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Specific impulse and absolute chemical hardness

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Abstract The present work is dedicated to show that there are relationships between the absolute chemical hardness (η) of monopropellants and their specific impulse (I_s). A total of sixteen monopropellants have been modelled and the absolute hardness obtained by quantum chemical calculations. The following equation was obtained: I_s = 17.562 η + 125.551, providing specific impulse results in very good agreement with reference values.

Keywords: Chemical propulsion; Specific impulse, absolute chemical hardness, empirical equations, semi-empirical.

INTRODUCTION

As is well known, the blend of a solid propellant is chosen by simultaneous considerations of processability, acceptable mechanical strength of cured propellant, and possible maximum specific impulse [1]. Specific impulse (I_s) is, of course, a paramount parameter in order to evaluate the performance of a given propellant. Due to its importance, be able to predict the value of I_s for a given propellant is a great advantage in aerospace research. The specific impulse rigorously defines the amount of useful energy which may be obtained from the combustion and expansion of a fuel and oxidizer. In addition to its thermodynamic significance, specific impulse also possesses an inherent ballistic importance [2].

Taking into account its maximum importance, empirical equations have been derived to allow the calculation of I_s based on the propellant´s chemical composition [3]

The molecular hardness η and electronegativity χ are defined from formal density functional theory. Electronegativity is formally defined as $(\partial E/\partial N)_V$ and hardness as $\frac{1}{2}(\partial^2 E/\partial N^2)_V$ where E is the energy, N is the number of particles, and V is the potential due to the nuclei. The χ of a molecule can be defined as the average of its (first) ionization potential (IP) and its electron affinity (EA), i.e. χ = (IP + EA)/2. By using a DFT variation for Koopmans' theorem (KT), we can obtain $\chi = -(E_{HOMO} + E_{LUMO})/2$. Absolute hardness (η) for a molecule is defined as η = IP - EA/2 and we can use KT to obtain $\eta = (E_{LUMO} - E_{HOMO})/2$.

Chemical hardness is a key parameter in order to rationalize and predict chemical and physical properties of elements and compounds. It has been shown, for example, that chemical hardness is very closely related with absolute ion hydration enthalpies [4] and with the physical properties of superheavy elements [5].

The present work is dedicated to show that there are relationships between the absolute chemical hardness of monopropellants and their specific impulse.

METHODOLOGY

The quantum chemical calculations were performed by using Spartan [6]. Specifically, the thermochemical parameters (E_{HOMO}, E_{LUMO} and $\Delta H_{f\ (g)}$) were calculated by using the T1 recipe.

The T1 recipe reproduces G3(MP2) heats of formation (but at significantly reduced computation cost) with a mean absolute error of <1 kJ/mol. [7]. T1 substitutes the MP2/6-31G* geometry used in G3(MP2) by a HF/6-31G* geometry, eliminates both the HF/6-31G* frequency and the QCISD(T)/6-31G* energy calculations and

approximates the MP2 energy calculation with the G3MP2 large basis set by an analogous calculation using dual basis set RI-MP2 techniques. Taken together, these changes reduce computation time by 2-3 orders of magnitude, and T1 calculations on molecules in the molecular weight range of 400-500 amu are practical. It reproduces the full set of ~2,000 experimental heats of formation in the NIST thermochemical database with a mean absolute error of 9 kJ/mol. [7].

For comparison, E_{HOMO} and E_{LUMO} energies were also calculated by using Hartree-Fock (6-311+G**) approach and no significant difference was observed to T1 values. Hence, all calculated thermochemical data shown in Table 1, are those obtained by using T1 thermochemical recipe.

Table 1. Calculated thermochemical data for selected monopropellants.

Propellant	Formula	mass /gmol^{-1}	E_{homo} /eV	E_{lumo} /eV	η /eV	$\Delta H_{f\,(g)}$ /kJmol^{-1}	$\Delta_c H°_{(s,l)}$ /kJmol^{-1}	I_s/s$^{\#}$
TNT	$C_7H_5N_3O_6$	227.1	-11.5	0.3	5.9	56.64 (24.1 ± 3.5)*	_ (-3410. ± 20)*	221.2
RDX	$C_3H_6N_6O_6$	222.1	-12.5	2.3	7.4	234.63 (192)*	_ (-2120. ± 5.0)*	262.0
HMX	$C_4H_8N_8O_8$	296.2	-12.5	2.2	7.3	262.12 (264.9)*[1]	_ (-2820 ± 2.8)*	262.0
NG	$C_3H_5N_3O_9$	227.1	-13.5	2.7	8.1	-273.17 (-279.1 ± 2.7)*	_ (-1529 ± 10)*	268.1
PETN	$C_5H_8N_4O_{12}$	316.1	-13.6	2.5	8.0	-385.09	_ (-2572.4 ± 0.8)*	260.0
NM	CH_3NO_2	61.0	-12.4	3.1	7.7	-66.34 (-81 ± 1)*	_ (-709.6 ± 0.4)*	259.0
HNS	$C_{14}H_6N_6O_{12}$	450.2	-11.1	-0.4	5.4	264.75 (238.4)*	_ (-6434.2 ± 5.0)*	223.2

*Reference values (Ref. 8); #Calculated using Eq. (1) (Ref. 3). [1]Using ΔH_f (s) + ΔH_{sub} = 103 + 161.9 (both from Ref. 7);

Dany Frem [4], have derived two empirical equations in order to predict the specific impulse of more than 165 compositions belonging to virtually all classes of propellants such as monopropellants, single-base, double-base, triple-base, and cast modified double-base (CMDB) propellants, pseudo-propellants, composite propellants, liquid mono- and bipropellants, and finally hybrid propellants. The obtained and tested empirical equations were really reliable, providing results in very good agreement with literature data. The obtained equation [3] is:

$$I_s\,(Nsg^{-1}) = (-4.459 + 121.81\,N_g + 4.697\,Q)^{1/2} \quad (1)$$

where (*Q*) and (*N***g**), are the heat of reaction in (kcal g^{-1}) and the number of moles of gaseous reaction products per gram of propellant, respectively, were calculated according to:

$$Q = [28.9b + 47\,[d-(b/2)] + \Delta H_f^{o}]/M_w \quad (2)$$

$$N_g = (2c + 2d + b)/(48a + 4b + 56c + 64d) \quad (3)$$

where: *a*, *b*, *c* and *d* are the number of carbon (C), hydrogen (H), nitrogen (N) and oxygen (O) atoms in the propellant composition, (ΔH_f^{o} kcal mol^{-1}) represents the condensed phase heat of formation, and *M***w** is the composition's molecular weight.

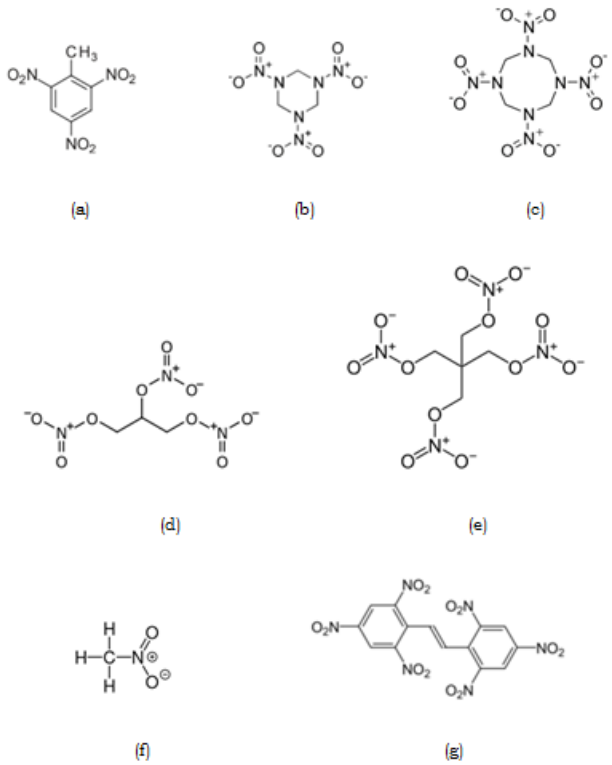

Figure 1. The modelled monopropellants (to obtain Eq. 4): (a) TNT, (b) RDX, (c) HMX, (d) NG, (e) PETN, (f) NM and (g) HNS.

The I_s values calculated using Eq. (1) are employed as reference values in the present work (Table 1), since they agree very well with those calculated by using ISPBKW code [3] but employ simple empirical data (number of atoms), as well as experimental ΔH_f^o values. Hence, they came from the propellant itself, with none especial or postulated theoretical assumption.

In order to shown the relationships between the absolute chemical hardness of monopropellants and their specific impulse, seven monopropellants were modelled: 2,4,6-trinitrotoluene (TNT), 1,3,5-Trinitro-1,3,5-triazinane (RDX), 1,3,5,7-Tetranitro-1,3,5,7-tetrazoctane (HMX), Propane-1,2,3-triyl trinitrate (nitroglycerin, NG), 2,2-Bis[(nitrooxy)methyl]propane-1,3-diyl dinitrate (PETN), nitromethane (NM) and 1,3,5-Trinitro-2-[2-(2,4,6-trinitrophenyl)ethenyl]benzene (hexanitrostilbene, HNS) (Figure 1).

In order to verify the reliability of the proposed relationships, a new set of monopropellants were modelled (Figure 2): 2,2´,4,4´,6,6´ hexanitroazobenzene (HNAB), 1-nitroguanidine (NQ), diazodinitrophenol (DDNP), 1,3,5-Triamino-2,4,6,-trinitrobenzene (TATB), Picric acid (PA), 2,4,6-Trinitrophenylmethylnitramine (Tetryl), Diethanolnitramine dinitrate (DINA), Ethriol trinitrate (ETN), and Ethylenedinitramine (EDNA).

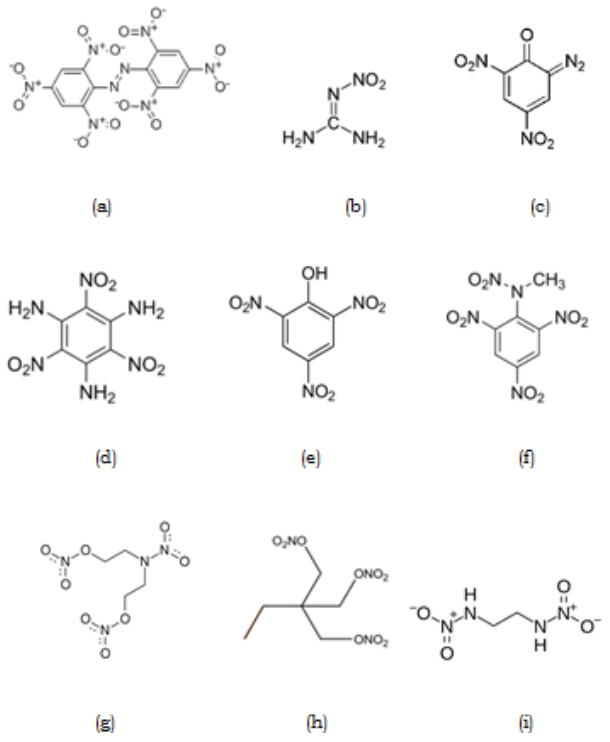

Figure 2. Modelled monopropellants to test Eq. (4) reliability: (a) HNAB, (b) NQ, (c) DDNP, (d) TATB, (e) PA, (f) Tetryl, (g) DINA, (h) ETN and (i) EDNA.

RESULTS AND DISCUSSION

The obtained results are summarized in Tables 1-3. The combustion enthalpy values are those provided by NIST [8]. The specific impulse values are those calculated using Eq. (1) [3].

As can be seen from Table 1 data, the investigated monopropellants have different chemical formulas and molar masses, as well as combustion enthalpies (a parameter directly related with the pressure and temperature in the combustion chamber, and hence, with specific impulse), with NM and HNS as the opposite extremes and TNT occupying an intermediary position. So, a very simplistic reasoning based only on the number of carbon atoms per formula, molar masses and combustion enthalpies could not explain the relatively close I_s values for such monopropellants. However, as can also be verified in the same Table, the absolute chemical hardness (η) values are very closely related.

As is well known, η values are related with polarizability (harder chemical species are less polarizable), and with, of course, E_{HOMO} and E_{LUMO} energies. That is, approximately (Koopman´s theorem) with ionization energies and electron affinities of such species. In other words, with their chemical reactivity and the possibility of to form lighter or heavier gaseous products (lighter gaseous products favours higher I_s values). So, it is not so surprisingly that a closer relationship between η and I_s values can be verified.

In Figure 3, the monopropellants I_s values (Eq. 1) are plotted as a function of η. As can be seen, a linear relationship (r= 0.9508) is obtained, providing the empirical equation:

$$I_s = 17.562\ \eta + 125.551 \qquad (4)$$

whose sell-consistency was verified (Table 2).

Furthermore, in order to verify the reliability of Eq. 4, it was applied to another set of monopropellants (Table 3), with good results, as can be verified.

Table 2. Self-consistence test to Eq. (4). Percentage deviations in parentheses.

Propellant	$I_s/s^{\#}$	I_s/s (Eq.4)
TNT	221.20	229.17 (+3.6%)
RDX	261.98	256.04 (-2.3%)
HMX	261.98	254.10 (-3.0%)
NG	268.10	267.80 (-0.1%)
PETN	259.94	266.75 (+2.6%)
NM	258.92	261.48 (+1.0%)
HNS	223.24	220.03 (-1.4%)

[#]Calculated using Eq. (1) (Ref. 3).

Table 3. Specific impulse to some selected monopropellants, calculated by using Eq. (4). Percentage deviations in parentheses.

Propellant	E_{homo} /eV	E_{lumo} /eV	η /eV	$I_s/s^{\#}$	I_s/s (Eq.4)
HNAB	-11.82	-0.09	5.87	234.45	228.64 (-2.5%)
NQ	-10.98	3.13	7.06	215.09	249.54 (+ 16.0)
DDNP	-9.75	-0.04	4.86	227.32	210.73 (-7.3%)
TATB	-9.88	1.54	5.71	206.93	225.83 (+7.2%)
PA	-11.12	0.07	5.60	219.16	223.81 (+2.1)
Tetryl	-12.06	-0.31	5.88	239.55	228.82 (-4.5%)
DINA	-11.78	3.02	7.40	259.94	255.51 (-1.7%)
ETN	-12.94	3.22	8.08	247.71	267.45 (+ 8.0%)
EDNA	-12.33	3.97	8.15	252.80	268.68 (+6.3%)

[#]Calculated using Eq. (1) (Ref. 3).

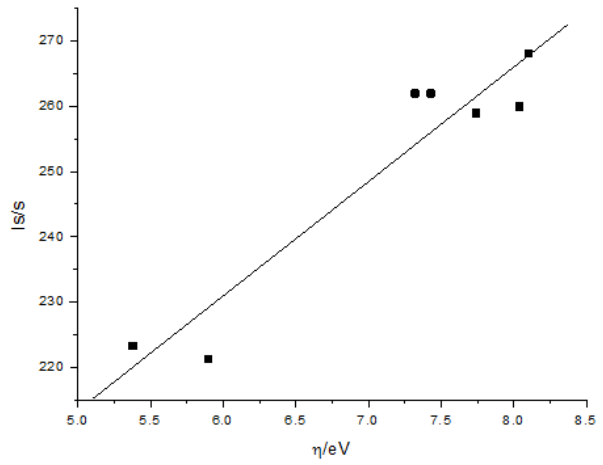

Figure 3. I_s (Eq. 1) as a function of η for Table 1 monopropellants.

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