

# Computational study on nitronium squarate – potential oxidizers for solid rocket propulsion?

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Received 19.03.2010

The enthalpies of formation for solid ionic nitronium squarate,  $[\text{NO}_2]_2[\text{C}_4\text{O}_4]$ , and covalent squaric acid dinitrate ester,  $\text{O}_2\text{N-C}_4\text{O}_4\text{-NO}_2$ , were calculated using the complete basis set (CBS-4M) method of Petersson and coworkers in order to obtain very accurate energies. The covalent form ( $\text{O}_2\text{N-C}_4\text{O}_4\text{-NO}_2$ ) was identified as the more stable isomer. The combustion parameters with respect to possible use as ingredients in solid rocket motors for both stable species were calculated using the EXPLO5 code. The performance of an aluminized formulation with covalently bound dinitrate ester ( $\text{O}_2\text{N-C}_4\text{O}_4\text{-NO}_2$ ) was shown to be comparable to that of ammonium perchlorate/aluminum. This makes squaric acid dinitrate ester a potentially interesting perchlorate-free and environmentally benign oxidizer for solid rocket propulsion.

**Key Words:** Ammonium perchlorate, combustion, nitronium, squaric acid, oxidizers, specific impulse, rocket propellants

## Introduction

Solid propellants of essentially all solid rocket boosters are based on a mixture of aluminum (Al, fuel) and ammonium perchlorate (AP, oxidizer).<sup>1</sup>

Ammonium perchlorate (AP) has applications in munitions, primarily as an oxidizer for solid rocket and missile propellants. It is also used as an air-bag inflator in the automotive industry, in fireworks, and as a

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component of agricultural fertilizers. Because of these uses and ammonium perchlorate's high solubility, chemical stability, and persistence, it has become widely distributed in surface and ground water systems. There is little information about the effects of perchlorate in these systems on the aquatic life that inhabits them. However, it is known that perchlorate is an endocrine disrupting chemical that interferes with normal thyroid function and that, in vertebrates, thyroid dysfunction impacts both growth and development. Because perchlorate competes for iodine binding sites in the thyroid, the addition of iodine to culture water was examined to determine if perchlorate effects can be mitigated. Finally, perchlorate is known to affect normal pigmentation of amphibian embryos. In the US alone the cost for remediation is estimated to be several billion dollars, money that is deeply needed in other defense areas.<sup>2-7</sup>

In the course of the global emerging interest in high-energetic, dense materials (HEDM)<sup>4</sup> we are currently developing new energetic materials preferentially with a positive oxygen balance value. Oxygen balance (OB, Eq. (1)) is defined as the ratio of the oxygen content of a compound  $C_aH_bN_cO_d$  to the total oxygen required for the complete oxidation of all carbon, hydrogen, and other elements that can be oxidized to form CO (Eq. (1)) or CO<sub>2</sub> (Eq. (2)), H<sub>2</sub>O, etc. and is used to classify energetic materials as either oxygen deficient (neg. oxygen balance) or oxygen rich (positive oxygen balance).<sup>1</sup>

$$\Omega_{CO} = \frac{[d - a - (b/2)] \times 1600}{M} \quad (1)$$

$$\Omega_{CO_2} = \frac{[d - (2a) - (b/2)] \times 1600}{M} \quad (2)$$

The objectives of our ongoing work are to explore the chemical synthesis of possible replacements for AP as oxidizer in tactical missile rocket motors.<sup>8</sup> We investigate the synthesis, sensitivities, thermal stability, binder compatibility, and decomposition pathways of these new high-oxygen materials. In the present study we now evaluate theoretically the suitability of nitronium (NO<sub>2</sub><sup>+</sup>) squarate as a potential ingredient for solid rocket propellants.

## Methodology

All calculations were carried out using the Gaussian G03W (revision B.03) program package.<sup>9</sup>

The structure of nitronium squarate (see Figure 1) was fully optimized without any symmetry constraints (in  $C_1$  symmetry) and optimized to  $C_2$  symmetry. A frequency analysis revealed that the  $C_2$  structure is a true minimum on the potential energy hypersurface ( $NIMAG = 0$ ). No other vibrationally stable conformers (with  $NIMAG = 0$ ) were identified.

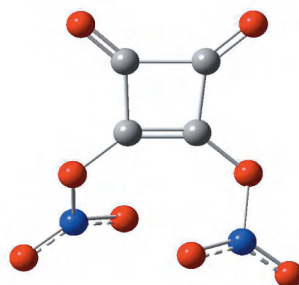
The enthalpies ( $H$ ) and free energies ( $G$ ) were calculated using the complete basis set (CBS) method of Petersson and coworkers in order to obtain very accurate energies. The CBS models use the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated complete basis set limit. CBS-4 begins with a HF/3-21G(d) geometry optimization; the zero point energy is computed at the same level. It then uses a large basis set SCF calculation as a base energy, and a MP2/6-31+G calculation with a CBS extrapolation to correct the energy through second order. A MP4(SDQ)/6-31+(d,p) calculation is used to approximate higher order contributions. In this study we applied

the modified CBS-4M method (**M** referring to the use of Minimal Population localization), which is a re-parametrized version of the original CBS-4 method and also includes some additional empirical corrections.<sup>10,11</sup>

## Results and discussion

### Thermodynamic aspects

The molecular structure of neutral  $O_2N-C_4O_4-NO_2$  was fully optimized without symmetry constraints to  $C_2$  symmetry (Figure 1).



**Figure 1.** Optimized molecular structures of  $O_2N-C_4O_4-NO_2$ .

The enthalpies of formation of the gas-phase species **M** were computed according to the atomization energy method (Eq. (3)) (Tables 1-3).<sup>12-14</sup> In Eq. (3)  $\Delta_f H_{(g,M)}^\circ$  stands for the gas-phase enthalpy of formation of the molecule **M** under investigation,  $H_{(M)}$  represents the CBS-4M calculated enthalpy of the molecule **M** ( $H^{298}$  in Table 1),  $atoms H^\circ$  denotes the CBS-4M calculated enthalpies for the individual atoms (see bottom of Table 1), and  $\Delta_{atoms} H^\circ$  stands for the experimentally reported literature values for the enthalpies of formation for the corresponding atoms ( $\Delta H_f^{298}$  in Table 2). All  $\Delta_f H_{(g,M)}^\circ$  values shown in Table 3 were calculated using Eq. (3). The excellent agreement between the reported experimental enthalpies of formation for  $NO_2^+$  with the CBS-4M calculated values (Table 3) gives credence to the idea that also the computed values for the squarate dianion and the neutral species are quite accurate.

$$\Delta_f H_{(g, Molecule)}^\circ = H_{(Molecule)}^\circ - \sum H_{(atoms)}^\circ + \sum \Delta_f (atoms) H^\circ \quad (3)$$

The lattice energies ( $U_L$ ) and lattice enthalpies ( $\Delta H_L$ ) were calculated from the corresponding molecular volumes ( $V_M$ ) (Table 4) according to the equations provided by Jenkins et al. (Eqs. (4), (5))<sup>17-19</sup> and are summarized in Table 5.

$$U_L = |z_+||z_-|\nu \left( \frac{\alpha}{\sqrt[3]{V_M}} + \beta \right) \quad (4)$$

$M_2X$  salt:  $\alpha = 165.3 \text{ kJ nm mol}^{-1}$ ,  $\beta = -29.8 \text{ kJ mol}^{-1}$ ,  $V$  in  $\text{nm}^3$

( $\alpha$ ,  $\beta$ : constants;  $V_M$ : molecular volume;  $z_+$ ,  $z_-$ : charges of the cation and anion;  $\nu$ : sum of the number of cations and anions per “molecular” unit)

**Table 1.** CBS-4M results<sup>a</sup>.

	p.g.	state	$-H^{298}$ / a.u.	$-G^{298}$ / a.u.	<i>NIMAG</i>	$\nu_1/\text{cm}^{-1}$
$\text{NO}_2^+$	$D_{\infty h}$	$^1\Sigma_g$	204.500147	204.524572	0	604
$\text{C}_4\text{O}_4^{2-}$	$D_{4h}$	$^1A$	452.752890	452.790776	0	98.9
$^1\text{C}_4\text{O}_4$	$C_{2v}$	$^1A_1$	452.642902	452.689307	0	19
$^3\text{C}_4\text{O}_4$	$D_{4h}$	$^3B_{1u}$	452.700312	452.738493	0	101.9
$\text{C}_4\text{N}_2\text{O}_8$	$C_2$	$^1A$	862.396203	862.448045	0	64.8
$\text{NO}_2$	$C_{2v}$	$^2A_1$	204.863140	204.890443	0	748
$\text{CO}$	$C_{\infty v}$	$^1S_g$	113.186814	113.209242	0	2315.3
$\text{C}$			37.786156	37.803062	0	–
$\text{N}$			54.522462	54.539858	0	–
$\text{O}$			74.991202	75.008515	0	–

<sup>a</sup>p.g. = point group, state = electronic state, *NIMAG* = number of imaginary frequencies

**Table 2.** Literature values for atomic enthalpies of formation  $\Delta H_f^\circ$  / kcal mol<sup>-1</sup>.

	Montgomery et al., ref. <sup>12</sup>	NIST <sup>15</sup>
H	52.6	52.1
C	170.2	171.3
N	113.5	113.0
O	60.0	59.6

**Table 3.** Enthalpies of formation of the gas-phase species M.

M	$\Delta_f H^\circ(\text{g}, \text{M})$ / kcal mol <sup>-1</sup>	$\Delta_f H^\circ(\text{g}, \text{M})$ / kcal mol <sup>-1</sup> , lit. value
$\text{NO}_2^+$	235.4	228.97 <sup>15, a</sup>
$\text{C}_4\text{O}_4^{2-}$	-107.8	—
$^3\text{C}_4\text{O}_4$	-74.8	—
$\text{C}_4\text{N}_2\text{O}_8$	-40.9	—
$\text{NO}_2$	+7.5	+7.9
$\text{CO}$	-26.1	-26.4

<sup>a</sup> Estimated from  $\Delta H_f^\circ(\text{NO}_2, \text{g}) = 7.9$  kcal mol<sup>-1</sup>, <sup>15</sup> and  $I_E(\text{NO}_2, \text{g}) = 9.586$  eV. <sup>15</sup>  $I_E$  = ionization energy. The value for  $\Delta H^\circ_f(\text{NO}_2^+, \text{g})$  was obtained according to:  $\Delta H_f^\circ(\text{NO}_2^+, \text{g}) = \Delta H_f^\circ(\text{NO}_2, \text{g}) + I_E(\text{NO}_2, \text{g})$ .

$$\Delta H_L(M_p X_q) = U_L + \left[ p \left( \frac{n_m}{2} - 2 \right) + q \left( \frac{n_x}{2} - 2 \right) \right] RT \quad (5)$$

( $n_M$ ,  $n_X$ : 3 monoatomic ions, 5 linear polyatomic ions, 6 non-linear ions;

$U_L$ : lattice energy, see Eq. (3); p, q: number of cations and anions per “molecular” unit)

**Table 4.** Molecular volumes ( $V_M$ ).

	$V_M / \text{Å}^3$	$V_M / \text{nm}^3$
$\text{NO}_2^+$	22	0.022 <sup>17-19</sup>
$\text{C}_4\text{O}_4^{2-}$	129.4	0.1294 <sup>20</sup>

<sup>a</sup>The molecular volume of the squarate dianion was calculated from the volume of the strontium squarate trihydrate,  $V(\text{SrC}_4\text{O}_4 \cdot 3\text{H}_2\text{O}) = 180.0 \text{ Å}^3$ ,<sup>20</sup> and the volumes of  $V(\text{Sr}^{2+}) = 8.6 \text{ Å}^3$ ,<sup>17,18</sup> and the volume for a structural water of  $V_M(\text{H}_2\text{O}, \text{hydrate}) = 14 \text{ Å}^3$ .<sup>19</sup>

**Table 5.** Lattice energies ( $U_L$ ) and lattice enthalpies ( $\Delta H_L$ ).

	$V_M / \text{nm}^3$	$U_L / \text{kJ mol}^{-1}$	$\Delta H_L / \text{kJ mol}^{-1}$	$\Delta H_L / \text{kcal mol}^{-1}$
$[\text{NO}_2]_2[\text{C}_4\text{O}_4]$	0.1734	1599.9	1604.8	383.9

The enthalpies of sublimation for the neutral  $\text{O}_2\text{N}-\text{C}_4\text{O}_4-\text{NO}_2$  were estimated according to Trouton's rule (Eq. (6), Table 6)<sup>21</sup> with estimated melting points of  $150 \text{ °C}$ . The validity of Trouton's rule reflects the fact that the entropy of vaporization is approximately constant for many compounds and that  $\Delta H_{sub.} \approx \Delta H_{vap.} + \Delta H_{fusion}$ , with  $\Delta H_{vap.} \gg \Delta H_{fusion}$  so that  $\Delta H_{sub.} \approx \Delta H_{vap.}$ .

$$\Delta H_{sub.} = 188T_m J mol^{-1} \quad (6)$$

The molar enthalpy of formation for the ionic compound (salt) was obtained by subtracting the lattice enthalpy  $\Delta H_L$  (Table 5) from the sum of the enthalpies of formation for the cation and anion (Table 3). The calculated molar enthalpies of formation for the ionic (salt) and neutral compound are summarized in Table 7.

**Table 6.** Enthalpies of sublimation ( $\Delta H_{sub.}$ ).<sup>21</sup>

	$T_m / \text{K}^a$	$\Delta H_{sub.} / \text{kcal mol}^{-1}$
$\text{O}_2\text{N}-\text{C}_4\text{O}_4-\text{NO}_2$	423	19.0

<sup>a</sup> The melting points  $T_m$  were taken equal to the estimated (from experience) decomposition temperatures.

**Table 7.** Enthalpies of formation ( $\Delta_f H^\circ$ ) of the condensed species M.

	$\Delta_f H^\circ(\text{s}, \text{M}) / \text{kcal mol}^{-1}$
$[\text{NO}_2]_2[\text{C}_4\text{O}_4]$	-20.9
$\text{O}_2\text{N}-\text{C}_4\text{O}_4-\text{NO}_2$	-59.9

Table 8 presents the calculated energies of formation for the solid neutral species and salts. The  $\Delta_f H^\circ(\text{s})$  values (Table 7) were converted into the  $\Delta_f U^\circ(\text{s})$  values using the correlation shown in Eq. (7).<sup>22</sup> From Table 8 we further see that the covalently bound form is favored over the ionic salt by  $39 \text{ kcal mol}^{-1}$

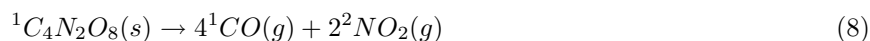
$$H_m = U_m + \Delta_n RT \quad (7)$$

**Table 8.** Solid state energies of formation ( $\Delta_f U^\circ$ ).<sup>22</sup>

	$\Delta_f H^\circ(\text{s}) /$ kcal mol <sup>-1</sup>	$\Delta n^a$	$\Delta_f U^\circ(\text{s}) /$ kcal mol <sup>-1</sup>	M / g mol <sup>-1</sup>	$\Delta_f U^\circ(\text{s}) /$ kJ kg <sup>-1</sup>
[NO <sub>2</sub> ] <sub>2</sub> [C <sub>4</sub> O <sub>4</sub> ]	-20.9	-5	-8.5	204	-174.4
O <sub>2</sub> N-C <sub>4</sub> O <sub>4</sub> -NO <sub>2</sub>	-59.9	-5	-47.5	204	-973.3

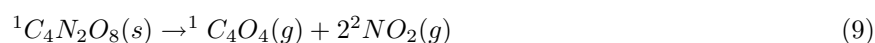
<sup>a</sup> change of molar number of gaseous species in the formation process of M from the elements (in their standard states).

Covalent nitronium squarate is a metastable compound with respect to its decomposition into CO and 2 NO<sub>2</sub> (Eq. (8))



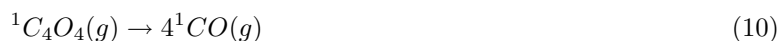
$$\Delta H^\circ (8) = -29.5 \text{ kcal mol}^{-1}$$

Since the first step of this decomposition is expected to be a bond cleavage of the relatively weak O-NO<sub>2</sub> bonds (see chapter below), we calculated the dissociation reaction according to Eq. (9) to be  $\Delta H^\circ(9) = +36.2$  kcal mol<sup>-1</sup> starting from singlet nitronium squarate and yielding singlet C<sub>4</sub>O<sub>4</sub> and 2 doublet NO<sub>2</sub> molecules in a spin-allowed reaction. (N.B. The also spin allowed reaction of singlet nitronium squarate into triplet-C<sub>4</sub>O<sub>4</sub> and NO<sub>2</sub> would be essentially thermoneutral with  $\Delta H = +0.1$  kcal mol<sup>-1</sup>; however, the following step of 3C<sub>4</sub>O<sub>4</sub> forming <sup>1</sup>CO would be spin-forbidden.)



$$\Delta H^\circ (9) = +36.2 \text{ kcal mol}^{-1}$$

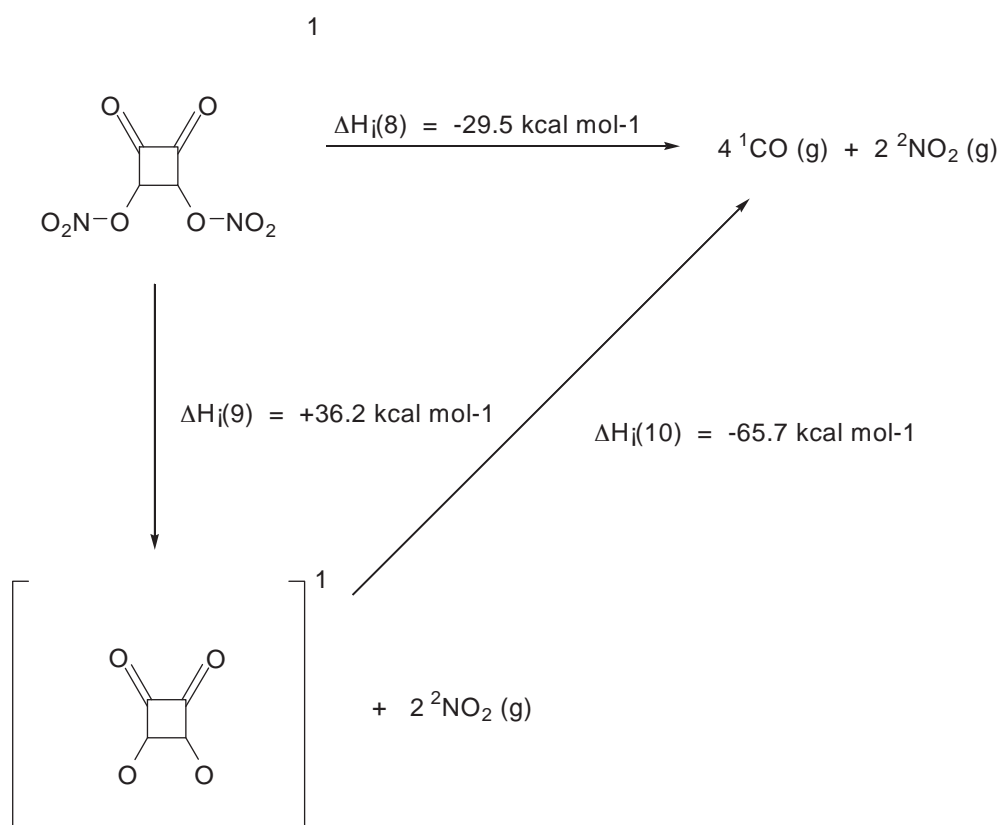
The final decomposition step would then be represented with the dissociation of <sup>1</sup>C<sub>4</sub>O<sub>4</sub> into 4 CO molecules (Eq. (10)).



$$\Delta H^\circ (10) = -65.7 \text{ kcal mol}^{-1}$$

The overall decomposition reaction would therefore be represented by a combination of reactions (8) and (9) and be exothermic with  $-29.5$  kcal mol<sup>-1</sup> with a barrier of at least  $36.2$  kcal mol<sup>-1</sup>.

Equations (8), (9), and (10) can be summarized as shown in the Scheme.



**Scheme.** Graphical representation of Eqs. (8), (9), and (10).

## Detonation parameters

The calculation of the combustion and detonation parameters was performed with the program package EXPLO5 (version 5.03).<sup>23</sup>

The detonation parameters were calculated using the EXPLO5 computer program.<sup>23</sup> The program is based on the chemical equilibrium, steady-state model of detonation. It uses the Becker-Kistiakowsky-Wilson's equation of state (BKW EOS) for gaseous detonation products and Cowan-Fickett's equation of state for solid carbon.<sup>24–26</sup> The calculation of the equilibrium composition of the detonation products is done by applying modified White, Johnson and Dantzig's free energy minimization technique. The program is designed to enable the calculation of detonation parameters at the CJ point. The BKW equation (11) in the following form was used with the BKWN set of parameters ( $\alpha$ ,  $\beta$ ,  $\kappa$ ,  $\theta$ ) as stated below the equations and  $X_i$  being the mol fraction of  $i$ -th gaseous product,  $k_i$  is the molar co-volume of the gaseous product.<sup>24–26</sup>

$$pV/RT = 1 + xe^{\beta x} \quad (11)$$

$$x = (\kappa \sum X_i k_i) / [V (T + \theta)]^\alpha$$

$$\alpha = 0.5, \beta = 0.176, \kappa = 14.71, \theta = 6620.$$

The detonation parameters calculated with the EXPLO5 program using the estimated determined densities are summarized in Table 9.

**Table 9.** Detonation parameters for O<sub>2</sub>N-C<sub>4</sub>O<sub>4</sub>-NO<sub>2</sub> and [NO<sub>2</sub>]<sub>2</sub>[C<sub>4</sub>O<sub>4</sub>].

	O <sub>2</sub> N-C <sub>4</sub> O <sub>4</sub> -NO <sub>2</sub>	[NO <sub>2</sub> ] <sub>2</sub> [C <sub>4</sub> O <sub>4</sub> ]
$\rho / \text{g cm}^{-3}$	1.8 <sup>a</sup>	1.8 <sup>a</sup>
$\Omega / \%$	0	0
$Q_v / \text{kJ kg}^{-1}$	-6147	-6756
$T_{ex} / \text{K}$	5340	5750
$P / \text{kbar}$	278	294
$D / \text{m s}^{-1}$	7964	8147
$V_0 / \text{L kg}^{-1}$	515	513

$\rho$  = density,  $\Omega$  = oxygen balance,  $Q_v$  = heat of detonation,  $T_{ex}$  = detonation temperature,  $P$  = detonation pressure,  $D$  = detonation velocity,  $V_0$  = Volume of detonation gases.

<sup>a</sup> A solid state density of 1.8 g cm<sup>-3</sup> was assumed reasonable for both the covalent and the ionic compound, based on a PM3 estimate of the density of covalent nitronium squarate of 1.99 g cm<sup>-3</sup> and for the ionic salt of 1.98 g cm<sup>-3</sup> <sup>27</sup>.

As we can see from Table 9, neither the nitrosonium ([NO<sub>2</sub>]<sup>+</sup>) salt nor the covalently bound nitrosonium (nitrate ester) compound possesses desirable detonation parameters in terms of their detonation pressure and velocity. For this reason, no further detonation parameters were studied.

## Combustion parameters

For a solid rocket propellant one can assume free expansion of the combustion products into space (or atmosphere) with  $p = \text{const.}$  and therefore Eq. (12) is a good approximation, i.e. one can consider the combustion process as isobaric:

$$\Delta U = Q_p - p\Delta V \quad (12)$$

In this study we assumed firing the rocket motor against ambient atmosphere ( $p = 1 \text{ bar}$ ) as it is commonly the case for tactical missiles.

The following combustion calculations were carried out under isobaric conditions, based on the assumptions that the combustion of the fuel proceeds without heat loss to the surrounding (i.e. adiabatically) and that in the combustion products the state of chemical equilibrium establishes. The calculation of the theoretical rocket performances was based on the following assumptions:

- (i) the pressure in the combustion chamber and the chamber cross-section area are constant
- (ii) the energy and momentum conservation equations are applicable
- (iii) the velocity of the combustion products at the combustion chamber is equal to zero
- (iv) there is no temperature and velocity lag between condensed and gaseous species
- (v) the expansion in the nozzle is isentropic (N.B. In thermodynamics, an isentropic process or isoentropic process is one during which the entropy of the system remains constant  $\Delta S = 0$ ).

The theoretical characteristics of the rocket motor propellant may be derived from the analysis of the expansion of the combustion products through the nozzle. The first step in the calculation of the theoretical rocket performance is to calculate the parameters in the combustion chamber, and the next step is to calculate

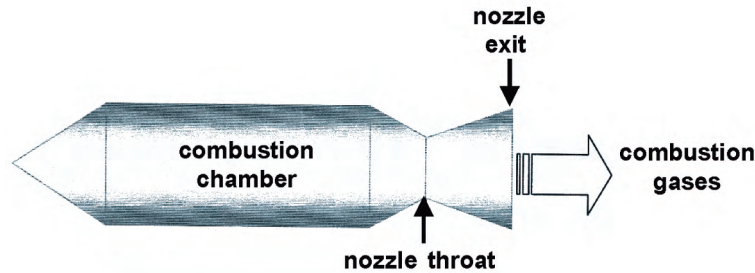


expansion through the nozzle (Figure 2). The expansion through the nozzle is assumed to be isentropic ( $\Delta S = 0$ ). The EXPLO5 and ICT program code<sup>28</sup> provide the following options:

(i) *frozen* flow (composition of combustion products remains unchanged, frozen, during the expansion through the nozzle, i.e. equal to composition in the combustion chamber)

(ii) *equilibrium* flow (composition of combustion products at any station in the nozzle is defined by chemical equilibrium).

The frozen performance is based on the assumption that the composition of combustion products remains constant (“frozen”), while equilibrium performance is based on the assumption of instantaneous chemical equilibrium during the expansion in the nozzle.



**Figure 2.** Schematic presentation of a rocket combustion chamber and nozzle.

The specific impulse  $I_{sp}^*$  is the change in the impulse (impulse = mass  $\times$  velocity, or force  $\times$  time) per propellant mass unit. The specific impulse is an important parameter for the characterization of rocket propellants and can be interpreted as the effective exhaust velocity of the combustion gases when exiting the expansion nozzle (Eq. (13)).

$$I_{sp}^* = \frac{\overline{F} \cdot t_b}{m} = \frac{1}{m} \int_0^{t_b} F(t) dt \quad (13)$$

The force  $F$  is the time-dependent thrust,  $F(t)$ , or the average thrust,  $\overline{F}$ ,  $t_b$  is the burning time of the motor, and  $m$  the mass of the propellant. Therefore, the unit of the specific impulse  $I_{sp}^*$  is  $\text{N s kg}^{-1}$  or  $\text{m s}^{-1}$ .

It is convention to divide the specific impulse  $I_{sp}^*$  by  $g_0$  (standard gravity,  $g_0 = 9.81 \text{ m s}^{-2}$ ) so that the resulting specific impulse  $I_{sp}$  has the unit s (seconds) (Eq. (5)).

$$I_{sp} = \frac{I_{sp}^*}{g_0} \quad (14)$$

The specific impulse  $I_{sp}$  can also be defined according to Eq. (15) with  $\gamma = C_p/C_v$ .

$$I_{sp}^* = \frac{1}{g} \sqrt{\frac{2\gamma RT_C}{(\gamma - 1)M}} \quad \gamma = \frac{C_P}{C_V} \quad (15)$$

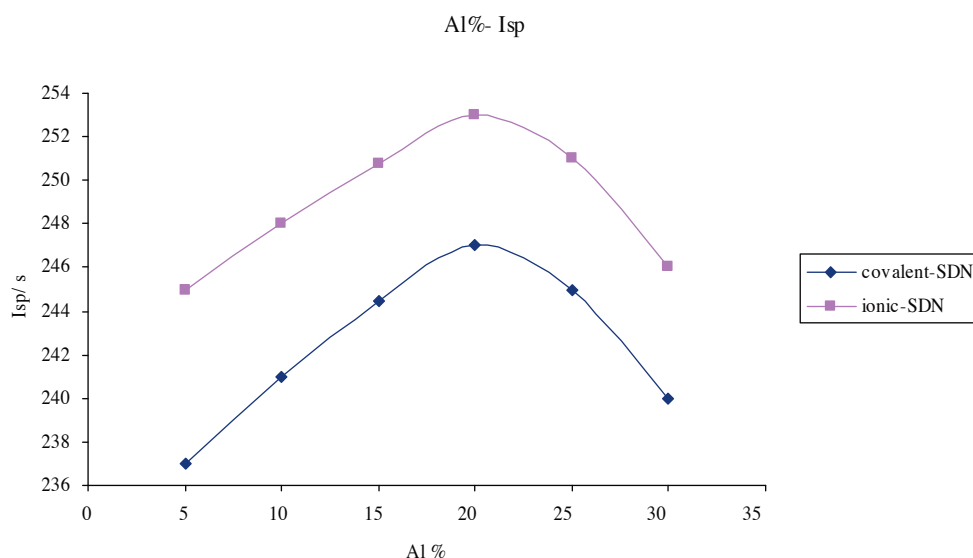
Table 10 summarizes the calculated rocket propellant performance parameters for an assumed chamber pressure of 70 bar for the neat propellants covalent  $\text{O}_2\text{N-C}_4\text{O}_4\text{-NO}_2$  and ionic  $[\text{NO}_2]_2[\text{C}_4\text{O}_4]$  used as mono-propellants ( $\Omega = 0$ ). Table 11 summarizes the calculated propulsion parameters for aluminized formulations

in which the Al content has been varied in order to achieve optimal performance (ca. 20% Al). Table 11 also contains the corresponding values for an AP/Al formulation for comparison. The results of Table 11 are graphically summarized in Figure 3.

**Table 10.** Combustion properties (solid rocket motor) of neat  $\text{O}_2\text{N-C}_4\text{O}_4\text{-NO}_2$  and  $[\text{NO}_2]_2[\text{C}_4\text{O}_4]$  (frozen expansion)<sup>a</sup>

	$\text{O}_2\text{N-C}_4\text{O}_4\text{-NO}_2$	$[\text{NO}_2]_2[\text{C}_4\text{O}_4]$
condition	isobaric	isobaric
p / bar	70	70
$\rho$ / $\text{g cm}^{-3}$	1.8	1.8
$\Omega$ / %	0	0
$Q_p$ / $\text{kJ kg}^{-1}$	-4255	-4468
$T_{comb.}$ / K	3636	3805
$I_{sp}$ / s	232	240

<sup>a</sup> $\Omega$  = oxygen balance,  $Q_p$  = heat of isobaric combustion,  $I_{sp}$  = specific impulse



**Figure 3.** Graphical representation of the calculated frozen specific impulses for covalent  $\text{O}_2\text{N-C}_4\text{O}_4\text{-NO}_2$  / Al and ionic  $[\text{NO}_2]_2[\text{C}_4\text{O}_4]$  / Al formulations (see Table 11).

From Table 11 and Figure 3 we can conclude that for both ionic and covalent nitronium squarate the best performance is achieved with an oxidizer:fuel ratio of 80:20. Although the oxygen balance of nitronium squarate is zero (with respect to  $\text{CO}_2$ ) this behavior can be explained by (i) the formation of CO rather than  $\text{CO}_2$  at high temperatures (Boudouard equilibrium) and (ii) the fact that aluminum oxide,  $\text{Al}_2\text{O}_3$ , is thermodynamically a very favorable compound. It is further apparent that the formulation with ionic  $[\text{NO}_2]_2[\text{C}_4\text{O}_4]$  and Al gives a better performance than the formulation using covalent  $\text{O}_2\text{N-C}_4\text{O}_4\text{-NO}_2$  and Al. However, realistically it can be expected that the more stable covalent species will eventually be synthesized in the laboratory. The specific impulse of the chlorine and perchlorate-free formulation with covalent  $\text{O}_2\text{N-C}_4\text{O}_4\text{-NO}_2$  and Al (**I**) is

**Table 11.** Combustion properties (solid rocket motor) of covalent and ionic nitronium squarate (oxidizer) / Al (fuel) formulations with varying oxidizer/fuel ratios.

	O <sub>2</sub> N <sub>2</sub> C <sub>4</sub> O <sub>4</sub> -NO <sub>2</sub>						[NO] <sub>22</sub> [C <sub>4</sub> O <sub>4</sub> ]						AP
	5	10	15	20	25	30	5	10	15	20	25	30	
Al %	5	10	15	20	25	30	5	10	15	20	25	30	30
condition	isobaric	isobaric	isobaric	isobaric	isobaric	isobaric	isobaric	isobaric	isobaric	isobaric	isobaric	isobaric	isobaric
p / bar	70	70	70	70	70	70	70	70	70	70	70	70	70
ρ / g cm <sup>-3</sup>	1.6	1.7	1.7	1.8	1.8	1.8	1.6	1.7	1.7	1.8	1.8	1.8	2.18
Ω / %	-4.45	-8.9	-13.34	-17.8	-22.2	-26.7	-4.45	-8.9	-13.34	-17.8	-22.2	-26.7	-2.8
Q <sub>p</sub> / kJ kg <sup>-1</sup>	-4645	-5092	-5583	-6182	-6448	-6286	-4856	-5307	-5774	-6338	-6516	-6381	-6787
T <sub>comb.</sub> / K	3797	4024	4273	4582	4741	4676	3955	4180	4417	4711	4827	4777	4290
I <sub>sp</sub> / s	237	241	243	246	245	240	244	248	250	253	250	246	243

slightly higher than that of the AP/Al (III) formulation. Therefore it can be concluded that bis(nitronium) squarate,  $\text{O}_2\text{N-C}_4\text{O}_4\text{-NO}_2$ , may be a promising new perchlorate-free and environmentally benign oxidizer for formulations to be used in solid rocket motors.

### Electrostatic potential of covalent $\text{O}_2\text{N-C}_4\text{O}_4\text{-NO}_2$

The electrostatic potential (ESP) of covalent  $\text{O}_2\text{N-C}_4\text{O}_4\text{-NO}_2$  was computed at the optimized structure at the B3LYP/6-31G(d) level of theory. Figure 4 shows the electrostatic potential for the 0.001 electron/bohr<sup>3</sup> isosurface of electron density evaluated at the B3LYP level of theory. The colors range from  $-0.06$  to  $+0.06$  hartrees with dark blue denoting extremely electron-deficient regions ( $V(r) > 0.06$  hartrees) and red denoting electron-rich regions ( $V(r) < -0.06$  hartrees). It has recently been found by Politzer, Murray et al.<sup>31</sup> and extensively used by Rice et al.<sup>32</sup> that the patterns of the computed electrostatic potential on the surface of molecules in general can be related to the sensitivity of the bulk material. The electrostatic potential at any point  $r$  is given by Eq. (16) in which  $Z_A$  is the charge on nucleus A, located at  $R_A$ .

$$V(r) = \sum \frac{Z_A}{|R_A - r|} - \int \frac{\rho(r')}{|r' - r|} dr' \quad (16)$$

Politzer et al. were able to show<sup>31</sup> that impact sensitivity can be expressed as a function of the extent of this anomalous reversal of the strengths of the positive and negative surface potentials. In most nitro ( $-\text{NO}_2$ ) and nitrate ( $-\text{O-NO}_2$ ) systems the regions of positive potential are stronger than the negative, contrary to the usual situation. This atypical imbalance between stronger positive regions and weaker negative ones can be related to the impact sensitivities. The calculated electrostatic potential of  $\text{O}_2\text{N-C}_4\text{O}_4\text{-NO}_2$  (Figure 4) shows strong positive regions over the nitro ( $-\text{NO}_2$ ) groups with the positive areas extending into the  $\text{O-NO}_2$  region (oxygen –  $\text{NO}_2$  bond). Moreover, there is also a strong positive region over the relatively weak C-C bond. This is in good accord with the labile  $\text{O-NO}_2$  and C-C bonds and also accounts for the easy bond cleavage. In comparison, free squaric acid (Figure 4) does not show any positive regions over the bonds in the molecule.



**Figure 4.** Electrostatic potential of  $\text{O}_2\text{N-C}_4\text{O}_4\text{-NO}_2$  and squaric acid (B3LYP/6-31G(d), 0.001 e bohr<sup>3</sup> isosurface, energy values  $-0.06$  H to  $+0.06$  H); color coding: red (very negative), orange (negative), yellow (slightly negative), green (neutral), turquoise (slightly positive), light blue (positive), dark blue (very positive).

## Conclusions

From this computational study the following conclusions can be drawn:

(i) Covalently bound and ionic nitronium squarate were investigated with respect to their potential use as energetic materials or oxidizers for solid rocket motors. None of these compounds can be expected to be a good high explosive. However, the covalent molecule squaric acid dinitrate ester,  $O_2N-C_4O_4-NO_2$ , was identified to be a potentially interesting oxidizer.

(ii) The computed specific impulse of an  $O_2N-C_4O_4-NO_2/Al$  formulation (80:20) is slightly higher than that of a conventional AP/Al (70:30) formulation, with the advantage of not having any toxic perchlorate or halogen present.

(iii) Squaric acid dinitrate ester,  $O_2N-C_4O_4-NO_2$ , is metastable with respect to decomposition into CO and  $NO_2$ . The enthalpy change for the decomposition reaction was calculated to be exothermic with  $-29.5 \text{ kcal mol}^{-1}$  with a barrier of at least  $36.2 \text{ kcal mol}^{-1}$ .

(iv) The computed electrostatic potential of  $O_2N-C_4O_4-NO_2$  shows strong positive areas at the  $0.001 \text{ s bohr}^{-3}$  isosurface over the O- $NO_2$  and C-C bonds, indicating the relative weakness of these particular bonds compared to the un-nitrated squaric acid.

The results obtained in this study should encourage synthetic work in order to prepare squaric acid dinitrate ester,  $O_2N-C_4O_4-NO_2$ , on a laboratory scale and to experimentally evaluate its properties, first and foremost its thermal stability. Such work is underway in our laboratories.

## Acknowledgments

Financial support of this work by the Ludwig-Maximilian University of Munich (LMU), the U.S. Army Research Laboratory (ARL), and the Strategic Environmental Research and Development Program (SERDP) under contract nos. W911NF-09-2-0018 (ARL) and 10 WPSEED01-002/WP-1765 (SERDP) is gratefully acknowledged. The authors acknowledge collaboration with Dr. Muhamed Sucesca (Brodarski Institute, Croatia) in the development of new computational codes to predict the detonation and propulsion parameters of novel explosives. We are indebted to and thank Drs. Betsy M. Rice and Brad Forch (ARL, Aberdeen Proving Ground, MD, USA) for many helpful and inspired discussions and support of our work. One of us (E.G.) acknowledges financial support by TÜBİTAK (PhD studies in Ankara) and the EU ERASMUS program (study leave in Munich). The authors also thank Mr. Norbert Mayr for many discussions and support with computational problems.

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