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Enthalpy of Formation of the Nitrogen-Rich Salt Guanidinium 5,5′-Azotetrazolate (GZT) and a Simple Approach for Estimating the Enthalpy of Formation of Energetic C, H, N, O Salts

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Abstract: The discrepancy between the calculated (CBS-4M/Jenkins) and experimentally determined enthalpies of formation recently reported for the 2:1 salt TKX-50 raised the important question of whether the enthalpies of formation of other 2:1 C, H, N, O salts calculated using the CBS-4M/Jenkins method are reliable values. The standard (p° = 0.1 MPa) enthalpy of formation of crystalline guanidinium 5,5′-azotetrazolate (GZT) (453.6 ± 3.2 kJ/mol) was determined experimentally using static-bomb combustion calorimetry and was found to be in good agreement with the literature's values. However, using the CBS-4M/Jenkins method, the calculated enthalpy of formation of GZT was again in poor agreement with the experimentally determined value. The method we used recently to calculate the enthalpy of formation of TKX-50, based on the calculation of the heat of formation of the salt and of the corresponding neutral adduct, was then applied to GZT and provided excellent agreement with the experimentally determined value. Finally, in order to validate the findings, this method was also applied to predict the enthalpy of formation of a range of 1:1 and 2:1 salts (M^+X^- and $(M^+)_2X^{2-}$ salts, respectively), and the values obtained were comparable to experimentally determined values. The agreement using this approach was generally very good for both 1:1 and 2:1 salts; therefore, this approach provides a simple and reliable method which can be applied to calculate the enthalpy of formation of energetic C, H, N, O salts with much greater accuracy than the current, commonly used method.

Keywords: enthalpy of combustion; enthalpy of formation; CBS-4M; CBS-QB3; Jenkins equation; GZT; energetic salts; TKX-50; combustion calorimetry

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1. Introduction

When designing and developing new secondary C, H, N, O explosives, it is of fundamental importance to be able to predict reliable values for the standard state heats of formation for potential new high explosives [1]. This is because the two most widely used computer programs (EXPLO5, CHEETAH) for calculating the energetic performance of an explosive (detonation velocity (D), Chapman–Jouguet pressure ($P_{C\text{–}J}$), energy of explosion ($\Delta_{ex}U^\circ$)) require the enthalpy of formation as an input [1].

Accurate predicted values for the enthalpy of formation are essential. For example, D is proportional to the heat of detonation and, therefore, also to the heat of formation. Consequently, inaccurate values for the enthalpy of formation will result in inaccurate predicted or calculated values for the energetic properties of the compound [1]. Predicted values for D are important because the experimental determination of D is only performed for compounds with exceptionally promising properties, since this generally requires over 1 kg of the explosive substance [1].

The enthalpies of formation for neutral, energetic C, H, N, O compounds can be quickly, easily, and reliably predicted using commonly used computer programs such as the Gaussian program [2] and have been reported to show excellent agreement with experimentally based values determined using combustion calorimetry [3–5]. This is not the case for energetic C, H, N, O salts (AB, A_2B or AB_2), for which the situation is currently unsatisfactory. Based on the often poor agreement between experimentally determined and calculated values for salts, there appear to be several problems in predicting the enthalpies of formation of these salts, and none of these problems have been rigorously addressed or solved [6].

Firstly, only a very small number of energetic high explosive salts have been investigated using combustion calorimetry, meaning that few experimentally determined standard enthalpies of formation in the solid phase, $\Delta_f H^\circ(\mathrm{s})$, have been reported in the literature. Secondly, detailed investigations of TKX-50 have shown that it can be tricky to determine the $\Delta_f H^\circ(\mathrm{s})$ for energetic salts using combustion calorimetry [7–13]. This appears to be a further problem in energetic salts. Thirdly, and finally, based on the results of multiple independent experimental determinations of the $\Delta_f H^\circ(\mathrm{s})$ of TKX-50 reported in the literature, the CBS-4M/Jenkins computational approach, which is widely used for estimating the $\Delta_f H^\circ(\mathrm{s})$ of energetic salts, resulted in extremely poor agreement with the experimentally determined values [7–13]. In the CBS-4M/Jenkins approach, the $\Delta_f H^\circ(\mathrm{g})$ values for the constituent ions are calculated at CBS-4M level of theory, followed by conversion to the $\Delta_f H^\circ(\mathrm{s})$ value for the salt by the addition of the lattice enthalpy for the salt, $\Delta_{\mathrm{latt}} H$, which is calculated using the Jenkins equation [14]. The Jenkins equation is an empirical method which requires the density, molecular weight, and ion ratios as inputs.

The experimentally determined enthalpy of formation for TKX-50 from independent research groups resulted in an average value of 190 kJ·mol^{-1} [7], which was in good agreement with our value from combustion calorimetry (175.3 $\pm$ 1.9 kJ·mol^{-1}) [7] but in extremely poor agreement with the original predicted value of 447 kJ·mol^{-1} (CBS-4M/Jenkins) [14]. Preliminary results comparing the experimentally determined enthalpies of formation of other 2:1 salts suggested that this very poor agreement is not restricted to TKX-50, and a re-parameterization of the CBS-4M/Jenkins method would not necessarily be a simple solution to this problem. Furthermore, changing the level of theory used for calculating the $\Delta_f H^\circ(\mathrm{g})$ of the constituent ions from CBS-4M to CBS-QB3 or PM7 [15] before calculation of $\Delta_{\mathrm{latt}} H$ did not solve the problem.

Currently, the heats of formation of energetic salts are generally estimated by applying either the atomization energies approach or the isodesmic approach, followed in both cases by the calculation of the lattice energy using the Jenkins equation [14]. However, debate in the literature about the best strategy for predicting the $\Delta_f H^\circ(\mathrm{s})$ for energetic salts has continued, with various strategies being proposed such as the isodesmic/Jenkins approach [16] or calculation of the molecular volumes of salts using the Monte Carlo method, followed by calculation of the lattice enthalpy using the Jenkins equation [17]. As far back as 2009, Byrd and Rice concluded that the "… prediction of lattice energies for 1:1 salts…. had significant errors when compared to experimental values" when using CBS-4M to calculate the enthalpies of formation of gas-phase ions combined with the Jenkins equation to calculate the lattice energy [6].

Several papers in the literature have discussed the origins of errors when using the CBS-4M/Jenkins approach, however, these remain unclear. Shreeve and co-workers showed in 2007 [16] that even for some "simple" salts such as $LiClO_4$ and $MgCl_2$, large differences in the agreement between the calculated and experimentally determined enthalpies of formation were observed. The predicted values for some salts showed good agreement, whereas for other salts only poor agreement was observed.

We therefore feel that in crystals where there is considerable interionic hydrogen bonding present, the purely spherical ion volume approach used in the Jenkins equation may be disadvantageous. Consequently, we wanted to try to find an approach that would eliminate this step. Furthermore, since it has been shown by others that the calculation of the enthalpy of formation of neutral molecules generally results in accurate predicted values, we also wanted to utilize a method in which no ions and only neutral molecules were calculated at the CBS-4M or CBS-QB3 levels of theory. Initial calculation of the enthalpy of formation of TKX-50 resulted in a value which was too exothermic if TKX-50 was treated purely as an ionic compound and too endothermic if TKX-50 was treated by calculation of the compound in the gas phase as a purely hypothetical adduct between the neutral acid and base, followed by conversion to the solid-state value using a coarse approach in which the enthalpy of sublimation of the components was used. Therefore, we decided to use a ratio of these two values, which we thought might very crudely reflect the solid-state crystal structure of TKX-50 which shows an ionic salt but has strong interionic hydrogen bonding. We found a ratio of 80:20 provided acceptable agreement.

We have shown in our recent paper on TKX-50 [7] that treating this energetic C, H, N, O salt both as a salt and as a neutral adduct (solid) with the corresponding calculated $\Delta_f H^\circ(s)$ values weighted in an 80:20 ratio results in a calculated $\Delta_f H^\circ(s)$ value which is in good agreement with the average value of $\Delta_f H^\circ(s)$ determined experimentally [7]. Considering that the method for calculating reliable values for the standard molar enthalpy of sublimation ($\Delta_{sub} H^\circ$) of the neutral adducts has not been established, an estimated value of $\Delta_f H^\circ(s)$ for the adduct was obtained using the standard molar enthalpies of sublimation ($\Delta_{sub} H^\circ$) or vaporization ($\Delta_{vap} H^\circ$) of the constituent acid and base, leading to an approximated value. This approach avoids calculation of ions at the CBS-4M level of theory and consequently avoids using the Jenkins equation. Our results for 1:1 (AB) and 2:1 (A_2B) salts show that this approach provides good agreement with experimentally determined values reported in the literature and excellent potential for predicting the values of the enthalpies of formation of energetic salts. This approach is not restricted to 1:1 salts (AB), but also shows excellent agreement for 2:1 salts (A_2B), which show particularly poor agreement between experimentally determined and CBS-4M/Jenkins calculated values.

However, in order to find a reliable approach for predicting the enthalpies of formation of energetic C, H, N, O salts, first of all, high-quality, reliable enthalpies of formation for as many energetic C, H, N, O salts as possible using combustion calorimetry must be obtained. Therefore, it is important to confirm the $\Delta_f H^\circ(s)$ of further important energetic salts using combustion calorimetry.

In this work, the enthalpy of formation of an energetic salt, guanidinium 5,5′-azotetrazolate (GZT—Figure 1), in the solid state was determined by combustion calorimetry. In addition, the CBS-4M/Jenkins method was used to derive the enthalpy of formation of GZT, which showed poor agreement. Therefore, a new method was used to provide better estimations of the enthalpy of formation of GZT. Finally, in order to validate the findings, this method was also applied to predict the enthalpy of formation of a range of 1:1 and 2:1 salts, and the values obtained were compared to experimentally determined values.

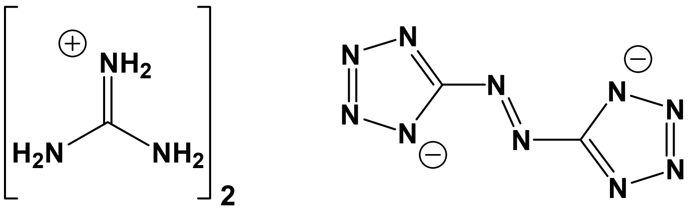


Figure 1. Molecular structure of guanidinium 5,5′-azotetrazolate (GZT).

2. Materials and Methods

CAUTION! Guanidinium 5,5′-azotetrazolate (GZT) is an energetic material and should be handled accordingly. Energetic materials can show unexpected sensitivities towards various external stimuli (e.g., elevated temperature, friction, impact). Although no hazards occurred, proper security precautions (safety glasses, face shield, earthed equipment and shoes, leather jacket, Kevlar sleeves, and earplugs) must be worn while synthesizing and handling GZT.

GZT was synthesized according to the literature and the purity was checked by elemental analysis (CHN) and NMR spectroscopy (^{1}H, ^{13}C) [18].

2.1. Combustion Calorimetry

The standard specific internal combustion energy of guanidinium 5,5′-azotetrazolate (GZT) was determined by static-bomb combustion calorimetry. The calorimetric system involves a twin valve bomb whose internal volume is 0.342 dm^3 (type 1108, Parr Instrument Company, IL, USA). The technique and equipment have been previously described in the literature [19,20].

The samples of GZT, in a pellet form, were ignited with a rich oxygen atmosphere (p = 3.04 MPa), with 1.00 cm^3 of deionized water added to the bomb.

For the compound studied, the standard (p° = 0.1 MPa) specific internal energy, $\Delta_c u^\circ$, at T = 298.15 K was calculated by a similar method to that developed by Hubbard et al. [21]. Further details about the experimental procedure are provided in the Supporting Information.

2.2. Computational Work

All quantum chemical calculations were carried out using the Gaussian 16 program package [2]. The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and coworkers in order to obtain very accurate energies. The CBS models used the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated the CBS limit. The CBS-QB3 was modified by the inclusion of diffuse functions in the geometry optimization step [22]. The five-step CBS-QB3 series of calculations starts with a geometry optimization at the B3LYP level, followed by a frequency calculation to obtain thermal corrections, zero-point vibrational energy, and entropic information. The next three computations are single-point calculations (SPCs) at the CCSD(T), MP4SDQ, and MP2 levels. The CBS extrapolation then computes the final energies [23].

The value for the enthalpy of the salt reaction ($\Delta_r H$) was calculated following the route proposed by Sinditskii [10], which requires accurate $\Delta_f H^\circ$ values for the neutral base in its standard state, for the liquid nitric acid, and for the corresponding $BH^+NO_3^-$(s) salt (Equation (1)). The value of $\Delta_f H^\circ$(s) for the $BH^+NO_3^-$(s) salt used should be determined experimentally, and where available, experimentally determined values are used for all terms. The value for $\Delta_r H$ for each individual base can then be calculated using Equation (2).

$$\mathrm{B(standard\ state)} + \mathrm{HNO_3(l)} \overset{\Delta_r H}{\rightarrow} \mathrm{BH} + \mathrm{NO_3}^-\mathrm{(s)} \tag{1}$$

$$\Delta_r H = \Delta_f H^\circ(\mathrm{BH^+NO_3}^-,\ \mathrm{s}) - \Delta_f H^\circ(\mathrm{B,\ standard\ state}) + \Delta_f H^\circ(\mathrm{HNO_3,\ l}) \tag{2}$$

In all cases, experimentally determined values which were available (NBS tables, NIST webbook, NRC handbook, etc. [24–28]) were used preferentially over calculated values. For values of $\Delta_f H^\circ$(s) or $\Delta_f H^\circ$(l) for which no experimentally determined values were available in the literature, the $\Delta_f H^\circ$(g) of the compound was calculated at CBS-4M or CBS-QB3 levels of theory and converted to the $\Delta_f H^\circ$(s) by subtracting the $\Delta_{sub} H^\circ$ (for solids) or $\Delta_{vap} H^\circ$ (for liquids) of the compound. If experimentally determined $\Delta_{sub} H^\circ$ and $\Delta_{vap} H^\circ$ values were not available, they were estimated using either the empirical method reported in the literature [29] or using the RoseBoom2.1© program [30].

For each salt (1:1 or 2:1 ion ratios), two separate values were calculated. In the first step, the $\Delta_f H^\circ$(s) of the salt A^+B^- or $(A^+)_2B^{2-}$ (Equation (3)) was calculated according to Equation (4) using the value obtained for the heat of salt reaction for the base outlined above.

$$\mathrm{Base(standard\ state)} + \mathrm{Acid(standard\ state)} \overset{\Delta_r H}{\rightarrow} \mathrm{BH^+A^-(s)} \tag{3}$$

$$\Delta_f H^{\circ}(\text{salt, s}) = \Delta_f H^{\circ}(\text{Base, standard state}) + \Delta_f H^{\circ}(\text{Acid, standard state}) + \Delta_r H \quad (4)$$

In the second step, the $\Delta_f H^{\circ}(g)$ of the neutral AB or A_2B (hypothetical) adduct was calculated at the CBS-4M (or CBS-QB3) level (Equation (5)) and converted to the $\Delta_f H^{\circ}(s)$ value according to Equation (6). Since a method for calculating reliable values for the $\Delta_{sub}H^{\circ}$ of the neutral adducts has not been established, this value had to be substituted by using the $\Delta_{sub}H^{\circ}$ or $\Delta_{vap}H^{\circ}$ of the constituent acid and base instead, which introduces a larger deviation to the value obtained. It is not assumed that this approach is equivalent to using the $\Delta_{sub}H^{\circ}$ for the adduct itself. For $\Delta_{sub}H^{\circ}$ and $\Delta_{vap}H^{\circ}$ values which had not been previously experimentally determined and reported in the literature, these values were calculated using either the empirical method reported in the literature [29] or using the RoseBoom2.1© program [30], where $\Delta_{trs}H^{\circ}$ represents the enthalpy of the phase transition (sublimation for solids and vaporization for liquids). The calculated enthalpies of vaporization and sublimation were predicted using a machine learning approach, in which the predicted value was obtained based on a database of compounds in which the enthalpies of sublimation or vaporization, as well as the connectivity of the compounds, were known. The values the machine learning approach predicts for a compound are based on patterns for specific structural features and the enthalpies of vaporization and sublimation for the known compounds in the dataset.

$$\text{Base(standard state)} + \text{Acid(standard state)} \rightarrow \text{Base}\bullet\text{Acid(s)} \quad (5)$$

$$\Delta_f H^{\circ}(\text{Base}\bullet\text{Acid, s}) \cong \Delta_f H^{\circ}(\text{Base}\bullet\text{Acid, g}) - \Delta_{trs}H^{\circ}(\text{Base, s or l}) - \Delta_{trs}H^{\circ}(\text{Acid, s or l}) \quad (6)$$

In the final step, the averages of the values obtained in the first and second steps were calculated, as well as the 80:20 value, which corresponds to a weighting ratio of 80:20 for the salt value obtained in step one vs. the (hypothetical) adduct value obtained in step two. Initial calculation of the enthalpy of formation of TKX-50 resulted in a value which was too exothermic when treating TKX-50 purely as an ionic compound and too endothermic if TKX-50 was treated purely as an adduct between the neutral acid and base. Therefore, we decided to use a ratio of these two values which we thought may very crudely reflect the solid-state crystal structure of TKX-50, which shows an ionic salt, but with strong interionic hydrogen bonding. We found a ratio of 80:20 provided acceptable agreement.

3. Results and Discussion

Before comparing the experimentally determined and calculated values for the $\Delta_f H^{\circ}(s)$ of further C, H, N, O energetic materials, it was first important to confirm the value of $\Delta_f H^{\circ}(s)$ for a further important compound. The compound GZT was chosen due to its importance, high nitrogen content, being a 2:1 salt, and also because the value for $\Delta_f H^{\circ}(s)$ has been reported previously in the literature [31–33], which therefore gives comparison results and increases confidence in the value of $\Delta_f H^{\circ}(s)$ of GZT, as was the case for TKX-50.

3.1. Enthalpy of Formation of GZT in Solid Phase

Typical values of a combustion experiment using guanidinium 5,5′-azotetrazolate are shown in Table 1. The internal energy for the isothermal bomb process, $\Delta U(\text{IBP})$, was calculated according to Equation (7). The energy correction to the standard state, ΔU_{Σ}, was calculated as recommended in the literature for organic compounds [21]. Details of all experiments performed are reported in Table S1 of the Supplementary Information.

$$\Delta U(\text{IBP}) = -\{\varepsilon_{cal} + \varepsilon_f\}\,\Delta T_{ad} + \Delta U(\text{ign}) \quad (7)$$

The standard specific internal combustion energy, $\Delta_c u^\circ$, of GZT is associated with the combustion reaction shown in Equation (8).

$$C_4H_{12}N_{16}(s) + 7O_2(g) \rightarrow 4CO_2(g) + 6H_2O(l) + 8N_2(g) \tag{8}$$

Results of six combustion experiments, the individual values of the standard specific internal energy of combustion with the mean value, and the corresponding standard deviation of the mean are reported in Table 2.

Table 1. Typical values of a combustion experiment of guanidinium 5,5′-azotetrazolate at T = 298.15 K and p° = 0.1 MPa.

m(cpd)/g [a]	0.25140
m(fuse)/g [b]	0.00252
m(n-hexadec.)/g [c]	0.25210
T_i/K [d]	298.1508
T_f/K [d]	299.1933
ΔT_{ad}/K [e]	0.95580
ε_i/J·K^{-1} [f]	16.31
ε_f /J·K^{-1} [f]	17.15
$-\Delta U$(IBP)/J [g]	15,310.98
ΔU(HNO$_3$)/J [h]	60.36
ΔU(ign)/J [i]	0.69
ΔU_Σ/J [j]	5.11
$-\Delta U$(n-hexadec.)/J [k]	11,883.16
$-\Delta U$(fuse)/J [l]	40.92
$-\Delta_c u^\circ$/(J·g^{-1}) [m]	13,211.73

[a] m(cpd) is the mass of compound burnt in each experiment; [b] m(fuse) is the mass of the fuse (cotton) used in each experiment; [c] m(n-hexadec.) is the mass of the n-hexadecane used in each experiment; [d] T_i and T_f denote the initial and final temperature rises, respectively; [e] ΔT_{ad} is the corrected temperature rise; [f] ε_i and ε_f are the energy equivalents of the contents in the initial and final state, respectively; [g] ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions; [h] ΔU(HNO$_3$) is the energy correction for the nitric acid formation; [i] ΔU(ign) is the electrical energy for ignition; [j] ΔU_Σ is the standard state correction; [k] ΔU(n-hexadec.) is the energy of combustion of the n-hexadecane; [l] ΔU(fuse) is the energy of combustion of the fuse (cotton); [m] $\Delta_c u^\circ$ is the standard specific internal combustion energy.

Table 2. Individual values of standard (p° = 0.1 MPa) specific internal combustion energy of the guanidinium 5,5′-azotetrazolate at T = 298.15 K.

$\Delta_c u^\circ$/(J·g^{-1})	−13,205.4 −13,225.8 −13,206.6 −13,223.6 −13,188.9 −13,211.7
<$\Delta_c u^\circ$>/(J·g^{-1})	−(13,210.3 ± 5.5) [a]

[a] Mean value and standard deviation of the mean.

The standard internal energy, $\Delta_c U^\circ(s)$, the standard enthalpy of combustion, $\Delta_c H^\circ(s)$, and the standard enthalpy of formation, $\Delta_f H^\circ(s)$, in the solid phase at T = 298.15 K are presented in Table 3. The uncertainties associated with the internal energy and enthalpy of combustion are the overall standard deviation of the mean and include the uncertainties in calibration with benzoic acid [34,35]. To calculate $\Delta_f H^\circ(s)$ from the enthalpy of combustion of GZT, the standard enthalpies of formation at T = 298.15 K were used for H_2O(l) (−(285.830 ± 0.040) kJ·mol^{-1}) [36] and CO_2(g) (−(393.51 ± 0.13) kJ·mol^{-1}) [36].

Table 3. Standard (p° = 0.1 MPa) molar energy of combustion, $\Delta_c U^\circ(s)$; enthalpy of combustion, $\Delta_c H^\circ(s)$; and enthalpy of formation in the solid phase, $\Delta_f H^\circ(s)$, for guanidinium 5,5′-azotetrazolate, at T = 298.15 K [a].

$\Delta_c U^\circ(s)$ / kJ·mol^{-1}	$\Delta_c H^\circ(s)$ / kJ·mol^{-1}	$\Delta_f H^\circ(s)$ / kJ·mol^{-1}
−3755.0 ± 3.2	−3742.6 ± 3.2	453.6 ± 3.2

[a] Uncertainties are twice the overall standard deviation of the mean and include the contributions from the calibration and from the auxiliary materials used.

A comparison of the value obtained in this work, (453.6 ± 3.2) kJ·mol^{-1}, with the previously reported values in the literature of 410.0 kJ·mol^{-1} [31], 452.2 kJ·mol^{-1} [32], and (387 ± 44) kJ·mol^{-1} [33] shows good agreement.

3.2. Computational Results for GZT

In order to estimate the $\Delta_f H^\circ(s)$ of GZT, first of all, the commonly used method was employed, in which the gas-phase enthalpies of the formation of the constituent ions (two equivalents of the guanidinium cation and one equivalent of the azotetrazolate anion) were calculated at both CBS-4M and CBS-QB3 levels of theory using atomization reactions. The value for $\Delta_f H^\circ(s)$ was then obtained through addition of the lattice energy, which was estimated using the Jenkins equation for an A_2B salt (Equation (9)) using the experimentally determined density of GZT (p = 1.538 g cm^{-3} [31]) and the molecular weight of GZT [14]. The value of +623 kJ·mol^{-1} estimated for GZT was much more endothermic than the value of (453.6 ± 3.2) kJ·mol^{-1} obtained experimentally in this work and also more than the experimentally determined values previously reported in the literature (+410 kJ·mol^{-1} [31], +452.2 kJ·mol^{-1} [32], and +387 kJ·mol^{-1} [33]). The discrepancy of 169 kJ·mol^{-1} between the experimental and computational values for $\Delta_f H^\circ(s)$ is less than the discrepancy of 254 kJ·mol^{-1} between the corresponding values for TKX-50 [7], but it is still very unsatisfactory.

$$U_{\mathrm{POT}}/\mathrm{kJ\ mol}^{-1} = 2\,I\,[10^{-7}\alpha\, N_A{}^{1/3}(\rho_m/M_m)^{1/3} + \beta] = \gamma(\rho_m/M_m)^{1/3} + \delta \quad (9)$$

Therefore, we searched for a different strategy to estimate the $\Delta_f H^\circ(s)$ of TKX-50 and GZT and found that a modified version using the enthalpy of the salt reaction ($\Delta_r H$) approach reported previously by Sinditskii [10] combined with the calculated $\Delta_f H^\circ(s)$ for the corresponding neutral adduct was much more successful. As we reported previously for TKX-50, using this approach [7], an estimated value for $\Delta_f H^\circ(s)$ of TKX-50 of +189.9 kJ·mol^{-1} using computational results from the CBS-4M level of theory and +180.9 kJ·mol^{-1} using computational results from CBS-QB3 was obtained [7], which are closer to the average experimentally determined value of $\Delta_f H^\circ(s)$ for TKX-50 of +193 kJ·mol^{-1} [7]. By employing the same approach for GZT, estimated values of +408.7 kJ·mol^{-1} (CBS-4M) and +405.8 kJ·mol^{-1} (CBS-QB3) were obtained, which are close to the experimental value obtained in this work (453.6 kJ·mol^{-1}) and those published in the literature (410 kJ·mol^{-1} [31], 452.2 kJ·mol^{-1} [32], and 387 kJ·mol^{-1} [33]). Using GZT as an example, the computational method used is outlined in detail below.

In the initial stage, the $\Delta_r H$ must be estimated according to Equation (2), as outlined previously by Sinditskii [10]. This is also described above in the computational section. The values of $\Delta_f H^\circ(s)$ of guanidinium nitrate (−386.9 kJ·mol^{-1}) [37], guanidine (−56.1 kJ·mol^{-1}) [37], and liquid nitric acid (−174.10 kJ·mol^{-1}) [24] are available in the literature. The value for $\Delta_r H$ can then be obtained from Equations (10) and (11).

$$(\mathrm{H_2N})_2\mathrm{C}=\mathrm{NH(s)} + \mathrm{HNO_3(l)} \overset{\Delta_r H}{\rightarrow} (\mathrm{H_2N})_3\mathrm{C^+NO_3{}^-(s)} \quad (10)$$

$$\Delta_r H = \Delta_f H^\circ((\mathrm{H_2N})_3\mathrm{C^+NO_3{}^-},\ \mathrm{s}) - \left[\Delta_f H^\circ\ (\mathrm{H_2N})_2\mathrm{C}=\mathrm{NH},\ (\mathrm{s}) + \Delta_f H^\circ\ (\mathrm{HNO_3},\ \mathrm{l})\right] \quad (11)$$

The value for $\Delta_r H$ is exothermic with respect to formation of the salt. In his original reports on the calculation of the $\Delta_r H$ for the base hydroxylamine, NH_2OH, Sinditskii used the value for $\Delta_r H$ of NH_2OH obtained based on the corresponding $NH_3OH^+NO_3^-$ and $NH_3OH^+ClO_4^-$ salts [10]. However, in the work reported herein, all of the values for the $\Delta_r H$ were calculated only using the corresponding nitrate salts, since the values for $\Delta_f H^\circ(s)$ of the corresponding perchlorate salts were not known for all bases. Table 4 shows a list of $\Delta_r H$ values for several bases, which were calculated based on the $\Delta_f H^\circ(s)$ of only the nitrate salt.

Table 4. Estimated values for the $\Delta H_{\text{salt reaction}}$ ($\Delta_r H$) calculated in this work based on the $\Delta_f H^\circ(s)$ of only the corresponding nitrate salts.

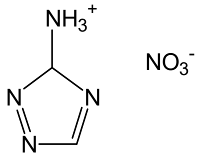
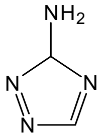
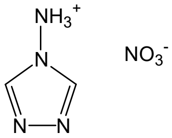
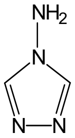
Salt	**$\Delta_f H^\circ$ (salt, s)/ kJ·mol^{-1}**	**$\Delta_f H^\circ$ (base)/ kJ·mol^{-1}**	**$\Delta_f H^\circ$ (acid)/ kJ·mol^{-1}**	**$\Delta_r H$/kJ·mol^{-1}**
$NH_3OH^+NO_3^-$	−366.5 [24]	NH_2OH(s) = −114.2 [24]	HNO_3(l) = −174.10 [24]	−78.2
$NH_4^+NO_3^-$	−365.56 [24]	NH_3(g) = −46.11 [24]	HNO_3(l) = −174.10 [24]	−145.35
$C(NH_2)_3^+NO_3^-$	−386.94 [24]	guanidine(s) = −56.1 [24]	HNO_3(l) = −174.10 [24]	−156.8
$AG^+NO_3^-$	−278.7 [37]	AG(s) = +58.5 [37]	HNO_3(l) = −174.10 [24]	−163.1
$DAG^+NO_3^-$	−157.3 [24]	DAG(s) = +167.4 [37]	HNO_3(l) = −174.10 [24]	−150.6
$TAG^+NO_3^-$	−50.2 [37]	TAG(s) = +287.7 [37]	HNO_3(l) = −174.10 [24]	−163.8
5-$AT^+NO_3^-$	−27.6 [24]	5-AT(s) = +207.9 [24]	HNO_3(l) = −174.10 [24]	−61.4
$N_2H_5^+NO_3^-$	−251.58 [24]	N_2H_4(l) = +50.63 [24]	HNO_3 (l) = −174.10 [24]	−128.1
$(H_2N)_2COH^+NO_3^-$	−564.0 [24]	urea(cr) = −333.51 [24]	HNO_3(l) = −174.10 [24]	−56.39
 3-amino-1,2,4-triazolium$^+NO_3^-$	−171.1 [24]	 3-amino-1,2,4-triazole (s) = +77.0 [24]	HNO_3(l) = −174.10 [24]	−74
Anilinium$^+NO_3^-$	−182. [27]	aniline (l) = +31.3 [27]	HNO_3(l) = −174.10 [24]	−40
$EtNH_3^+NO_3^-$	−366.9 [24]	$EtNH_2$(l) = −74.1 [24]	HNO_3(l) = −174.10 [24]	−118.7
$Me_2NH_2^+NO_3^-$	−352.0 [24]	Me_2NH(l) = −43.9 [27]	HNO_3(l) = −174.10 [24]	−134.0
$Me_3NH^+NO_3^-$	−343.9 [24]	Me_3N(l) = −46.0 [24]	HNO_3(l) = −174.10 [24]	−123.8
$MeNH_3^+NO_3^-$	−354.4 [24]	$MeNH_2$(l) = −47.3 [24]	HNO_3(l) = −174.10 [24]	−132.6
$Et_2NH_2^+NO_3^-$	−418.8 [24]	Et_2NH(l) = −103.3 [24]	HNO_3(l) = −174.10 [24]	−141.7

Table 4. *Cont.*

Salt	$\Delta_f H^{\circ}$ **(salt, s)/ kJ·mol^{-1}**	$\Delta_f H^{\circ}$ **(base)/ kJ·mol^{-1}**	$\Delta_f H^{\circ}$ **(acid)/ kJ·mol^{-1}**	$\Delta_r H$**/kJ·mol^{-1}**
$Et_3NH^+NO_3^-$	−447.7 [37]	$Et_3N(l)$ = −169.0 [27]	$HNO_3(l)$ = −174.10 [24]	−104.6
 4-amino-1,2,4-triazolium nitrate	+2 [38]	 4-amino-1,2,4-triazole(s) = +223.13 [39]	$HNO_3(l)$ = −174.10 [24]	−47.03

Using the value for $\Delta_r H$ obtained as described above, in the first step, the value of $\Delta_f H^{\circ}(s)$ for the GZT salt was then estimated according to Equations (12) and (13), in which $H_2C_2N_{10}$ is the acid of the azotetrazolate dianion. Since the $\Delta_f H^{\circ}(s)$ value for this acid is not known, the $\Delta_f H^{\circ}(g)$ was calculated for $H_2C_2N_{10}$ at CBS-4M (+935 kJ·mol^{-1}) or CBS-QB3 (+929 kJ·mol^{-1}) levels of theory and converted to the $\Delta_f H^{\circ}(s)$ value by subtraction of the value of $\Delta_{sub} H^{\circ}$. The $\Delta_{sub} H^{\circ}$ value for $H_2C_2N_{10}$ used was either approximated as being the same as the value estimated for the similar acid of the TKX-50 dianion (129 kJ·mol^{-1}) [7], estimated using the empirical approach reported previously in the literature (98 kJ·mol^{-1}) [29], or estimated using the empirical approach implemented in the RoseBoom© program (103.3 kJ·mol^{-1}) [30]. Since the base undergoes double protonation in Equation (12), the value for $\Delta_r H$ has to be included twice in Equation (13).

$$2(H_2N)_2C = NH(s) + H_2C_2N_{10}(s) \overset{\Delta_r H}{\rightarrow} ((H_2N)_3C)_2C_2N_{10}(s) \tag{12}$$

$$\Delta_f H^{\circ}(GZT,\ s) = 2 \times \Delta_f H^{\circ}(H_2N)_2C = NH,\ s) + \Delta_f H^{\circ}(H_2C_2N_{10},\ s) + 2 \times \Delta_r H \tag{13}$$

This value was slightly more exothermic than the experimentally determined value, as was also the case for TKX-50. In contrast to step one, which estimated the $\Delta_f H^{\circ}(s)$ of GZT purely as a salt, in the second step, the $\Delta_f H^{\circ}(s)$ of the neutral adduct formed between two neutral guanidine molecules and one $H_2C_2N_{10}$ acid was estimated. In order to do this, the $\Delta_f H^{\circ}(g)$ of the neutral adduct was calculated at the CBS-4M (or CBS-QB3) level, and the values for the $\Delta_{sub} H^{\circ}$ or $\Delta_{vap} H^{\circ}$ for both the neutral acid and neutral base were subtracted. The, resulting value is only an approximate value of the $\Delta_f H^{\circ}(s)$ for the neutral adduct, since the correct value can only be obtained by subtraction of the $\Delta_{sub} H^{\circ}$ of the adduct, which is not known. Experimentally determined values for $\Delta_{sub} H^{\circ}$ and $\Delta_{vap} H^{\circ}$ were used preferentially when available in the literature. In cases where no experimentally determined values for $\Delta_{sub} H^{\circ}$ and $\Delta_{vap} H^{\circ}$ were available, these values were estimated using either the empirical approach previously reported in the literature [29], or using the RoseBoom© program [30]. In this step, the value for $\Delta_r H$ is not required.

As stated by Sinditskii [10], the $\Delta_r H$ is a different value for each base, i.e., the $\Delta_r H$ for NH_3 is different from the value for N_2H_4. However, Sinditskii states that for a given base, e.g., NH_3, the $\Delta_r H$ remains the same regardless of whether the acid forming the salt is HNO_3, $HClO_4$, or HN_3 [10]. This means that for every "new" base which is used for preparing energetic salts, the $\Delta_f H^{\circ}(s)$ of the nitrate salt of the "new" base has to be determined using combustion calorimetry in order for the value for the $\Delta_r H$ to be estimated. However, once the $\Delta_r H$ is known for a given base, this value is used as the value for $\Delta_r H$ for every energetic salt containing that base.

Using GZT as a working example, the calculated value for $\Delta_f H^{\circ}(g)$ for the GZT adduct at the CBS-4M level of theory was +806.8 kJ·mol^{-1}, the experimentally determined value of

$\Delta_{\mathrm{sub}}H^{\circ}$ for neutral guanidine was reported in the literature as being 78.3 kJ·mol^{-1} [38], and the estimated value of $\Delta_{\mathrm{sub}}H^{\circ}$ for $H_2C_2N_{10}$ was 129 kJ·mol^{-1} using the empirical approach reported in the literature [29] and 103.1 kJ·mol^{-1} using the RoseBoom© program [30]. Subtraction of the $\Delta_{\mathrm{sub}}H^{\circ}$ values from the $\Delta_{\mathrm{f}}H^{\circ}(\mathrm{g})$ of the GZT adduct calculated at the CBS-4M level of theory resulted in an estimated value for the $\Delta_{\mathrm{f}}H^{\circ}(\mathrm{s})$ GZT adduct of +521.2 kJ·mol^{-1}, which is 141 kJ·mol^{-1} more endothermic than the calculated values in step one for the GZT salt. Using the $\Delta_{\mathrm{sub}}H^{\circ}$ value estimated by RoseBoom© [30] for the $H_2C_2N_{10}$ acid of 103.1 kJ·mol^{-1} results in a value for the $\Delta_{\mathrm{f}}H^{\circ}(\mathrm{s})$ of the GZT adduct of 547.1 kJ·mol^{-1}. Calculation of the $\Delta_{\mathrm{f}}H^{\circ}(\mathrm{g})$ for the GZT adduct at the CBS-QB3 level of theory results in a value of +818 kJ·mol^{-1} and a value for the $\Delta_{\mathrm{f}}H^{\circ}(\mathrm{s})$ of the GZT-adduct of +532.4 kJ·mol^{-1} (Equations (14) and (15)).

$$2(\mathrm{H_2N})_2\mathrm{C}=\mathrm{NH(s)}+\mathrm{H_2C_2N_{10}(s)}\ \rightarrow(\mathrm{N_2N})_2\mathrm{C}=\mathrm{NH}\bullet\mathrm{H_2C_2N_{10}}\bullet\mathrm{NH}=\mathrm{C(NH_2)_2(s)} \tag{14}$$

$$\begin{aligned}\Delta_{\mathrm{f}}H^{\circ}(\mathrm{GZT-adduct,\ s}) = {}& \Delta_{\mathrm{f}}H^{\circ}((\mathrm{N_2N})_2\mathrm{C}=\mathrm{NH}\bullet\mathrm{H_2C_2N_{10}}\bullet\mathrm{NH}=\mathrm{C(NH_2)_2,\ g}) - \\ & 2\ \times\ \Delta_{\mathrm{sub}}H^{\circ}\ ((\mathrm{H_2N})_2\mathrm{C}=\mathrm{NH,\ s}) - \Delta_{\mathrm{sub}}H^{\circ}(\mathrm{H_2C_2N_{10},\ s})\end{aligned} \tag{15}$$

Since the calculated value for the GZT salt in step one is slightly too exothermic and the value calculated in step wo for the GZT adduct is too endothermic with respect to the experimentally determined value, the average of the two values was calculated (+451 kJ·mol^{-1} using values calculated at CBS-4M level of theory), as well as the 80:20 weighted ratio of the salt:adduct values, which gave a value of 409 kJ·mol^{-1} (using values calculated at the CBS-4M level of theory). These values are in good agreement with the experimentally determined value of +453.6 kJ·mol^{-1} reported in this work and the two values available in the literature: +410 kJ·mol^{-1} [31] and 452.2 kJ·mol^{-1} [32].

Using this approach, it is not necessary to calculate the constituent ions in the gas phase or the lattice enthalpy. Since the source of the problems using the CBS-4M/Jenkins approach has still not been unambiguously identified, a different approach is appealing. However, in order to determine whether the approach described in this work generally provides $\Delta_{\mathrm{f}}H^{\circ}(\mathrm{s})$ values for the energetic salts which show good agreement with experimentally determined values, this approach was used for series of 2:1 and 1:1 salts and the results were compared with the experimentally determined $\Delta_{\mathrm{f}}H^{\circ}(\mathrm{s})$ values for the salts. The results are summarized for 2:1 salts in Table 5 and details of the values used and obtained in steps one and two for these compounds are given in the Supplementary Information.

Table 5. Estimated values for the $\Delta_{\mathrm{f}}H^{\circ}(\mathrm{s})$ for 2:1 salts using values calculated at the CBS-4M level of theory where necessary, as well as the experimentally determined $\Delta_{\mathrm{f}}H^{\circ}(\mathrm{s})$ values previously reported in the literature (all values in kJ·mol^{-1}).

Compound	**$\Delta_{\mathrm{f}}H^{\circ}$ CBS-4M: Cation** *Anion* **$\Delta_{\mathrm{latt}}H$ (Jenkins)**	**$\Delta_{\mathrm{f}}H^{\circ}$ CBS-4M/Jenkins**	**$\Delta_{\mathrm{f}}H^{\circ}$ Salt**	**$\Delta_{\mathrm{f}}H^{\circ}$ Neutral Adduct**	**Average of Salt + Adduct**	**80:20**	**Exptl. Value**	**Δ (Exptl. and 80:20 Values)**
TKX-50	**2 × +685.8** *1 × +566.8* −1488.95	+449.45	+168.1	+302.3	+235.2	+194.94	+193 (average) [7]	+1.94
TKX-50	**2 × +685.8** *1 × +566.8* −1488.95	+449.45	+156.2	+290.4	+223.3	+183.04	+193 (average) [7]	−9.96
GZT	**2 × 570.31** *1 × +770.5* −1287.98	+623.14	+380.6	+521.2	+450.9	+408.72	+410 [31] +452 [32] +387 [33]	−1.28, −43.28, +21.72
AG_2AzT	**2 × 669.73** *1 × +770.5* −1246.01	+863.95	+597.2	+739.9	+668.55	+625.74	+462 [31], +434 [32], +782 [32]	+163.74, +191.74 −156.26

Table 5. *Cont.*

Compound	**$\Delta_f H^\circ$ CBS-4M: Cation** *Anion* **$\Delta_{latt}H$ (Jenkins)**	**$\Delta_f H^\circ$ CBS-4M/Jenkins**	**$\Delta_f H^\circ$ Salt**	**$\Delta_f H^\circ$ Neutral Adduct**	**Average of Salt + Adduct**	**80:20**	**Exptl. Value**	**Δ (Exptl. and 80:20 Values)**
DAG_2AzT	**2 × 814.9** *1 × +770.5* −1215.11	+1185.19	+840	+1021.23	+930.62	+876.25	+709 [32]	+167.25
TAG_2AzT	**2 × 923.88** *1 × +770.5* −1177.40	+1440.9	+11,054.2	+1199.6	+1126.9	+1083.28	+1075 [31], +1065 [32]	+8.28, +18.28
$(NH_4)_2AzT$	**2 × 634.6** *1 × +770.5* −1467.43	+572.27	+423.48	+610.8	+517.14	+460.94	+443.9 [32] +452 [32]	+17.04, +8.94
$(N_2H_5)_2AzT$	**2 × +772.48** *1 × +770.5* —	density unknown	+651.5	+794.4	+722.95	+680.08	+659 [32]	+21.08
G_2CO_3	**2 × +570.31** *1 × −247.78* −1415.0	−522.16	−1033.58	−889.1	−961.34	−1004.68	−971.1 [27]	−33.58
$(NH_4)_2SO_4$	**2 × +634.6** *1 × −608.8* −1806.74	−1146.34	−1196.9	−948.97	−1072.94	−1147.31	−1180.9 [24]	+33.59
$(NH_3OH)_2SO_4$	**2 × +685.8** *1 × −608.8* −1712.2	−949.2	−1200.0	−1076.09	−1138.05	−1175.2	−1181.98 [24]	+6.78
$(NH_4)_2C_2O_4$	**2 × +634.6** *1 × −566.21* —	density unknown	−1210.2	−981.43	−1095.82	−1164.45	−1123.0 [24]	−41.45

A comparison of the experimentally determined values of $\Delta_f H^\circ(s)$ for the 2:1 salts in Table 5 with the estimated values based on the approach used in this work resulted in a maximum deviation of 44 $kJ \cdot mol^{-1}$, except for AG_2AzT and DAG_2AzT, which showed a particularly large deviation between the experimental and estimated values of over 150 $kJ \cdot mol^{-1}$. For AG_2AzT, there are widely different values reported in the literature for $\Delta_f H^\circ(s)$: 462, 434, and 782 $kJ \cdot mol^{-1}$. Therefore, it would also be beneficial for this value to be determined again experimentally. It is interesting to note the relatively similar values reported for the experimentally determined values of $\Delta_f H^\circ(s)$ for the guanidinium and aminoguanidinium salts. For all other 2:1 salts, the agreement was satisfactory and much better than that using the previous CBS-M/Jenkins method. The results using the CBS-QB3 higher level of theory (Table 6) were very similar, however, they required much longer computational times for the neutral Base•Acid•Base adducts which were calculated in C_1 symmetry.

Therefore, in order to establish whether this approach was also valid for estimating the $\Delta_f H^\circ(s)$ values for 1:1 salts of the AB type, the $\Delta_f H^\circ(s)$ of a series of such compounds was estimated using an analogous procedure to that described above for the 2:1 salts, using values calculated at either the CBS-4M level of theory (Table 7) or the CBS-QB3 (Table 8) level of theory. Tables giving more detail about the values used are included in the Supplementary Information.

Table 6. Estimated values for the $\Delta_f H^\circ(s)$ for 2:1 salts using values calculated at the CBS-QB3 level of theory where necessary, as well as the experimentally determined $\Delta_f H^\circ(s)$ values previously reported in the literature (all values in kJ·mol^{-1}).

Compound	$\Delta_f H^\circ$ CBS-QB3: Cation *Anion* $\Delta_{latt}H$ (Jenkins)	$\Delta_f H^\circ$ CBS-B3/ Jenkins	$\Delta_f H^\circ$ Salt	$\Delta_f H^\circ$ Neutral Adduct	Average of Salt + Adduct	80:20	Exptl. Value	Δ (Exptl. and 80:20 Values)
TKX-50	**2 × +669.2** *1 × +541.05* −1488.95	+390.5	+168.3	+240.49	+204.4	+182.74	+193 (average) [7]	−10.26
TKX-50	**2 × +669.2** *1 × +541.05* −1488.95	+390.5	+168.3	+252.39	+210.3	+185.12	+193 (average) [7]	−7.88
GZT	**2 × 570.31** *1 × +790.5* −1287.98	+643.14	+374.2	+532.37	+453.3	+405.83	+410 [31], +452 [32], +387 [33]	−4.17, +18.83, −46.17
AG_2AzT	**2 × 668.9** *1 × +790.5* −1246.01	+882.29	−509.8	+737.9	+664.4	+620.22	+462 [32], +434 [32], +782 [32]	+158.22, +186.22, −161.78
DAG_2AzT	**2 × 813.1** *1 × +790.5* −1215.11	+1201.59	+833.6	+885.56	+859.6	+843.99	+709 [32]	+134.99
TAG_2AzT	**2 × 920.8** *1 × +790.5* −1177.40	+1454.7	+1047.8	+1167.04	+1107.42	+1071.65	+1075 [31], +1065 [32]	−3.35, +6.65
$(NH_4)_2AzT$	**2 × 632.12** *1 × +790.5* −1467.43	+587.31	+417.08	+623.03	+520.1	+458.27	+443.9 [32], +452 [32], +551 [32]	+14.37, +6.27, −92.73
$(N_2H_5)_2AzT$	**2 × 765.52** *1 × +790.5* -	density unknown	+645.06	+784.88	+714.97	+673.02	+659 [32] +858 [32]	+14.02, −184.98
G_2CO_3	**2 × +570.31** *1 × −232.2* −1415.0	−505.68	−1044.6	−902.36	−973.48	−1016.15	−971.1 [27]	−45.05
$(NH_4)_2SO_4$	**2 × +632.12** *1 × −607.3* −1806.74	−1149.8	−1196.9	−989.22	−1093.1	−1155.36	−1180.9 [24]	+25.54
$(NH_3OH)_2SO_4$	**2 × +669.2** *1 × −607.3* −1712.2	−981.1	−1200.0	−1143.6	−1171.8	−1188.72	−181.98 [24]	−6.74

Table 7. Estimated values for the $\Delta_f H^\circ(s)$ for 1:1 salts using values calculated at the CBS-4M level of theory where necessary, as well as the experimentally determined $\Delta_f H^\circ(s)$ values previously reported in the literature (all values in kJ·mol^{-1}).

Compound	$\Delta_f H^\circ$ CBS-4M: Cation *Anion* $\Delta_{latt}H$ (Jenkins)	$\Delta_f H^\circ$ CBS-4M/ Jenkins	$\Delta_f H^\circ$ Salt	$\Delta_f H^\circ$ Neutral Adduct	Average of Salt + Adduct	80:20	Exptl. Value	Δ (Exptl. and 80:20 Values)
$NH_4^+C(NO_2)_3^-$	**+634.59** *−219.3* −531.92	−116.6	−239.7	−113.7	−176.7	−214.5	−197.9 [39]	−16.6
$NH_4^+N_3^-$	**+634.59** *+188.96* −660.0	+163.55	+72.54	+202.56	+137.55	+98.54	+115.6 [24]	−17.06
$NH_4^+HCO_2^-$	**+634.59** *−481.0* −638.99	−485.4	−616.18	−495.3	−555.74	−592.0	−567.48 [24]	−24.52
$NH_4^+HCO_3^-$	**+634.59** *−735.70* −639.70	−740.81	−891.11	−740.29	−815.7	−860.9	−849.4 [24]	−11.5

Table 7. *Cont.*

Compound	Δ_fH° CBS-4M: Cation *Anion* $\Delta_{latt}H$ (Jenkins)	Δ_fH° CBS-4M/ Jenkins	Δ_fH° Salt	Δ_fH° Neutral Adduct	Average of Salt + Adduct	80:20	Exptl. Value	Δ (Exptl. and 80:20 Values)
$NH_4^+CH_3COO^-$	**+634.59** *−523.13* −591.78	−480.32	−675.96	−558.97	−617.47	−652.6	−616.14 [24]	−36.46
NH_4^+picrate$^-$	**+634.59** *−376.1* −480.15	−221.6	−409.36	−288.01	−348.69	−385.09	−400.9, −389, −377.2 [40]	+15.31, +3.91, −7.89
NH_4^+3,5-dinitrobenzoate$^-$	**+634.59** *−546.2* −486.10	−397.7	−624.06	−571.44	−597.75	−613.5	−500.8 [40]	−112.7
$NH_4^+N(NO_2)_2^-$	**+634.59** *−123.93* −585.49	−74.83	−137.06	+1.09	−67.99	−109.43	−148 [41,42]	+38.57
$NH_4^+H_2NCOO^-$	**+634.59** *−521.5* −617.47	−504.38	−738.46	−518.3	−628.38	−694.43	−645.05 [24]	−49.38
$NH_4^+H_2NCOO^-$	**+634.59** *−521.5* −617.47	−504.38	−626.16	−630.6	−628.4.23	−627.0	−645.05 [24]	+18.05
$(H_2N)_3C^+$picrate$^-$	**+570.31** *−376.1* −444.73	−250.5	−430.8	−384.8	−407.8	−421.6	−396.6 [43]	−25.0
$(H_2N)_3C^+N(NO_2)_2^-$	**+570.31** *−123.93* −529.24	−82.86	−158.5	−90.08	−124.29	−166.4	−157.8, −170.3 [39]	−8.6, +3.9
$(H_2N)_3C^+$3,5-dinitrobenzoate$^-$	**+570.31** *−546.2* −460.0	−435.9	−645.5	−588.5	−617	−634.1	−593.5 [40]	−40.6
$AG^+N(NO_2)_2^-$	**+669.73** *−123.93* —	density unknown	−50.9	+17.81	−16.45	−37.16	−44 [39]	+6.84
$TAG^+N(NO_2)_2^-$	**+923.88** *−123.93* −488.07	+311.88	+178.3	+263.7	+221	+195.38	+182.9 [39]	−12.48
$N_2H_5^+C(NO_2)_3^-$	**+772.48** *−219.3* −532.0	+21.18	−125.67	−7.2	−66.44	−101.98	−71.69, −76.9 [44]	−30.29, −25.08
$N_2H_5^+NTO^-$	**+772.48** *−203.49* −545.0	+23.98	−206.87	−125.2	−166.04	−190.54	−231.4 [43]	+40.86
$N_2H_5^+N(NO_2)_2^-$	**+772.48** *−123.93* −568.86	+79.69	−23.07	+83.47	+30.2	−1.76	−13.6 [39]	+11.84
$N_2H_5^+CH_3NNO_2^-$	**+772.48** *−106.49* —	density unknown	−128.76	−34.18	−81.47	−109.84	−74.43 [45]	−35.41
$NH_3OH^+N(NO_2)_2^-$	**+685.76** *−123.93* —	density unknown	−138.6	−64.67	−101.64	−123.81	−139 [41,42]	+15.19

Table 7 shows that the agreement between the estimated values using values calculated at the CBS-4M level of theory and the experimentally determined values from the literature was generally very good. However, some problems were encountered. For example, H_2CO_3 is an unstable acid under ambient conditions, which complicates estimation of the value of the Δ_fH°(s) of G_2CO_3. Furthermore, the acid of the dinitramide anion $HN(NO_2)_2$ has also not been isolated as a pure compound in macroscopic amounts and has been presumed to be a liquid in this work. Similarly, the acid H_2NCOOH is stated in the literature as being unstable above −23 °C. Despite these issues, poor agreement between the estimated and experimentally determined values for Δ_fH°(s) was only observed for the ammonium salt of 3,5-dinitrobenzoate. It was found for the 1:1 salts that using the higher CBS-QB3 level of theory (Table 8) did not result in estimated values with significantly better agreement with the experimentally determined values in comparison with the values estimated using the CBS-4M level of theory.

Table 8. Estimated values for the $\Delta_fH^\circ(s)$ for 1:1 salts using values calculated at the CBS-QB3 level of theory where necessary, as well as the experimentally determined $\Delta_fH^\circ(s)$ values previously reported in the literature (all values in kJ·mol^{-1}).

Compound	**Δ_fH° CBS-4M: Cation** ***Anion*** **$\Delta_{latt}H$ (Jenkins)**	**Δ_fH° CBS-4M / Jenkins**	**Δ_fH° Salt**	**Δ_fH° neutral Adduct**	**Average of Salt + Adduct**	**80:20**	**Exptl. Value**	**Δ (Exptl. and 80:20 Values)**
$NH_4^+C(NO_2)_3^-$	**+632.12** *−243.16* −531.92	−142.96	−239.66	−144.95	−192.31	−220.72	−197.9 [44]	−22.82
$NH_4^+N_3^-$	**+632.12** *+190.84* −660.0	+163.0	+82.38	+193.7	+138.04	+104.6	+115.6 [24]	+11
$NH_4^+HCO_2^-$	**+632.12** *−481.0* −638.99	−482.5	−616.18	−505	−560.59	−593.94	−567.48 [24]	−26.46
$NH_4^+HCO_3^-$	**+632.12** *−735.70* −639.70	−742.92	−891.11	−743.57	−817.34	−861.60	−849.4 [24]	−12.2
$NH_4^+CH_3COO^-$	**+632.12** *−511.21* −591.78	−470.87	−675.96	−560.12	−618.04	−652.79	−616.14 [24]	−36.65
NH_4^+picrate$^-$	**+632.12** *−376.1* −480.15	−240.01	−409.36	−324.91	−367.14	−392.47	−400.9, −389 [40] −377.2	+8.43, −3.47, −15.27
$NH_4^+N(NO_2)_2^-$	**+632.12** *−123.93* −585.49	−95.75	−157.33	−59.27	−108.3	−137.72	−148 [41,42]	+10.28
$NH_4^+H_2NCOO^-$	**+632.12** *−521.5* −617.45	−501.63	−741.21	−524.89	−633.1	−697.9	−645.05 [24]	−52.9
$NH_4^+H_2NCOO^-$	**+632.12** *−521.5* −617.45	−501.63	−629.91	−637.19	−633.6	−636.5	−645.05 [24]	+8.55
$(H_2N)_3C^+N(NO_2)_2^-$	**+570.31** *−123.93* −529.24	−101.31	−178.77	−123.39	−151.08	−167.69	−157.8, −170.3 [39]	−9.89, +2.61
$N_2H_5^+C(NO_2)_3^-$	**+765.52** *−243.16* −532.0	−9.64	−125.67	−51	−88.34	−110.74	−71.69, −76.9 [44]	−39.05, −33.84
$N_2H_5^+NTO^-$	**+765.52** *−204.4* −545.0	+16.1	−206.87	−135.01	−170.94	−192.50	−231.4 [43]	+38.9
$N_2H_5^+N(NO_2)_2^-$	**+765.52** *−142.38* −568.86	+54.32	−43.34	+33.8	−4.77	−27.91	−13.6 [39]	−14.31
$N_2H_5^+CH_3NNO_2^-$	**+765.52** *−113.42* —	density unknown	−138.47	−47.71	−93.09	−120.32	−74.43 [45]	−45.89
$NH_3OH^+N(NO_2)_2^-$	**+669.15** *−142.38* —	density unknown	−158.87	−104.19	−131.53	−147.93	−139 [41,42]	−8.93

Again, the method of estimating the $\Delta_fH^\circ(s)$ for 1:1 salts described in this work appears to result in better predicted values than the widely used combination of calculations for the $\Delta_fH^\circ(g)$ values of the constituent ions in the gas phase and conversion into the $\Delta_fH^\circ(s)$ value for the salt, using the Jenkins equation for the lattice enthalpy [14]. However, in order to make this computational approach more simple and applicable for more salts, it is essential for further combustion calorimetry studies to be performed to obtain the $\Delta_fH^\circ(s)$ for nitrate salts of commonly-used C, H, N, O-containing bases and also, ideally to obtain the $\Delta_fH^\circ(s)$ of the commonly used neutral bases. It is also important that previously reported values for $\Delta_f H^\circ(s)$ determined experimentally for energetic salts are reinvestigated and confirmed. Only through multiple, independent, experimentally determined values of $\Delta_f H^\circ(s)$ for TKX-50 [7] was the unsatisfactory performance of the CBS-4M (ions in the gas phase)/Jenkins (lattice enthalpy) method established.

4. Conclusions

The enthalpy of formation of the salt guanidinium 5,5′-azotetrazolate (GZT) was determined experimentally, using static-bomb combustion calorimetry, to be (453.6 ± 3.2) kJ·mol^{-1}. Using the method described in this work and previously used for TKX-50, the enthalpy of formation of GZT(s) was estimated to be 406 kJ·mol^{-1}, which is in good agreement with the experimentally determined value. This value is in better agreement than the value of 643 kJ·mol^{-1} calculated using the widely used method of calculation of the enthalpy of formation of the gaseous ions at the CBS-4M level, followed by addition of the lattice enthalpy estimated using the Jenkins equation. The current unsatisfactory discrepancies of often 100 kJ·mol^{-1} between theory and combustion calorimetry values for 1:1 salts (AB), and even 200 kJ·mol^{-1} for 2:1 salts (A_2B) using the CBS-4M/Jenkins method, were investigated for a range of salts using the calculation of the enthalpy of formation of the salts using the $\Delta_r H$ approach combined with calculation of the $\Delta_f H^\circ(s)$ of the corresponding neutral adduct and the value obtained from an 80:20 weighting of these values. The agreement using this approach with the experimentally determined values is reasonable, and significantly better than the values obtained using the CBS-4M/Jenkins method. Until now, only very few $\Delta_f H^\circ(s)$ values for A_2B salts have been determined using combustion calorimetry, but agreement with the calculated values using this method has been shown to lead to a better coherency than using the CBS-4M/Jenkins approach.

Supplementary Materials: The following supporting information can be downloaded at: https://www.mdpi.com/article/10.3390/thermo3040033/s1, Table S1: Data of all the combustion calorimetry experiments of guanidinium 5,5′-azotetrazolate; Table S2: data of computational results on 1:1 salts at CBS-4M level of theory; Table S3: data of computational results on 1:1 salts at CBS-QB3 level of theory; Table S4: data of computational results on 1:1 adducts at CBS-4M level of theory; Table S5: data of computational results on 1:1 adducts at CBS-QB3 level of theory; Table S6: data of computational results on 2:1 salts at CBS-4M level of theory; Table S7: data of computational results on 2:1 salts at CBS-QB3 level of theory; Table S8: data of computational results on 2:1 adducts at CBS-4M level of theory; Table S9: data of computational results on 2:1 adducts at CBS-QB3 level of theory. References [21,24,31,36,46–48] are cited in the supplementary materials.

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Data Availability Statement: Detailed information of individual calculations can be obtained from the authors on request.

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