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Ab initio quantum chemical predictions of enthalpies of formation, heat capacities, and entropies of gas-phase energetic compounds

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Abstract

This paper presents the thermochemical properties of 42 energetic materials commonly used in explosives and/or propellants. The standard enthalpies of formation at 298.15 K and heat capacities and entropies in the temperature range of 300–5000 K have been computed by means of the density functional theory in quantum chemistry along with a protocol developed for these energetic compounds. The resulting data, currently not available in the literature, are critical for modeling reaction mechanisms and combustion-wave structures of these materials.

Keywords: Propellants; Explosives; Thermochemistry; HEDM

1. Introduction

The combustion of solid propellants is a complex phenomenon involving many intricate physiochemical processes in the gas-phase, near-surface, and subsurface regions [1–4]. Despite the extensive efforts made over the past 5 decades, the thermochemical properties of many propellant ingredients and related molecules and radicals in the reaction pathways are not available [1,5]. Even for such nitramine compounds as RDX and HMX, whose gas-phase reaction mechanisms have been reasonably well established by Yetter et al. [2], Melius [6], and Manaa et al. [7], thermochemical data for many participating species are still lacking. The situation becomes more severe when a new energetic material is formulated and its combustion needs to be characterized. The lack of data hampers the development of detailed chemical kinetic models for the decomposition and subsequent combustion chemistry of the new compound. Experimental measurements are always preferred, but the amount of data needed is so vast that validated theoretical tools must be employed to make available the required information. The purpose of this paper is to provide such fundamental thermochemical properties as standard enthalpies of formation, heat capacities, and entropies for selected energetic compounds in the gas phase. It is not certain whether all the molecules considered below exist in the gas phase near the burning surface of a given energetic material. Many of them, including RDX [8], Keto-RDX [8],

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and TNAZ [9], however, have been observed both experimentally and theoretically due to evaporation or ejection from the condensed phase. The subsequent thermal decomposition and reactions then lead to ignition and combustion in the gas phase.

2. Computational method

The energetic materials under consideration have large molecules containing one or several nitro, nitrate, or amino groups. The most reliable existing ab initio methods, G2 and G3, are computationally too expensive [10] to be of interest for the present work. Moreover, these methods have been benchmarked only for relatively small molecules, and their validity for large molecules remains to be demonstrated. Density functional methods (such as the B3LYP/6-311G(d,p) method) using a conventional atomization approach have been shown [11] to provide a reasonable treatment of naphthalene ($C_{10}H_8$), quite a large molecule. The molecules investigated in the present study, however, are even larger. For this reason, a method with a smaller basis set is desired. Rice et al. [12] used a B3LYP/6-31G(d)//B3LYP/6-31G(d) method based on the atomization approach and atomic corrections to predict enthalpies of formation of several energetic materials. A total of seven atomic corrections were defined, four for C, H, N, and O atoms involved in single bonds and three for C, N, and O atoms involved in multiple bonds. Unfortunately, this method was not validated because all of the 35 gaseous species considered [12] were used to determine atomic corrections. It should be noted, however, that validation for those energetic materials poses practical challenges because of the scarcity of experimental data. Wilcox and Russo [13] proposed a B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) method for C, H, and N compounds with parametric corrections for these atoms. The method, derived with 35 compounds, was not validated in a strict sense. Moreover, it is of limited use for the energetic materials considered here because calculations with O atoms are not feasible, although it is expected to be slightly more accurate than the B3LYP/6-31G(d)//B3LYP/6-31G(d) method employed by Rice et al. [12]. A comparative study of several existing approaches, including the semiempirical PM3 method, indicates that the B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) technique appears to offer the best compromise between numerical accuracy and expense.

The model employed in this paper includes zero-point energies and several new atomic corrections. Rice et al. [12] considered only two classes of atoms involved in either single or multiple bonds. We introduce a distinction between nitrogen atoms in a 'normal' environment (trivalent according to the octet rule) and nitrogen atoms in a hypervalent state (pentavalent), such as those in nitro and nitrate groups. Many energetic materials are fluorinated and an atomic correction for F atoms is required. A total of nine atomic corrections are derived in the present work: two for H and F atoms, three for C, N, and O atoms involved in single bonds, three for C, N, and O atoms involved in multiple bonds, and one for hypervalent N atoms.

The gas-phase standard enthalpy of formation of molecule j at 298.15 K can be determined from the equation

$$\Delta_f H^0_{298.15\mathrm{K(g)}} = 627.51 \times \Big(E_j + \mathrm{ZPE}_j + \text{thermal corrections} + \sum_i \alpha_i c_i^*\Big),$$

where α_i is the number of atoms i in molecule j and c_i^* is the atomic correction for atom i. E_j and ZPE_j denote, respectively, the absolute electronic energy and zero-point energy, calculated using the Gaussian 98W [14] and Gaussian 03 [15] software packages. The units are Hartree molecule^{-1} for E_j, ZPE_j, and thermal corrections and Hartree atom^{-1} for c_i^*, whereas $\Delta_f H^0_{298.15\mathrm{K(g)}}$ is in kcal mol^{-1}. The method employed in the present study is based on 28 energetic and nonenergetic compounds having well-calibrated enthalpies of formation with uncertainty less than 1 kcal mol^{-1}. The atomic corrections c_i^* are determined by least-square fitting of the 28 selected experimental gas-phase standard enthalpies of formation at 298.15 K. Table 1 reports the comparison between experimental and computed standard enthalpies of formation at 298.15 K for some of the 28 compounds considered. Table 2 gives the atomic corrections. The work of Rice et al. [12] was recently refined [16] with the introduction of group-based corrections and modification of the values of the atom-based corrections. Such refinements allow computation of the gas-phase enthalpies of formation of molecules containing all types of N atoms described above.

3. Validation of model

The ab initio method developed here was validated for 16 nitro or nitrate compounds, including RDX. Table 3 shows the measured and calculated gas-phase enthalpies of formation. The corresponding statistical analysis is given in Table 4. Good agreement is obtained with experimental data, indicating that the predicted results are sufficiently accurate. It is usually recognized that the level of accuracy required

Table 1
Measured and calculated gas-phase standard enthalpies of formation at 298 K of selected compounds for the derivation of the ab initio method used in this study[a]

Compound	Name	$\Delta_f H^0_{\mathrm{exp(g)}} \pm \Delta_{\mathrm{exp}}$	$\Delta_f H^0_{\mathrm{calc(g)}}$	Δ
CH_3NO_2	Nitromethane	-19.3 ± 0.3	-19.6	-0.3
CH_3NO_3	Methyl nitrate	-29.2 ± 0.3	-30.9	-1.7
$C_2H_5NO_3$	Ethyl nitrate	-37.0 ± 0.8	-39.8	-2.8
$C_3H_5N_3O_9$	Nitroglycerine	-66.71 ± 0.65	-67.5	-0.8
$C_4H_9NO_2$	*Tert*-nitrobutane	-42.3 ± 0.8	-43.2	-0.9
$C_5H_8N_4O_{12}$	Pentrite PETN	-92.4 ± 0.7	-91.9	0.5
$C_7H_5N_3O_6$	TNT	5.8 ± 0.8	8.7	2.9

[a] Unit in kcal mol^{-1}. 1 cal = 4.184 J. $\Delta = \Delta_f H^0_{\mathrm{calc(g)}} - \Delta_f H^0_{\mathrm{exp(g)}}$.

Table 2
Atomic corrections used in the present model

Atom	c_i^* (Hartree atom^{-1})
H	0.58188704
C	38.11447874
N	54.76547900
O	75.15682281
F	99.74611074
C_d	38.11542265
N_d	54.75925621
O_d	75.15439445
N_{hyp}	54.75799267

for a useful standard enthalpy of formation at 298 K is ±2–3 kcal mol^{-1}, depending on the application. Our predictions generally match the data reported by Rice et al. [12], except in the cases of 4 compounds. Previously in [12], the energy of the minimum obtained was assumed to be within a few kcal mol^{-1} of the global minimum. The different stable conformations of a molecule were assumed to be similar in energy. The situation in reality, however, is more complicated in that two stable conformations can have quite different energies. For instance, at the same level of theory, we found a minimum for pernitroethane that was lower by 13.5 kcal mol^{-1} than that reported in [12]. On the other hand, the present work predicts an energy minimum for DNPN higher than Rice et al.'s value [12] by 8.1 kcal mol^{-1}. Thus discrepancies for these two compounds appear to exist. For the other two, (hexahydro-1,3,5-trinitroso-1,3,5-triazine) (TTT) and (hexanitrostilbene) (HNS), the energies reported are approximately equal and the methods themselves may be responsible for the discrepancies. For instance, Rice et al.'s method [12] performs better for TTT. The resulting deviation from the data in the literature is −1.3 kcal mol^{-1}, compared with −5.8 kcal mol^{-1} for our method. This may be at-

Table 3
Measured and calculated gas-phase standard enthalpies of formation at 298 K for selected compounds for validation of the ab initio method used in this study[a]

Compound	Name	$\Delta_f H^0_{\mathrm{exp(g)}} \pm \Delta_{\mathrm{exp}}$	$\Delta_f H^0_{\mathrm{calc(g)}}$	Δ
CHN_3O_6	Trinitromethane	-3.2	2.3	5.5
$CH_2N_2O_4$	Dinitromethane	-14.1 ± 1.0	-11.1	3.0
$C_3H_6N_6O_6$	RDX (hexogen)	45.8	44.4	-1.4
$C_3H_7NO_2$	1-Nitropropane	-29.8	-33.1	-3.3
$C_3H_7NO_2$	2-Nitropropane	-33.5	-35.9	-2.4
$C_3H_7NO_3$	*n*-Propyl nitrate	-41.6	-44.9	-3.3
$C_3H_7NO_3$	Isopropyl nitrate	-45.6	-48.4	-2.8
$C_4H_4N_4O_7$	4,5-Furazandimethanol dinitrate	2.6 ± 0.6	3.0	0.4
$C_4H_8N_4O_4$	1,4-Dinitropiperazine	13.9 ± 0.6	13.0	-0.9
$C_4H_9NO_2$	1-Nitrobutane	-34.4	-38.6	-4.2
$C_4H_9NO_2$	2-Nitrobutane	-39.1	-40.5	-1.4
$C_5H_{10}N_2O_2$	1-Nitropiperidine	-10.6 ± 0.6	-11.3	-0.7
$C_6H_6N_2O_2$	*m*-Nitroaniline	14.9 ± 0.4	17.0	2.1
$C_7H_6N_2O_4$	*o*,*p*-Dinitrotoluene	7.9 ± 0.8	4.0	-3.9
$C_7H_7NO_2$	*p*-Nitrotoluene	7.4 ± 0.9	4.5	-2.9
$C_8H_9NO_2$	2-Nitro-*m*-xylene	2.1 ± 0.4	1.6	-0.5

[a] Unit in kcal mol^{-1}. 1 cal = 4.184 J. $\Delta = \Delta_f H^0_{\mathrm{calc(g)}} - \Delta_f H^0_{\mathrm{exp(g)}}$.

Table 4
Statistical analysis of the ab initio method used in this study[a]

	Number of compounds	Maximum negative deviation	Maximum positive deviation	$\overline{\Delta}$	$\overline{\lvert\Delta\rvert}$	$\sqrt{\overline{(\Delta-\overline{\Delta})^2}}$
Determination	28	−3.6	3.7	−0.06	1.72	2.09
Validation	16	−4.2	5.5	−1.06	2.43	2.61

[a] Unit in kcal mol^{-1}. 1 cal = 4.184 J. $\overline{\lvert\Delta\rvert}$: mean absolute deviation.

tributed to the exclusion of nitroso molecules from our derivation set, and as a consequence our method is not appropriate for a molecule containing three nitroso groups. It is worth mentioning that the standard enthalpy of formation at 298 K in the literature for TTT is 94.3 kcal mol^{-1} without any experimental uncertainty reported. Thus the issue of whether the method of Rice et al. [12] functions better overall or simply provides a superior result for this particular compound remains to be clarified. Both methods perform reasonably well for another nitroso molecule, namely nitrosobenzene. It should furthermore be borne in mind that some data given in the literature are either erroneous or just rough estimates [17].

For the remaining 31 species included in the derivation set of Rice et al. [12], the two methods appear to be approximately equivalent. It is, however, noteworthy that all those 31 compounds are included in the derivation set of Rice et al. [12], whereas only 8 of them are included in the derivation set in the present work.

4. Results and discussion

Table 5 gives the calculated gas-phase standard enthalpies of formation at 298.15 K for a total of 42 common energetic compounds taken from the common military list of the European Union [18]. Only those compounds whose data are not available elsewhere are considered here. Tables 6 and 7 provide, respectively, the values of C_p and S over a wide temperature range of 300–5000 K. These properties are needed in the detailed modeling of reaction mechanisms. They are also required for calculating combustion-wave characteristics and burning properties. The entropies and heat capacities are calculated following the harmonic oscillator approximation. This approximation is the one generally used in the combustion chemistry field. Heat capacities and entropies corrected for anharmonic molecular motions, in particular internal rotations, are seen to be approximately equal to uncorrected C_p^0 and S^0 [19]. Furthermore, if one considers that the heat capacities and entropies are computed at ±2 cal K^{-1} mol^{-1} for C_p^0 and at ±3 cal K^{-1} mol^{-1} for S^0, then the corrections due to the neglect of internal rotations are not significant here (they are generally within the computational error). Figs. 1 and 2 show a comparison between uncorrected C_p^0 and S^0, presented in Tables 6 and 7, and C_p^0 and S^0 corrected for internal rotations, as reported by Lyman et al. [20]. Because of the lack of experimental measurements for the gas-phase enthalpies of formation of these compounds, the results presented here can be compared only with predictions from other theoretical work, where available, to assess the model's accuracy. Such a comparison is still limited; the comprehensive study of Byrd and Rice [16], for instance, allows the estimation of the gas-phase enthalpies of formation for only 7 of the 42 compounds listed in Table 5.

Politzer et al. [21] computed at the B3P86/6-31 + G(d,p) level the standard enthalpy of formation at 298.15 K for gaseous DADE (FOX-7) and reported a value of −1 kcal mol^{-1}. By using the two methods reported in Byrd and Rice [16], we derived values of −2.1 kcal mol^{-1} and of −2.3 kcal mol^{-1}. These results appears to be consistent with the prediction of 0.1 kcal mol^{-1} from the present analysis.

For DNGU (DINGU), Türker and Atalar [22] did semiempirical PM3 calculations with a B3LYP/6-31G(d,p)-optimized geometry. The resulting gas-phase enthalpy of formation of −26.23 kcal mol^{-1} (temperature and pressure not specified) agrees well with the value of −28.7 kcal mol^{-1} obtained here.

Several different values have been given for the standard enthalpy of formation of HMX at 298.15 K. These include 67.9 ± 2 kcal mol^{-1} by Cobos [23] using DFT calculations for selected isodesmic reactions. Other reported values are 65.2 ± 0.7 kcal mol^{-1} [20], 65.7 ± 7 kcal mol^{-1} [24], and 59.5 kcal mol^{-1} [25]. We derived two values of 51.8 kcal mol^{-1} (method of atom equivalents) and 67.0 kcal mol^{-1} (method of group equivalents) using the methods and data reported by Byrd and Rice [16]. The method of atom equivalents is seen to be in better agreement with the experimental data than the method of group equivalents according to Byrd and Rice [16]. This is probably not the case for HMX. The present prediction of 61.7 kcal mol^{-1} is consistent with other predictions, except for the 51.8 kcal mol^{-1} value derived from the data reported in Byrd and Rice [16].

Table 5

Calculated gas-phase standard enthalpies of formation at 298.15 K for selected energetic materials for which no experimental data are available in the literature, except HNS

Abbreviation	Formula	CAS registry No.	$\Delta_f H^0_{(g)}$ (kcal mol^{-1})	$E_j + \mathrm{ZPE}_j +$ thermal corrections (Hartree molecule^{-1})
Nitroguanidine	$CH_4N_4O_2$	556-88-7	10.7	−409.782849
5-Azido-2-nitrotriazole	$C_2HN_7O_2$	53566-50-0	121.6	−610.246164
NTO (ONTA)	$C_2H_2N_4O_3$	932-64-9	−0.9	−521.907475
ADNT	$C_2H_2N_6O_4$		79.2	−706.451485
DADE (FOX-7)	$C_2H_4N_4O_4$		0.1	−598.222684
FDIA	$C_3HN_4O_4F$		44.4	−734.261791
DNI	$C_3H_2N_4O_4$	5213-49-0	28.9	−635.122260
DNAM	$C_3H_3N_7O_5$	19899-80-0	24.4	−875.158410
TNAZ	$C_3H_4N_4O_6$	97645-24-4	26.5	−786.594550
K-6 (Keto-RDX)	$C_3H_4N_6O_7$	115029-35-1	24.4	−971.284271
NNHT	$C_3H_6N_6O_4$	130400-13-4	40.4	−746.960617
DBT	$C_4H_2N_8O_4$	30003-46-4	94.1	−892.177038
DNBT	$C_4H_2N_8O_4$	70890-46-9	104.3	−892.160876
TNGU (Sorguyl)	$C_4H_2N_8O_{10}$	55510-03-7	25.8	−1343.220276
DDPO (PZO)	$C_4H_4N_6O_5$	194486-77-6	25.1	−859.091568
DNFP	$C_4H_4N_6O_5$		90.1	−858.983605
DINGU (DNGU)	$C_4H_4N_6O_6$	55510-04-8	−28.7	−934.337279
DAAzF	$C_4H_4N_8O_2$	78644-90-3	145.3	−742.957862
DAAOF	$C_4H_4N_8O_3$		138.5	−818.121751
K-55 (Keto-bicyclic HMX)	$C_4H_4N_8O_9$	130256-72-3	48.0	−1269.193326
BNNII	$C_4H_6N_8O_4$		61.4	−894.567263
HMX	$C_4H_8N_8O_8$	2691-41-0	61.7	−1196.343791
DDFP	$C_4N_8O_6$		173.1	−1041.201005
ADNBF	$C_6H_3N_5O_6$	97096-78-1	58.2	−955.072889
CL-14	$C_6H_4N_6O_6$	117907-74-1	54.2	−1010.426755
DATB	$C_6H_5N_5O_6$	1630-08-6	0.5	−956.332511
TATB	$C_6H_6N_6O_6$	3058-38-6	−0.7	−1011.681760
HNIW (CL-20)	$C_6H_6N_{12}O_{12}$	135285-90-4	141.0	−1790.947001
TEDDZ	$C_6H_8N_8O_4F_8$		2.8	−1770.032757
TNFX	$C_6H_8N_8O_8F_4$		15.4	−1671.630874
TNAD	$C_6H_{10}N_8O_8$	135877-16-6	75.5	−1273.714492
TNP	$C_6N_8O_8$	229176-04-9	235.3	−1267.621752
PAT	$C_7H_4N_8O_6$		107.7	−1157.972953
Tetryl	$C_7H_5N_5O_8$	479-45-8	36.4	−1144.691116
PDNT	$C_8H_2N_8O_{10}$		94.8	−1495.553991
PATO	$C_8H_5N_7O_6$		69.2	−1141.972373
SAT	$C_8H_5N_{13}O_6$		192.9	−1470.343230
PTIA	$C_9H_2N_8O_{12}$		87.6	−1683.988481
BTATNB	$C_{10}H_7N_{11}O_6$		129.3	−1438.320591
TACOT	$C_{12}H_4N_8O_8$	25243-36-1	152.0	−1498.785660
HNS	$C_{14}H_6N_6O_{12}$	20062-22-0	69.0	−1767.398024
PYX	$C_{17}H_7N_{11}O_{16}$	38082-89-2	73.6	−2456.42568

No experimental value is reported for this enthalpy in the literature. It is, however, possible to estimate it indirectly from the following experimental data: $\Delta_f H^0_{298\mathrm{K}\,(\mathrm{solid\,HMX})} = 18.0\ \mathrm{kcal\,mol^{-1}}$ [26], $\Delta_{\mathrm{sub}} H^0$ (371–403 K) $= 41.9\ \mathrm{kcal\,mol^{-1}}$ [27], $C^0_{\mathrm{p\,solid}} = 69.36\ \mathrm{cal\,mol^{-1}\,K^{-1}}$ in the temperature range of 290–345 K [28], and $C^0_{\mathrm{p\,gas}} = 0.16T + 18.6\ \mathrm{cal\,mol^{-1}\,K^{-1}}$ in the temperature range of 300–400 K obtained here. These numbers can be substituted into the following equation to obtain the value of 59.7 kcal mol^{-1} for the standard enthalpy of formation for gaseous HMX at 298 K.

$$\Delta_f H^0_{\mathrm{gas},298\mathrm{K}} = \Delta_f H^0_{\mathrm{solid},298\mathrm{K}} + \Delta_{\mathrm{sub}} H^0_{371\mathrm{K}} + \int_{371}^{298} \left(C^0_{\mathrm{p\,gas}} - C^0_{\mathrm{p\,solid}}\right) \mathrm{d}T.$$

Table 6a
Calculated C_p^0 (cal mol^{-1} K^{-1}) in the temperature range of 300–1500 K

Species	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
ONTA	28.1	34.2	39.1	42.9	48.1	51.4	55.9
ADNT	37.5	45.1	51.4	56.3	63.1	67.3	72.9
DADE (FOX-7)	36.4	43.8	49.6	54.2	60.6	64.9	71.1
5-Azido-2-nitrotriazole	33.0	39.6	44.9	49.0	54.6	58.1	62.5
DNI	33.2	40.7	46.8	51.5	58.0	62.0	67.3
DNAM	47.7	58.1	66.3	72.7	81.5	87.0	94.4
TNAZ	42.4	52.1	60.0	66.3	75.1	80.8	88.4
K6	51.4	62.7	72.1	79.4	89.7	96.3	105.1
Nitroglycerine	51.7	62.7	71.7	78.9	89.0	95.6	104.6
NNHT	43.5	54.4	63.4	70.6	81.0	87.8	97.3
RDX	49.2	61.5	71.7	79.7	91.2	98.7	108.9
FDIA	36.5	43.8	49.6	54.1	60.3	64.0	68.6
TNGU	67.8	81.9	93.2	101.8	113.6	120.8	129.7
DBT	46.7	57.4	66.1	72.9	82.2	87.9	95.2
DNBT	46.6	57.3	66.1	73.0	82.3	88.1	95.3
DDPO	50.9	61.6	70.0	76.4	85.5	91.2	99.2
DNFP	46.3	57.7	66.9	74.2	84.4	90.9	99.5
DINGU	50.2	62.1	71.7	79.1	89.4	96.0	104.7
DAAzF	46.9	57.2	65.3	71.6	80.2	85.8	93.4
DAAOF	49.9	60.9	69.5	76.2	85.3	91.2	99.1
K55	65.5	80.5	92.6	102.0	114.9	123.0	133.4
BNNII	52.3	65.6	76.3	84.6	96.2	103.7	114.0
HMX	66.9	83.0	96.5	107.2	122.6	132.7	146.4
DDFP	51.5	62.7	71.4	78.0	86.8	91.8	97.8
TNAD	72.7	91.8	107.8	120.5	138.7	150.6	167.0
o,*p*-Trinitrobenzene	46.5	57.1	65.6	72.2	81.4	87.2	94.7
ADNBF	53.1	65.1	74.5	81.7	91.6	97.8	105.9
CL-14	57.8	71.1	81.4	89.3	100.2	107.0	116.1
DATB	56.0	69.0	79.3	87.3	98.4	105.4	115.1
CL-20	91.1	114.2	132.6	146.8	166.1	178.1	193.4
TATB	60.3	74.8	86.1	94.9	106.9	114.7	125.4
TEDDZ	92.5	112.8	128.6	140.7	157.4	167.9	182.0
TNFX	90.0	109.8	125.7	138.1	155.4	166.4	181.3
TNP	65.9	79.4	89.8	97.6	107.9	113.8	120.7
PAT	64.9	80.0	92.1	101.5	114.4	122.5	133.0
TNT	52.5	64.4	74.2	82.0	93.0	100.1	109.8
Tetryl	65.5	79.6	91.2	100.3	113.2	121.4	132.4
PDNT	78.9	95.4	108.6	118.9	133.0	141.5	152.0
SAT	82.6	102.3	118.1	130.4	147.2	157.6	171.1
PATO	65.5	81.2	93.8	103.7	117.4	126.0	137.5
PTIA	88.9	107.0	121.5	132.8	148.2	157.5	169.0
Nitroguanidine	26.8	32.4	36.9	40.4	45.4	48.9	54.1
TACOT	52.5	64.4	74.2	81.9	92.9	100.1	109.7
HNS	101.7	124.2	142.4	156.6	176.2	188.5	204.5
PYX	138.4	169.2	193.9	213.0	239.3	255.7	276.7

If Byrd and Rice's value [16] for the standard enthalpy of formation of solid HMX at 298 K is used, the value for gaseous HMX at 298 K becomes 66.2 kcal mol^{-1}. Other estimates are possible if one considers different experimental data in the calculation. It is not easy to determine which of these results is the most reliable. Nevertheless, in light of the similar chemical structures of HMX and RDX and the accurate prediction of the standard enthalpy of formation of gaseous RDX at 298 K (see Table 3), the value for HMX calculated from the present analysis should be considered reliable.

Türker [29] reported an enthalpy of formation of 47.1 kcal mol^{-1} (state, temperature, and pressure not specified) for nitroguanidine by means of the semiempirical method AM1, whereas we derived two values, 11.4 kcal mol^{-1} (method of atom equivalents) and 15.2 kcal mol^{-1} (method of group equivalents), with methods and data reported by Byrd and Rice [16]. The result of Türker [29] disagrees with our prediction of

Table 6b
Calculated C_p^0 (cal mol^{-1} K^{-1}) in the temperature range of 2000–5000 K

Species	2000 K	2500 K	3000 K	3500 K	4000 K	4500 K	5000 K
ONTA	58.1	59.2	59.9	60.3	60.6	60.8	61.0
ADNT	75.5	76.8	77.6	78.1	78.4	78.6	78.8
DADE (FOX-7)	74.2	75.9	76.9	77.5	78.0	78.3	78.5
5-Azido-2-nitrotriazole	64.5	65.5	66.1	66.5	66.7	66.9	67.0
DNI	69.8	71.0	71.7	72.2	72.5	72.7	72.8
DNAM	97.8	99.6	100.7	101.4	101.8	102.1	102.3
TNAZ	91.9	93.7	94.8	95.4	95.9	96.2	96.4
K6	109.1	111.2	112.3	113.1	113.6	113.9	114.2
Nitroglycerine	108.7	110.9	112.2	112.9	113.5	113.8	114.1
NNHT	101.8	104.2	105.7	106.6	107.2	107.6	107.9
RDX	113.6	116.1	117.6	118.5	119.1	119.6	119.9
FDIA	70.6	71.6	72.2	72.5	72.7	72.9	73.0
TNGU	133.5	135.4	136.5	137.2	137.6	137.9	138.1
DBT	98.4	100.0	101.0	101.6	102.0	102.2	102.4
DNBT	98.5	100.1	101.0	101.6	102.0	102.3	102.5
DDPO	103.0	105.0	106.2	107.0	107.5	107.9	108.1
DNFP	103.3	105.3	106.5	107.2	107.7	108.0	108.2
DINGU	108.8	110.9	112.1	112.9	113.5	113.8	114.1
DAAzF	97.1	99.1	100.3	101.0	101.6	101.9	102.2
DAAOF	102.9	105.0	106.2	107.0	107.5	107.9	108.1
K55	138.0	140.4	141.7	142.6	143.1	143.5	143.8
BNNII	118.9	121.6	123.2	124.2	124.9	125.3	125.7
HMX	152.8	156.2	158.1	159.3	160.2	160.7	161.1
DDFP	100.1	101.2	101.9	102.2	102.5	102.7	102.8
TNAD	174.6	178.6	181.0	182.4	183.4	184.1	184.6
o,*p*-Trinitrobenzene	98.1	99.8	100.8	101.5	101.9	102.2	102.4
ADNBF	109.5	111.4	112.5	113.2	113.7	114.0	114.2
CL-14	120.3	122.6	123.9	124.7	125.3	125.7	125.9
DATB	119.7	122.1	123.5	124.5	125.1	125.5	125.8
CL-20	200.2	203.7	205.7	206.9	207.8	208.3	208.8
TATB	130.5	133.3	134.9	136.0	136.7	137.1	137.5
TEDDZ	188.5	191.8	193.8	195.0	195.9	196.4	196.9
TNFX	188.0	191.5	193.6	194.9	195.7	196.3	196.8
TNP	123.4	124.7	125.4	125.9	126.2	126.4	126.5
PAT	137.7	140.1	141.6	142.4	143.0	143.5	143.8
TNT	114.2	116.5	117.9	118.7	119.3	119.7	120.0
Tetryl	137.3	139.9	141.4	142.3	142.9	143.4	143.7
PDNT	156.4	158.7	159.9	160.7	161.2	161.6	161.8
SAT	177.2	180.4	182.2	183.4	184.1	184.7	185.1
PATO	142.7	145.4	147.0	148.1	148.7	149.2	149.5
PTIA	173.8	176.2	177.5	178.4	178.9	179.3	179.6
Nitroguanidine	56.8	58.3	59.2	59.8	60.2	60.5	60.7
TACOT	114.1	116.5	117.8	118.7	119.2	119.6	119.9
HNS	211.6	215.3	217.4	218.7	219.6	220.2	220.7
PYX	285.9	290.6	293.4	295.1	296.2	297.0	297.6

10.7 kcal mol^{-1}, although both calculations lead to a positive enthalpy of formation. The AM1 calculations are generally regarded very rough estimates. Our value is consistent with the data derived from Byrd and Rice [16].

For gas-phase TNAZ at 298.15 K, Wilcox et al. [30] reported a standard enthalpy of formation of 26.22 kcal mol^{-1} using G3(MP2)//B3LYP/6-31G(d) calculations together with an atom-based correction protocol. This result agrees well with our prediction of 26.5 kcal mol^{-1}, demonstrating the effectiveness of the present approach since the G3 method is of the highest accuracy among the existing techniques. Politzer et al. [31] reported a value of 30.7 kcal mol^{-1} using a less accurate technique than the G3(MP2)//B3LYP/6-31G(d) method employed by Wilcox et al. [30].

For TNAD, Liu et al. [32] reported two different values for the gas-phase enthalpy of formation at 298 K, 64.7 and 59.4 kcal mol^{-1}, obtained, respec-

Table 7a
Calculated S^0 (cal mol^{-1} K^{-1}) in the temperature range of 300–1500 K

Species	300 K	400 K	500 K	600 K	800 K	1000 K	1500 K
ONTA	85.2	94.2	102.4	109.9	123.0	134.1	156.0
ADNT	101.3	113.2	124.0	133.8	151.0	165.6	194.1
DADE (FOX-7)	95.4	106.9	117.4	126.8	143.4	157.4	185.1
5-Azido-2-nitrotriazole	94.7	105.2	114.6	123.2	138.1	150.7	175.2
DNI	94.5	105.1	114.9	123.9	139.7	153.1	179.4
DNAM	117.7	132.9	146.8	159.5	181.7	200.6	237.5
TNAZ	109.8	123.4	135.9	147.5	167.8	185.3	219.7
K6	125.6	142.0	157.0	170.8	195.2	216.0	257.0
Nitroglycerine	132.6	149.1	164.1	177.8	202.0	222.6	263.3
NNHT	108.7	122.7	135.9	148.1	170.0	188.8	226.4
RDX	116.4	132.3	147.2	161.0	185.6	206.8	249.0
FDIA	100.9	112.5	122.9	132.4	148.9	162.8	189.7
TNGU	146.0	167.5	187.1	204.9	235.9	262.1	313.0
DBT	117.5	132.4	146.2	158.9	181.2	200.3	237.5
DNBT	117.3	132.3	146.0	158.7	181.1	200.1	237.5
DDPO	112.9	129.1	143.7	157.1	180.4	200.2	238.9
DNFP	112.0	126.9	140.8	153.7	176.6	196.1	234.9
DINGU	116.5	132.7	147.6	161.4	185.7	206.4	247.2
DAAzF	108.7	123.7	137.3	149.8	171.7	190.2	226.7
DAAOF	113.8	129.8	144.3	157.6	180.9	200.6	239.3
K55	142.2	163.1	182.5	200.2	231.5	258.0	310.2
BNNII	119.3	136.2	152.1	166.7	192.8	215.1	259.4
HMX	141.5	163.0	183.1	201.6	234.8	263.3	320.1
DDFP	122.1	138.5	153.5	167.1	190.9	210.8	249.4
TNAD	144.3	167.9	190.2	211.0	248.3	280.7	345.3
o,*p*-Trinitrobenzene	113.7	128.6	142.2	154.8	177.0	195.8	232.8
ADNBF	116.1	133.1	148.7	162.9	187.9	209.0	250.4
CL-14	120.1	138.6	155.7	171.2	198.5	221.7	267.1
DATB	121.4	139.4	155.9	171.1	197.9	220.6	265.5
CL-20	167.3	196.8	224.3	249.8	295.0	333.4	409.0
TATB	129.8	149.2	167.2	183.7	212.8	237.6	286.4
TEDDZ	164.1	193.6	220.6	245.2	288.1	324.5	395.7
TNFX	164.5	193.2	219.5	243.6	285.9	321.9	392.6
TNP	134.9	155.7	174.7	191.8	221.4	246.2	293.9
PAT	138.0	158.8	178.0	195.7	226.8	253.3	305.2
TNT	120.1	136.9	152.3	166.6	191.8	213.4	256.0
Tetryl	139.6	160.5	179.5	197.0	227.8	254.0	305.6
PDNT	165.2	190.2	213.0	233.8	270.1	300.7	360.4
SAT	160.7	187.3	211.9	234.5	274.6	308.6	375.5
PATO	137.3	158.4	177.9	195.9	227.8	255.0	308.6
PTIA	180.4	208.6	234.1	257.3	297.8	331.9	398.4
Nitroguanidine	82.1	90.6	98.3	105.4	117.7	128.3	149.2
TACOT	120.0	136.8	152.3	166.5	191.7	213.3	256.0
HNS	195.7	228.1	257.9	285.2	333.2	373.9	453.9
PYX	236.8	280.9	321.4	358.5	423.7	479.0	587.3

tively, by means of atom-based-corrected B3LYP/6-31++G//B3LYP/6-31G(d,p) and B3LYP/6-31+G(d)//B3LYP/6-31G(d,p) calculations. Both results differ from the present prediction by about 10–15 kcal mol^{-1}, although the three estimation procedures follow almost identical computational methods. Liu et al. [32] also performed calculations for RDX (34.0 and 32.3 kcal mol^{-1}). The discrepancy from the measured data of 45.8 kcal mol^{-1} is about 10 kcal mol^{-1}. Further calculations were conducted for HMX by Liu et al. [32]. The results of 42.7 and 44.3 kcal mol^{-1} differ from other theoretical estimations [16,20,23–25], and from the present work by $\sim$10–20 kcal mol^{-1}. These discrepancies may result from the use of a standard enthalpy of formation of 44.9 kcal mol^{-1} at 298 K for gas-phase HMX, as recommended by Burcat [5]; the value was considered erroneous by Cobos [23]. This demonstrates the importance of the quality of the data selected for the derivation set. The bias introduced

Table 7b
Calculated S^0 (cal mol^{-1} K^{-1}) in the temperature range of 2000–5000 K

Species	2000 K	2500 K	3000 K	3500 K	4000 K	4500 K	5000 K
ONTA	172.4	185.5	196.3	205.6	213.7	220.8	227.3
ADNT	215.5	232.5	246.6	258.6	269.0	278.3	286.6
DADE (FOX-7)	206.0	222.7	236.7	248.6	259.0	268.2	276.4
5-Azido-2-nitrotriazole	193.5	208.1	220.1	230.3	239.2	247.1	254.1
DNI	199.1	214.9	227.9	239.0	248.6	257.2	264.8
DNAM	265.2	287.2	305.5	321.0	334.6	346.6	357.4
TNAZ	245.6	266.4	283.6	298.2	311.0	322.3	332.4
K6	287.9	312.5	332.9	350.2	365.4	378.8	390.8
Nitroglycerine	294.1	318.6	338.9	356.3	371.4	384.8	396.8
NNHT	255.1	278.1	297.3	313.7	327.9	340.6	352.0
RDX	281.1	306.7	328.1	346.3	362.1	376.2	388.8
FDIA	209.8	225.7	238.8	249.9	259.6	268.2	275.9
TNGU	350.9	380.9	405.7	426.8	445.2	461.4	475.9
DBT	265.4	287.5	305.9	321.5	335.1	347.1	357.9
DNBT	265.4	287.5	305.9	321.5	335.1	347.1	357.9
DDPO	268.0	291.2	310.5	326.9	341.2	353.9	365.3
DNFP	264.1	287.4	306.7	323.2	337.5	350.2	361.6
DINGU	278.0	302.5	322.8	340.2	355.3	368.7	380.7
DAAzF	254.1	276.0	294.2	309.7	323.2	335.2	346.0
DAAOF	268.4	291.6	310.9	327.3	341.6	354.3	365.7
K55	349.3	380.4	406.1	428.0	447.1	464.0	479.1
BNNII	293.0	319.8	342.1	361.2	377.8	392.6	405.8
HMX	363.2	397.7	426.3	450.8	472.1	491.0	508.0
DDFP	277.9	300.4	318.9	334.6	348.3	360.4	371.2
TNAD	394.5	433.9	466.7	494.7	519.2	540.8	560.2
o,*p*-Trinitrobenzene	260.5	282.6	300.9	316.5	330.1	342.1	352.9
ADNBF	281.5	306.1	326.5	343.9	359.1	372.5	384.5
CL-14	301.1	328.2	350.7	369.9	386.6	401.3	414.6
DATB	299.3	326.3	348.7	367.8	384.5	399.2	412.5
CL-20	465.7	510.8	548.2	580.0	607.7	632.2	654.2
TATB	323.3	352.8	377.2	398.1	416.3	432.5	446.9
TEDDZ	449.0	491.5	526.7	556.6	582.8	605.9	626.6
TNFX	446.8	488.2	523.3	553.3	579.4	602.5	623.2
TNP	329.1	356.8	379.6	399.0	415.8	430.7	444.0
PAT	344.2	375.2	400.9	422.8	441.9	458.8	473.9
TNT	288.3	314.1	335.4	353.7	369.6	383.6	396.3
Tetryl	344.5	375.4	401.1	422.9	442.0	458.8	474.0
PDNT	404.9	440.0	469.1	493.8	515.3	534.3	551.3
SAT	425.6	465.5	498.6	526.8	551.3	573.0	592.5
PATO	348.9	381.1	407.8	430.5	450.3	467.9	483.6
PTIA	447.7	486.8	519.1	546.5	570.4	591.5	610.4
Nitroguanidine	165.2	178.0	188.7	197.9	205.9	213.0	219.4
TACOT	288.2	314.0	335.4	353.6	369.5	383.6	396.2
HNS	513.8	561.4	600.9	634.5	663.8	689.7	712.9
PYX	668.3	732.7	785.9	831.3	870.8	905.7	937.0

was so substantial that the values estimated for TNAD by Liu et al. [32] cannot be considered reliable.

Türker and Atalar [33] reported three different values for the enthalpy of formation of NTO (ONTA) based on three PM3 calculations with different optimized geometries: 8.4, 10.6, and −3.0 kcal mol^{-1}. No indication, however, was given about the relative accuracy of these results. The last value is consistent with the present prediction of −0.9 kcal mol^{-1}.

For DATB, we derive two values according to the methods and data reported by Byrd and Rice [16]: −3.1 kcal mol^{-1} (method of atom equivalents) and −3.4 kcal mol^{-1} (method of group equivalents). These results are in agreement with the value reported in the present work: 0.5 kcal mol^{-1}. Wang et al. [34] report a value of −6.6 kcal mol^{-1} for DATB using the PM3 method.

For TATB, we derive two values according to the methods and data reported by Byrd and Rice [16]:

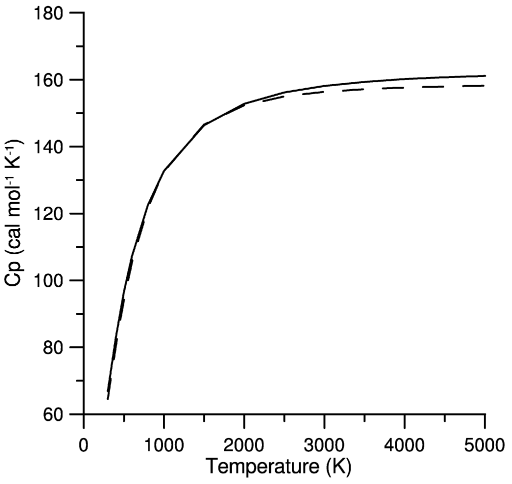

Fig. 1. Comparison between uncorrected C_p^0 and corrected C_p^0 for internal rotations for HMX. Dashed line: corrected C_p^0 according to Lyman et al. [20].

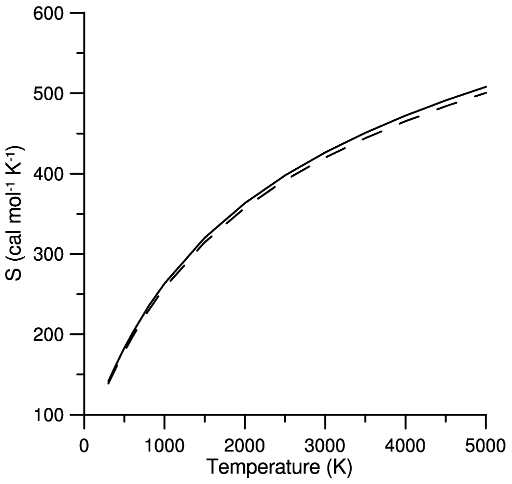

Fig. 2. Comparison between uncorrected S^0 and corrected S^0 for internal rotations for HMX. Dashed line: corrected S^0 according to Lyman et al. [20].

−4.1 kcal mol^{-1} (method of atom equivalents) and −4.4 kcal mol^{-1} (method of group equivalents). These results are in agreement with the value reported in the present work: −0.7 kcal mol^{-1}. Wang et al. [34] report a value of −10.8 kcal mol^{-1} for TATB using the PM3 method.

For Tetryl, we derive two values according to the methods and data reported by Byrd and Rice [16]: 32.9 kcal mol^{-1} (method of atom equivalents) and 36.4 kcal mol^{-1} (method of group equivalents). These results are in agreement with the value reported in the present work: 36.4 kcal mol^{-1}.

For CL-20, we derive two values according to the methods and data reported by Byrd and Rice [16]: 120.7 kcal mol^{-1} (method of atom equivalents) and 143.6 kcal mol^{-1} (method of group equivalents). Although the two methods proposed by Byrd and Rice [16] lead to comparable results for FOX-7, DATB, TATB, and Tetryl, they lead to quite different enthalpies of formation for CL-20. This is also the case for HMX. The value obtained with the method of group equivalents is consistent with the value reported in this study: 141.0 kcal mol^{-1}.

For PYX, the largest molecule in our list, Wang et al. [34] report a value of 52.9 kcal mol^{-1}, which is not consistent with our data of 73.6 kcal mol^{-1}. Wang et al. [34] do not discuss the validity of the PM3 method that they used because they needed only a rough estimate of this enthalpy for their purposes.

Data are available [35] for some of the energetic compounds considered here (DAAzF, TATB, FOX-7), but the capability of the method employed in this paper to predict reliable thermodynamic data for energetic materials has not been demonstrated. In particular, the authors did not thoroughly validate their method with known energetic materials. For instance, Zhang et al. [35] report a value of 32 kcal mol^{-1} for the gas-phase standard enthalpy of formation of DADE (FOX-7), which is far off the other available values obtained with four different methods (−1, −2.1, −2.3, 0.1 kcal mol^{-1}). Zhang et al. [35] report a value of 74 kcal mol^{-1} for gas-phase standard enthalpy of formation of TATB, which is also far off the other estimates (−4.1, −4.4, −0.7 kcal mol^{-1}). Therefore, the value reported by Zhang et al. [35] for DAAzF (121 kcal mol^{-1}) is doubtful and is not reported here.

5. Conclusions

Ab initio quantum chemical calculations based on the B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) technique have been used to determine the enthalpies of formation, heat capacities, and entropies of 42 selected energetic compounds in the gas phase. These properties are available, experimentally or theoretically, for only a few of the 42 energetic compounds considered. Information of this kind is essential for modeling combustion-wave structures and burning properties of energetic materials. Although the present ab initio technique has been benchmarked against the thermochemical properties of several energetic compounds, more experimental measurements are always needed to validate these computations. Future work will predict the thermodynamic properties of molecules and radicals formed during the thermal decomposition and combustion of the materials considered in this study. Results from these efforts will facilitate the development of detailed reaction mechanisms.

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Supplementary material

The online version of this article contains additional supplementary material.

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