
STUDIES IN THE FIELD OF CHEMISTRY OF NITRO COMPOUNDS
(TO 100TH BIRTHDAY ANNIVERSARY OF S. S. NOVIKOV)

Application of Dinitramide Salts (Review)

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Received April 29, 2009

Abstract—Published data on application areas of ammonium and other salts of dinitramide, new components of condensed energetic systems, are discussed. Originally suggested as nearly exclusively oxidants for rocket propellants and explosives, these compounds have significantly expanded their application areas, and this occurred not only in defense, but also in nondefense fields.

DOI: 10.1134/S1070427209100036

The ammonium salt of dinitramide (ADN) $\text{NH}_4+\text{N}(\text{NO}_2)_2^-$, synthesized nearly 40 years ago [1–3], was primarily regarded as a promising oxidant for solid propellants. By the end of the 1980s, it was industrially manufactured, but the defense conversion and economical crisis made this unique product unnecessary and its industrial production was terminated. Owing to the recently revived interest in dinitramide salts upon a number of publications about their synthesis and properties [2–6], a rather ample body of literature dedicated to this topic, including that concerned with various presumed application areas of these salts, has appeared.

This review cannot pretend to be complete: all developments in the Soviet Union were of secrete nature and, presumably, only their part was declassified after dinitramide (DN) was synthesized by American researchers in 1990 [4–6]. The indubitable attractiveness of the ammonium (ADN), potassium (PDN), and other DN salts as components in various defense applications gives reason to believe that, at present too, the available information (both domestic and foreign) is only the “visible part of an iceberg.”

By now, several tens of dinitramide salts have been synthesized [2, 3, 7]. Although no reliable evidence about industrial use of some of these salts is available for the above-mentioned reasons, the whole set of functional and service properties of some compounds belonging to

this class gives a certain reason to believe that they will be used in the industry.

The classification of the compounds under consideration just by their application areas is primarily caused by the desire to outline their increasing applied importance. The commonly accepted division is largely conditional because rate (decrease in the exponent in the combustion law to 0.5 [9]), caused by the key role of processes in the condensed phase [9, 14, 15]; and even lower sensitivity to various mechanical impacts [12].

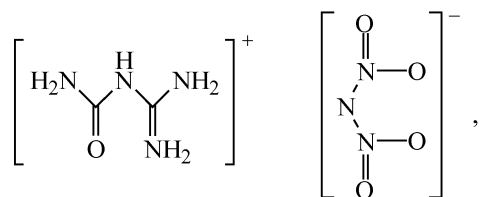
Use of ADN presumably lifts certain psychological limitations and, occasionally, propellants contain as propellants such exotic components as, e.g., lithium borohydrides or aluminohydrides [11], which are suggested to be preliminarily encapsulated in hydrocarbons, or aluminum hydride, which “exhibits a good compatibility with oxidants and binder components” [16].

Problems associated with the high hygroscopicity and poor compatibility with some components of the propellant mass can be eliminated by encapsulating oxidant particles in a protective sheath composed of various polymers [18, 19] and the easy fusibility at a sufficiently large difference between the melting and decomposition points is used to obtain rounded particles (with the technological properties improved on mixing the propellant mass) [20–32]. Crystallization in the presence of additives, salts of magnesium and calcium [33], yields nearly isometric particles, but fails to produce a shape

perfection similar to that furnished by granulation.

An attractive property of DN salts is their comparatively low combustion point, which makes them promising powder components for barrel artillery. A composite powder based on ADN and a binder, thermoplastic copolymer of ethylene and vinyl acetate, has been suggested [34].

In 2005, the development and tests have been reported of a new modular powder charge UNIFLEX for the ARCHER artillery system, containing 60% guanylurea salt (GUS) of DN:



hexogen, and a binder. The system was intended to be supplied to Swedish and Danish armies in 2008 [35]. The same report mentioned that the cost of DN GUS industrially manufactured by EURENCO BOFORS mostly as a component of gas-generating formulations for automobile safety bags “is comparable with that of ordinary energetic materials.”

Use of ADN-based solid propellants is not limited to rocket and artillery industries. For example, a fire-extinguishing formulation has been suggested in which there are combustible components, binder, thermally scattered component (mainly inorganic salts), and ADN salts or their mixtures with nitrates and(or) perchlorates as oxidants. The formulation is intended for use in volume fire-extinguishing systems as a compound that minimizes the release of toxic and ecologically hazardous combustion products [36].

Owing to the high electrical conductivity of its combustion products, the potassium salt of DN is regarded as an oxidant for promising plasma-forming fuels for MHD generators [2]. Probably, of interest in this regard are salts of other elements with low ionization potential, e.g., cesium and rubidium.

(2) Liquid DN-based propellants. The high solubility of ADN in water and numerous combustible liquids, e.g., alcohols, and its good compatibility with other component make it possible to regard this compound as a promising oxidant in liquid mono- and binary propellants.

It has been noted that such a propellant has the

following advantages over hydrazine: enhanced thermal stability; lower fire hazard, sensitivity, and toxicity; high specific impulse and density; and storage temperatures of up to +50°C [37].

ECAPS, a joint enterprise of the Swedish space agency and Volvo Aero Co., has suggested a liquid monopropellant LMP 101 (HPGP 101), a high-performance green propellant containing ADN, water, and propellant, e.g., an alcohol (methanol, glycerol) [38, 39]. The propellant contains as a combustion stabilizer ammonia or a weaker or sterically hindered base (hydrazine, hydroxylamine, urea, urotropin) in amounts of 0.1–5% relative to the formulation mass [38].

The effect of the composition on the specific impulse, sensitivity, and thermal stability of monopropellants based on ADN, water, and an alcohol has been studied [40]. The results obtained were used to choose a formulation that provides an impulse of 255 kg s kg⁻¹, does not detonate at a diameter shorter than 25 mm, and has an acceptable thermal stability. An additional variant suggests a monopropellant composed of a mixture of ADN, water, and formamide [41], with a specific impulse as large as 2560 N s kg⁻¹ (261 kg s kg⁻¹).

The thermal stability of ADN-based monopropellants thickened with aerosil has been studied [42, 43].

In some cases, ADN is mentioned as a possible oxidizing component [44–47]. For example, a liquid oxidant for a “safe and convenient” hybrid propellant has been patented. It contains hydroxylammonium nitrate and at least one oxidant from the following group: hydrazine nitroformate, ADN, ammonium nitrate, and hydrogen peroxide [44].

(3) Explosives based on DN salts. The chemical composition of ADN is far from being stoichiometrically optimal (excess of oxygen is 2 g-at mol⁻¹, or more than 16 g-at kg⁻¹), and, therefore, the salt has rather poor detonation properties. Determination of the explosive properties and sensitivity of cast and compacted charges based on ADN and its mixtures with aluminum and nanodispersed diamonds has been reported [48–50]. Addition of 1% magnesium oxide makes it possible to reach a casting density of 97% relative to the theoretical value for pure ADN and 95–99% for mixtures with aluminum. It is maintained that a technology for mixing and casting has been developed, which can produce charges with masses up to 6 kg.

The detonation velocity is strongly dependent on the charge diameter, at least up to a diameter of 100 mm, and

reaches a value 6 km s^{-1} at a density 1760 kg m^{-3} . This velocity is presumably close to the limiting value because extrapolation to an infinite diameter yields a detonation velocity 6300 m s^{-1} [48].

For cast charges of compositions ADN/ZnO (99.5/0.5 wt %), ADN/nanodiamond/ZnO (92.4/7.2/0.4), ADN/ NH_4NO_3 /ZnO (95.5/4.0/0.5), and ADN/ NH_4NO_3 /ZnO/nanodiamond (88.0/4.5/0.5/7.0), the detonation velocity is $3.9\text{--}4.5 \text{ km s}^{-1}$ at a diameter of 1.3 cm [50].

The comparatively easy fusibility of ADN has given an impetus to development of synthesis of cast formulations with the optimal oxygen balance, including high-power disruptive explosives. Explosive formulations have been suggested in which ADN serves as a matrix, with octogen, hexogen, CL-20, and mixtures of these used as fillers [51]. It is stated that the ADN/octogen mixture (30/70 wt %) has the same power as octogen, and the ADN/CL-20 mixture (30/70), a 12% higher explosive power which markedly exceeds the value for the same cast formulation on a TNT matrix.

Complexes of ADN and PDN with some energetic compounds forming needle-like crystals have been suggested as promising thermally stable explosives [52]. It has been reported that ADN complexes with CL-20 at 1 : 1 to 3.5 : 1 molar ratios of the components decompose without melting at 250°C , and PDN complexes with CL-20 at molar ratios of 1 : 2 to 6 : 1, at 200°C . ADN complexes with 1,3-trinitroazetidine (1 : 1 and 2 : 1) melt at 99.2 and 98.6°C (decomposition onset temperature 150°C according to DSC data). The 1 : 1 ADN complex with trinitrobenzene (TNB), produced by fusing together the components, has a melting point 149°C (compared with 92°C for ADN and 120°C for TNB) and a density 1.83 g cm^{-3} (1.81 and 1.66 g cm^{-3} , respectively, for pure components). However, the high thermal stability is combined with a very high sensitivity comparable with that of lead azide [53].

Mixed explosive formulations with a polymeric binder seem to be considerably more promising as regards their functional and service characteristics. For example, nitrocellulose-based formulations containing explosives, metals, and oxidants have been suggested, among which are ADNs with a detonation velocity of no less than 8 km s^{-1} [54].

In contrast to ADNs, salts with some other cations are more balanced in oxygen and, accordingly, are higher power explosives. Of these, mention should be primarily made of the guanidinium salt (GS) $[\text{C}(\text{NH}_2)_3]^+[\text{N}(\text{NO}_2)_2]^-$

[55] and GUS [56], whose power exceeds that of TNT. The last salt deserves a particular attention, because, containing explosives in amounts comparable with those in TG-50 and TG-40 formulations (detonation velocity 7966 m s^{-1} and pressure 26 GPa on the Chapman–Zhuge surface for a compacted charge with a density of 1662 kg m^{-3}) it has a sensitivity to mechanical impacts comparable with that of TNT and a thermal stability unique to DN salts (its intense decomposition onsets at $196\text{--}215^\circ\text{C}$, which exceeds by $15\text{--}35^\circ\text{C}$ the decomposition points of other DN salts [57, 58]). These properties are attributed to the mutual stabilization of the cation and anion, which form a dense network of hydrogen bonds in the crystal.

(4) DN salts in gas-generating and other pyrotechnical formulations. DN salts, and especially guanylurea and guanidinium salts, yield in decomposition and combustion a large volume of gases, mostly nitrogen, water vapor, and CO_2 . Therefore, a rather widely represented area of their use is as basic components in gas-generating formulations and, in particular, those for automobile safety bags [59–62]. The low sensitivity of these compounds to mechanical impacts provides their safe use. As a rule, a gas-generating formulation includes DN GUS or GS and an oxidant whose role can be played by nitrates of alkaline-earth metals. A gas-generating formulation based on DN GUS, to which DN GS is added to raise the detonation velocity, has been suggested [62].

It is suggested to use nitrogen-rich metal-complex salts of DN, instead of GUS. For example, a mixture of 26.2% guanidine nitrate and 73.8% dinitraze salt of tetramminecopper(II), $[\text{Cu}(\text{NH}_3)_4]^{2+} 2\text{N}(\text{NO}_2)_2^-$, yields in combustion 3.65 mol of gases per 100 g [63].

Gas-generating formulations in which ADN is used as oxidant has been patented [64–66].

DN salts, and commonly that with potassium, are promising as oxidants for various luminous pyrotechnical formulations [67–71], in which they replace the corresponding nitrates because of having a higher enthalpy of formation. Metal-ammine salts have also been studied as oxidants for initiating pyrotechnical formulations [72].

(5) Use of DN salts for stabilization of ammonium nitrate. One the main disadvantages of ammonium nitrate as a component of propellant and pyrotechnical formulations is the occurrence of phase transitions in the temperature range from -17 to $+169^\circ\text{C}$. The most undesirable of these occurs at 32.3°C and may lead to

disintegration of the material. A most important advantage of DN salts over other additives suggested to control this phenomenon is that the energy properties of the system are, at least, preserved. It has been suggested to use for phase stabilization of ammonium nitrate the potassium salt individually or with addition of lithium, cesium, and zinc salts of DN [73, 74].

(6) Use of a lithium salt of DN as an electrolyte component for power cells and batteries. It is suggested to use a lithium dinitramide solution (in glymes, carbonates), individually, or as an additive to lithium hexafluorophosphate, as the electrolyte of lithium power cells with a liquid sulfur-containing cathode. In this case, the surface of the lithium cathode is covered by a protective layer which markedly decelerates the self-discharge caused by the reaction of the metal with sulfur-containing components of the cathode system (lithium polysulfides). However, this layer has a rather high conductivity by lithium ions which provides a moderate polarization of the anode [75]. As a result, the rate of self-discharge decreases by approximately a factor of 30.

(7) DN salts as surfactants. The comparatively strong delocalization of the charge of the $[N(NO_2)_2]^-$ provides a good affinity of its numerous salts for organic substances and also its ability to solubilize organic bases in a lipophilic medium via formation of low-polar ion pairs. Because of the high cost, such a use of surfactants should be regarded as rather exotic and only justified in the case of a very high value of the objects being dissolved or of the products of their dissolution, e.g., for improving the efficiency of medicinal preparations. Data on an approximately twofold increase in the distribution coefficient of protriptyline (preparation for curing Alzheimer's disease) and quinine in their extraction from an aqueous solution of, respectively, hydrochloride and sulfate [76].

(8) Chemical transformations and synthetic prospects of DN salts. Numerous examples of reactions in which the dinitrimine moiety remains unchanged have been reported [2, 7]. The decomposition of this moiety is an object of analysis of the thermal decomposition of various salts, to which a large number of theoretical and experimental studies have been devoted [77].

The reactivity of dinitramide and its aci-isomer toward alkenes was theoretically studied using the apparatus of the density functional B3LYP/6-31+G(d,p) and the nonempirical CBS-QB3 method [78]. It was demonstrated that the rate of 1,3-dipolar cycloaddition to the double

bond of the N–N–O fragment is comparable with the rate of interaction of nitril oxides and azides with olefins, but decreases in the presence of electron-acceptor substituents at the double bond.

An interesting synthetic application of DN salts is the controlled stage-by-stage substitution of fluorine atoms with oxygen in interhalides [79]. It has been reported that, in these reactions, the $N(NO_2)_2^{2-}$ anion is preferable to the nitrate. For example, $KN(NO_2)_2$ smoothly reacts with BrF_5 at $-45^\circ C$ to quantitatively give $KBrOF$, N_2O , and FNO_2 , and its interaction with ClF_5 at $-13^\circ C$ yields an equimolar mixture of $KClOF_4$ and $KClF_4$. It is remarkable that $KClOF_4$ is formed, because, with most of exchange reagents, e.g., NO_3^- , it is difficult to terminate the process in this stage and $FClO_2$ is the only product.

In the reaction of PDN with IF_7 , IOF_6^- is deoxygenated to give, instead, KIF_6 , which yields a new adduct in the presence of an excess amount of the starting heptafluoride.

CONCLUSIONS

Dinitramide salts, originally regarded as promising oxidants of solid propellants and mixed explosive formulations, have found new applications, including those in nondefense industries possessing a considerably larger consumer capacity than military applications. This gives reason to expect that the amount of their production will further increase and their cost will, accordingly, decrease, with these compounds becoming more easily available, and their use, wider.

ACKNOWLEDGMENTS

The authors are grateful to N.V. Kozyrev and R.Yu. Mitrofanov for assistance in analysis of the literature and to V.A. Shandakov, N.I. Popka, and G.I. Russkikh for a number of valuable critical remarks.

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