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RESEARCH ARTICLE

On the Enthalpy of Formation and Enthalpy of Sublimation of Dihydroxylammonium 5,5′-bitetrazole-1,1′-dioxide (TKX-50)

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Abstract

The thermodynamic characterization of dihydroxylammonium 5,5′-bitetrazole-1,1′-dioxide (TKX-50) was reinvestigated. Although TKX-50 is one of the most promising new-generation energetic materials, contradictory reports are found in the literature with regard to its solid enthalpy of formation. The standard ($p^\circ = 10^5$ Pa) molar enthalpy of formation of crystalline TKX-50, $(175.3 \pm 1.9)\ \mathrm{kJ \cdot mol^{-1}}$, was determined experimentally based on the measured standard massic energy of combustion, determined through static-bomb combustion calorimetry. Additionally, the standard molar enthalpy of sublimation of TKX-50, at $T = 298.15$ K, $(165.0 \pm 2.4)\ \mathrm{kJ \cdot mol^{-1}}$, was derived from vapor pressure measurements determined by a Knudsen mass-loss effusion technique. Finally, different approaches were used in attempts to calculate the standard enthalpy of formation of TKX-50 in the solid state. A critical overview and assessment of the data on the enthalpy of formation of TKX-50 is also presented.

KEYWORDS

CBS-QB3 level of theory, combustion calorimetry, enthalpy of formation, enthalpy of sublimation, TKX-50, vapor pressures

1 | INTRODUCTION

Dihydroxylammonium 5,5′-bitetrazole-1,1′-dioxide (TKX-50) is a high explosive which was first reported in 2012 [1]. It has been extensively investigated in the decade since, due to its excellent properties [2]. Since in-depth reviews have been dedicated to TKX-50, the properties which make is a highly promising candidate for use as a future high-explosive can be simplified here to being a combination of low sensitivity to external stimuli (impact, friction, ESD)

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with high thermal stability, high density and detonation velocity as well as low toxicity. Equally important is that fact that TKX-50 can be prepared using a simple and inexpensive synthetic route. In contrast to the high explosives RDX, HMX and TNT which are all neutral molecules, TKX-50 is a salt containing the $C_2N_8O_2^{2-}$ dianion and two NH_3OH^+ cations making it a 2:1 (ratio of ions) salt (Figure 1).

The detonation velocity (D) of TKX-50 has been determined experimentally by various groups, and all of the experimental values for the detonation velocity of TKX-50 (Table 1) are in good agreement. Furthermore, the agreement between the experimentally determined D and calculated D using EXPLO5 are also in excellent agreement.

However, the same cannot be said for the heat of formation of TKX-50, which has resulted in a plethora of values and discussion as to not only which value is best, but also which method should be used to calculate the enthalpy of formation of such a compound [7–12]. There is a large discrepancy between the value for the enthalpy of formation ($\Delta_f H^\circ_m$(cr)) originally reported (447 kJ·mol^{-1} calculated [1, 7], 439 kJ·mol^{-1} combustion calorimetry) [7, 12] and more recently reported experimental and calculated values which are given in tables 2 and 3 respectively [6, 8–12].

The experimentally determined (combustion calorimetry) value of Sinditskii of (111 ± 16) kJ·mol^{-1} [8] appears to be too low and the original reported value (combustion calorimetry) of 439 kJ·mol^{-1} is too high [1, 12]. The other experimentally determined results [6, 9, 10, 11] given in Table 2 are all relatively similar and result in an average value $\Delta_f H^\circ_m$(cr) of 197.4 kJ·mol^{-1}. This is considerably lower than calculated value of 447 kJ·mol^{-1} originally reported [1, 7, 12]. This discrepancy is problematic, since an accurate value for $\Delta_f H^\circ_m$(cr) is important for calculating the energetic properties of a compound such as the detonation velocity [13].

The calculation of $\Delta_f H^\circ_m$(cr) for neutral energetic molecules using the computational CBS-4M method is widespread [13, 14], as is calculation of the $\Delta_f H^\circ_m$(g) of constituent ions of a salt using CBS-4M followed by estimation of the lattice energy using the Jenkins equation in order to obtain $\Delta_f H^\circ_m$(cr) for salts [13, 14].

If, however, the calculated values for $\Delta_f H^\circ_m$(cr) for TKX-50 given in Table 3 are compared, then it is clear that the CBS-4M/Jenkins approach [7] results in a value which is too endothermic for TKX-50. The same approach using B3LYP/6-31G*/PM7/Jenkins was reported [15] to give a lower value which was in good agreement with the experimentally obtained value of 111 kJ·mol^{-1} by Sinditskii [8].

The main difference between the CBS-4M/Jenkins and B3LYP/6-31G*/PM7/Jenkins was optimization of the structures of the ions at B3LYP/6-31G* level in the latter calculation as opposed to HF/3-21G* in the CBS-4M method, and calculation of the energies of the ions at composite CBS-4M or PM7 level. The authors proposed

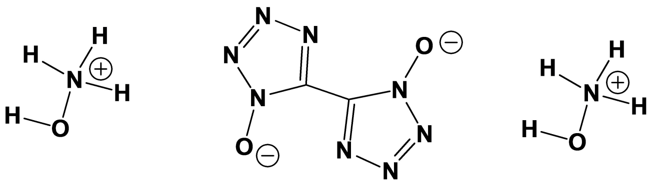

FIGURE 1 Structural formula of TKX-50.

TABLE 2 Experimentally determined enthalpies of formation for crystalline TKX-50 previously reported in the literature.

Method	$\Delta_f H^\circ_m$(cr)/kJ·mol^{-1}	Ref.
Combustion calorimetry	111 ± 16	[8]
Combustion calorimetry	194.1 ± 0.9	[9]
Combustion calorimetry	193	[10]
Combustion calorimetry	189	[11]
Combustion calorimetry	213.4 ± 1.2	[6]
Combustion calorimetry	439	[12]
Combustion calorimetry	175.3 ± 1.9	this work
Average of results marked	197.4	

TABLE 1 Results of detonation velocities (D) of TKX-50 and TKX-50 based formulations.

Condition	Density/ g·cm^{-3}	Method	D/m·s^{-1}	Ref.
Neat compound	1.877	LASEM	9560 ± 280	[3]
TKX-50/binder = 95.5/4.5	1.80	60 mm tube	9037	[4]
TKX-50/wax = 94.5/4.5	1.776	50 mm tube	9020	[5]
TKX-50/wax = 97/3	1.735	50 mm tube	9248	[6]
Calculated value (EXPLO5)	1.877		9698	[1]

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TABLE 3 Calculated enthalpies of formation for crystalline TKX-50 previously reported in the literature.

Method	$\Delta_f H^\circ_m$(cr)/ kJ·mol^{-1}	Ref.
CBS-4M $\Delta_f H^\circ_m$(g) of ions, lattice enthalpy determined using Jenkins' equation	447	[7]
Experimental $\Delta_f H^\circ_m$(cr) of NH_2OH, estimated $\Delta_f H^\circ_m$(cr) of $C_2H_2N_8O_2$ based on value for bistetrazole and estimated value for $\Delta H_{\text{salt reaction}}$	119	[8]
B3LYP/6-31G* structure optimization of gas phase ions followed by $\Delta_f H^\circ_m$(g) ions calculated using PM7, lattice enthalpy determined using Jenkins' equation	112.6	[15]
Calculated sum of ions model	171.1	[16]
Calculated isodesmic model	164.1	[16]

that the poor agreement between the originally calculated CBS-4M value and experimental value was the result of the wrong level of theory being use in the CBS-4M calculations [15]. However, we re-calculated the energies of the TKX-50 constituent ions by performing the same calculations as Christopher et al. [15] by performing geometry optimizations at B3LYP/6-31G* level of theory followed by PM7 single point energy calculations and obtained different results. We then recalculated the ions by performing structure optimizations at PM7 level of theory, followed by energy calculations at PM7 level of theory and obtained the same results as Christopher et al. reported [15]. Therefore, the value of 112.6 kJ·mol^{-1} [15] likely results from a semi-empirical PM7 calculation of the structures and energy and not B3LYP/6-31G* optimized structures as previously published [15]. Furthermore, in order to assess whether this approach (PM7 structure optimization and PM7 energy) was in fact, applicable to other related salts, we calculated a second 2 : 1 (ratio of ions) salt GZT using the PM7 method, and found the resulting heat of formation to be in poor agreement with experimentally obtained results, therefore, this approach is not to be recommended.

Sinditskii calculated the $\Delta_f H^\circ_m$(cr) for TKX-50 to be 119 kJ·mol^{-1} [8] by using the $\Delta_f H^\circ_m$(cr) for NH_2OH reported in the literature (−114.8 kJ·mol^{-1} [17]), as well as an estimated $\Delta_f H^\circ_m$(cr) for the acid of the anion, namely $C_2H_2N_8O_2$ (~481 kJ·mol^{-1}), by subtracting 50.7 kJ·mol^{-1} from the value for the enthalpy of formation of solid 5,5'-bistetrazole (531.7 kJ·mol^{-1}) reported in the literature [8]. No specific information was given for the 50.7 kJ·mol^{-1} subtracted. Finally, the heat of salt reaction was also used in this calculation. Sinditskii reported this value to be 67 kJ·mol^{-1} as the average value obtained for the reaction of NH_2OH (cr) with HNO_3 (l) forming $NH_3OH^+NO_3^-$ (cr) and NH_2OH (cr) with $HClO_4$ (l) forming $NH_3OH^+ClO_4^-$ (cr) [8]. However, using the $\Delta_f H^\circ_m$(cr) reported for $NH_3OH^+ClO_4^-$ in the literature of −276.8 kJ·mol^{-1} [18] results in values for the salt reaction of 78.2 kJ·mol^{-1} (NO_3^- salt) and 122.0 kJ·mol^{-1} (ClO_4^- salt) resulting in an average value of 100.1 kJ·mol^{-1} which is over 30 kJ·mol^{-1} higher than the value of 67 kJ·mol^{-1} reported by Sinditskii [8]. This discrepancy is probably the result of the different value used for $\Delta_f H^\circ_m$(cr) for $NH_3OH^+ClO_4^-$ in this work, since unfortunately, the value used by Sinditskii [8] in his work is a value from a 1968 US military report [19], which we have been unable to obtain a copy of. Therefore, in order to obtain an average value for the salt reaction with hydroxylamine as the base, we used the values in the NBS tables for $NH_3OH^+NO_3^-$ (cr), NH_2OH (cr), liquid HNO_3, $(NH_3OH)_2SO_4$ (cr) and liquid H_2SO_4 [17] and obtained an average value of 74 kJ·mol^{-1}, which is the value we used in the work reported herein. The value for the enthalpy of salt reaction for the formation of $NH_3OH^+NO_3^-$ (cr) was calculated to be 78.2 kJ·mol^{-1} and for $(NH_3OH)_2SO_4$ a value of 69.8 kJ·mol^{-1} per NH_2OH was calculated.

The calculated sum of ions model and calculated isodesmic model reported recently provides a much better calculated value for the $\Delta_f H^\circ_m$(cr) of TKX-50 [16]. However, it requires calculation of the molecular volumes of the constituent ions.

Since the standard enthalpy of formation is an important value to accurately know for predicting the energetic performance of a high explosive, and the determination of this value for TKX-50 produced so many contradictory results, we decided to re-determine the standard enthalpy of formation of TKX-50, in the crystalline phase, at T = 298.15 K, using high-accurate equipment of combustion calorimetry and compare this with results from quantum chemical calculations at the highest possible levels. In addition, the sublimation vapor pressures of the title compound were determined at several temperatures using the Knudsen effusion method. The experimental results enabled the determination of the standard molar enthalpy, entropy and Gibbs energy of sublimation, at T = 298.15 K, of TKX-50.

In addition, the standard enthalpy of formation of TKX-50 in the crystalline phase was calculated using

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different approaches that combined experimental results and quantum chemical calculations at the CBS-4M and also at the CBS-QB3 levels of theory, in order to find a more accurate predictive route for estimating the $\Delta_f H_m^\circ$ (cr) of TKX-50.

2 | EXPERIMENTAL SECTION

CAUTION! *TKX-50 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) have to be worn while synthesizing and handling TKX-50.*

2.1 | Materials characterization

TKX-50 was synthesized according to the literature and the purity checked by elemental analysis (CHN) and NMR spectroscopy (^{1}H, ^{13}C) [1].

The Hitachi-DSC7020 heat flow calorimeter was used to check whether phase transitions occurred in the crystalline phase of TKX-50, as well as to study the behavior of TKX-50 at different temperatures. The sample was sealed in an airtight aluminum crucible of 7.5 μL and scanned at 0.033 $K \cdot s^{-1}$ from $T \approx 301$ K to $T \approx 460$ K under a controlled nitrogen flux which was used to prevent eventual contamination of the calorimeter. Calibration of the equipment was performed using benzoic acid (NIST SRM 39j), indium (Sigma-Aldrich, mass fraction > 0.99999) and tin (Sigma-Aldrich, mass fraction > 0.99999). Figure 2 shows the thermogram obtained during the DSC experiment performed on TKX-50. This confirms the absence of crystalline phase transitions in the temperature range used for the volatility study of this compound (411.2 and 431.2) K (more details in section 3.2.). In a previous study, the thermal stability of TKX-50 was also evaluated, and showed that the onset of decomposition occurred at 495 K (heating rate of 0.083 $K \cdot s^{-1}$) [1]. In addition, the thermal behavior of TKX-50 was evaluated using differential scanning calorimetry (DSC), thermal gravimetric analysis-Fourier transform infrared spectroscopy (TG-FTIR) and thermal gravimetric analysis-differential scanning calorimetry-mass spectrometry (TG-DSC-MS) [20]. The critical temperature of thermal explosion and the initial decomposition temperature were determined to be 523.39 K and 513.80 K, respectively.

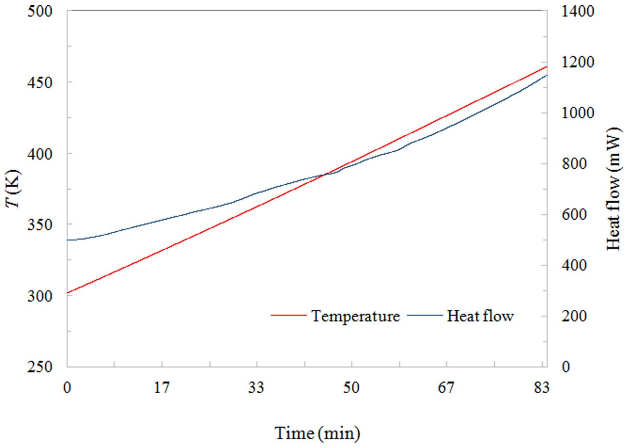

FIGURE 2 DSC thermogram of TKX-50 (heating rate 2 K/min).

2.2 | Combustion calorimetry

The combustion calorimetric experiments were achieved using a macro-combustion calorimeter previously described [21, 22]. The static-bomb used is a twin valve bomb whose internal volume is 0.342 dm^3 (type 1108 of Parr Instrument Company). The energy equivalent of the calorimeter and its standard deviation of the mean, $\varepsilon_{cal} = (16002.6 \pm 1.7)\ J \cdot K^{-1}$, were determined from the combustion of benzoic acid (NBS 39j) whose massic energy of combustion under the certificate conditions is $-(26434 \pm 3)\ J \cdot g^{-1}$. The calorimeter temperatures were measured to $\pm(1 \times 10^{-4})$ K, at time intervals of 10 s, with a quartz crystal thermometer (HP 2804A), interfaced to a PC; the ignition occurs at $T = (298.150 \pm 0.001)$ K.

Samples of TKX-50 were burnt in pellet form, under oxygen at $p = 3.04$ MPa, with 1.00 cm^3 of deionised water added to the bomb. *n*-Hexadecane (Aldrich, mass fraction > 0.999), stored under nitrogen, was used as auxiliary combustion in most of the experiments, in order to obtain an adequate temperature rise. The energetic correction for the nitric acid formation, $\Delta U(HNO_3)$, was based on $-59.7\ kJ \cdot mol^{-1}$ for the molar energy of formation of 0.1 $mol \cdot dm^{-3}$ $HNO_3(aq)$ from $N_2(g)$, $O_2(g)$ and $H_2O(l)$ [17].

The standard massic energy of combustion, $\Delta_c u^\circ$, was calculated by a similar procedure to that developed by Hubbard et al. [23]. Further details about the experimental procedure are provided in ESI.

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2.3 | Knudsen effusion method

The vapor pressures of the crystalline phase of TKX-50 were measured, at different temperatures, using the Knudsen mass-loss effusion method. The apparatus used in this work lets the simultaneous operation of nine effusion cells that are inserted into cylindrical holes inside three aluminum blocks. Each of these blocks is kept at a constant temperature, different from the other two, and contains three cells with differently sized effusion orifices, made on platinum foil of (0.0125±0.001) mm thickness and with the following areas: $A_o(A_1)=A_o(A_2)=A_o(A_3)=(0.636\pm0.004)\ \mathrm{mm}^2$, $A_o(B_1)=A_o(B_2)=A_o(B_3)=(0.785\pm0.004)\ \mathrm{mm}^2$ and $A_o(C_1)=A_o(C_2)=A_o(C_3)=(0.985\pm0.004)\ \mathrm{mm}^2$. The Clausing factors for the orifices of the series A, B and C were calculated as 0.986, 0.988 and 0.989, respectively, using $w_o=1/\{1+(l/2r)\}$, where r is the radius of the orifices and l is the thickness of the platinum foil [24]. More information about this installation, procedure and testing has already been described in detail [25].

In each experiment, the mass of the sublimed sample due to the effusion process, Δm, was determined by weighing the cells before and after the effusion period, t, with an estimated uncertainty of 1×10^{-5} g. Equation (1) was used to calculate the vapor pressure p of the crystalline sample, contained in each effusion cell, at the temperature T.

$$p=\frac{\Delta \mathrm{m}}{A_o w_o t}\left(\frac{2\pi RT}{M}\right)^{0.5} \tag{1}$$

In this equation, M is the molar mass of the effusing vapor and R is the molar gas constant ($8.314462618\ \mathrm{J\cdot K^{-1}\cdot mol^{-1}}$) [26]. The standard uncertainties of the vapor pressure and temperatures measurements were estimated as $u(p/\mathrm{Pa})=0.02$ and $u(T/\mathrm{K})=0.01$.

2.4 | Computational methods

All quantum chemical calculations were carried out using the Gaussian G16 W program package [27]. The enthalpies (H) and free energies (G) were calculated using the complete basis set (CBS) method of Petersson and co-workers in order to obtain very accurate energies. The CBS models are using the known asymptotic convergence of pair natural orbital expressions to extrapolate from calculations using a finite basis set to the estimated CBS limit.

The CBS-QB3 has been modified by the inclusion of diffuse functions in the geometry optimization step to give CBS-QB3 [28]. 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 [29].

3 | RESULTS AND DISCUSSION

3.1 | Experimental enthalpy of formation of solid TKX-50

Detailed results of each combustion experiment for TKX-50 are presented in Table S1 of the supplementary information. Some results of the seven combustion experiments and the individual values of the massic energy of combustion, $\Delta_c u^\circ$, for TKX-50 are given in Table 4. The values of $\Delta_c u^\circ$ refer to the quantitative combustion reaction represented by equation (2).

TABLE 4 Experimental data from combustion experiments for TKX-50.[a]

m(TKX-50)/g	m(n-hexadec.)/g	ΔT_{ad}/K	$-\Delta U$(IBP)/J	$\Delta U(\mathrm{HNO_3})$/J	$-\Delta U$(n-hexadec.)/J	$-\Delta_c u^\circ/(\mathrm{J\cdot g^{-1}})$
0.66454	–	0.37699	6039.14	33.43	–	8962.30
0.65357	–	0.37182	5956.30	48.66	–	8963.19
0.64754	0.23768	1.06974	17137.86	62.69	11203.47	8983.05
0.64742	0.21020	0.98832	15833.31	63.88	9908.29	8976.76
0.60282	0.20928	0.96016	15381.84	57.55	9864.87	8966.42
0.60045	0.21696	0.98079	15712.73	55.04	10226.90	8954.94
0.60856	0.17112	0.85137	13639.09	55.52	8066.07	8977.59
						$-(8969.2\pm3.8)$[b]

[a] m(n-hexadec.) is the mass of n-hexadecane used in each experiment; ΔT_{ad} is the corrected temperature rise; ΔU(IBP) is the energy change for the isothermal combustion reaction under actual bomb conditions and includes ΔU(ign); $\Delta U(\mathrm{HNO_3})$ is the energy correction for the nitric acid formation; ΔU(n-hexadec.) is the energy of combustion of the n-hexadecane; $\Delta_c u^\circ$ is the standard massic energy of combustion. Detailed information about all the corrections considered is provided in Table S1 of Supplementary Information.

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

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$$\begin{aligned} C_2H_8N_{10}O_4(\mathrm{cr}) \ + \ 2O_2(\mathrm{g}) \ \rightarrow \\ 2CO_2(\mathrm{g}) \ + \ 4H_2O(\mathrm{l}) \ + \ 5\,N_2(\mathrm{g}) \end{aligned} \tag{2}$$

The internal energy for the isothermal bomb process, $\Delta U(\mathrm{IBP})$, was calculated through equation (3), where ΔT_{ad} is the corrected temperature rise obtained in each experiment, ε_{f} is the energy equivalent of contents in the final state and $\Delta U(\mathrm{ign})$ is the electrical energy for ignition.

$$\Delta U(\mathrm{IBP}) = -\{\varepsilon_{\mathrm{cal}} \ + \ \varepsilon_{\mathrm{f}} \ \} \ \Delta T_{\mathrm{ad}} \ + \ \Delta U(\mathrm{ign}) \tag{3}$$

The mean value of the standard ($p^\circ = 0.1$ MPa) massic energy of combustion of TKX-50, as well as, the derived standard molar internal energy of combustion, $\Delta_{\mathrm{c}}U^{\circ}_{\mathrm{m}}(\mathrm{cr})$ and enthalpy of combustion, $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{cr})$, and the standard molar enthalpy of formation, in the crystalline phase, $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{cr})$, at $T = 298.15$ K, are reported in Table 5. The uncertainties associated with the standard molar energy and enthalpy of combustion are twice the overall standard deviation of the mean and include the uncertainties in calibration with benzoic acid [30, 31]. To derive $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{cr})$ from $\Delta_{\mathrm{c}}H^{\circ}_{\mathrm{m}}$ (cr), the standard molar enthalpies of formation, at $T = 298.15$ K, were used for $H_2O(\mathrm{l})$, $-(285.830 \pm 0.040)$ $\mathrm{kJ \cdot mol^{-1}}$, and $CO_2(\mathrm{g})$ $-(393.51 \pm 0.13)$ $\mathrm{kJ \cdot mol^{-1}}$ [32].

3.2 | Thermodynamic properties of sublimation

The effusion vapor pressures of TKX-50, reported in Table 6, are the mean of the results determined through the different effusion orifices at each temperature, listed in detail in Table S2. The volatility study of this compound was performed over the range (0.03 and 0.33) Pa, between (411.2 and 431.2) K. At higher temperatures the effusion vapor pressure results showed significant deviations and therefore were not considered. The experimental (p,T) results of this compound were fitted by the Clarke and Glew equation (truncated form) [33], eq. 4.

$$R\ln\left(\frac{p}{p^{\mathrm{o}}}\right) = -\frac{\Delta^{\mathrm{g}}_{\mathrm{cr}}G^{\mathrm{o}}_{\mathrm{m}}(\theta)}{\theta} + \Delta^{\mathrm{g}}_{\mathrm{cr}}H^{\mathrm{o}}_{\mathrm{m}}(\theta)\left(\frac{1}{\theta} - \frac{1}{T}\right) + .$$

$$\Delta^{\mathrm{g}}_{\mathrm{cr}}C^{\mathrm{o}}_{p,\mathrm{m}}(\theta)\left[\left(\frac{\theta}{T}\right) - 1 + \ln\left(\frac{T}{\theta}\right)\right]\mathrm{S} > (4)$$

In this equation, p^{o} is a selected reference pressure (in this work, $p^{\mathrm{o}} = 10^5$ Pa), p is the vapor pressure at the temperature T, θ is a reference temperature (in this work, unless stated otherwise, $\theta = 298.15$ K) and R is the molar gas constant. The differences between gaseous and crystalline phases of standard Gibbs energy, enthalpy, and heat capacity at constant pressure, are represented, respectively, by $\Delta^{\mathrm{g}}_{\mathrm{cr}}G^{\circ}_{\mathrm{m}}$, $\Delta^{\mathrm{g}}_{\mathrm{cr}}H^{\circ}_{\mathrm{m}}$, and $\Delta^{\mathrm{g}}_{\mathrm{cr}}C^{\circ}_{p,\mathrm{m}}$. The values of these properties, the assigned uncertainties and the results of $\Delta^{\mathrm{g}}_{\mathrm{cr}}S^{\circ}_{\mathrm{m}}(\theta)$ – calculated through equation (5) – are listed in Table 7.

$$\Delta^{\mathrm{g}}_{\mathrm{cr}}S^{\circ}_{\mathrm{m}}(\theta) = \frac{\Delta^{\mathrm{g}}_{\mathrm{cr}}H^{\mathrm{o}}_{\mathrm{m}}(\theta) - \Delta^{\mathrm{g}}_{\mathrm{cr}}G^{\mathrm{o}}_{\mathrm{m}}(\theta)}{\theta} \tag{5}$$

The results of vapor pressure obtained using the well-known equation (6) are also reported in this table.

$$\Delta^{\mathrm{g}}_{\mathrm{cr}}G^{\mathrm{o}}_{\mathrm{m}}(\theta) = -R\theta\ln\left(\frac{p}{p^{\mathrm{o}}}\right) \tag{6}$$

TABLE 5 Standard ($p^\circ = 0.1$ MPa) massic energy of combustion, $\Delta_{\mathrm{c}}u^{\circ}(\mathrm{cr})$, molar energy of combustion, $\Delta_{\mathrm{c}}U^{\circ}_{\mathrm{m}}(\mathrm{cr})$, enthalpy of combustion, $\Delta_{\mathrm{c}}H^{\circ}_{\mathrm{m}}(\mathrm{cr})$, and enthalpy of formation, $\Delta_{\mathrm{f}}H^{\circ}_{\mathrm{m}}(\mathrm{cr})$, for TKX-50, at $T = 298.15$ K.[a]

$\Delta_{\mathrm{c}}u^{\circ}$ (cr)/kJ·mol^{-1}	$\Delta_{\mathrm{c}}U^{\circ}_{\mathrm{m}}$(cr)/kJ·mol^{-1}	$\Delta_{\mathrm{c}}H^{\circ}_{\mathrm{m}}$(cr)/kJ·mol^{-1}	$\Delta_{\mathrm{t}}H^{\circ}_{\mathrm{m}}$(cr)/kJ·mol^{-1}
−8969.2 ± 3.8	−2118.1 ± 1.9	−2105.7 ± 1.9	175.3 ± 1.9

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

TABLE 6 Vapor pressure results.[a]

T/K	p/Pa	100Δp/p[b]	T/K	p/Pa	100Δp/p[b]	T/K	p/Pa	100Δp/p[b]
411.19	0.037	0.5	421.39	0.114	0.0	429.56	0.274	1.3
413.38	0.047	−0.3	423.36	0.139	−1.3	431.22	0.329	2.4
415.34	0.059	0.5	425.22	0.168	−2.2			
419.20	0.091	1.3	427.31	0.209	−2.4			

[a] The reported effusion pressures are the mean of the values obtained using the small, medium, and large effusion orifices. The standard uncertainties are $u(T/\mathrm{K}) = 0.01$ for the temperature and $u(p/\mathrm{Pa}) = 0.02$ for the effusion pressures. [b] $\Delta p = p - p_{\mathrm{calc}}$, where p_{calc} is calculated from the Clarke and Glew, Eq. (4), with parameters given in Table 7.

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TABLE 7 Standard ($p^o = 10^5$ Pa) thermodynamic properties of sublimation of TKX-50.

ΔT/K	θ/K	$\Delta_{cr}^{g}G_{m}^{\circ}(\theta)^{a}$/ kJ·mol^{-1}	p^{b}/Pa	$\Delta_{cr}^{g}H_{m}^{\circ}(\theta)^{a}$/ kJ·mol^{-1}	$\Delta_{cr}^{g}S_{m}^{\circ}(\theta)^{a}$/ J·K^{-1}·mol^{-1}	R^2	$\Delta_{cr}^{g}C_{p,m}^{\circ}(\theta)^{a}$/ J·K^{-1}·mol^{-1}	σ_r^{d}
411.2 to 431.2	298.15	81.46 ± 0.69	5.36×10^{-10}	165.0 ± 2.4	280.2 ± 8.4	0.9996	−45.0^{e}	0.0165
	421.20^{f}	48.00 ± 0.04	1.11×10^{-1}	159.4 ± 2.0	264.5 ± 4.7			

[a] Uncertainties are expressed as the expanded uncertainty (0.95 level of confidence, $k=2$).

[b] Calculated from Clarke and Glew equation for two different temperatures ($\theta = 2981.5$ K and θ = mean temperature of the experiments).

[c] Calculated using equation 5; uncertainties calculated through the RSS method.

[d] σ_r is the relative standard deviation of the fit, defined as $\sigma_r = \left[\sum_{i=1}^{n}(\ln p - \ln p_{\text{calc}})_i^2/(n-m)\right]^{1/2}$.

[e] Estimated value.

[f] Mean temperature.

The value of $\Delta_{cr}^{g}C_{p,m}^{\circ}$ was introduced in equation (4) after being estimated through equation (7), suggested by Monte *et al.* [34, 35], that is a reorganization of equation (8) proposed by Chickos *et al.* [36]. The value $C_{p,m}^{o}(g) = 250.49$ J·K^{-1}·mol^{-1}, determined at the temperature 298.15 K for TKX-50, was derived from statistical thermodynamics, calculated by means of the Gaussian G16 W software package [27], using the vibrational frequencies calculated at the B3LYP/6-31G(d) level of theory (scaled by a factor of (0.960 ± 0.022) [37].

$$\Delta_{cr}^{g}C_{p,m}^{\circ}(\theta)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = -\{0.9 + 0.176\ (C_{p,m}^{\circ}(\mathrm{g})/\mathrm{J\cdot K^{-1}\cdot mol^{-1}})\} \tag{7}$$

$$\Delta_{cr}^{g}C_{p,m}^{\circ}(\theta)/\mathrm{J\cdot K^{-1}\cdot mol^{-1}} = -\{0.75 + 0.15\ (C_{p,m}^{\circ}(\mathrm{cr})/\mathrm{J\cdot K^{-1}\cdot mol^{-1}})\} \tag{8}$$

Figure 3 shows the plot of vapor pressures against the reciprocal temperatures of TKX-50. To the best of our knowledge no (p,T) study was reported before for this compound.

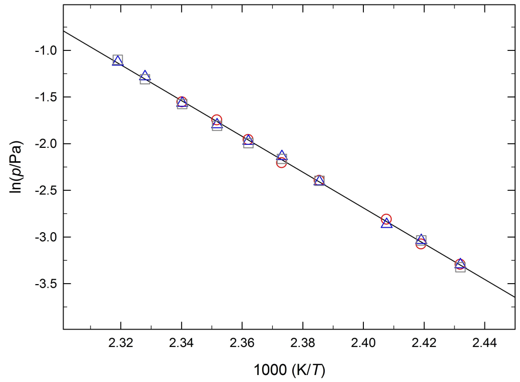


FIGURE 3 Plot of ln$p$ against $1/T$ for TKX-50. ○, small effusion orifices; △, medium effusion orifices and □, large effusion orifices.

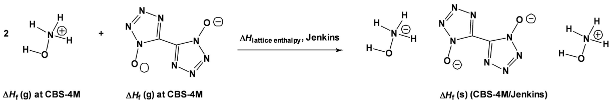
3.3 | Estimates of enthalpy of formation of solid TKX-50 using computational approaches

This experimental determination of the enthalpy of formation of TKX-50 was necessary, due to the fact that the enthalpies of formation $\Delta_f H_m^{\circ}$ for crystalline TKX-50 determined experimentally (Table 2) deviated substantially from the calculated value using the widely applied method of CBS-4M/Jenkins (Table 3) [1, 7]. For example, the CBS-4M calculated enthalpy of formation of the corresponding ions in the gas phase ($H_3N{-}OH^+$ and $C_2O_2N_8^{2-}$) converted into the solid state using the Jenkin's equations for the lattice energy and lattice enthalpy yielded a value of $\Delta_f H_m^{\circ}$ (TKX-50, cr) = 447 kJ·mol^1 [1, 7]. On the other hand, using an isodesmic model in which the molecular volumes for two methyl-substituted tetrazoles were calculated as additive using the molecular volume of ethane gave a value of $\Delta_f H_m^{\circ}$ (TKX-50, cr) = 164.1 kJ·mol^{-1} (Table 3) [16].

An equally important reason to investigate experimentally the $\Delta_f H_m^{\circ}$ for TKX-50 was the substantial difference in the experimentally determined values of Sinditskii (111 ± 16) kJ·mol^{-1} (Table 2) [8], with those of four other groups (189–213.4 kJ·mol^{-1}, average value = 197.4 kJ·mol^{-1}) (Table 2).

Furthermore, using the experimentally obtained results, the suitability of the CBS-4M/Jenkins approach for predicting the $\Delta_f H_m^{\circ}$ of energetic salts would be able to be re-assessed and a different strategy assessed to allow better prediction of the $\Delta_f H_m^{\circ}$ of high explosives which are salts. Several different computational approaches were adopted and different levels of theory were applied. Each of the different strategies which were used will be discussed in more detail below.

The initial strategy involved again treating TKX-50 computationally as an ionic salt (Figure 1), in which the enthalpies of formation of the individual ions in the gas-phase were calculated at various higher levels (CBS-QB3, G3MP2B3 and W1BD (data in Table S3 of Supplementary Information) and conversion of these values into the solid-state using Jenkin's equation (eq. 9) [7]. This approach was the same as that which is widely used for energetic salts using CBS-4M level of theory [14], and which resulted in the originally predicted values of 447 $kJ \cdot mol^{-1}$ at CBS-4M level of theory [1, 7].



(9)

Regardless of which level of theory was selected (CBS-4M, CBS-QB3, G3MP2B3 or W1BD), the value for $\Delta_f H^\circ_m$ was much more endothermic (Table 8) than the experimentally determined value of 175.3 $kJ \cdot mol^{-1}$ determined in this work (Table 5) and also than the average value of 197.4 $kJ \cdot mol^{-1}$ (Table 2) discussed in the introduction section for previously reported experimentally determined values. Despite being a widely-used approach for calculating the $\Delta_f H^\circ_m$ of energetic salts [14], this method was shown to produce unsatisfactory results for TKX-50. Preliminary results show that also for other 2:1 (ratio of ions), the calculated $\Delta_f H^\circ_m$ values show unsatisfactory agreement with experimentally determined $\Delta_f H^\circ_m$ values [14], with the calculated values generally being too endothermic.

The second strategy involved treating TKX-50 as being a neutral adduct between two hydroxylamine molecules with one bitetrazole-1,1'-diol (Figure 4). The enthalpy of formation of a neutral TKX-50 adduct was calculated in the gas phase at CBS-4M and CBS-QB3 levels of theory (data in Table S3 of Supplementary Information) and each of these values was converted into the corresponding enthalpy of formation in the solid state using the enthalpy of sublimation of TKX-50 of 165.0 $kJ \cdot mol^{-1}$ determined in this work (Table 7) (eq. 10).

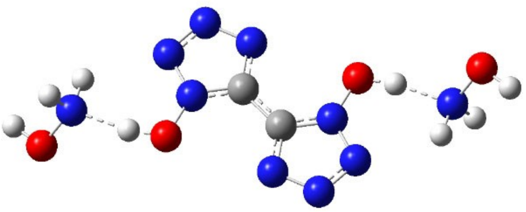
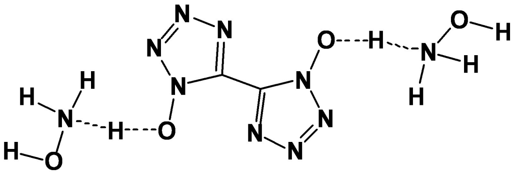


FIGURE 4 Calculated structure of TKX-50 in the gas phase as a neutral adduct (CBS-QB3).



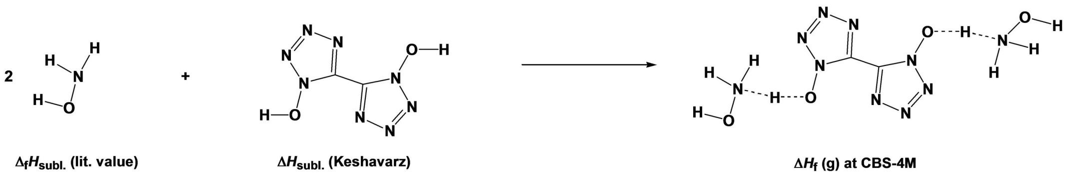
$$\Delta_f H^\circ_m(\text{cr}) \; = \; \Delta_f H^\circ_m(\text{g}) \text{ at CBS-4M } - \Delta^{\text{g}}_{\text{cr}} H^\circ_m \text{ adduct} \quad (10)$$

This approach resulted at CBS-QB3 level of theory in a value for $\Delta_f H^\circ_m$ for TKX-50 of 337 $kJ \cdot mol^{-1}$ which is less endothermic than the values calculated for the ionic salt using the CBS-4M/Jenkins or CBS-QB3/Jenkins methods, and closer to the experimentally determined value of 175.3 $kJ \cdot mol^{-1}$ in this work. However, the value is still in poor agreement with the experimentally determined value. Utilizing the same approach, but using the enthalpy of sublimation for TKX-50 predicted using the method by Keshavarz ($\Delta^{\text{g}}_{\text{cr}} H^\circ_m = 176.9$ $kJ \cdot mol^{-1}$) [38] instead of the value determined experimentally in this work did not result in any significant improvement in the agreement between the experimentally determined and calculated values for $\Delta_f H^\circ_m$.

A third strategy comprised again calculation of the enthalpy of formation of the neutral TKX-50 in the gas phase (adduct between two hydroxylamine molecules with one bitetrazole-1,1'-diol, Figure 4) at CBS-4M and also at CBS-QB3 levels of theory and subtraction of the enthalpies of sublimation of the neutral component compounds ($2 \times NH_2OH$ and $C_2H_2N_8O_2$), instead of subtracting the enthalpy of sublimation of TKX-50 (eq. 11).

The value for the enthalpy of sublimation of the neutral diol was estimated using Keshavarz' method (128.9 $kJ \cdot mol^{-1}$) [38], and the value for the enthalpy of sublimation of hydroxylamine (2×64.2 $kJ \cdot mol^{-1}$) was taken from the literature [35], which resulted in a value of 244.7 $kJ \cdot mol^{-1}$ at CBS-QB3 and 290.5 $kJ \cdot mol^{-1}$ at CBS-4M, which were significantly lower than the calculated values obtained using the other strategies. However, the agreement with the experimentally determined values was still unsatisfactory.

As was discussed in the introduction, Sinditskii has proposed [8] that $\Delta_f H^\circ_m$ for TKX-50 can be more accurately predicted using an approach in which the $\Delta_f H^\circ_m$ of the acid and base are summed together with the enthalpy for the salt reaction which occurs between a base



(11)

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TABLE 8 Overview of the different methods used to calculate the enthalpy of formation for crystalline TKX-50.

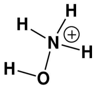
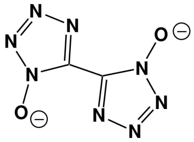
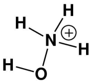
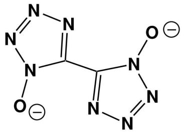
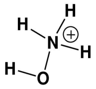
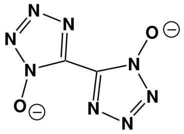
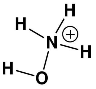
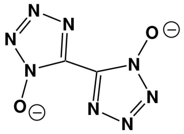
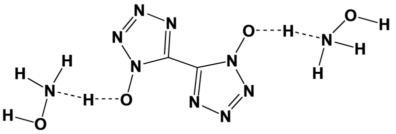
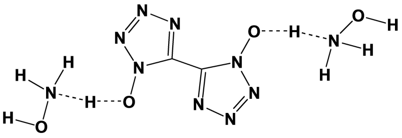
Method	$\Delta_f H^\circ_m$(cr)/ kJ·mol^{-1}
a) CBS-4M $\Delta_f H^\circ_m$(g) calculated for  and  ions, lattice enthalpy determined using Jenkins' equation	447 [1, 7, 12]
b) CBS-QB3 $\Delta_f H^\circ_m$ calculated for  and  gas-phase ions, lattice enthalpy determined using Jenkins' equation [7]	376.9
c) G3MP2B3 $\Delta_f H^\circ_m$(g) calculated for  and  ions, lattice enthalpy determined using Jenkins' equation [7]	462.2
d) W1BD $\Delta_f H^\circ_m$(g) calculated for  and  ions, lattice enthalpy determined using Jenkins' equation [7]	437.0
e) CBS-QB3 $\Delta_f H^\circ_m$(g) calculated for neutral TKX-50 adduct,  converted to $\Delta_f H^\circ_m$(cr) value, using exptl. $\Delta^g_{cr} H^\circ_m$ value (this work, 165 kJ·mol^{-1}) for neutral TKX-50 adduct	337.0
f) CBS-QB3 $\Delta_f H^\circ_m$(g) calculated for neutral TKX-50 adduct,  converted to $\Delta_f H^\circ_m$(cr) value using estimated $\Delta^g_{cr} H^\circ_m$ value (176.9 kJ·mol^{-1}, Keshavarz eq.) [38] for neutral TKX-50 adduct	325.1

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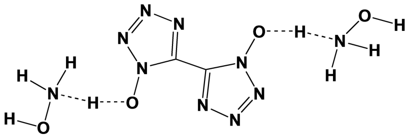
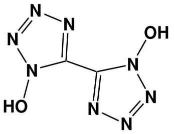
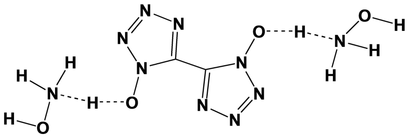
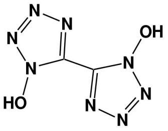
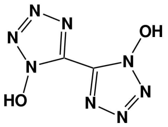
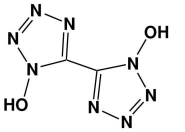
TABLE 8 (Continued)

Method	**$\Delta_f H_m^\circ$(cr)/ kJ·mol^{-1}**
g) CBS-QB3 $\Delta_f H_m^\circ$(g) calculated for neutral TKX-50 adduct,  converted to $\Delta_f H_m^\circ$(cr) value using 2 × exptl. $\Delta_{cr}^{g} H_m^\circ$ value for NH_2OH (2×64.2 kJ·mol^{-1}) [35] and estimated $\Delta_{cr}^{g} H_m^\circ$ value (128.9 kJ·mol^{-1}, Keshavarz eq.) [38] for 	244.7
h) CBS-4M $\Delta_f H_m^\circ$ calculated for neutral TKX-50 adduct  in gas-phase, converted to $\Delta_f H_m^\circ$(cr) value using 2×exptl. $\Delta_{cr}^{g} H_m^\circ$ value for NH_2OH (2×64.2 kJ·mol^{-1}) [35] and estimated $\Delta_{cr}^{g} H_m^\circ$ value (128.9 kJ·mol^{-1}, Keshavarz eq. [38]) for 	290.5
i) 2×$\Delta_f H_m^\circ$(cr) NH_2OH, CBS-4M $\Delta_f H_m^\circ$(g) for  converted to $\Delta_f H_m^\circ$(cr) using Keshavarz eq. [38] for $\Delta_{cr}^{g} H_m^\circ$, and $\Delta H_{\mathrm{salt\,reaction}}$ estimated based on value for NH_2OH(cr) + HNO_3(l) → $NH_3OH^+NO_3^-$(cr)	164.7
j) 2×$\Delta_f H_m^\circ$(cr) NH_2OH, CBS-QB3 $\Delta_f H_m^\circ$(g) for  converted to $\Delta_f H_m^\circ$(cr) using Keshavarz eqn. [38] for $\Delta_{cr}^{g} H_m^\circ$, and $\Delta H_{\mathrm{salt\,reaction}}$ estimated based on value for NH_2OH(cr) + HNO_3(l) → $NH_3OH^+NO_3^-$(cr)	164.9
k) Average of values calculated (CBS-4M) for of neutral adduct h) and ionic salt i)	227.6
l) Average of values calculated (CBS-4M) for of neutral adduct h) and ionic salt i) weighted 20:80	189.9
m) Average of values calculated (CBS-QB3) for of neutral adduct g) and ionic salt j)	204.8
n) Average of values calculated (CBS-QB3) for of neutral adduct g) and ionic salt j) weighted 20:80	180.9

and an acid. According to Sinditskii, the value for the salt reaction remains relatively constant for a particular base, regardless of which acid is involved, but not vice versa [8]. Using this approach, Sinditskii obtained a calculated value of $\Delta_f H_m^\circ$ for TKX-50 of 119 kJ·mol^{-1} [8] which was in good agreement with his experimentally determined value, but which is over 70 kJ·mol^{-1} lower than the average value for the experimentally determined values (excluding the original value of 447 kJ·mol^{-1} and 111 kJ·mol^{-1} reported by Sinditskii) (Table 2). We were unable to repeat exactly the calculation of the enthalpies of salt reaction for the formation of the $NH_3OH^+NO_3^-$ and $NH_3OH^+ClO_4^-$ salts to obtain the average value used by Sinditskii [8], since the value for $\Delta_f H_m^\circ$ used by Sinditskii for $NH_3OH^+ClO_4^-$ [8] is contained in a report [19] which we have been unable to access. However, using instead the values for $\Delta_f H_m^\circ$ of $NH_3OH^+NO_3^-$ and $(NH_3OH)_2SO_4$ that are easily available in the literature [18], we obtained an average value for the enthalpy of salt reaction for hydroxylamine base

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of 74 kJ·mol^{-1} which is less than that obtained by Sinditskii [8]. The other difference in our calculation of $\Delta_f H^\circ_m$ using the salt reaction method from that reported by Sinditskii [8] was that we calculated at CBS-4M the $\Delta_f H^\circ_m$(g) of the diol and converted this value to the $\Delta_f H^\circ_m$ value by estimating the enthalpy of sublimation using the Keshavarz method [38], whereas Sinditskii used a value of ~481 kJ·mol^{-1} for $\Delta_f H^\circ_m$ of the diol, based on the value of 531.7 kJ·mol^{-1} for bistetrazole [8]. Specific information for the difference in the values of bistetrazole and the value of ~481 kJ·mol^{-1} used for the diol of the dianion of TKX-50 was not given [8]. Using our modified approach, we obtained a value of $\Delta_f H^\circ_m$ for TKX-50 of 164.7 kJ·mol^{-1} (eq. 12). This value was much closer to the average experimentally determined value of 193.0 kJ·mol^{-1} (Table 2) and our experimentally re-determined value of 175.3 kJ·mol^{-1} reported herein.

Finally, since there is strong hydrogen bonding in TKX-50 between cations and anions [1], we calculated the average calculated value of $\Delta_f H^\circ_m$ TKX-50 using the value obtained for the neutral adduct after subtraction of the enthalpies of sublimation of the neutral component acid and base, and the value obtained for the ionic description of TKX-50 using the modified Sinditskii approach [8], and obtained a value of 228 kJ·mol^{-1}, which was relatively close to the average value of the experimentally determined $\Delta_f H^\circ_m$ values. Reconsideration of the crystal structure [1] suggested that the ionic description should have more weight than a neutral description, and by adopting a ratio 80 % ionic: 20 % neutral adduct, a calculated estimated value for the $\Delta_f H^\circ_m$ of TKX-50 of 190 kJ·mol^{-1} was obtained, which is in excellent agreement with the average value obtained from combustion calorimetry experiments of 193.0 kJ·mol^{-1} (Table 2), and also with the experimentally determined value of 175.3 kJ·mol^{-1} reported in this work. An overview of the different computational methods which were used in this work to estimate the $\Delta_f H^\circ_m$ for TKX-50 is given in Table 8.

In order to assess whether this approach calculating the $\Delta_f H^\circ_m$ of an energetic salt using a combined neutral adduct/ionic salt with 20:80 percent contribution can be applied to other salts of 2:1 ratio or 1:1 ratio, we are undertaking similar computational work on other related compounds and will report on these findings in subsequent work.

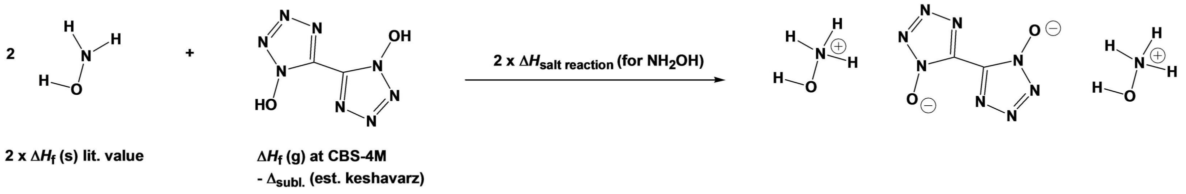
4 | CONCLUSION

The standard molar enthalpy of formation of the crystalline TKX-50, $\Delta_f H^\circ_m$(TKX-50, cr, 298.15 K) = (175.3 ± 1.9) kJ·mol^{-1}, was determined experimentally based on the measured standard massic energy of combustion enthalpies of combustion determined by static-bomb combustion calorimetry. This experimental study highlights the relevance on the direct measurement of the combustion energy of the compound, for deriving with accuracy its enthalpy of formation in crystalline phase.

To extend the thermodynamic characterization of TKX-50, the corresponding standard molar enthalpy of sublimation, $\Delta^g_{cr} H^\circ_m$(TKX-50, 298.15 K) = (165.0 ± 2.4) kJ·mol^{-1}, was also determined from vapor pressure measurements using the Knudsen effusion method.

In addition, several approaches were used to calculate the enthalpy of formation of TKX-50, and the values compared with the experimentally determined value of (175.3 ± 1.9) kJ·mol^{-1} determined in this study. Calculation of the gas phase heat of formation for the constituent ions and conversion to the solid-state enthalpy of formation for TKX-50 resulted in values which were too endothermic, regardless of which level of theory (CBS-4M, CBS-QB3, G3MP2B3 or W1BD) was applied. Therefore, this approach does not provide an accurate value for the enthalpy of formation for TKX-50. Calculation of the enthalpy of formation of TKX-50 using optimization of the gas-phase structures at B3LYP/6-31G* followed by single point energy calculation at the semi-empirical PM7 level of theory which was previously reported in the literature [15] was repeated and the literature value of 112.6 kJ·mol^{-1} [15] was shown to correspond to the value obtained from structure optimization and energy calculation at PM7 level of theory. Repeating this approach for a related 2:1 (ratio of ions) salt gave a value which showed poor agreement with the experimentally determined (combustion calorimetry) value.

The calculated value showing the best agreement with the experimental value was obtained by combining two approaches in an 80 %:20 % ratio, using summation of the standard enthalpy of formation of neutral hydroxylamine base from the literature [35] with the calculated (CBS-QB3, sublimation energy estimated by Keshavarz method [38]) enthalpy of formation of the neutral diol



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with the enthalpy of salt reaction for hydroxylamine base (80 %), as well as calculation of the neutral TKX-50 adduct in the gas-phase and subtracting the heats of sublimation of the components (20 %). Thus, a model was used in which the heat of formation doesn't correspond to a strictly ionic TKX-50, or to a strictly neutral TKX-50 adduct.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflicts of interest.

DATA AVAILABILITY STATEMENT

Data may be requested via the authors.

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