al-I₂ composite powders. *Combust. Flame* **2012**, *159*, 1980–1986. [[CrossRef](#)]

137. Wang, S.; Corcoran, A.; Leybova, V.; Dreizin, E.L. Metal-based iodine bearing materials prepared by mechanical milling. *Mater. Res. Soc. Symp. Proc.* **2015**, *1758*, 38–43. [[CrossRef](#)]
138. Abraham, A.; Obamedo, J.; Schoenitz, M.; Dreizin, E.L. Effect of composition on properties of reactive Al-B-I₂ powders prepared by mechanical milling. *J. Phys. Chem. Solids* **2015**, *83*, 1–7. [[CrossRef](#)]
139. Wang, S.; Abraham, A.; Zhong, Z.; Schoenitz, M.; Dreizin, E.L. Ignition and combustion of boron-based Al-B-I₂ and Mg-B-I₂ composites. *Chem. Eng. J.* **2016**, *293*, 112–117. [[CrossRef](#)]
140. Grinshpun, S.A.; Yermakov, M.; Indugula, R.; Abraham, A.; Schoenitz, M.; Dreizin, E.L. Aluminium-based materials for inactivation of aerosolized spores of *Bacillus Anthracis* surrogates. *Aerosol Sci. Technol.* **2017**, *51*, 224–234. [[CrossRef](#)]
141. Zhou, W.; DeLisio, J.B.; Li, X.; Liu, L.; Zachariah, M.R. Persulfate salt as an oxidizer for biocidal energetic nano-thermites. *J. Mater. Chem. A* **2015**, *3*, 11838–11846. [[CrossRef](#)]
142. Abraham, A.; Zhong, Z.; Liu, R.; Grinshpun, S.A.; Yermakov, M.; Indugula, R.; Schoenitz, M.; Dreizin, E.L. Preparation, ignition and combustion of Mg-S reactive nanocomposites. *Combust. Sci. Technol.* **2016**, *188*, 1345–1364. [[CrossRef](#)]
143. Nakpan, W.; Grinshpun, S.A.; Yermakov, M.; Indugula, R.; Reponen, T.; Wang, S.; Schoenitz, M.; Dreizin, E.L. Inactivation of aerosolized surrogates of *Bacillus anthracis* spores by combustion products of aluminium- and magnesium-based reaaactive materials: Effect of exposure time. *Aerosol Sci. Technol.* **2018**, *52*, 579–587. [[CrossRef](#)]
144. Liu, X.; Schoenitz, M.; Dreizin, E.L. Combustion of Mg and composite Mg-S powders in different oxidizers. *Combust. Flame* **2018**, *195*, 292–302. [[CrossRef](#)]
145. Stoimenov, P.K.; Zaikovski, V.; Klabunde, K.J. Novel halogen and interhalogen adducts of nanoscale magnesium oxide. *J. Am. Chem. Soc.* **2003**, *125*, 12907–12913. [[CrossRef](#)] [[PubMed](#)]
146. Reverberi, A.P.; Vocciante, M.; Salerno, M.; Ferretti, M.; Fabiano, B. Green synthesis of silver nanoparticles by low-energy wet bead milling of metal spheres. *Materials* **2020**, *13*, 63. [[CrossRef](#)]
147. Sullivan, K.T.; Wu, C.; Piekielek, N.W.; Gaskell, K.; Zachariah, M.R. Synthesis and reactivity of nano-Ag₂O as an oxidizer for energetic systems yielding antimicrobial products. *Combust. Flame* **2013**, *160*, 438–446. [[CrossRef](#)]
148. Wu, T.; Zachariah, M.R. Silver ferrite: A superior oxidizer for thermite-driven biocidal nanoenergetic materials. *RSC Adv.* **2019**, *9*, 1831–1840. [[CrossRef](#)]
149. Johnson, C.E.; Higa, K.T. Iodine-rich biocidal reactive materials. *MRS Online Proc. Libr.* **2013**, *1521*, 307. [[CrossRef](#)]
150. Abraham, A.; Zhang, S.; Aly, Y.; Schoenitz, M.; Dreizin, E.L. Aluminum-iodoform composite reactive material. *Adv. Eng. Mater.* **2014**, *16*, 909–917. [[CrossRef](#)]
151. Muravyev, N.K.; Monogarov, K.A.; Schaller, U.; Fomenkov, I.V.; Pivkina, A.N. Progress in additive manufacturing of energetic materials: Creating a reactive microstructures with high potential of applications. *Propellants Explos. Pyrotech.* **2019**, *44*, 941–969. [[CrossRef](#)]
152. Groven, L.J.; Mezger, M.J. Printed energetics: The path toward additive manufacturing of munitions. In *Energetic Materials: Advanced Processing Technologies for Next-Generation Materials*; Mezger, M.J., Tindle, K.J., Pantoya, M., Groven, L.J., Kalyon, D.M., Eds.; CRC Press: Boca Raton, FL, USA, 2017; p. 115.
153. Kline, D.J.; Alibay, Z.; Rehwoldt, M.C.; Idrogo-Lam, A.; Hamilton, S.G.; Biswas, P.; Xu, F.; Zachariah, M.R. Experimental observation of heat transfer mechanisms that drive propagation in additively manufactured energetic materials. *Combust. Flame* **2020**, *215*, 417–424. [[CrossRef](#)]
154. Egan, G.C.; Zachariah, M.R. Commentary on the heat transfer mechanisms controlling propagation in nanothermites. *Combust. Flame* **2015**, *162*, 2959–2961. [[CrossRef](#)]
155. Shancita, I.; Woodruff, C.; Campbell, L.L.; Pantoya, M.L. Thermal analysis of an iodine rich binder for energetic material applications. *Thermochim. Acta* **2020**, *690*, 178701. [[CrossRef](#)]
156. Huang, C.; Jian, G.; DeLisio, J.B.; Wang, H.; Zachariah, M.R. Electro spray deposition of energetic polymer nanocomposites with high mass particle loadings: A prelude to 3D printing of rocket motors. *Adv. Eng. Mater.* **2015**, *17*, 95–101. [[CrossRef](#)]
157. Li, X.; Guerieri, P.; Zhou, W.; Huang, C.; Zachariah, M.R. Direct deposit laminate nanocomposites with enhanced propellant properties. *ACS Appl. Mater. Interfaces* **2015**, *7*, 9103–9109.
158. Hu, X.; DeLisio, J.B.; Li, X.; Zhou, W.; Zachariah, M.R. Direct deposit of highly reactive Bi(IO₃)₃—polyvinylidene fluoride biocidal energetic composite and its reactive properties. *Adv. Eng. Mater.* **2017**, *19*, 1500532. [[CrossRef](#)]
159. Wang, H.; Holdren, S.; Zachariah, M.R. Preparation and combustion of laminated iodine containing aluminium/polyvinylidene fluoride composites. *Combust. Flame* **2018**, *197*, 120–126. [[CrossRef](#)]
160. Mei, X.; Zhong, G.; Cheng, Y. Ignition and combustion characteristics of aluminium/manganese iodate/nitrocellulose biocidal nanothermites. *J. Therm. Anal. Calorim.* **2019**, *138*, 425–432. [[CrossRef](#)]
161. Oxley, J.C.; Smith, J.L.; Porter, M.M.; Brady, J.E.; Levine, R.M. Polymer packaging of I₂ producing pyrotechnic biocides. *J. Energ. Mater.* **2018**, *36*, 493–501. [[CrossRef](#)]
162. Zaky, M.G.; Elbeih, A.; Elshenawy, T. Review of nano-thermites: A pathway to enhanced energetic materials. *Cent. Eur. J. Energ. Mater.* **2021**, *18*, 63–85. [[CrossRef](#)]
163. Vocciante, M.; Finocchi, A.; D’Auris, A.F.; Conte, A.; Tonziello, J.; Pola, A.; Reverberi, A.P. Enhanced oil spill remediation by adsorption with interlinked multilayered graphene. *Materials* **2019**, *12*, 2231. [[CrossRef](#)]
164. Wu, T.; Wang, X.; DeLisio, J.B.; Holdren, S.; Zachariah, M.R. Carbon addition lowers initiation and iodine release temperatures from iodine oxide-based biocidal energetic materials. *Carbon* **2018**, *130*, 410–415. [[CrossRef](#)]

165. Zhang, J.; Hooper, J.P.; Zhang, J.; Shreeve, J.M. Well-balanced energetic cocrystals of H₅IO₆/HIO₃ achieved by a small acid-base gap. *Chem. Eng. J.* **2021**, *405*, 126623. [[CrossRef](#)]
166. Kumar Chinnam, A.; Shlomovich, A.; Shamis, O.; Petrutik, N.; Kumar, D.; Wang, K.; Komarala, E.P.; Tov, D.S.; Sućeska, M.; Yan, Q.L.; et al. Combustion of energetic iodine-rich coordination polymer—Engineering of new biocidal materials. *Chem. Eng. J.* **2018**, *350*, 1084–1091. [[CrossRef](#)]
167. Bushuyev, O.S.; Peterson, G.R.; Brown, P.; Maiti, A.; Gee, R.H.; Weeks, B.L.; Hope-Weeks, L.J. Metal–organic frameworks (MOFs) as safer, structurally reinforced energetics. *Chem.—Eur. J.* **2013**, *19*, 1706–1711. [[CrossRef](#)]
168. Du, Y.; Su, H.; Fei, T.; Hu, B.; Zhang, J.; Li, S.; Pang, S.; Nie, F. Structure–property relationship in energetic cationic metal–organic frameworks: New insight for design of advanced energetic materials. *Cryst. Growth Des.* **2018**, *18*, 5896–5903. [[CrossRef](#)]
169. Zhang, J.; Zhu, Z.; Zhou, M.; Zhang, J.; Hooper, J.P.; Shreeve, J.M. Superior high-energy-density biocidal agent achieved with a 3D metal-organic framework. *ACS Appl. Mater. Interfaces* **2020**, *12*, 40541–40547. [[CrossRef](#)]
170. Chattopadhyay, K.; Mandal, M.; Maiti, D.K. Smart metal-organic frameworks for biotechnological applications: A mini-review. *ACS Appl. Bio Mater.* **2021**, *4*, 8159–8171. [[CrossRef](#)]
171. Greenberg, D.L.; Busch, J.D.; Keim, P.; Wagner, D.M. Identifying experimental surrogates for Bacillus Anthracis spores: A review. *Investig. Genet.* **2010**, *1*, 4. [[CrossRef](#)]
172. Grinshpun, S.A.; Li, C.; Adhikari, A.; Yermakov, M.; Reponen, T.; Schoenitz, M.; Dreizin, E.; Hoffman, V.; Trunov, M. Method for studying survival of airborne viable microorganisms in combustion environments: Development and evaluation. *Aerosol Air Qual. Res.* **2010**, *10*, 414–424. [[CrossRef](#)]
173. Grinshpun, S.A.; Adhikari, A.; Yermakov, M.; Reponen, T.; Dreizin, E.; Schoenitz, M.; Hoffmann, V.; Zhang, S. Inactivation of aerosolized Bacillus Atrophaeus (BG) endospores and MS2 viruses by combustion of reactive materials. *Environ. Sci. Technol.* **2012**, *46*, 7334–7341. [[CrossRef](#)] [[PubMed](#)]
174. Li, L.; Mendis, N.; Trigui, H.; Oliver, J.D.; Faucher, S.P. The importance of the viable but non-culturable state in human bacterial pathogens. *Front. Microbiol.* **2014**, *5*, 258. [[CrossRef](#)] [[PubMed](#)]
175. Grinshpun, S.A.; Adhikari, A.; Li, C.; Reponen, T.; Yermakov, M.; Schoenitz, M.; Dreizin, E.; Trunov, M.; Mohan, S. Thermal inactivation of airborne viable Bacillus Subtilis spores by short-term exposure in axially heated air flow. *J. Aerosol Sci.* **2010**, *41*, 352–363. [[CrossRef](#)]
176. Aly, Y.; Zhang, S.; Schoenitz, M.; Hoffmann, V.K.; Dreizin, E.L.; Yermakov, M.; Indugula, R.; Grinshpun, S.A. Iodine-containing aluminium-based fuels for inactivation of bioaerosols. *Combust. Flame* **2014**, *161*, 303–310. [[CrossRef](#)]
177. Nakpan, W.; Yermakov, M.; Indugula, R.; Jandarov, R.; Reponen, T.; Grinshpun, S.A. Inactivation of aerosolized Bacillus anthracis surrogate spores in close proximity to the flame: Simulation study. *J. Aerosol Sci.* **2019**, *128*, 72–78. [[CrossRef](#)]
178. Santarpia, J.; Ratnesar-Shumate, S.; Haddrell, A. Laboratory study of bioaerosols: Traditional test systems, modern approaches, and environmental control. *Aerosol Sci. Technol.* **2020**, *54*, 585–600. [[CrossRef](#)]
179. Wang, S.; Schoenitz, M.; Grinshpun, S.A.; Yermakov, M.; Dreizin, E.L. Biocidal effectiveness of combustion products of iodine-bearing reactive materials against aerosolized bacterial spores. *J. Aerosol Sci.* **2018**, *116*, 106–115. [[CrossRef](#)]
180. Zhou, W.; Orr, M.W.; Lee, V.T.; Zachariah, M.R. Synergistic effects of ultrafast heating and gaseous chlorine on the neutralization of bacterial spores. *Chem. Eng. Sci.* **2016**, *144*, 39–47. [[CrossRef](#)]
181. Zhou, W.; Orr, W.M.; Jian, G.; Watt, K.S.; Lee, V.T.; Zachariah, M.R. Inactivation of bacterial spores subjected to sub-second thermal stress. *Chem. Eng. J.* **2015**, *279*, 578–588. [[CrossRef](#)]
182. Mulamba, O.; Hunt, E.M.; Pantoya, M.L. Neutralizing bacterial spores using halogenated energetic reactions. *Biotechnol. Bioprocess Eng.* **2013**, *18*, 918–925. [[CrossRef](#)]
183. Henderson, J.; Longbottom, A.W.; Milne, A.M.; Lightstone, J.M.; Milby, C.; Stamatis, D.; Svingala, F.R.; Daniels, A.L.; Bensman, M.; Bohmke, M.; et al. Experiments and modeling for biocidal effects of explosives. *Propellants Explos. Pyrotech.* **2015**, *40*, 712–719. [[CrossRef](#)]
184. Knott, A.; Stamatis, D.; Svingala, F.; Lightstone, J.; Miller, K.; Bensman, M.; Bohmke, M. Subscale testing of prompt agent defeat formulations. In Proceedings of the Shock Compression of Condensed Matter—AIP Conference Proceedings 2015, Tampa Bay, FL, USA, 14–19 June 2015; Volume 1793, p. 040035.
185. Tringe, J.W.; Létant, S.E.; Dugan, L.C.; Levie, H.W.; Kuhl, A.L.; Murphy, G.A.; Alves, S.W.; Vandersall, K.S.; Pantoya, M.L. Comparison of Bacillus Atropaeus spore viability following exposure to detonation of C4 and to deflagration of halogen-containing thermites. *J. Appl. Phys.* **2013**, *114*, 234903. [[CrossRef](#)]
186. Pang, Y.-L.; Kalume, A.; Wang, C.; Santarpia, J. Atmospheric aging processes of bioaerosols under laboratory-controlled conditions: A review. *J. Aerosol Sci.* **2021**, *155*, 105767.
187. Fröhlich-Nowoisky, J.; Kampf, C.J.; Weber, B.; Huffman, J.A.; Pöhlker, C.; Andreae, M.O.; Lang-Yona, N.; Burrows, S.M.; Gunthe, S.S.; Elbert, W.; et al. Bioaerosols in the earth system: Climate, health, and ecosystem interactions. *Atmos. Res.* **2016**, *182*, 346–376. [[CrossRef](#)]
188. La, A.; Zhang, Q. Experimental validation of CFD simulations of bioaerosol movement in a mechanically ventilated airspace. *Can. Biosyst. Eng.* **2019**, *61*, 5.01–5.14. [[CrossRef](#)]
189. Fabiano, B.; Pistritto, F.; Reverberi, A.; Palazzi, E. Ethylene-air mixtures under flowing conditions: A model-based approach to explosion conditions. *Clean Technol. Environ. Policy* **2015**, *17*, 1261–1270. [[CrossRef](#)]
190. Moulay, S. Molecular iodine in monomer and polymer designing. *Des. Monomers Polym.* **2014**, *17*, 501–527. [[CrossRef](#)]

191. Makhayeva, D.N.; Irmukhametova, G.S.; Khutoryanskiy, V.V. Polymeric iodophors: Preparation, properties, and biomedical applications. *Rev. J. Chem.* **2020**, *10*, 40–57. [[CrossRef](#)]
192. Jander, J. Non-aqueous solvents for preparation and reactions of nitrogen halogen compounds. *Pure Appl. Chem.* **1977**, *49*, 67–73. [[CrossRef](#)]
193. Marinho, G.S.; de Farias, R.F. The structure, thermodynamic instability and energetics of NI_3 , its specific impulse and a strategy for its stabilization. *J. Mol. Struct.* **2021**, *1232*, 130075. [[CrossRef](#)]
194. Jander, J. Recent chemistry and structure investigation of nitrogen triiodide, tribromide and trichloride, and related compounds. In *Advances in Inorganic Chemistry and Radiochemistry*; Emeléus, H.J., Sharpe, A.G., Eds.; Academic Press: New York, NY, USA, 1976; Volume 19, pp. 2–59.

Disclaimer/Publisher's Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.