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REGULAR ARTICLE

Estimation of heats of formation for nitrogen-rich cations using G3, G4, and G4 (MP2) theoretical methods

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Abstract

Gas-phase heats of formation of 48 commonly used nitrogen-rich cations in energetic salts composed of H, C, N, and O atoms have been calculated at the Gaussian-3 (G3), Gaussian-4 (G4), and G4 (MP2) theories using the atomization reaction. The discrepancies between the predicted and the reported HOFs vary in the range of 0.28–470.78 kJ/mol. The reported HOFs for twenty cations were observed within 5 kJ/mol deviation, ten cations within 6–10 kJ/mol deviation, eleven cations within 11–50 kJ/mol, five cations within 51–100 kJ/mol, while two cations differed by more than 420 kJ/mol with respect to G4 data. The calculated HOFs with the G4 composite method at 298.15 K were recommended for selected cations as being more reliable than the reported data.

Keywords Heat of formation · Cations · Gaussian-4 · Energetic salts · Energetic materials

1 Introduction

In modern civil and military uses, explosives with high performance with lower sensitivity to thermal shock, friction, and electric discharge have been a principal requirement and always desirable. However, the combination of performance and insensitivity is challenging, complicated, and also mutually exclusive because improvement in performance brings upsurge in sensitivity (e.g., in CL–20) [1, 2] and vice versa. One promising approach to overcome this challenge is to explore energetic materials based on ionic salts containing nitrogen-rich compounds with large number of C–N and N–N bonds in the chemical structure [3–5]. Ionic salts have been established as a diverse class of materials due to their possible chemical manipulation to achieve desired energetic properties. These salts can be chemically altered with selection of cations, anions, functional groups such as $–NO_2$, $–NH_2$, and $–N_3$ allowing tuning energy content, altering the physical properties, and developing a library of compounds with extreme diversity. Performance parameters (detonation velocity and pressure) are more relying on the heat of formation (HOF) and reflect the energy content of explosive, and the density, which indicates amount of material that can be packed into the charge. Our specific interest is in the design and assessment of new energetic materials for which the HOF plays a crucial role in the preliminary assessment of energy content, stability, reactivity, and potential performance. Considering the hazards of explosives, it is a complicated and unsafe task to measure HOF experimentally, and hence, theoretical methods have received considerable attention. To obtain HOF experimentally, differential scanning calorimetry is commonly employed [6]; however, these calorimetric measurements are resource consuming and difficult due to unknown intermediates and hazardous nature of explosives. Several methods have been proposed for neutral energetic molecules including group additive contributions, isodesmic reactions, atomic or group corrections to Hartree–Fock molecular energies, bond additivity corrections, and composite methods [7–25]. For judging the energy content of the ionic salts, it is most significant to know the HOFs of anion and cation in gas phase. Despite the extensive studies on ionic salts, available thermochemical data for cations are frequently scarce and reveal significant inconsistency among the reported results. In case of ionic compounds, Born–Haber energy cycle (Fig. 1) has been

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Electronic supplementary material The online version of this article (https://doi.org/10.1007/s00214-018-2300-6) contains supplementary material, which is available to authorized users.

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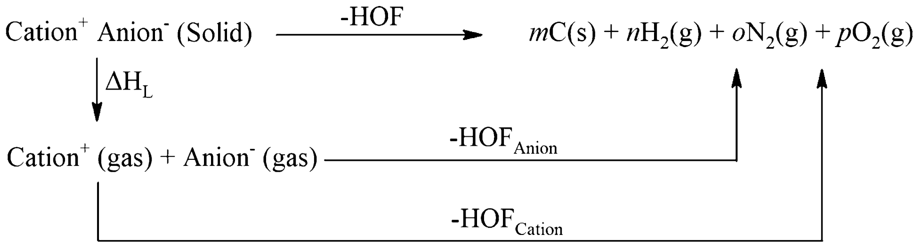


Fig. 1 Born–Haber cycle for the formation of energetic salts

used to predict the HOF of salts [26–28] and is given by the formula:

$$\text{HOF(ionic salt, 298 K)} = \text{HOF(cation, 298 K)} + \text{HOF(anion, 298 K)} - \Delta H_L$$

where ΔH_L is the lattice energy of the salt. The HOFs of cations and anions are mostly predicted with isodesmic reactions. Most of the reported salts in the literature [29–46] show the variation in anion, while cations are commonly the nitrogen-rich compounds. To investigate the HOF of ionic salt, knowledge of the reliable HOF of cation and anion is an essential requirement. In recent years, there have been several accurate first-principle techniques proposed to evaluate the thermochemistry of molecules. In particular, G3, G4, and G4 (MP2) theories [47–65] are popular composite theoretical techniques which have been successfully applied and established as an accurate method to calculate the HOF of a wide variety of molecules. Experimental data of HOFs for cations are rare, and reliable values are required for quantitative interpretation of performance and energetic nature of material. In this work, we report the calculation of HOFs for commonly used cations in the formation of ionic salts by G3, G4, and G4 (MP2) methods. Curtiss et al. [60, 61] reported the HOFs for different classes of compounds using G3, G4, and G4 (MP2) methods where G4 theory shows minimum deviation from experiment values. The calculated HOFs of cation were compared with that of reported results and recommend in thermochemical models to compute HOF of ionic salts precisely.

2 Results and discussion

A set of 48 commonly used CHNO cations belonging to a different nitrogen-containing molecules (with $-NO_2$, $-NH_2$, $-CH_3$, $-N_3$, $-C(O)NH_2$, –CN, –OH, and five-membered heterocycles) were taken from the literature [29–46] and studied in this work. All ab initio and density functional theory (DFT) computations were performed via the Gaussian 09 package [66]. The structures of selected cations were optimized at the B3PW91/6-31G(*d*,*p*) level, and the resulting structures were used as inputs for further G3, G4, and G4 (MP2) calculations. The G3, G4, and G4 (MP2) HOFs at 298.15 K were calculated using the atomization reaction procedures, which includes experimental HOFs of gaseous atoms at 0 K and thermal corrections for elements in their standard states [50]. The optimized Cartesian coordinates of the cations at G3, G4, and G4 (MP2) calculations are summarized in Table S5-148 of Supporting Information.

The computed HOFs for cations using G3, G4, and G4 (MP2) methods are compared in Table 1 together with the reported values from the literature. To the best of our knowledge, HOFs from quantum-chemical calculations for these nitrogen-rich cations are not available in the literature. Figure 2 shows Bland–Altman plot of the calculated HOFs using G4 method and reported data. Figures S1 and S2 in Supporting Information represent the Bland–Altman plots using G3 and G4 (MP2) methods, respectively. 2,2′-Carbonyldihydrazinium and 2,2-dimethyltriazan-2-ium appear as an outlier for which all three methods consistently calculate lower values of the HOF at 298.15 K. In general, the agreement between the calculated HOFs using G3, G4, and G4 (MP2) methods is extremely good. In Table 1, the HOFs computed from G3, G4, and G4 (MP2) atomization reaction are compared and reveal that the HOFs obtained from G3 and G4 (MP2) methods are always overestimated than that of the G4 method. Inspection of Table 1 shows that G3 values differ by 0.84–15.09 kJ/mol and G4 (MP2) values vary from 2.05 to 12.97 kJ/mol relative to G4 HOFs. Overall, the close agreement can be seen in HOFs calculated using G3 and G4 (MP2) methods with the results of G4 level and provides support to assume that G4 method with the atomization reaction will be capable of calculating the accurate HOFs for cations.

The G4 HOFs derived in this work for C^+ and N^+ containing cations (1–2, 3–5, 6–7, and 8–9) show similar results, while HOFs for cations 10–11, 12–13, and 14–15 differ from each other by 2–37 kJ/mol. As shown in Table 1, the HOFs obtained using G4 method for twenty cations (1–7, 10, 20, 26, 27, 29, 30, 35, 38–41, 46, and 47) show variation within 0.4–5 kJ/mol and close agreement with reported values, while the reported values show 6–10 kJ/mol deviation for ten cations and 11–50 kJ/mol difference for eleven cations concerning to those calculated with the G4 method. The uncertainty in reported values is greater than 50 kJ/mol for seven cations. The HOF obtained for cation 14 and 19 in the present work shows deviation of 55–68 kJ/mol compared to the values reported by Klapotke et al. [30].

Table 1 HOF (kJ/mol) of various cations computed using G3, G4, and G4 (MP2) methods

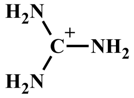
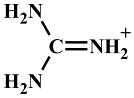
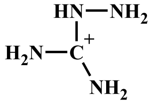
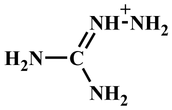
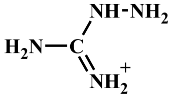
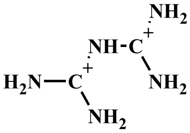
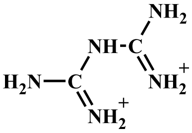
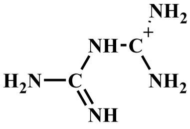
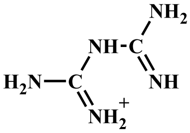
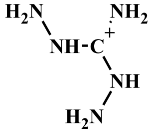
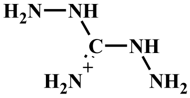
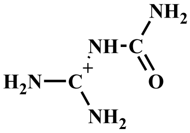
No.	Cation	Calculated HOF (kJ/mol)			Reported HOF (kJ/mol)
		G3	G4	G4(MP2)	
1.		574.1	572.4	579.9	571.5 [30]
2.		574.1	572.4	579.9	566.7 [31] 575.9 [32]
3.		675.9	671.7	680.1	671.1 [30]
4.		675.9	671.7	680.0	667.4 [33]
5.		675.9	671.7	680.0	667.4 [31]
6.		1616.9	1614.6	1627.3	1618.0 [33]
7.		1616.9	1614.4	1627.4	1618.0 [33]
8.		619.3	612.3	622.5	620.9 [35]
9.		619.3	612.3	622.5	621.0 [36]
10.		779.1	773.0	782.2	771.95 [30]
11.		804.3	797.5	806.7	769.0 [37]
12.		419.7	417.2	427.8	350.6 [34]

Table 1 (continued)

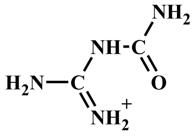
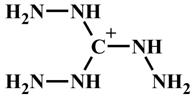
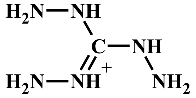
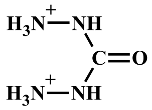
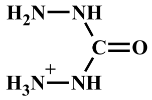
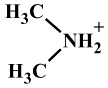
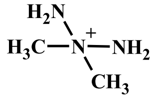
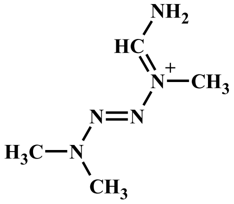
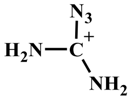
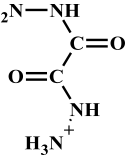
No.	Cation	Calculated HOF (kJ/mol)			Reported HOF (kJ/mol)
		G3	G4	G4(MP2)	
13.		383.9	380.2	391.2	350.6 [34] 351.0 [36]
14.		936.1	926.9	936.7	873.6 [30] 871.5 [32]
15.		933.5	924.1	933.6	871.5 [33]
16.		1725.5	1721.2	1730.5	1764.6 [33] 2192.0 [39]
17.		678.6	670.9	679.2	663.0 [38] 663.4 [35] 651.0 [30]
18.	NH_4^+	634.8	636.8	638.9	635.5 [30] 626.4 [37] 631.7 [67]
19.	$H_3\overset{+}{N}-OH$	676.9	675.6	678.1	744.3 [30] 669.5 [33]
20.	$H_3\overset{+}{N}-NH_2$	771.	769.5	771.7	770.0 [34]
21.		586.2	587.3	590.8	579.5 [31]
22.		779.4	775.5	780.0	1196.7 [40]
23.		899.2	889.9	899.5	884.0 [41]
24.		967.1	955.7	965.6	982.8 [30]
25.		551.5	548.2	558.1	561.8 [42]

Table 1 (continued)

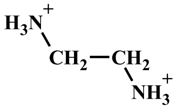
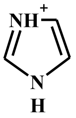
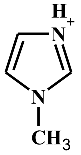
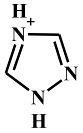
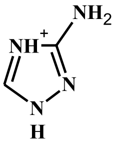
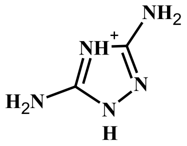
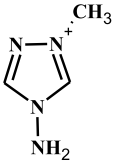
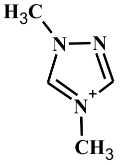
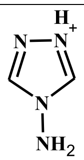
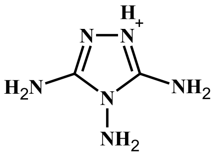
No.	Cation	Calculated HOF (kJ/mol)			Reported HOF (kJ/mol)
		G3	G4	G4(MP2)	
26.		1635.2	1636.0	1640.1	1630.5 [37]
27.		724.5	719.3	722.4	711.5 [34] 720.2 [37]
28.		695.7	690.7	694.1	680.6 [32]
29.		844.4	836.3	840.5	835.0 [31]
30.		812.6	802.3	809.9	804.5 [31]
31.		782.8	775.6	786.3	764.0 [33]
32.		913.4	903.8	909.4	895.6 [34]
33.		772.3	765.0	770.2	756.9 [43]
34.		955.5	945.4	950.5	936.3 [31]
35.		882.4	874.1	886.2	877.6 [33]

Table 1 (continued)

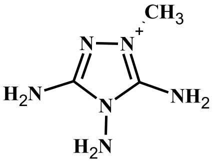
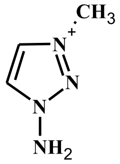
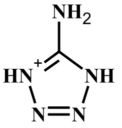
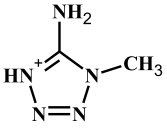
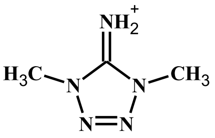
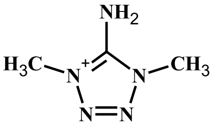
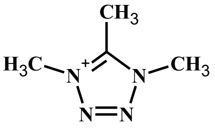
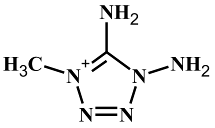
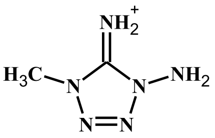
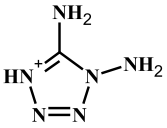
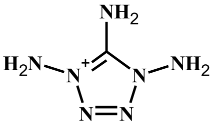
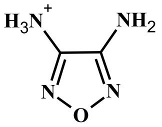
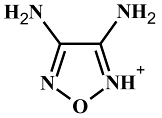
No.	Cation	Calculated HOF (kJ/mol)			Reported HOF (kJ/mol)
		G3	G4	G4(MP2)	
36.		849.5	840.8	853.2	913.7 [37]
37.		960.3	948.8	953.6	963.2 [34]
38.		987.1	975.3	983.1	975.6 [39]
39.		944.9	933.5	941.7	937.2 [44]
40.		904.2	893.2	901.9	887.7 [45]
41.		904.4	893.2	901.9	885.5 [43] 888.0 [36]
42.		868.8	856.2	862.5	844.8 [43]
43.		1021.4	1008.4	1017.8	998.0 [43] 974.0 [36]
44.		1021.4	1008.4	1017.8	974.3 [45]
45.		1062.3	1048.8	1057.7	1042.2 [39] 1055.2 [44]

Table 1 (continued)

No.	Cation	Calculated HOF (kJ/mol)			Reported HOF (kJ/mol)
		G3	G4	G4(MP2)	
46.		1140.9	1125.8	1135.8	1129.0 [46]
47.		946.6	934.0	941.1	935.3 [42]
48.		888.5	884.6	894.8	935.0 [38]

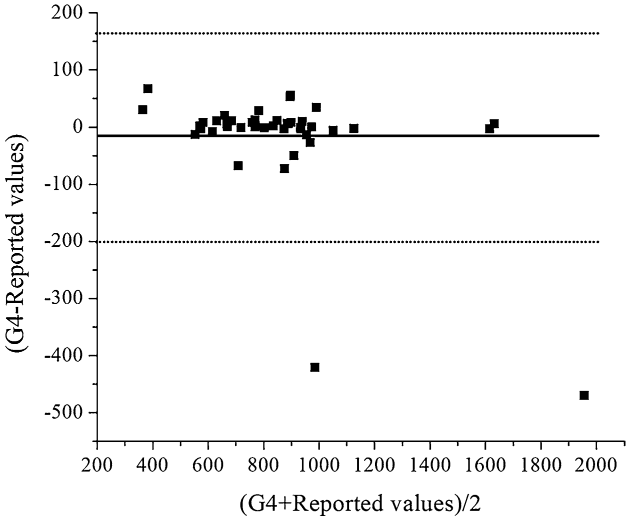


Fig. 2 Bland–Altman analysis: correlation between calculated HOFs using G4 method and reported data

The HOFs for cations 12, 14, and 15 predicted in the present work are higher (by 52–66 kJ/mol) than the values of Shreeve et al. [32–34]. Similarly, Huang et al. [37] reported HOF for cation 36 to be 73 kJ/mol higher than the G4 value. The HOFs of cation 16 (1721 kJ/mol) and 22 (775 kJ/mol) obtained by Shreeve et al. [39, 40] are substantially higher (> 420 kJ/mol) than calculated in this work. The reason for this considerable disagreement is not quite clear. In summary, the values of HOF obtained by G3, G4, and G4 (MP2) theories with atomization reaction method are very close. Therefore, the obtained G4 HOFs for cations for which no experimental data are available may be used to calculate the energy content of energetic ionic salts and it is hoped that our computed HOFs will serve as reliable estimates.

3 Conclusions

Gas-phase HOFs for a set of widely used nitrogen-rich cations were calculated with a number of methods; G4 performs best against experiment and recommended for calculations. Taking into account the available inconsistent HOF values of cations, significant errors can occur in the HOF calculations for energetic salts. The HOFs computed in the present work will help to avoid significant errors in the calculation of energy content and precisely compute HOF-dependent performance parameters. The major differences between the HOF values for fourteen cations calculated by G4 method and reported results are above 15 kJ/mol. The results of the present calculations is supported by G3 and G4 (MP2) calculations, which shows that the predicted values are consistent and can give reasonable estimations.

4 Supporting information

Deviation in predicted HOFs with G3 and G4 (MP2) methods and reported data from G4 values for selected cations is listed in Table S1. Tables S2 to S4 contain the calculated energies at 0 and 298.15 K for selected cations at G3, G4, and G4 (MP2) level, respectively. Cartesian coordinates (Å) of the cations studied in the present work at the G3, G4, and G4 (MP2) level are summarized in Table S5-S148. Table S149 lists the experimental HOFs (in kcal/mol) and enthalpy corrections of the atomic elements. Total G3, G4, and G4 (MP2) energies (in hartrees) of atomic species are summarized in Table S150-152. Figures S1 and S2 show the Bland–Altman plots between calculated HOFs using G3 and G4 (MP2) methods and reported data.

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Compliance with ethical standards

Conflict of interest The authors declare that they have no conflict of interest.

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