Determination of Enthalpies of Formation of Energetic Molecules with Composite Quantum Chemical Methods

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Abstract

We report gas-phase enthalpies of formation for the set of energetic molecules NTO, DADE, LLM-105, TNT, RDX, TATB, HMX, and PETN using the G2, G3, G4, and ccCA-PS3 quantum composite methods. Calculations for HMX and PETN hitherto represent the largest molecules attempted with these methods. G3 and G4 calculations are typically close to one another, with a larger difference found between these methods and ccCA-PS3. Although there is significant uncertainty in experimental values, the mean absolute deviation between the average experimental value and calculations are 12, 6, 7, and 3 kcal/mol for G2, G3, G4, and ccCA-PS3, respectively.

The enthalpy of formation (ΔH_f^0) of energetic materials such as explosives and propellants is an essential thermodynamic quantity that is a prerequisite to determine a variety of functions associated with the performance of these materials. Heat of explosion, detonation velocity and pressure, and specific impulse, are all important thermodynamic characteristics of energetic materials that are related to their ΔH_f^0 . [1,2] In designing new energetic materials, therefor, it is very advantageous to determine the enthalpy of formation as accurately as possible *a priori* in order to establish the desired performance characteristics of the candidate materials before embarking on a costly synthesis effort. Even for existing energetic materials, such as organic solids containing the elements C, H, N, and O, experimental measurements of the enthalpy of formation are often based on a single determination. This makes it difficult to assess the accuracy of the determined ΔH_f^0 , considering that various factors such as sample impurity and assumptions of final equilibrium detonation products can greatly produce variable results.[3] These are clearly manifested in the case of existing multiple measurements such as for the explosives TATB and TNT (see Table I). Finally, due to low vapor pressure of most energetic solids and liquids, ΔH_f^0 gas-phase measurements are virtually nonexistent.

Computationally, several schemes have been devised for calculating ΔH_f^0 of energetic molecules at various levels of complexity. Empirical methods provide values based on group additivity, where groups of atoms within the molecule are assigned certain enthalpy values. [4] More elaborate atom and group-equivalent schemes based on density functional theoretical (DFT) calculations were also developed to predict gas-phase enthalpy of formation with modest computational requirements. [5,6] These semi-

empirical methods rely on a set of “training” molecules for which their experimental ΔH_f^0 data is available and electronic energies are calculated. DFT calculations with added empirical atomic corrections were also implemented. [7]

Even though the condensed phase enthalpy of formation is usually of most interest in the performance of energetic systems, a tractable way to determine its value is through separate calculations of the gas-phase enthalpy of formation and the enthalpy of sublimation. We confine the present study to the gas-phase enthalpy of formation. As it has been described previously, [8] accurate predictions of gas-phase enthalpy of formations for molecules, $\Delta H_{f(g)}^0$, with composition $C_wH_xN_yO_z$ can be determined at $T=298$ K from the known enthalpies of formation of the isolated atoms and the calculated atomization energies:

$$\begin{aligned} \Delta H_f^0(C_wH_xN_yO_z, 298 \text{ K}) = & \Delta H_f^0(C_wH_xN_yO_z, 0 \text{ K}) + [H^0(C_wH_xN_yO_z, 298 \text{ K}) - \\ & H^0(C_wH_xN_yO_z, 0 \text{ K})] - w[H^0(C, 298 \text{ K}) - H^0(C, 0 \text{ K})]_{ST} - x[H^0(H, 298 \text{ K}) - \\ & H^0(H, 0 \text{ K})]_{ST} - y[H^0(N, 298 \text{ K}) - H^0(N, 0 \text{ K})]_{ST} - z[H^0(O, 298 \text{ K}) - H^0(O, 0 \text{ K})]_{ST} \end{aligned} \quad (1)$$

The enthalpy of formation at 0 K in (1) is given by:

$$\begin{aligned} \Delta H_f^0(C_wH_xN_yO_z, 0 \text{ K}) = & w\Delta H_f^0(C, 0 \text{ K}) + x\Delta H_f^0(H, 0 \text{ K}) + y\Delta H_f^0(N, 0 \text{ K}) + \\ & z\Delta H_f^0(O, 0 \text{ K}) - \sum D_0 \end{aligned} \quad (2)$$

The atomization energy of $C_wH_xN_yO_z$, $\sum D_0$, is determined as:

$$\sum D_0 = wE_e(C) + xE_e(H) + yE_e(N) + zE_e(O) - E_0(C_wH_xN_yO_z) \quad (3)$$

where E_e is the calculated electronic energy of the atom, and E_0 is the calculated molecular energy with zero-point energy correction (ZPE). The Gn methods use nonrelativistic calculations for Eq. (3). In the ccCA, the same scalar relativistic correction is applied to atoms and molecules. In equations (1)-(3) above, accurate experimental values for the atomic ΔH_f^0 and for the standard state of the elements, $[H^0(298\text{ K}) - H^0(0\text{ K})]_{ST}$, are usually used. [9] The atomization energies, $\sum D_0$, and the enthalpies $H^0(C_wH_xN_yO_z)$ at 298 and 0 K in equation (1) can be determined from accurate electronic structure computational methods such as the quantum chemical Gaussian-n (Gn) series, which have been shown to achieve chemical accuracy for the determination of molecular energies on test sets of relatively small molecules. Achieving similar accuracies for large molecules, however, is a significant challenge. Since the atomization energy $\sum D_0$ is approximately a linear function of the number of atoms, we expect that computational errors in $\Delta H_{f(g)}^0$ will scale linearly with molecule size.

In this work, we calculate the zero and room-temperature enthalpies of formation as defined in equations (1) and (2) for the set of energetic molecules listed in Table I using the Gaussian G2, [8,10] G3, [11,12] and G4 methods, [13] and a variant of the parameter-free correlation consistent Composite Approach (ccCA-PS3). [14,15] The Gaussian-n methods were performed as implemented in Gaussian 09 program, [16] while the steps described in ref. [15] of the ccCA-PS3 method were performed using the electronic structure codes GAMESS. [17] Individual GAMESS input files were generated for each step in the composite method, using locally developed computer programs. The NWCHEM[18] program was used to perform coupled cluster calculations on PETN and HMX, since that code was found to scale more effectively to very large molecule size.

The ccCA-PS3 method variant was chosen since it was shown previously to be the most effective among the family of ccCA methods for highly energetic nitrogen-containing molecules. [19] The ccCA-PS3 calculation in Ref. 19 of RDX was repeated here for completeness and to validate the method as implemented locally with GAMESS. The list of energetic molecules in Table I includes some of the most commonly known explosive materials of current interest, such as TNT, RDX, HMX, and PETN. Even for TNT, a material that has been known for over a century, experimental ΔH_f^0 values differ by more than 7 kcal/mol, and advanced computational methods may help settle these differences. Further, the computational methods we implement in this study have been shown to produce successively more accurate molecular energies, with the G3 and G4 theories having been benchmarked against 454 experimental energies and yielding average absolute difference of 1.13 and 0.83 kcal/mol, respectively. [13,20] The ccCA methodology was also reported to yield enthalpies of formation similar to G3 theory for a set of 40 nitrogen-containing molecules, with a mean absolute difference of 1.1 kcal/mol from the experimental values. [19] Being computationally intensive and too expensive to perform, the application of these methods has been understandably limited mainly to small molecular species, while resorting to modified schemes based on variation of these methods for larger species. [21,22] Molecules containing as many as 29 atoms (with 21 second-row elements) such as PETN represent a significant computational challenge that dedicated runs on a specialty computer platform with 500 GB of physical memory distributed among 32 CPUs had to be performed for over a period of 21 days. The largest calculation with ccCA-PS3 was a single-point CCSD(T) energy calculation of PETN with a cc-pVTZ basis set. The NWCHEM code running on the LLNL Sierra cluster used

6144 processors (1024 nodes) for a period of 7 hours to perform this calculation.

Table II reports the results of the calculated zero-point-corrected electronic energies (E_0), the zero-point energies (E_{ZPE}), the enthalpies at $T=298\text{ K}$ (H_{298}), and the enthalpies of formation $\Delta H_f^0(0\text{ K})$ and $\Delta H_f^0(298\text{ K})$ at 0 and 298 K, respectively. For each molecule, the reported values are listed from top to bottom at the G2, G3, G4, and ccCA-PS3 level of theory. Where available, the average of the experimental enthalpy of formation in Table II is given in the last row. Where two experimental values are given in Table I, the absolute difference between these values is used as an estimated experimental error. When only one experimental value is reported, the experimental error in Table II is taken to be the largest of the reported errors for the enthalpy of formation and enthalpy of sublimation. In determining $\Delta H_f^0(0\text{ K})$ and $\Delta H_f^0(298\text{ K})$ via equations (1) and (2), the JANAF values for the atomic ΔH_f^0 and for the standard state of the elements, $[H^0(298\text{ K}) - H^0(0\text{ K})]_{ST}$, were used in combination with the G2, G3, and G4 results.[8,9] For atomic carbon, the ccCA-PS3 method uses $\Delta H_f^0(\text{C}, 0\text{ K}) = 170.11\text{ kcal/mol}$ instead of the JANAF value 169.98 kcal/mol . [19] For a molecule with 6 carbon atoms, such as TATB, this different choice in the experimental atomic enthalpy of formation leads to a 0.8 kcal/mol difference in the calculated value. Results from all methods of the total energies for C, N, O, and H atoms that are required in evaluating the atomization energies, $\sum D_0$, are presented in Table III.

The results of the room-temperature enthalpies of formation, $\Delta H_f^0(298\text{ K})$, in Table II reveal several important comparisons. First, the G2 $\Delta H_f^0(298\text{ K})$ values are consistently lower for all molecules on the list than values obtained with the other

methods. The range of deviation of the G2 values from G3, G4, and ccCA-PS3 values, respectively, are: 2.7 (TATB)-9.3 (HMX and PETN) kcal/mol, 1.6 (NTO and TATB)-9.6 (PETN) kcal/mol, and 3.4 (NTO)-17.3 (PETN) kcal/mol. Second, the G3 method gives enthalpies of formation values that are consistently higher than the G4 method, but with a significantly low difference between the two methods: 0.3 (PETN)-2.5 (LLM-105) kcal/mol. This difference is in accord with previous extensive studies on a wide range of smaller size molecules. [13,23] Third, the results in Table II indicate a large difference between G3 and ccCA for at least three molecules: TNT (5.9), HMX (6.5), and PETN (8.0) kcal/mol.

Comparison with experimentally determined enthalpies of formation in Table I is next considered. For these solid materials, the gas-phase reported $\Delta H_f^0(298\text{ K})$ values are obtained via Hess's law as the difference between two measured enthalpies: the condensed-phase $\Delta H_{f(s)}^0$ and the enthalpy of sublimation:

$$\Delta H_{f(s)}^0 = \Delta H_{f(g)}^0 - \Delta H_{sub}$$

Measurements of ΔH_{sub} are not available for NTO, DADE, or LLM-105, and subsequently, no $\Delta H_f^0(298\text{ K})$ values are available. For these three materials, and for TATB, however, the G3, G4, and ccCA-PS3 values are comparable to within ~2 kcal/mol. Multiple experimental measurements exist for TNT, TATB, and HMX. For TNT, G3 and G4 results agree well with the experimental value 5.75 ± 0.84 kcal/mol, [24] while the ccCA-PS3 result of 11.9 kcal/mol is in agreement with the other experimental result of 12.3 ± 1.2 kcal/mol. [3]. Since we prefer to obtain agreement between theoretical methods before choosing preferred experimental values, no definitive conclusion as to the

more accurate result can be drawn from this comparison. Similarly for TATB, the two experimental data of -6.2 [25,26] and 6.8 [25,27] kcal/mol conflict with the G4 value of 1.4 kcal/mol, while the G3 and ccCA-PS3 values of 2.5 and 3.7 kcal/mol, respectively, are in closer agreement with the experimental measurement of 6.8 kcal/mol.

The ccCA-PS3 $\Delta H_f^0(298\text{ K})$ results for RDX, HMX, and PETN are in better agreement with the measured data than those obtained from G3 and G4 methods. For RDX, the calculated ccCA-PS3 $\Delta H_f^0(298\text{ K})=45.3$ kcal/mol is in a remarkable agreement with the experimental value of 45.9 kcal/mol, [25,28] while the calculated G4 value compares poorly at 40.8 kcal/mol. Similarly for HMX, the ccCA-PS3 $\Delta H_f^0(298\text{ K})=59.8$ kcal/mol is in much closer agreement with either of the two experimental measurements 58.9 [25,28] and 62.9 [29] kcal/mol than either of the G3 or the G4 of 53.3 and 52.3 kcal/mol, respectively. For PETN, while the experimental value of -91.1 kcal/mol [30,31] differs significantly from the ccCA-PS3 value of -98.0 kcal/mol, it also compares very poorly with either the G3 value of -106.0 kcal/mol or the G4 value of -105.7 kcal/mol. The above comparisons clearly indicate better agreement of the ccCA-PS3 results with the available experimental values for RDX, HMX, and PETN.

Although there is significant uncertainty in experimental values, we find that the mean absolute deviation between the average experimental value and calculations based on values in Table II are 12, 6, 7, and 3 kcal/mol for G2, G3, G4, and ccCA-PS3, respectively. The root mean square of the estimated experimental errors in Table II is 7 kcal/mol, which limits our ability to unambiguously determine the accuracy of the methods. Nonetheless, we find a trend of increasing accuracy in comparing earlier and more recent methods. The non-empirical ccCA-PS3 method performs best overall. The

mean absolute deviations are larger than those quoted for small molecules (4-5 atoms) [12-15]. This is expected, since errors will increase proportionally to the number of atoms in the molecule.

The large difference between the ccCA-PS3 and the G4 (and G3) results for the molecules TNT, RDX, HMX and PETN is manifested in differences between their correspondingly calculated atomization energies, which are listed in Table IV. The ccCA-PS3 method consistently yields lower atomization energies for these molecules, 6.82 and 6.90 kcal/mol lower than the G4 values in the case of HMX and PETN for instance. Comparing the computational steps of the G3, G4, and ccCA-PS3 methods in obtaining the molecular energies, it may well be that level of computation at which the optimized molecular structure is determined is at play. With the G3 method, the equilibrium structure is obtained using the fully correlated MP2 level with the 6-31G* basis set and the zero-point energy (ZPE) correction is calculated at the Hartree-Fock (HF) level with the same basis. [12] With the G4 method, the equilibrium structure and the ZPE correction are determined at the B3LYP/6-31G(2*df*, *p*) level of theory, [13] while these calculations are performed at the B3LYP/cc-pVTZ level with the ccCA-PS3. [19] The use of the correlation-consistent, cc-pVXZ instead of the “Pople-style” basis sets, along with different extrapolation schemes in conjunction with the ccCA-PS3 method as the reference for the various additive corrections, is probably responsible for the observed differences in the calculated energies. We note, however, that despite the implemented level of computation, the calculated ZPE in Table II is very comparable between the three methods, with a maximum difference of 1.4 kcal/mol for PETN between G3 and the ccCA-PS3 values.

The largest difference between calculated and experimental values was found for PETN. This molecule is also the “floppiest” of the molecules studied, with 4 nitrate ester chains emanating from an sp^3 carbon center. It may be that the use of DFT without dispersion correction (as in G3, G4, and ccCA-PS3) could generate a larger error in the structure of PETN than for the other molecules. In addition, vibrational anharmonicity, which is not accounted for in the methods considered here, could be more important for PETN than for the other molecules.

One obvious difference between ccCA-PS3 and the Gn methods is the inclusion of a scalar relativistic energy calculation in the ccCA. The net relativistic energy correction may be calculated as the difference between the molecular relativistic correction and the sum of the atomic relativistic corrections. For PETN, we obtain a net relativistic correction of 3.7 kcal/mol, while for TATB we obtain a net correction of 3.6 kcal/mol. This is large enough to explain a significant portion of the difference between ccCA and G4, although the empirical “higher level correction” in Gn could be interpreted as including relativistic effects.

In conclusion, we applied advanced quantum chemical composite methods for calculating enthalpies of formation of some of the largest molecules ever attempted. Although computationally very demanding and exhaustive, our results based on these methods did not allow us to unambiguously distinguish between varying experimental values for several molecules. Nonetheless, we found evidence of significant progress in the development of accurate gas phase thermochemistry for large molecules, since the earliest method studied (G2, 12 kcal/mol) has four times the average error when compared to experiment as the latest method studied (ccCA-PS3, 3 kcal/mol).

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Table I. Available experimental enthalpies of formation of energetic molecules considered in this study.^a

Name	Stoichiometry	$\Delta H_f^0(s)$	ΔH_{sub}	$\Delta H_f^0(g)$
NTO (3-nitro-1,2,4-triazol-5-one)	$C_2H_2N_4O_3$	-30.9 ± 0.3^b	NA	NA
DADE (2,2-Dinitroethene-1,1-diamine)	$C_2H_4N_4O_4$	-32.0^c	NA	NA
LLM-105 (2,6-diamino-3,5-dinitropyrazine-1-oxide)	$C_4H_4N_6O_5$	NA	NA	NA
TNT (2-Methyl-1,3,5-trinitrobenzene)	$C_7H_5N_3O_6$	-19.25 ± 0.74^d -16.03 ± 0.65^{d1} -15.1 ± 1.2^{d2}	24.7^{e1} 28.3^{e2}	5.75 ± 0.84^d 12.3 ± 1.2^{d1}
RDX (1,3,5-Trinitroperhydro-1,3,5-triazine)	$C_3H_6N_6O_6$	17 ± 1.2^f	31.11^g	45.9^h
TATB (1,3,5-triamino-2,4,6-trinitrobenzene)	$C_6H_6N_6O_6$	-33.4 ± 1.2^{d2} -46.4 ± 1.8^i	40.21^g	6.8^m -6.2^m
HMX (Octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine)	$C_4H_8N_8O_8$	21 ± 0.7^f 18^j	41.89^g	62.9^m 58.9^m
PETN ([3-Nitrooxy-2,2-bis(nitrooxymethyl)propyl] nitrate)	$C_5H_8N_4O_{12}$	-128.7 ± 0.2^k	37.6 ± 0.8^l	-91.1^m

^a Enthalpy of formation in kcal/mol.

^b Ref. [32], ^c Ref. [33], ^d Ref. [24], ^{d1} Ref. [3], ^{d2} Ref. [26], ^{e1} Ref. [34], ^{e2} Ref. [35], ^f

Ref. [28], ^g Ref. [25], ^h Ref. [36], ⁱ Ref. [27], ^j as quoted in Ref. [29], ^k Ref. [31], ^l Ref.

[30]. $^m \Delta H_f^0(g)$ calculated using Hess's law from the corresponding reported data of $\Delta H_f^0(s)$ and ΔH_{sub} .

Table II. Gas phase energies and enthalpies of formation.^a

Molecule	E_0	E_{ZPE}	H_{298}	$\Delta H_f^0(0 \text{ K})$	$\Delta H_f^0(298 \text{ K})$
NTO	-521.292618	41.2	-521.284505	-0.3	-5.0
	-521.708365	41.2	-521.700255	3.2	-1.6
	-521.805736	41.3	-521.797705	1.4	-3.4
	-522.198871	41.2	-522.190848	3.1	-1.6
					N/A
DADE	-597.527794	56.8	-597.517292	3.1	-3.2
	-597.993140	56.8	-597.982638	7.4	1.1
	-598.105038	57.0	-598.094765	6.2	-0.3
	-598.564396	57.0	-598.554146	7.2	0.8
					N/A
LLM-105	-858.069576	73.5	-858.056077	27.7	19.7
	-858.761908	73.4	-858.748404	33.0	25.0
	-858.921830	73.8	-858.908311	30.5	22.5
	-859.563058	73.8	-859.549571	33.9	25.9
					N/A
TNT	-883.829536	83.4	-883.814953	10.1	3.1
	-884.566857	83.4	-884.552274	13.0	6.0
	-884.729931	83.7	-884.715348	12.5	5.5
	-885.377776	83.8	-885.363141	18.8	11.9
					9.±7
RDX	-896.226904	88.9	-896.213406	45.3	34.5
	-896.922771	88.9	-896.909274	53.1	42.3
	-897.090086	88.3	-897.076480	51.6	40.8
	-897.774461	88.2	-897.760810	56.0	45.3
					46.±1
TATB	-1010.449419	98.1	-1010.433001	9.5	-0.2
	-1011.283609	98.1	-1011.267191	12.3	2.5
	-1011.469035	98.3	-1011.453214	11.5	1.4
	-1012.217890	98.2	-1012.201922	13.7	3.7
					0.±13
HMX	-1194.972672	119.1	-1194.954397	58.2	44.0
	-1195.902220	119.1	-1195.883945	67.6	53.3
	-1196.123877	118.5	-1196.105446	66.4	52.3
	-1197.033986	118.3	-1197.015470	73.8	59.8
					61.±4
PETN	-1314.799504	118.2	-1314.778085	-102.8	-115.3
	-1315.782691	118.2	-1315.761273	-93.4	-106.0
	-1316.029668	116.9	-1316.007883	-93.4	-105.7
	-1317.076741	116.8	-1317.054931	-85.8	-98.0
					-91±1

^a Results from top to bottom are from G2, G3, G4, and ccCA-PS3 levels of theory, respectively. The last row in $\Delta H_f^0(298 \text{ K})$ is the average of available experimental gas phase enthalpies of formation. Total energies (E_0) and enthalpies at 298 K (H_{298}) are in Hartrees. Heat of formation at 0 K and 298 K ($(\Delta H_f^0(0 \text{ K}))$, $(\Delta H_f^0(298 \text{ K}))$) calculated from equation 1 in the text are in kcal/mol. $E_0 = E_e + E_{\text{ZPE}}$, where E_e is the electronic energy, and E_{ZPE} is the zero-point energy (in kcal/mol).

Table III. Calculated total energies of atomic species (in Hartrees).

Atom	G2	G3	G4	ccCA-PS3
C	-37.784301	-37.827717	-37.834168	-37.854215
H	-0.500000	-0.501003	-0.501420	-0.499986
N	-54.517960	-54.564343	-54.573666	-54.612301
O	-74.982030	-75.030991	-75.045501	-75.113399

Table IV. Calculated atomization energies (in kcal/mol).

Molecule	G2	G3	G4	ccCA-PS3
TNT	2129.42	2126.59	2127.09	2121.71
RDX	1803.55	1795.72	1797.27	1793.28
TATB	2349.25	2346.49	2347.26	2345.99
HMX	2406.90	2397.56	2398.72	2391.90
PETN	2523.78	2514.38	2514.36	2507.46

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$\Delta H_f^0(298\text{ K})$

G2= -115.3

G3= -106.0

G4= -105.7

cc-CA-PS3= -98.0

PETN

Enthalpy of Formation