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Possible Chemical Mechanisms for Boron Hydride Acceleration of Nitramine Decomposition: Literature Review

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This paper is a summary of observations and possible chemical mechanisms for the acceleration of the thermal decomposition of nitramines octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), and of propellants derived from them, by salts containing the anions $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$. Available literature on the thermal behavior of salts containing these anions are reviewed as well as available information on the effects of these salts on the decomposition and combustion of HMX and RDX. The emphasis is on thermal decomposition and salts with alkali metal cations. The pure salts appear stable under vacuum or inert gas to ~700–800°C, but there are reports of H_2 evolution at about 620–650°C. In the presence of air, thermo-oxidative degradation at somewhat lower temperatures (~300–600°C, depending on the nature of the salt) is observed. When the salts are heated together with RDX, considerable enhancement of the decomposition rate of RDX is observed; this begins at the melting temperature of pure RDX and becomes intense, leading to a lower, much sharper decomposition exotherm. These observations seem consistent with an acceleration mechanism involving attack on the nitramine by the B–H hydrogens of the boron hydride salt, but it is difficult to evaluate the role of other processes or the reaction of the accelerant with products, particularly nitrogen oxides.

Introduction

THERE are a number of propellant applications for which very high burning rate (VHBR) propellants are needed. These propellants generally contain octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX) and/or triaminoguanidinium nitrate (TAGN), together with a borohydride. The borohydride, which is often a $B_nH_n^{=}$ salt such as $K_2B_{10}H_{10}$ or $K_2B_{12}H_{12}$, greatly accelerates the burning rate of the propellant. This effect is well known and has been the subject of several workshops and of a large number of reports.[1–7]

The purpose of the work described here was to elucidate the chemical mechanisms responsible for the burning-rate acceleration of HMX and RDX propellants by $B_nH_n^{=}$ salts, with the ultimate goal of obtaining maximum acceleratory effects with minimum sensitivity. This work focuses on the initial stages of the nitramine decomposition process; however, it should be remembered that acceleration may also occur at a later stage of the combustion process, when the initial product gases are reacting with each other.

References 8–12 describe pyrolysis and pyrolysis-gas-chromatography-mass-spectroscopy (GCMS) studies on RDX and on RDX-$K_2B_{12}H_{12}$ mixtures, and on a series of HMX–TAGN propellant compositions,[11] some containing $K_2B_{10}H_{10}$.

This paper is a summary and critical analysis of literature data on borohydride acceleration of the initial stages of nitramine decomposition, together with a discussion of some possible chemical mechanisms that may be involved.

This paper tends to be focused on the condensed phase, although it is possible that a significant amount of reaction, including the acceleratory effect, may in fact take place in the gas phase. This seems reasonable because some evidence (see the section entitled "Effect of Added Accelerant on Decomposition Rates") at least suggests the presence of an acceleratory effect on the condensed-phase decomposition of RDX, and since the primary and acceleratory mechanisms might well be similar in the liquid and gaseous phases.

Note also that most of the data discussed here pertain to slow decomposition, whereas the time scale in VHBR combustion is several orders of magnitude faster because of the much higher temperatures and pressures involved. However, it should be remembered that slow-decomposition studies are still relevant to the fast-reaction conditions characteristic of combustion, because they can lead to an understanding of the reaction steps involved. Once these reaction steps are understood at low temperatures and pressures, their activation parameters can be measured or estimated. These parameters can then be inserted in models and used to estimate their rates under the more severe conditions characteristic of combustion and explosive behavior.

Effect of Added $K_2B_{10}H_{10}$ and $K_2B_{12}H_{12}$ on Thermal Decomposition of HMX and RDX

In this section we will consider the effect of added $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ salts on the rates and product distributions obtained from thermal decomposition of the nitramines HMX and RDX.[8–19] The decomposition of mixtures, pure salts, and pure nitramines will each be considered separately.[8–19]

Effect of Added Accelerant on Decomposition Rates

There are few, if any, quantitative kinetic studies of the decomposition of HMX and RDX in the presence of $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ salts; however, there is some qualitative information in support of the view that addition of these salts does accelerate the early stages of thermal decomposition of these materials.

On the pyroprobe pyrolysis of RDX, the addition of accelerant resulted in a decrease in the time to the appearance of products.[13]

Thermal analysis studies have been performed[19] on mixtures of RDX with $K_2B_{12}H_{12}$ with $((CH_3)_4N)_2B_{12}H_{12}$ and with $NaBH_4$; these show that the normal RDX exotherm at ~240°C is shifted to the noticeably lower temperature of ~200°C and appears to coincide with the normal RDX melting endotherm at this temperature. The mixtures used contained 15–50% of the boron compound. The melting endotherm of RDX at

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~205°C and its broad, intense decomposition exotherm at ~225–250°C disappear and are replaced by a sharp, exothermic spike in the region 203–224°C; this spike is so narrow and intense that it appears to have no width at all. Examination of these curves[19] suggests that the rate enhancement occurs immediately on melting of the RDX, because for the catalyzed samples the melting endotherm disappears and the reaction becomes rapid at precisely the temperature (~205°C) at which pure RDX melts. Because these studies were done in open pans,[19] which enabled the gaseous products such as nitrogen oxides to escape, it was suggested that direct nitramine–borohydride interactions occurred. However, some gas–borohydride interactions could still occur under these conditions.

This same effect is also observed when RDX is mixed with $((CH_3)_4N)_2B_{12}H_{12}$ that has been heat-treated at 480°C[19]; but the acceleration effect is almost eliminated when the heat treatment takes place at 760°C. Little if any acceleration is observed when elemental boron is substituted for the previously mentioned salts.[19]

The preceding differential scanning calorimetry (DSC) studies employed open pans (no lids) with argon purge flow of 30 ml/min.[19] It was pointed out that there was little chance for gas to collect over the sample; the preceding effects were believed to be a result of solid/liquid phase interactions.

Second, a series of experiments was reported[8,16,17] in which RDX, alone and in mixtures containing 29% $K_2B_{12}H_{12}$, was partially decomposed at temperatures of 200–215°C. The residues from the incomplete decomposition of these samples were analyzed by high-pressure liquid chromatography (HPLC); it was found that the addition of $K_2B_{12}H_{12}$ led to a more rapid disappearance of RDX and the appearance of its mono-*N*-nitrosoderivative (MRDX). This indicates that $K_2B_{12}H_{12}$ accelerates the decomposition of RDX, in agreement with the DSC results described in the preceding paragraphs. It was found that the weight of the material remaining after decomposition was approximately equal to the sum of 1) the weight of RDX remaining, 2) the weight of nitrosoamines formed, 3) the amount of borohydride catalyst added, and 4) the residue (~5%) from the amount of RDX that had decomposed.

Effect of Added Boron Hydride Salt on Product Distributions: Gaseous-Product Accelerant Effects

There is little quantitative information available on the effect of added $B_nH_n^{=}$ salts on gaseous-product distributions. It was found from Pyroprobe-GC studies[15,17] that the relative amounts of HCN, NO, and NO_2 were greater for RDX decomposed in the presence of boron hydride salts than for RDX decomposed alone. Tantalum hydride and tantalum oxide did not affect the decomposition products to the same degree as did the borohydride salts. Pyroprobe-gas-chromatography-Fourier-transform-infrared (GC–FTIR) spectroscopy studies indicated that the main effect of added borohydride accelerant was an increase in CO_2 formation relative to N_2O.[19]

Effect of Added Boron Hydride Salt on Product Distributions: Accelerant Effects on Formation of Less-Volatile Products

A number of less-volatile products have been identified as being formed from the decomposition of HMX and RDX.[8–12,19–26] These include 1,3,5-triazine[8–12]; a material(s) with parent peak at *m*/*e* = 97 (protonated form, *m*/*e* = 98)[20–26] usually written as a 1,3,5-triazine oxide; formamide[8,19]; *N*-methylformamide[20–26]; *N*,*N*-dimethylformamide[20–26]; dimethylnitrosoamine[20–26]; dimethylamino-acetonitrile[9–12,20–22]; an unidentified compound[8–12] referred to as "Unknown A" (1,2,4-oxadiazole, *N*-cyanoformamide, or *C*-cyanoformamide) (note that this is a discrete chromatographic peak, corresponding to a discrete chemical substance, the mass spectrum of which has its highest-mass peak at *m*/*e* 70); and a number of other compounds discussed later in this paper.[8–12,19]

The effect of added $K_2B_{10}H_{10}$ and $K_2B_{12}H_{12}$ on the formation of 1,3,5-triazine seems to be to reduce the relative extent to which it is formed.[8–12] These accelerants also reduce (Ref. 13) the formation of the 1,3,5-triazine oxide,[20–22] at least relative to dimethylformamide, dimethylaminoacetonitrile, and dimethylnitrosoamine. On the other hand, the addition of a borohydride accelerant led to a sharp decrease in the amounts [relative to *m*/*e* 60 (CH3NH–C(=O)H), *m*/*e* 74 ($(CH_3)_2N{-}C({=}O)H$), *m*/*e* 75 ($(CH_3)_2N{-}NO$), and *m*/*e* 85 ($(CH_3)_2N{-}CH_2CN$)] of *m*/*e* 46 [now known to be $H_2N{-}C({=}O)H$, not NO_2] and to a noticeable increase in the relative amount of *m*/*e* 44.[13] This raises the possibility that the preceding methylated compounds may be formed by a mechanism that does not involve formamide.

However, added $K_2B_{10}H_{10}$ and $K_2B_{12}H_{12}$ lead to an increase in the relative amounts of dimethylaminoacetonitrile,[11] *N*-methylformamide, *N*,*N*-dimethylformamide, and dimethylnitrosoamine formed.[19]

Unknown A exhibits an interesting dependence on the addition of boron hydride salt[9–12]: At low temperatures (250 and 400°C) added $K_2B_{12}H_{12}$ leads to a decrease in its formation from RDX decomposition, while at higher temperatures (800°C) an apparent increase in its formation is observed when $K_2B_{12}H_{12}$ is added.

Thermal Behavior of Pure Salts of Anions $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$

In understanding the mechanisms by which the anions $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ accelerate the decomposition and combustion of HMX and RDX, it is necessary to understand the thermal behavior of these materials separately. In this section, the thermal behavior of salts of $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ will be summarized; the emphasis will be on thermally stable, inorganic cations such as metals because this will eliminate complications caused by decomposition reactions involving organic anions. In the following section, relevant aspects of the thermal behavior of pure HMX and pure RDX will be summarized.

It has been reported that when metal (or other not-readily-reduced cation) salts such as $Cs_2B_{10}H_{10}$ and $Cs_2B_{12}H_{12}$ were heated under vacuum in sealed tubes to temperatures of 600–800°C, they were recovered unchanged except for melting.[27] Because cesium and potassium are both alkali metals, the potassium salts $K_2B_{10}H_{10}$ and $K_2B_{12}H_{12}$ that are of interest as propellant combustion catalysts may behave similarly.

Kuznetsov and Klimchuk[28] described the preparation, infrared (IR) spectra, and thermal properties of the $B_{12}H_{12}^{=}$ salts of sodium, rubidium, cesium, lithium, and hydronium. The thermal studies were mainly of the thermogravimetric and differential thermal analysis (DTA) types, and were carried out under air. It was found that the thermo-oxidative degradation of all of the compounds began with a distinct exothermic effect at ~300°C, with the stability increasing appreciably from the lithium to the cesium salt. This thermo-oxidative degradation was accompanied by an increase in weight of the compounds; the increase in weight was linked by IR studies to the replacement of B–H bonds by B–O bonds. However, no definite composition could be assigned to these pyrolysis products.

Note that in the studies described in Kuznetsov and Klimchuk,[28] thermo-oxidative degradation of these materials was observed, whereas in Muetterties et al.[27] it was stated that the materials were unchanged. This discrepancy is probably because the the studies of Kuznetsov and Klimchuk were carried out under air, while those of Muetterties et al. were carried out in a sealed tube. This seems relevant to the question of the behavior of these materials in the presence of nitro compounds such as HMX and RDX because such materials would also be expected to provide an oxidizing environment.

In a study of $Na_2B_{12}H_{12}$ tetrahydrate, it was found that the material gave two endotherms at 140 and 195°C[29]; these were connected with the two-stage elimination of water (two molecules at each stage). The anhydrous salt existed in the region 195–505°C, and above 505°C this was found to undergo exothermic thermo-oxidative degradation marked by an increase in weight corresponding to one oxygen atom per formal unit of the anhydrous salt. This mono-oxygenated product burned when heated above 830°C. Presumably the heating was carried out under air, in view of the occurrence of oxidative processes.

Reference 30 describes thermogravimetric and DTA studies on a series of mixed potassium, rubidium, and cesium dodecahydro-closo-dodecaborate halides. The salts investigated had the composition $M_2B_{12}H_{12} \cdot MX$, where M was K, Rb, or Cs, and X was Cl, Br, or I. The thermoanalytical studies were performed under air at a heating rate of 9 K/min, and it was found that the thermo-oxidative degradation of the mixed salts began in the range 510–570°C, regardless of the nature of the cation and the halogen. This degradation was accompanied by an increase in weight; this increase was attributed to replacement of the B–H bond by B–O and to a gradual conversion of the tetrahydroborate ion into alkali metal borates and B_2O_3.

The thermal decomposition of the hydrogen analogs $H_2B_{12}X_{12} \cdot nH_2O$, where X is H, Cl, Br, or I, and n is 4–12, has been investigated by mass spectrometry and IR spectroscopy in the temperature range 20–800°C.[31] When $H_2B_{12}H_{12} \cdot 6H_2O$ was heated to 400°C, the evolution of water and hydrogen was observed. Above 400°C, boron ions (B^+) were seen for all compounds investigated. The $B_{12}Cl_{12}^{=}$ and $B_{12}Br_{12}^{=}$ ions also showed BX^+, BX_2^+, and BX_3^+. It was argued that the B^+ ions resulted from the ionization of elementary boron, because their temperature dependence had the same form as that of elementary boron.

In the course of studies on a variety of boron hydride derivatives, thermal analysis studies were performed on some $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ salts.[32] The cesium salts of $B_{12}H_{12}^{=}$ gave only two exothermic effects with "insignificant" gassing at 616–655°C. It was stated that nearly 1 mole of H_2 was given off per mole of salt in this temperature range; however, the identification of H_2 as the gas was not described. The IR spectrum for $Cs_2B_{12}H_{12}$ after heating to 700°C retained all primary absorption bands of the untreated salt. Curves were also given for $Cs_2B_{10}H_{10}$, which suggested that this compound behaves similarly. If substantiated, this report of H_2 evolution suggests that slight changes involving H_2 evolution may also have taken place in the sealed-tube vacuum heatings described in Muetterties et al.,[27] and quite possibly in all such experiments on these compounds. The preceding studies were carried out in vacuum. The effect of medium was noted only for the cesium and tetramethylammonium $B_{12}H_{12}^{=}$ salts. When the experiments were carried out in argon the behavior was similar to that in a vacuum, and when it was carried out in air exothermal thermo-oxidative behavior was observed at 200–300°C, accompanied by an increase in weight. This behavior was attributed to an "exchange of chemical bonds B–H for B–O;" i.e., to the formation of boron oxides.

Thermolysis studies on $((CH_3)_4N)_2B_{12}H_{12}$ were also described[32]; the situation is complicated by the presence of the tetramethylamino group. The authors felt that the decomposition involved destruction of the tetramethylamino cation and possibly the formation of a B–N bond. Thermal studies on $(NH_3)_2B_{10}H_{12}$ and $(NH_4)_2B_{10}H_{10}$ were also described.

Kaste[19] described a variety of thermoanalytical studies on $K_2B_{12}H_{12}$ and on $((CH_3)_4N)_2B_{12}H_{12}$. These studies were performed in an atmosphere of argon. It was found that the potassium salt gave a weak endotherm at 78°C, corresponding to about 7% weight loss, and was thereafter stable to at least 460°C. The tetramethylammonium salt, on the other hand, remained stable until a temperature of about 360°C was reached, at which temperature it exhibited an endotherm and an 18.5% weight loss. The accelerative ability of these salts toward RDX decomposition was not decreased by preheating at 360°C.

It is tempting to try to explain these weight losses in terms of loss of water of hydration.[19] This would be in agreement with the fact that these weight losses do not remove the acceleratory effect of the salts on RDX decomposition. However, the water-loss hypothesis alone does not explain the slight discoloration that was noted.[19]

The boron cage compounds $M_2(B_{10}H_{10})_3$, where M is gadolinium or cerium, have been used as sources of boron in synthesis of gadolinium and cerium borides.[33] The synthesis was carried out by heating the $M_2(B_{10}H_{10})_3$ with metal hydride at temperatures of 1000–1400°C. Yields were not reported; however, the basic result seems consistent with the idea that most of the weight of the anion stays behind and goes into the nonvolatile residue.

The pyrolysis of ammonium and alkylammonium salts with $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ has been investigated under argon and under ammonia[34,35]; the products were investigated by nuclear magnetic resonance and IR spectroscopy. The salts underwent intense oxidation when heated in air. Under argon the $B_{10}H_{10}^{=}$ anion rearranged, as did the $B_{20}H_{18}^{=}$ and $B_{20}H_{19}^{3-}$ to the more stable $B_{12}H_{12}^{=}$ anion, and simultaneous interaction with the onium cations resulted in the formation of polymeric compounds containing B–N bonds. When decomposition of the ammonium salt was carried out under ammonia, ring opening and incorporation of ammonia occurred; this raises questions concerning the possibility that even under an inert atmosphere the ammonium cations, or amines in equilibrium with them, might be playing a role in facilitating the decomposition. Further heating in an inert atmosphere to 1900°C resulted in ordering of the structure and formation of crystalline boron nitride.

When heated in air $(CH_2NH_3)_2B_{10}H_{10}$ was stable, except for a polymorphic change at 200°C, until an exothermic reaction took place at 290°C; this resulted in changes in the IR spectrum of the sample.[36] The discrete NH and BH bands were replaced by diffuse bands, and a broadband appeared near 1000 cm^{-1}; these bands were attributed to thermo-oxidative destruction of the $B_{10}H_{10}^{=}$ anion.

The pyrolysis of $Cu_2B_{10}H_{10}$ has been studied under argon over the temperature range 25–800°C, using DTA, volumetric, IR spectroscopic, and x-ray phase analytical methods.[37] It was found that $Cu_2B_{10}H_{10}$ decomposes with the liberation of H_2 on heating to 292–340°C; there were exothermal effects at 292, 330, and 340°C. There were then no thermal effects until 800°C, although there was gradual release of the last traces of hydrogen as H_2. The pyrolysis products produced at 250–350°C were air- and moisture-sensitive, but those from pyrolysis to 800°C were not. The products included amorphous and crystalline phases of CuB_{24}, copper, and boron.

A study has been made of the thermal behavior of a series of double salts of $B_{10}H_{10}^{=}$ with monovalent copper and alkali metal (potassium, cesium) or alkylammonium (di, tri- or tetramethyl, -ethyl or -butyl) cations.[38] It was found that on heating in air at 10 K/min, the copper salts began decomposing at ~235–300°C, whereas the alkylammonium salts began decomposing above 300°C and the alkali–metal salts above 350°C.

When hydrazonium ($N_2H_5^+$) salts, hydrazine-Ni(II) or hydrazine-Pb(II) complex salts of the anions $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ were heated in air, polymorphic transitions and elimination of solvated hydrazine molecules at temperatures of around 140–200°C were observed.[39] Further heating led to a vigorous exothermal reaction resulting in the formation of a complex mixture of oxidation products. The Pb(II) complexes were somewhat more stable; they gave no effect on heating to 325°C, after which there was a vigorous exothermic reaction that "ceased prior to transition of all of the mass of the samples to the gaseous phase."

The thermal stability of the $(B_{12}H_{11}SCN)^{=}$ anion has also been studied by thermogravimetric analysis in a flow of inert gas.[40] The cesium salt of this anion was heated to 385°C without mass change or thermal effect; at 395°C it gave a strong exothermal effect, with mass loss corresponding to loss of the thiocyante (SCN) grouping. Further heating to 600°C gave no mass change or thermal effect. Infrared and ^{11}B nuclear magnetic resonance (NMR) spectroscopy showed that the parent $B_{12}H_{12}^{=}$ anion was the only boron-containing product.

Several other publications appear to contain information on the thermal properties of $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ salts, but the abstracts contain little information and it has not yet been possible to obtain copies or English translations of these papers.[41–50]

On the basis of the preceding text, it is possible to draw several conclusions about the thermal behavior of the pure $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ salts. First, in the absence of air they seem stable to temperatures well above the initial decomposition temperatures of HMX and RDX. Second, at elevated temperatures they seem to undergo oxidation reactions with the oxygen of air; it does not seem unreasonable to suppose that analogous, possibly rapid, reactions might occur in the presence of other oxidizing atmospheres such as might be provided by nitrogen oxides, or by the nitro groups in liquified HMX or RDX. Third, there appears to be a tendency to evolve H_2 on heating to high temperatures in an inert atmosphere or vacuum. These conclusions seem relevant to acceleration, by $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ salts, of nitro-compound decomposition and combustion.

Thermal Decomposition Behavior of Pure RDX and HMX

The thermal decomposition chemistry of pure HMX and RDX, together with some possible chemical mechanisms, have been reviewed previously.[51–60] This paper will therefore be concerned only with updating these reviews with regard to new results that seem most relevant to the question of mechanisms of rate acceleration by borohydride salts. These include primarily the identification of a number of products involving reduction, as well as reassignment of the structures assigned to some very common ion masses (such as *m/e* 46, 74, and 75) that have been previously observed in mass spectrometric studies of HMX and RDX decomposition.

Products Involving Reduction

The one recent development that seems to be most pertinent to the question of acceleration of HMX and RDX decomposition by $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ is the detection of products such as *N*-methylformamide, *N,N*-dimethylformamide, dimethylaminoacetonitrile, etc.[19–26]; the formation of which appears to involve reduction, from the decomposition of pure HMX and RDX.

Some of these products have most likely been detected in previous mass spectrometric studies on HMX and RDX decomposition, but misidentified because their molecular weights are similar to those of materials that are, or logically might be, products of HMX or RDX decomposition. Typical examples of such products include formamide [detected (Refs. 20–22) as its protonated form, *m/e* 46, the same as NO_2]; dimethylformamide [detected (Refs. 20–22) as its protonated form *m/e* 74, the same as $H_2C{=}N{-}NO_2$]; and dimethylnitrosamine (detected as its unprotonated form *m/e* 74, the same as $H_2C{=}N{-}NO_2$, or protonated *m/e* 75, the same as protonated $H_2C{=}N{-}NO_2$).

We have alluded to the effects of added $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ on the formation of these products. Initially, formic acid, formamide, *N*-methylformamide, *N,N*-dimethyl-formamide, and dimethylnitrosamine were detected by GC-FTIR studies on HMX and RDX decomposition.[19] Also detected were several unidentified compounds, which were believed to contain C-nitroso, C=N double-bonded, ketone, and amide groupings.

The use of pyrolysis together with atmospheric pressure chemical ionization mass spectrometry atmospheric pressure chemical ionization mass spectrometry (APCI–MS) led to the detection, from the RDX decomposition at a Pyroprobe® set temperature of 360°C under a flow of air, of principal nongaseous products with molecular ions of *m/e* 46, 60, 74, 75, 85, and 98.[20] The results that emerged from examination of the daughter–ion mass spectra of the decomposition products from isotopically labeled (deuterium and ^{15}N) and unlabeled RDX seemed surprising at the time: *m/e* 46 proved to not be NO_2 (which was not detected in these experiments), but to be protonated formamide; *m/e* 60 proved to be protonated *N*-methylformamide; *m/e* 74 proved to not be $H_2C{=}N{-}NO_2$ but instead protonated *N,N*-dimethylformamide; and *m/e* 75 proved to not be protonated $H_2C{=}N{-}NO_2$ but protonated *N,N*-dimethylnitrosamine. These results seemed surprising at the time because up until then *m/e* 46 had always been assumed to be NO_2, whereas *m/e* 74 and 75 had been assumed to be unprotonated and protonated $H_2C{=}N{-}NO_2$. The products with *m/e* 85 and 98 proved to be the protonated forms of dimethylaminoacetonitrile and of a 1,3,5-triazine oxide, respectively. (The protonation takes place inside the mass spectrometer, the original products being the unprotonated forms; therefore, a condition for detectability by APCI–MS is that the molecule in question must be capable of being protonated.) The effects of added $K_2B_{10}H_{10}$ and $K_2B_{12}H_{12}$ salts were also studied; these were described earlier in this paper.

Under slightly modified sample introduction conditions, an ion at *m/e* 44 was detected from RDX decomposition and identified as protonated dimethylimine ($CH_3N{=}CH_2$)[21]; in addition, a second component at *m/e* 60 was identified as protonated acetaldoxime ($CH_3C(H){=}OH$).

Pyrolysis of HMX and its ^{2}D- and ^{15}N-isotopomers under a flow of air at a Pyroprobe set temperature of 420°C gave all of the species identified previously for RDX.[22] In addition, HMX provided additional ions at *m/e* 30, 58, 69, 71, 83, and 141. The ion at 30 was identified as protonated methyleneimine ($CH_2{=}NH$), and the ion at *m/e* 58 as protonated methyleneformamide ($CH_2{=}NC(H){=}O$). The ions at 69 and 71 were identified as protonated methyleneaminoacetonitrile ($CH_2{=}NCH_2CN$) and methylaminoacetonitrile (CH_3NHCH_2CN). The ion at *m/e* 141 was identified as being caused by hexamethylenetetramine. The identity of the ion at *m/e* 83 was uncertain; its mass spectra were similar to, but not identical with, those of 1-methylimidazole and 3-methylpyrazole. Again, note that the original products were the unprotonated molecules; protonation occurred inside the mass spectrometer.

Several of these same products were also detected from studies where small samples of HMX and RDX were heated under vacuum in an alumina reaction cell.[23–26] HMX was studied at temperatures of 210–237°C, well below its melting point of ~280°C (Refs. 25 and 26), whereas RDX was studied at 180–225°C, just below and above its melting point of ~204°C (Ref. 24). Product concentrations during pyrolysis were studied by allowing small amounts of products to escape through an orifice into a low-pressure chamber and studying the electron ionization (EI) mass spectra of the products. Time of flight velocity spectra were used to determine the molecular weight of the products contributing to each ion-mass signal arriving at the detector; in this way it was possible to eliminate the ion-fragmentation peaks and concentrate on the actual products of thermal decomposition. This method is known as simultaneous thermogravimetric modulated beam mass spectrometry (STMBMS). Both gaseous and nongaseous products were studied. Although the EIMS technique did not permit structures to be determined as in the APCI study the use of deuterated and ^{15}N-labeled samples gave formulas consistent with the structures determined under APCI conditions.[20–22]

Nongaseous decomposition products of HMX and RDX identified in this way included formamide (Refs. 24 and 26); *N*-methylformamide (Refs. 24 and 26) (or a dimer thereof); dimethylformamide (Ref. 26); methylnitrosamine (Ref. 26); 1-nitroso-3,5,7-trinitro-1,3,5,7-tetrazocine (ONTNTA) (Ref. 26) (from HMX only), 1-nitroso-3,5,-dinitro-1,3,5,-triazine (ONDNTA) (Ref. 24) (from RDX only); and a 1,3,5-triazine oxide (Ref. 24) (from RDX only). The methylated formamides and dimethylnitrosoamine were generally minor products, formed in yields of about 0.1 mole or less per mole of RDX decomposed. Formamide was an exception; it was not mentioned among the direct products of HMX decomposition, only among the products of residue decomposition.[26] However, in the case of RDX decomposition, it was formed in the amount of 0.29 mole per mole of RDX decomposed, placing it almost among the major products.[24] No quantitative information could be obtained from atmospheric pressure chemical ionization mass spectrometry (APCIMS), but it does not seem unreasonable to suppose that, to a first approximation, all products detected by APCIMS but not by STMBMS are relatively minor products or they would have also been detected by STMBMS.

Isotope-scrambling results for these products were as follows:

1) The HCN incorporates a ring nitrogen from the original HMX/RDX molecule.[26,54]

2) The dimethylnitrosoamine incorporates only one nitrogroup nitrogen, the other presumably being from the ring.[26]

3) The *N*-methylformamide does not incorporate nitrogen from the nitro group.[26]

4) Only one of the C–N bonds in *N*-methylformamide undergoes isotopic scrambling.[23]

5) At least one of the products $(CH_3)_2N{-}NO$ or $(CH_3)_2NCHO$ is formed with complete rearrangement of all C–N bonds; because their *m/z* values (73 and 74 if unlabeled) overlap it is impossible to tell which.[23]

Some possible chemical mechanisms for formation of the reduced, hydrogenated products are discussed next.

Chemical Mechanisms for Decomposition of Pure HMX and RDX

Overall Decomposition Mechanisms

Possible chemical mechanisms for decomposition of pure HMX and RDX have been discussed previously.[54–56] The details are still almost as uncertain as they were at the time of the earlier discussion; one change seems to be that the concerted decomposition pathway [concerted depolymerization to three (RDX) or four (HMX) molecules of $H_2C{=}N{-}NO_2$], which was mentioned previously (Ref. 54), has had its credibility greatly enhanced by the IR multiphoton decomposition (IRMPD) results of Zhao et al.[61]

The paper of Zhao et al. includes results suggesting that RDX decomposition proceeds primarily by concerted depolymerization to three molecules of $H_2C{=}N{-}NO_2$, which decompose either to N_2O and formaldehyde or, by HONO elimination, to HCN and HONO. However, this result corresponds to a thermal decomposition at a very high temperature (~1000°C). There is at least one piece of evidence suggesting that at a lower temperature either 1) the stepwise decomposition of RDX involving initial $N{-}NO_2$ cleavage, followed by breakup of the resulting nitrogen-centered radical to $H_2CN\cdot$ and two molecules of $H_2C{=}N{-}NO_2$ or 2) $N{-}NO_2$ cleavage of $H_2C{=}N{-}NO_2$ may take place. This is the detection, by electron spin resonance (ESR), of the radical $H_2CN\cdot$ from thermal decomposition of the very similar molecule HMX.[62] The formation of $H_2CN\cdot$ seems hard to explain except by one of the mechanisms 1 or 2.[54] The $H_2CN\cdot$ was detected from decomposition of HMX below its melting point; it was present in amounts ranging from 1/2000 to about 1/25 of the amount of NO_2 present. It was not detected above the melting point, possibly because of a shorter lifetime as a result of greater reactivity in the gaseous and liquid phases.

Thus, it still seems possible that the stepwise ring cleavage and the loss of two molecules of $H_2C{=}N{-}NO_2$ from the nitrogen-centered denitro-RDX radical, and/or $N{-}NO_2$ cleavage of $H_2C{=}N{-}NO_2$ to give $H_2CN\cdot$ and NO_2 could be taking place at the lower temperature ranges (200–300°C), in which the decomposition of HMX and RDX is being studied.

Formation of Reduced and Hydrogenated Species

Because of their possible importance to the mechanisms of rate acceleration by boron hydrides, it seems appropriate to discuss possible mechanisms for the formation of hydrogenated materials such as *N*-methylformamide ($HCONHCH_3$), *N,N*-dimethylformamide ($HCON(CH_3)_2$), dimethylnitrosamine ($CH_3N(NO)CH_3$), and dimethylaminoacetonitrile ($(CH_3)_2\cdot NCH_2CN$) from pure HMX and RDX.

One possible reaction mechanism that might be involved in the formation of the hydrogenated products was suggested by Refs. 63–65, which reported the formation of an amine nitrate from RDX decomposition in a static system just below its melting point at 195°C. The identity of the amine was not identified, but it was suggested that it might have been trimethylamine, which could have been formed from the decomposition of hydroxymethylformamide (a known decomposition product of HMX and RDX) with formaldehyde, via the following mechanisms:

$$\begin{aligned} 2HOCH_2{-}NH{-}C({=}O)H &\longrightarrow CH_2(NH{-}C({=}O)H)_2 + H_2O + CH_2O \\ HOCH_2{-}NH{-}C({=}O)H + 3CH_2O &\longrightarrow (CH_3)_3N + CO_2 + CH_2O \end{aligned} \tag{1}$$

It is then possible that reduction of $CH_2(NH{-}C({=}O)H)_2$ and/or $2HOCH_2{-}NH{-}C({=}O)H$ might lead, possibly via $CH_2(NH{-}CH_3)_2$ or $HOCH_2{-}NH{-}C({=}O)H$, respectively, to dimethylamine ($(CH_3)_2NH$). Furthermore, the oxidation of trimethylamine ($(CH_3)_3N$) might lead to such compounds as dimethylformamide.

It is not clear why hydroxymethylformamide was reported by Refs. 63 and 64, but not in the APCI-MS work[20–22] and the STMBMS work.[23–26] One possible explanation might arise out of consideration of exactly how the experiments were carried out. The APCIMS and STMBMS experiments[20–26] were carried out, respectively, by decomposing the samples in a stream of inert gas at atmospheric pressure and by decomposing them under vacuum in a small cell from which they could escape only through a small orifice. The experiments of Refs. 63 and 64 on the other hand, were carried out by decomposing the samples in a relatively large vessel over a long period of time. The hydroxymethylformamide was found when the reaction was over, in material that had condensed on the walls of the vessel; possibly carrying out the reaction and workup in this way resulted in the gas-phase formation of hydroxymethylformamide from some combination of HCN, formaldehyde, formamide, and water.

Another possible mechanism for the formation of some of these products was suggested by Behrens[26]; this consisted of the addition of $H_2CN\cdot$ to formaldehyde, forming $\cdot H_2CNHCHO$, which, it was suggested, could either abstract a hydrogen atom to form *N*-methylformamide, or polymerize to an amide-containing polymer, with cross-linking involving formaldehyde. The source of the hydrogen atom could be either the H_2 formed[54,66,67] in RDX and HMX decomposition, or a precursor such as $HCO\cdot$ or $H_2CN\cdot$. Note also that loss of a hydrogen atom from $\cdot H_2CNHCHO$ could lead to $H_2C{=}NCHO$, which as mentioned previously was detected from HMX pyrolysis.[22]

It is difficult to predict just how HCN, formamide, and related compounds might react under the exact conditions present in molten or liquefied HMX/RDX at temperatures in the range ~200–800°C. However, possible sources for formamide include 1) decomposition of residue, at least in the case of HMX decomposition,[26] and 2) incomplete hydrolysis of the known HMX/RDX decomposition products HCN (Ref. 54) or 1,3,5-triazine (Refs. 8 and 9) by water that is also known to be formed from HMX/RDX decomposition.[23–26,54]

It has been reported that H_2 is formed in the low-temperature (200–300°C) thermal decomposition of RDX and HMX.[54,66,67] Robertson[66] reported formation of H_2 in the amount of 0.05–0.1 mole per mole of RDX decomposed neat or in solution in dicyclohexyl phthalate; for decomposition in solution in 2,4,6-trinitrotoluene (TNT), the amount rose to 0.2–0.3 mole of H_2 per mole of RDX decomposed. The mechanisms for formation of H_2 are uncertain, but presumably involve either dimerization of $H\cdot$ or reaction of some possible source of $H\cdot$, e.g., $H_2CN\cdot$ or $HCO\cdot$, with another H-source molecule or with $H\cdot$. Because their large hydrogen content suggests that the formamide derivatives, dimethylaminoacetonitrile, etc., are the product of reduction/hydrogenation reactions, it seems reasonable to suspect that they might share a common source with or possibly be formed from the H_2.

The formation of $(CH_3)_2NCH_2CN$ and related compounds could be explained by dimerization or oligomerization of $H_2CN\cdot$, which is known to be formed in thermal decomposition of HMX and RDX.[62] Tail to tail dimerization of $H_2CN\cdot$, followed by the rearrangement of hydrogen atoms could lead to H_2NCH_2CN. The formation of $H_2C{=}NH$ could be explained by disproportionation between two molecules of $H_2CN\cdot$, giving $H_2C{=}NH$ and HCN.

Possibly, the hydrogen atoms or precursor could participate in the formation of methylated compounds such as $(CH_3)NHCH_2CN$ by a mechanism such as the following (illustrated for the formation of $(CH_3)NHCH_2CN$ from H_2NCH_2CN):

$$\begin{array}{c}
O{=}CH_2 + H_2N\text{-}CH_2\text{-}CN \longrightarrow [\overset{\ominus}{O}\text{-}CH_2\text{-}H_2\overset{\oplus}{N}\text{-}CH_2\text{-}CN] \longrightarrow HO\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CN \\
HO\text{-}CH_2\text{-}NH\text{-}CH_2\text{-}CN \longrightarrow H\overset{\ominus}{O} + \overset{\oplus}{C}H_2{=}NH\text{-}CH_2\text{-}CN \\
\overset{\oplus}{C}H_2{=}NH\text{-}CH_2\text{-}CN \xrightarrow{[H]} \overset{\oplus\cdot}{CH_3\text{-}NH\text{-}CH_2\text{-}CN} \xrightarrow{[H]} CH_3\text{-}\overset{\oplus}{N}H_2\text{-}CH_2\text{-}CN \\
CH_3\text{-}\overset{\oplus}{N}H_2\text{-}CH_2\text{-}CN \longrightarrow \overset{\oplus}{H} + CH_3\text{-}NH\text{-}CH_2\text{-}CN
\end{array} \tag{2}$$

Repetition of this process could lead to the formation of $(CH_3)_2NCH_2CN$; similar steps could possibly result in the formation of hydroxymethylformamide and of methylated formamides from formamide, and of $H_2C{=}NCH_3$ from $H_2C{=}NH$.

Furthermore, it is known that catalytic hydrogenation of nitriles and amides or reduction with many common reducing agents generally leads to the corresponding amines.[68–70] Therefore, it seems conceivable that HCN, formamide, $H_2C{=}NH$, or $H_2C{=}N{-}CH_3$ could be reduced to methylamine, CH_3NH_2, or to dimethylamine, CH_3NHCH_3, by the hydrogen atoms or precursor present:

$$\begin{array}{rcl}
HCN & \xrightarrow{[H]} & CH_3NH_2 \\
HCONH_2 & \xrightarrow{[H]} & CH_3NH_2 \\
CH_3NH_2 + HCONH_2 & \longrightarrow & HCONHCH_3 + NH_3 \\
HCONHCH_3 & \xrightarrow{[H]} & CH_3NHCH_3 \\
CH_3NHCH_3 + HCONHR & \longrightarrow & HCON(CH_3)_2 + H_2NR \ (R = H \text{ or } CH_3) \\
HCON(CH_3)_2 \text{ or } CH_3NHCH_3 & \xrightarrow[\text{Nitrosation}]{\text{Hydrolysis}} & CH_3N(NO)CH_3
\end{array} \tag{3}$$

Methylamine formed in one of these ways could then react with formamide to give *N*-methylformamide, which could be reduced to dimethylamine; this could then react, by nucleophilic displacement at the carbonyl group, with formamide or *N*-methylformamide to give dimethylformamide. Nitrosation of dimethylamine, by nitrogen oxides (NO and NO_2) known to be formed in HMX and RDX decomposition, could lead to dimethylnitrosoamine.[54] Another possible mode for the formation of methylamine and dimethylamine might involve the hydrogenation of $H_2C{=}NH$ and of $H_2C{=}NCH_3$. Note, however, that as far as the author is aware, neither methylamine nor dimethylamine have been detected among the products of HMX/RDX decomposition.

The preceding reactions could continue with the chain lengths building up by polymerization reactions involving H_2CN, HCN, formaldehyde, and amides; this is presumably how the residue is formed. The main feature of the preceding text is most likely the source of the reduction; it presumably arises from the hydrogen atom source(s) that also give rise to the H_2 formed in HMX and RDX decomposition.[66,67]

These apparent H-atom hydrogenation pathways would be particularly significant because 1) their occurrence suggests that the H-atoms should also be available for autocatalysis by attack on the nitro-oxygens of HMX and RDX[54,55] and, 2) it is shown in this paper that thermal decomposition of salts of the $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ anions yields hydrogen; therefore the addition of these salts to decomposing HMX and RDX should generate additional hydrogen atoms or hydrogen sources that could explain both the acceleration in decomposition and combustion rates and the increased formation of hydrogenated/reduced products caused by addition of these salts.

All of the mechanisms discussed in the preceding text seem consistent with the isotope-scrambling results also mentioned previously, as well as with the following facts.

1) There seems to be sufficient H_2 present (0.05–0.3-moles/mole RDX decomposed, Ref. 66) to account for the amounts of methylated and reduced products formed.

2) Time-formation plots for dimethylnitrosoamine and for an amide product from decomposition of HMX below its melting point resemble those from the major products.[26]

3) Time-formation plots for formamide and for *N*-methylformamide (or its dimer) from RDX decomposition at 180–225°C rise slowly throughout the decomposition and go through a maximum late in the decomposition.[24]

Possible Chemical Mechanisms for Acceleration of HMX and RDX Decomposition by $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$

In this section we will discuss some possible chemical mechanisms that may be responsible for the acceleration of HMX and RDX decomposition and combustion by $K_2B_{10}H_{10}$ and $K_2B_{12}H_{12}$.

There are at least three general classes of initial steps that might contribute to the acceleration of HMX and RDX decomposition by borohydride salts such as $K_2B_{10}H_{10}$ and $K_2B_{12}H_{12}$.

1) Decomposition of nitramine is initiated by a direct reaction between nitramine and borohydride; for example, as discussed in the previous text, by electron transfer, by attack of a B–H hydrogen on nitro-oxygen of the nitramine, or by some combination of these mechanisms.

2) An early decomposition product of the nitramine, for example NO_2, reacts with the accelerant to form products, possibly free radicals, which react further with nitramine and result in rate acceleration.

3) Unimolecular decomposition of the accelerant generates products or radicals that react with nitramine, causing it to decompose faster than would otherwise be the case.

At low temperatures, class 3 may be less likely than the others, in view of the reports that when heated in vacuum or in an inert atmosphere, alkali metal salts of $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ are stable up to temperatures in the range of 600–800°C.[19,27,32] Note, however, the reports of hydrogen evolution on heating of such compounds to higher temperatures; this H_2 may well have been formed from hydrogen atoms, which could also react with the nitro groups of HMX and RDX.[30,31,37] The available data offer support for both class 1 and class 2 as dominant mechanisms, and, in fact, both may operate. The intense nature of the previously mentioned rate enhancement, its correlation with increased contact due to melting of the RDX, and the open-pan nature of the studies are consistent with the idea that class 1 mechanisms may be operating.[19] Note, however, that 1) RDX and HMX decompose below their melting points; 2) that the decomposition accelerates on melting, presumably causing an increase in evolution of nitrogen oxides[53]; and 3) that there appears to be some evidence that borohydride anions like $B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$ may react rapidly with nitrogen oxides. This follows from the report that the reaction of $B_{12}H_{12}(NH(C_2H_5)_3)_2$ with NO_2 in CH_2Cl_2 at 0°C gave a dark-blue solution from which $B_{14}H_{12}NO(NH(C_2H_5)_3)_2$ was isolated; the use of gaseous NO_2 in acetonitrile gave products having more than one NO group per molecule.[71] This reaction, in a dilute solution at 0°C, suggests that similar reactions under combustion conditions could be very rapid and proceed further. Therefore, explanations of class 2 seem quite believable, particularly with regard to gaseous, strongly oxidizing products such as NO_2.

Possible types of chemical mechanisms that might be operating include the following.

A: Attack of a *B–H* hydrogen of the accelerant on the HMX or RDX molecule, most likely at the oxygen of the nitro group.

B: An electron-transfer reaction between the accelerant and the nitramine molecule, with the nitramine assuming a negative charge and the boron-containing anion assuming one less negative charge than before.

C: Primary decomposition of the nitramine, followed by reaction of one or more of the products (most likely NO_2, although other products, particularly other nitrogen oxides such as NO and N_2O, are also plausible candidates) with the boron hydride, most likely at a B–H bond, generating more radicals or other intermediates that further catalyze the decomposition. In addition to the previous chemical catalysis by radicals formed by a reaction between the nitrogen-oxides and the boron hydride salt, it should be remembered that the reaction of nitrogen oxides with these boron hydride salts could generate heat because of the formation of boron oxides, and that this heat-release within the sample could cause an increase in temperature and, hence, an additional increase in the observed rate of reaction. It is difficult to be quantitative about the relative importance of these effects without more detailed information than is currently available about the actual chemical species and the mechanisms that are involved.

D: Another possibility might be an equilibrium involving the boron-containing salt in which a B–H bond breaks thermally to give a hydrogen atom and a boron-centered radical; hydrogen atoms formed in this way could dimerize to H_2. The hydrogen atoms could also react with nitramine, presumably at the oxygen atom of the nitro group, and the resulting hydroxynitroxide could decompose to give OH· and nitrosoamine; or to give HONO and nitrogen-centered denitro-RDX radical.

Mechanisms *A* and *B* are examples of class 1, mechanism *C* is an example of class 2, whereas mechanism *D* is an example of class 3, and accordingly may be less likely except at higher temperatures.

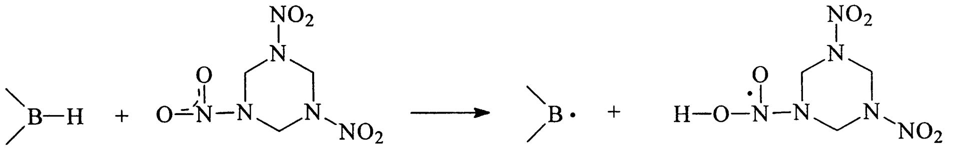
A number of the observations in the preceding sections are consistent with the idea that the subject acceleration may involve hydrogen-atom donation by the borohydride ($B_{10}H_{10}^{=}$ and $B_{12}H_{12}^{=}$) anions. These include the following:

1) The relative amount of reduced products (methylated formamide derivatives, etc.) tends to increase on addition of catalyst.[19]

2) It was reported (see preceding text) that the heating of $Cs_2B_{10}H_{10}$ and $Cs_2B_{12}H_{12}$ in vacuum led to the evolution of almost 1 mole of H_2 per mole of salt, accompanied by a slight endotherm in the region around 600–650°C.[32] Examination of the gas-evolution curves shows that while evolution is fastest in the 600–650°C region, there is for both compounds a long tail to the low-temperature side of the volume-time plot. This remains visible down to just above 400°C, and there may conceivably be a very small amount of H_2 evolved at even lower temperatures. In any case, the high-temperature evolution of hydrogen gas (H_2) suggests the possibility that even at low temperatures the B–H bonds might be sufficiently labile as to be susceptible to attack, possibly by the nitro oxygens of the nitramine.

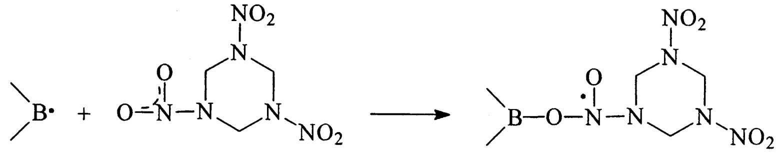
3) In connection with 2, it seems worthwhile to mention the observations that when $((CH_3)_4N)_2B_{12}H_{12}$ was heat-treated at 460°C, it retained its acceleratory activity toward RDX decomposition but lost it when the heat treatment took place at 760°C.[19] Elemental boron had no acceleratory activity. These observations are consistent with the idea that loss of acceleratory activity may have been a result of the loss of hydrogen as H_2.

One possible mechanistic scheme for the initial phases of acceleration might be as follows:

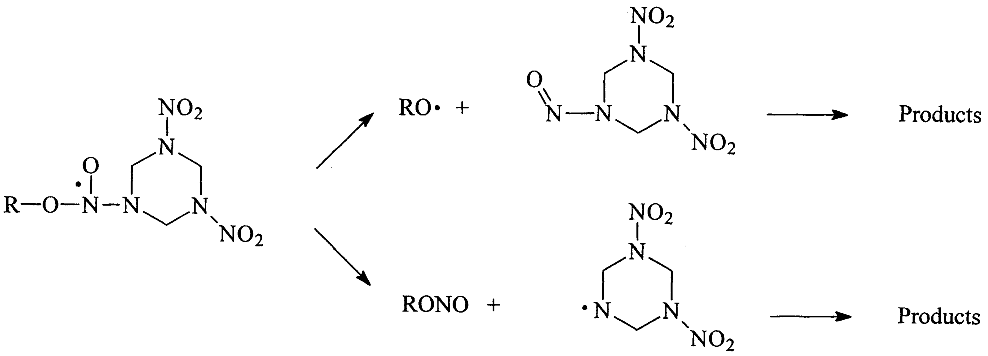


(4)

where a nitro group of RDX reacts with a B–H bond of the anion of the boron hydride salt ($B_{10}H_{10}^{=}$ or $B_{12}H_{12}^{=}$):



(5)



(6)

In reaction 5, R = H· or >B·. Note, however, that the exact details in the preceding reaction schemes are uncertain. In particular, there is at present not enough information to evaluate the importance, if any, of electron-transfer reactions.

A variation on the theme of electron transfer reactions might be a combination of electron-transfer and hydrogen-transfer mechanisms; such a combination has been suggested for the reaction of difluorodinitromethane with a variety of nucleophilic reagents, including sodium borohydride.[72] The radicals produced were studied by ESR and trapping techniques and identified as H· and ·CF_2NO_2. Their formation was rationalized in terms of the following mechanism:

$$\begin{aligned} \mathrm{CF_2(NO_2)_2} + \mathrm{BH_4}^{\ominus} &\longrightarrow \mathrm{CF_2(NO_2)_2}^{\dot{\ominus}} + \mathrm{H}^{\bullet} + \mathrm{BH_3} \\ \mathrm{CF_2(NO_2)_2}^{\dot{\ominus}} &\longrightarrow {}^{\bullet}\mathrm{CF_2NO_2} + \mathrm{NO_2}^{\ominus} \end{aligned} \tag{7}$$

An analogous mechanism for the acceleration of HMX/RDX decomposition by $B_{10}H_{10}^{=}$ or $B_{12}H_{12}^{=}$ could be written as follows:

$$\begin{aligned} \mathrm{RDX} + \mathrm{B_{12}H_{12}}^{\textcircled{=}} &\longrightarrow \mathrm{RDX}^{\dot{\ominus}} + \mathrm{H}^{\bullet} + \mathrm{B_{12}H_{11}}^{\ominus} \\ \mathrm{RDX} + \mathrm{B_{12}H_{11}}^{\ominus} &\longrightarrow \mathrm{RDX}^{\dot{\ominus}} + \mathrm{H}^{\bullet} + \mathrm{B_{12}H_{10}} \\ \mathrm{RDX}^{\dot{\ominus}} &\longrightarrow \mathrm{Products} \\ \mathrm{RDX} + \mathrm{H}^{\bullet} &\longrightarrow \mathrm{Products} \end{aligned} \tag{8}$$

The initial steps are similar to those in reaction 7, and the decompositions then go to completion with the evolution of the same gaseous products as those obtained from decomposition without additives. What is left behind might then be most or all of the boron and potassium, in the form of oxides and/or nitrides. This seems consistent with the following facts.

1) Thermal decomposition of pure salts of $B_{10}H_{10}^{=}$ or $B_{12}H_{12}^{=}$ has been reported to leave behind metal boride, or some combination of metallic and boron oxides or nitrides.[28-30,32-36]

2) The residue after combustion of a propellant composition [84% RDX, 6% $K_2B_{10}H_{10}$, 10% Hycar (hydroxy-terminated polyacrylate) binder plus additives] was analyzed by x-ray photoelectron spectroscopy[5]; the results suggested that boron nitride was present in large quantities, that the borate present was $K_2B_4O_7$, and that the boron hydride initially present had fully reacted.

3) Schroeder et al.[8] reported that when RDX was decomposed in the presence and absence of $K_2B_{12}H_{12}$, the weight of the residue could be estimated approximately by assuming that any $K_2B_{12}H_{12}$ present contributed its full weight to the residue; the failure of the borohydride to contribute more than its own weight in this case may be related to the fact that these samples were heated only to a little over 200°C.

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