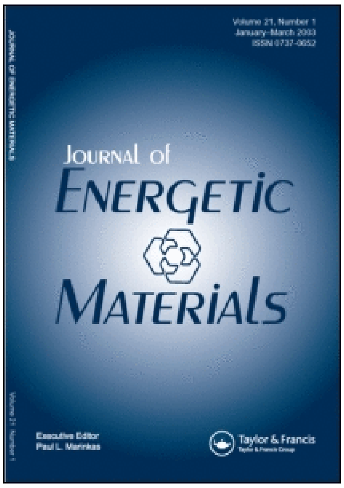

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Two potential energetic compounds: Ammonium superoxide and ammonium ozonide

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Two Potential Energetic Compounds: Ammonium Superoxide and Ammonium Ozonide

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Abstract

Two proposed ionic compounds, NH_4O_2 and NH_4O_3, are discussed in terms of several properties related to energetic performance. These include oxygen content, moles of gas produced and heat released upon decomposition, and specific impulse. The heat release was calculated in each instance using the predicted lattice energy, which was obtained from the computed electrostatic potential on the surface of the negative ion. NH_4O_2 is found to be superior to HMX in each property considered, while NH_4O_3 is better than HMX in some and comparable in the others.

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Introduction

Our objective in this paper is to draw attention to two proposed energetic compounds, ammonium superoxide (NH_4O_2) and ammonium ozonide (NH_4O_3). These would be ionic solids, composed of the NH_4^+ cation and either the O_2^- or the (nonlinear) O_3^- anion. Some key features that shall be discussed are (1) stoichiometry, including both oxygen content and the number of moles of gases produced upon decomposition, and (2) the heat release upon decomposition. Oxygen content is important if the compound is to be used as an oxidizer, while the number of moles of gaseous products and the heat release (both given per unit mass) are directly related to energetic performance [1-3]. The monopropellant specific impulse is computed for each compound. The results for NH_4O_2 and NH_4O_3 shall be compared to those for HMX (cyclotetramethylenetetranitramine) and RDX (cyclotrimethylene-trinitramine), which have long been among the leading secondary explosives and propellant ingredients [2,3].

Stoichiometry

(a) *Oxygen Content*

The percents by mass of oxygen in several different explosives and propellants are presented in Table 1. NH_4O_3 is by far the most oxygen-rich, with NH_4O_2 second.

(b) *Moles of Gases Produced Upon Decomposition*

Assuming the ideal decompositions shown in eqs. (1) and (2),

$$NH_4O_2(s) \longrightarrow \frac{1}{2}N_2(g) + 2H_2O(g) \tag{1}$$

$$NH_4O_3(s) \longrightarrow \frac{1}{2}N_2(g) + \frac{1}{2}O_2(g) + 2H_2O(g) \tag{2}$$

then for NH_4O_2,

$$\frac{\text{2.5 moles gases per mole compound}}{\text{50 grams per mole compound}} = 0.0500 \text{ moles/g} \tag{3}$$

and for NH_4O_3,

$$\frac{3.0 \text{ moles gases per mole compound}}{66 \text{ grams per mole compound}} = 0.0455 \text{ moles/g} \quad (4)$$

In contrast, the corresponding numbers for HMX and RDX for the processes,

$$\underset{\text{(HMX)}}{C_4H_8N_8O_8} \longrightarrow 4N_2 + 4H_2O + 4CO \quad (5)$$

and

$$\underset{\text{(RDX)}}{C_3H_6N_6O_6} \longrightarrow 3N_2 + 3H_2O + 3CO \quad (6)$$

are 0.0405 moles/g in each case. The latter are among the highest heretofore known.

Heat Release Upon Decomposition

The heat releases associated with the decompositions of NH_4O_2 (s) and NH_4O_3 (s), reactions (1) and (2), can be found from the heats of formation of the reactants and products. This quantity is known for H_2O (g) [4] and is equal to zero for N_2 (g) and O_2 (g). The heats of formation of the ionic solids NH_4O_2 and NH_4O_3 can be determined from their lattice enthalpies ΔH_L and the heats of formation of the respective ions. For NH_4O_2, for example, the lattice enthalpy is ΔH for the process,

$$NH_4O_2\,(s) \longrightarrow NH_4^+\,(g) + O_2^-(g) \quad (7)$$

Thus

$$\Delta H_L(NH_4O_2) = \Delta H_f(NH_4^+) + \Delta H_f(O_2^-) - \Delta H_f(NH_4O_2) \quad (8)$$

Experimental values are available for $\Delta H_f(NH_4^+)$, $\Delta H_f(O_2^-)$ and $\Delta H_f(O_3^-)$ [4], all at 298 K. $\Delta H_f(NH_4O_2)$ and $\Delta H_f(NH_4O_3)$ can then be found once $\Delta H_L(NH_4O_2)$ and $\Delta H_L(NH_4O_3)$ are known. These can be estimated by means of a relationship that we have shown to exist between the lattice energies of ammonium salts and certain properties of the electrostatic potentials on the surfaces of the negative ions [5]:

$$\text{Lattice Energy} = -287.8Q - 0.6246V_{S,min} - 1.72 \times 10^{-7}[(\text{area})(\overline{V}_S^-)]^2 - 199.4 \qquad (9)$$

In eq. (9), $\overline{V}_S^-$ is the average negative potential on the anion surface, and $V_{S,min}$ is its minimum. For O_2^- and O_3^-, $Q = -1$. The lattice energy, $V_{S,min}$ and $\overline{V}_S^-$ are all in kcal/mole, and the surface area is in $Å^2$. Following Bader *et al* [6], the surface is defined as the 0.001 au contour of the electronic density. These quantities are to be computed at the HF/6-31+G* level. The lattice energy obtained with eq. (9), which is at 298 K, can readily be converted to the lattice enthalpy, ΔH_L(298 K) [7].

The calculated surface properties of O_2^- and O_3^- are given in Table 2. These data, plus the enthalpies of formation of NH_4^+, O_2^- and O_3^- (151, −10 and −14 kcal/mole, respectively [4]), were used to find the lattice energies, lattice enthalpies and heats of formation of NH_4O_2 and NH_4O_3. These are listed in Table 3.

Eq. (9), and analogous relationships for sodium and potassium salts, were developed using a database that included a variety of singly- and doubly-charged anions, but not O_2^- or O_3^- [5]. In order to assess the reliability of these procedures for superoxides and ozonides, we calculated the lattice energies and enthalpies, plus the heats of formation, for NaO_2, KO_2 and KO_3, for which some experimental data are available. We used the equations appropriate for Na^+ and K^+ salts [5], and the heats of formation of Na^+ and K^+ [4]. The results are included in Table 3, along with some experimental values. The average absolute deviation is 6.2 kcal/mole, which is similar to what was obtained in developing the original relationships.

With the heats of formation of NH_4O_2 and NH_4O_3 that are given in Table 3, and the experimentally-determined −57.80 kcal/mole for H_2O (g) [4], the heat releases in the idealized decomposition processes shown in eqs. (1) and (2) can be evaluated. These are found to be −1.5 kcal/g for NH_4O_2 and −1.2 kcal/g for NH_4O_3. For comparison, the values for HMX and RDX, for the decompositions in eqs. (5) and (6), are −1.198 kcal/g and −1.214 kcal/g, respectively, taking their heats of formation from Köhler and Meyer [8]. Thus NH_4O_2 is significantly superior to both RDX and HMX in this respect, while NH_4O_3 is comparable to them.

It should further be noted in Table 3 that the calculated lattice energies for NaO_2, KO_2 and KO_3 are all somewhat higher than the experimental, and correspondingly the calculated heats of formation of NaO_2 and KO_2 are too negative. If the same pattern would hold for NH_4O_2 and NH_4O_3, then the actual heat releases for the latter two would be even greater in magnitude (i.e. more negative), and the specific impulses higher (next section), than is being predicted.

Specific Impulse

The specific impulse is a measure of the thrust developed by a propellant, and is one of the key quantities used to assess performance [8,9]. It depends primarily upon the number of moles of gaseous combustion products per unit mass of propellant and the temperature achieved in the combustion chamber. The latter is of course determined in part by the heat of formation of the propellant.

We have estimated the specific impulse for both NH_4O_2 and NH_4O_3, using the Newpep code [10], into which were input the heats of formation in Table 3. The predicted specific impulse of NH_4O_2 is 5.8% greater than that of HMX, while that of NH_4O_3 is 2.7% less than HMX.

Discussion

NH_4O_2 is predicted to be superior to HMX in each of the four categories considered: specific impulse, heat release, moles of gas produced and oxygen content. NH_4O_3 is expected to be comparable to HMX in the first two respects, and better in the last two.

An important property of energetic materials is the density [1-3]. We have not attempted to predict this for NH_4O_2 and NH_4O_3. However it may be relevant to look at the known values for some related compounds. Table 4 compares the densities of some ammonium, sodium and potassium salts. If the ammonium systems follow a pattern similar to the sodium and potassium, then the density of NH_4O_2 would be in the neighborhood of 1.7 g/cm^3. That of NH_4O_3 might be higher, due to the compact (bent) structure and greater mass of the O_3^- ion.

With regard to the feasibility of preparation of NH_4O_2 and NH_4O_3, some encouragement can be obtained from the fact that tetraalkylammonium superoxides and ozonides, NR_4O_2 and NR_4O_3, are well known [11-14]. Perhaps the observed acidity of the hydroperoxy radical, HO_2 ($pK_a = 4.7$ [15]), could be exploited. The predicted properties of NH_4O_2 and NH_4O_3 suggest that some exploration of synthetic routes may be warranted.

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Table 1. Percents of oxygen by mass in some energetic compounds.

Compound	Percent oxygen by mass
NH_4O_3	72.7
NH_4O_2	64.0
NH_4NO_3	60.0
NH_4ClO_4	54.5
$NH_4N(NO_2)_2$	51.6
HMX, RDX	43.2

Table 2. Computed (HF/6-31+G*) surface properties of O_2^- and O_3^-.

Anion	Area (Å^2)	$V_{S,min}$ (kcal/mole)	$\overline{V}_S^-$ (kcal/mole)
O_2^-	59.39	−166.75	−151.14
O_3^-	72.63	−163.08	−137.88

Table 3. Thermochemical properties of some ionic solids at 298 K, in kcal/mole.[a]

Compound	Lattice energy		Lattice enthalpy, ΔH_L		Heat of formation, ΔH_f	
	calc.	exp.	calc.	exp.	calc.	exp.
NH_4O_2	179	---	180	---	−39	---
NH_4O_3	173	---	174	---	−37	---
NaO_2	203	191	203	---	−69	−62.31
KO_2	181	177	181	---	−70	−68.00
KO_3	173	167	173	---	−66	---

[a] Experimental data are from reference 7.

Table 4. Some experimental densities, in g/cm^3.[a]

Anion/Cation	NH_4^+	Na^+	K^+
ClO_4^-	1.95	2.52	2.52
O_2^-	----	2.2	2.16
NO_3^-	1.72	2.26	2.11
N_3^-	1.346	1.846	2.04

[a] Reference 7.