Vapor Pressures and Standard Molar Sublimation Enthalpies of Three 6-Methylthio-2,4-di(alkylamino)-1,3,5-triazine Derivatives: Simetryn, Ametryn, and Terbutryn

Stefano Vecchio[*,†] **and Bruno Brunetti**[‡]

Dipartimento di Ingegneria Chimica Materiali Ambiente, Università di Roma “La Sapienza”,
Via del Castro Laurenziano 7, 00161 Rome, Italy, and Istituto per lo Studio dei Materiali Nanostrutturati,
CNR Dipartimento di Chimica, Università di Roma “La Sapienza”, P.le A. Moro 5, 00185 Roma, Italy

The standard sublimation enthalpies of simetryn (*N,N′*-diethyl-6-(methylthio)-2,4-diamine-1,3,5-triazine), ametryn (*N*-ethyl-*N′*-(1-methylethyl)-6-(methylthio)-2,4-diamine-1,3,5-triazine), and terbutryn (*N*-(1,1-dimethylethyl)-*N′*-ethyl-6-(methylthio)-2,4-diamine-1,3,5-triazine) were determined by nonisothermal differential scanning calorimetry and nonisothermal and isothermal thermogravimetry, both techniques based on the Langmuir equation. For simetryn, ametryn, and terbutryn, the sublimation enthalpy values $\Delta_{sub}H°(298\ K) = \{(117 \pm 5), (121 \pm 5), \text{and } (112 \pm 5)\}\ kJ{\cdot}mol^{-1}$, respectively, were selected from nonisothermal and isothermal thermogravimetry data. The temperature dependence of the vapor pressures was selected from isothermal thermogravimetry data for the examined compounds: $\ln(p/kPa) = (23.86 \pm 0.38) - (10410 \pm 160)/(T/K)$ (from (391.4 to 456.0) K), $\ln(p/kPa) = (23.30 \pm 0.44) - (10458 \pm 189)/(T/K)$ (from (400.1 to 470.6) K), and $\ln(p/kPa) = (21.80 \pm 0.41) - (9978 \pm 178)/(T/K)$ (from (402.8 to 464.3) K) for liquid simetryn, ametryn, and terbutryn, respectively. From the isothermal thermogravimetry data, the standard sublimation entropies for simetryn, ametryn, and terbutryn equal to $\Delta_{sub}S°(298\ K) = \{(243), (244), \text{and } (214)\}\ J{\cdot}K{\cdot}mol^{-1}$, respectively, were derived with an estimated uncertainty of $\pm 10\ J{\cdot}K^{-1}{\cdot}mol^{-1}$ for all the studied triazines.

Introduction

Triazines are systemic herbicides with a six-membered ring structure, consisting of alternating N and C atoms joined by alternating single and double bonds.[1] Because of their capacity to inhibit photosynthesis, they are used to control annual grass and broad-leaved weeds in different cultures.

Moreover, many authors[2,3] indicated that volatilization from the soil surface may be an important pathway for loss of many pesticides, and it is largely controlled by the vapor pressure.[4] They were introduced in 1958, and some of them are among the most widely used herbicides in agriculture and industrial applications.[3]

Therefore, because of the persistence of several triazine herbicides after the application in soil, the knowledge of the vapor pressures as well as of other physicochemical properties (melting point; melting, vaporization, and sublimation enthalpies; water solubility) is important for the assessment of the environmental fate and behavior of these environmental pollutants. Some authors[5,6] have determined the values of properties such as the standard sublimation enthalpies and the vapor pressure data of different classes of organic substances using more classical effusion techniques.

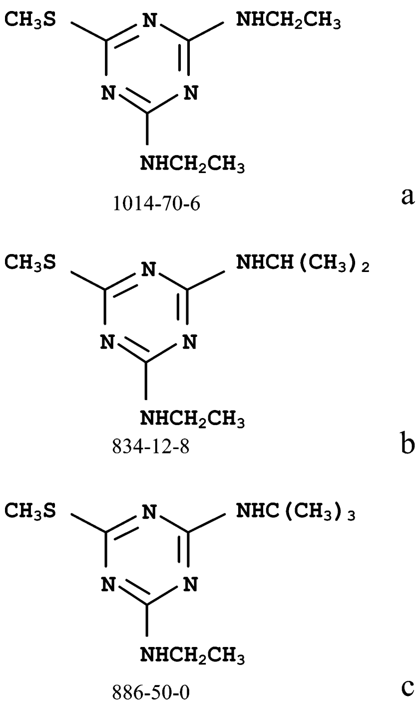

Figure 1. Molecular structures of the investigated herbicides: a, simetryn; b, ametryn; c, terbutryn.

As a follow-up of our previous study on phenoxyherbicides,[7,8] the standard molar sublimation enthalpies of simetryn, ametryn, and terbutryn, belonging to the class of the 6-methylthio-2,4-di(alkylamino)-1,3,5 triazines, were determined. Their molecular structures are given in Figure 1. The thermal behavior of these herbicides has been studied, and some enthalpy data related to melting and vaporization processes have been given.[9] In a previous work by Rodante et al.,[9] the combined gas chromatography−mass spectrometry technique has been used on the gaseous product of the three herbicides tested concluding that the decomposition process did not occur in the compounds

---

* Corresponding author. Phone: 0039.06.49766906. Fax: 0039.06.49766749. E-mail: stefano.vecchio@uniroma1.it.
[†] Dipartimento di Ingegneria Chimica Materiali Ambiente.
[‡] CNR Dipartimento di Chimica.

10.1021/je600580r CCC: $37.00

Table 1. Temperature Dependence of Q and Vaporization Enthalpies of the Reference Compounds from I-TG and NI-TG Data

compd	process	technique (n. exps.)	no. of points	ΔT K	$A^{a,b}$	B/K^{a,b}	$\Delta H(T)$ kJ·mol^{-1}	$\Delta_{sub}H°$(298 K) kJ·mol$^{-1\,b,c}$
benzoic acid	sub	I-TG (1)	8	333 − 356	20.73 ± 0.54	10287 ± 184	85.5 ± 1.5	87.7 ± 1.5
	sub	I-TG (2)	8	361 − 393	20.88 ± 0.37	10321 ± 140	85.8 ± 1.2	
	sub	NI-TG (3)	13	363 − 391	20.66 ± 0.23	10262 ± 88	85.3 ± 0.7	
	sub	NI-TG (4)	13	365 − 393	20.58 ± 0.25	10227 ± 95	85.0 ± 0.8	
	sub	average (2−4)		361 − 393	20.68 ± 0.27	10263 ± 100	85.3 ± 0.9	89.1 ± 1.0
	vap	I-TG (5)	12	415 − 458	15.38 ± 0.30	8022 ± 130	66.7 ± 1.1	
	vap	NI-TG (6)	8	396 − 410	15.45 ± 0.18	8215 ± 74	68.3 ± 0.6	
	vap	NI-TG (7)	8	397 − 409	15.42 ± 0.18	8207 ± 73	68.2 ± 0.6	
	vap	average (5−7)		396 − 458	15.41 ± 0.23	8130 ± 100	67.6 ± 0.8	90.3 ± 2
ferrocene	sub	I-TG (8)	10	313 − 353	17.00 ± 0.54	8702 ± 179	72.3 ± 1.5	73.6 ± 1.7
	sub	I-TG (10)	6	396 − 436	16.37 ± 0.48	8392 ± 198	69.7 ± 1.6	74.1 ± 2.2
	sub	I-TG (9)	14	357 − 396	16.72 ± 0.37	8566 ± 139	71.2 ± 1.2	
	sub	NI-TG (11)	26	372 − 402	13.73 ± 0.18	8500 ± 69	70.6 ± 0.6	
	sub	NI-TG (12)	26	372 − 403	13.70 ± 0.12	8479 ± 45	70.5 ± 0.4	
	sub	NI-TG (13)	26	372 − 403	13.70 ± 0.25	8493 ± 96	70.6 ± 0.8	
	sub	NI-TG (14)	26	373 − 403	13.71 ± 0.20	8493 ± 78	70.6 ± 0.6	
	sub	average (9−14)		357 − 403	14.22 ± 0.22	8496 ± 86	70.6 ± 0.7	73.7 ± .8

[a] $\ln Q = A - B/(T/\mathrm{K})$. [b] The quoted errors are standard deviations. [c] Recommended standard enthalpies of sublimation, $\Delta_{sub}H°(298\ \mathrm{K}) = (89.7 \pm 1.0$ and $73.4 \pm 1.1)$ kJ·mol^{-1}, for benzoic acid and ferrocene, respectively, were found in the literature.[21]

examined. However, to the best of our knowledge, only one paper concerning the sublimation for simetryn and ametryn has been published,[10] which reported the vapor pressures of the two solid triazines, determined by gas chromatography. Some doubts concerning the reliability of these published results arise from the very low number of experimental values used and from the temperature range studied (from (323 to 403) K). In addition, some authors have confirmed that results derived from this technique are largely scattered and higher than most results derived by other methods.[11]

In the present work, the sublimation and vaporization enthalpies of the compounds were derived both directly by differential scanning calorimetry (DSC) and indirectly through the temperature dependence of the vapor pressure evaluated by the Langmuir method[12] using nonisothermal and isothermal thermogravimetry (NI-TG and I-TG, respectively). Finally, the vapor pressures of the three herbicides were calculated above their liquid lines after a suitable calibration with benzoic acid and ferrocene, whose vapor pressures are known in the experimental temperature range investigated.

Experimental Section

Chemicals. Simetryn (CAS No.: 1014-70-6), ametryn (CAS No.: 834-12-8), and terbutryn (CAS No.: 886-50-0) were supplied by Polyscience; benzoic acid and ferrocene were supplied by Merck. The suppliers certified that the purity of all examined compounds is over 99 %. In this work, benzoic acid, ferrocene, simetryn, ametryn, and terbutryn were purified by sublimation under reduced pressure. By contrast, PL Thermal Science that supplied indium, gallium, lead, and tin used in this work certified that their purity is 99.999 %. Therefore, they were used without further purification.

Apparatus and Procedure. The TG and DSC measurements were carried out on a Stanton-Redcroft 625 simultaneous TG/DSC connected to a 386 IBM-compatible personal computer. The instrument calibration necessary to convert the area of DSC curves into enthalpy values was performed by using several very pure standards (i.e., indium and tin in this study) having well-known temperatures and fusion enthalpies.[13−15]

Increasing temperature experiments were carried out in triplicate on the sample, under a stream of argon, from room temperature to about 600 K at 1 K·min^{-1}, and the experimental data were collected every 1 K to give accuracy to the results. The uncertainty in the temperature measurements was estimated to be ± 0.5 K for all the experiments. An open aluminum crucible, with a cross sectional area of $2.0 \cdot 10^{-5}$ m^2, containing the sample and an empty one of equivalent mass as the reference were used. Samples with sizes of about (4 to 6) mg were placed in the crucible in an argon-filled drybox. The surface area of the molten compounds was considered equal to the area of the crucible bottom. The simultaneous TG/DSC system was flushed with a pure gas stream both below (flow rate 0.83 mL·s^{-1}) and above (flow rate 1.33 mL·s^{-1}) the open pans, to remove the vapor during the vaporization of the sample.

Table 2. Onset Temperatures and Mass Loss Percentage Obtained from NI-TG Data and Onset, Peak Temperatures Obtained from NI-DSC Data at 1 K·min^{-1}

	from NI-TG measurements		from NI-DSC measurements			
			melting		vaporization	
	T_{onset}	Δm	T_{onset}	T_{peak}	T_{onset}	T_{peak}
compd	K	%	K	K	K	K
simetryn	438.1	98.8	350.5	352.2 (355.1)^a	408.0	473.5
ametryn	445.4	97.8	356.7	359.1 (361.1)^a	404.5	476.8
terbutryn	441.8	98.1	372.3	376.0 (375.9)^b	418.7	478.4

[a] Melting temperatures (K) reported by the Merck Index[22] are given in parentheses. [b] Melting temperature (K) reported by Donnely et al.[23] is given in parentheses.

The vaporization enthalpy of a compound can be determined by the temperature dependence of its vapor pressure. The vapor pressure p of a compound at a temperature T is related to its mass-loss rate $\Delta m/\Delta t$ by the Langmuir equation,[12] which can be modified assuming the following form

$$p = \frac{\Delta m}{\Delta t}\cdot\sqrt{\frac{T}{M}}\cdot\frac{\sqrt{2\pi R}}{\alpha' S} = Qk_{\alpha'} \qquad (1)$$

where M is the molecular weight of the compound; S is the surface of the sample considered equal to the area of the bottom of the crucible; $k_{\alpha}' = \sqrt{2\pi R}/\alpha'$ is the instrumental constant where α' is the vaporization constant and R is the gas constant. The temperature dependence of the rate of mass loss is derived both by the first derivative of the NI-TG data at 1 K·min^{-1} and by the I-TG experiments, where the temperature is increased at 2 K·min^{-1}, from room temperature to the selected temperature

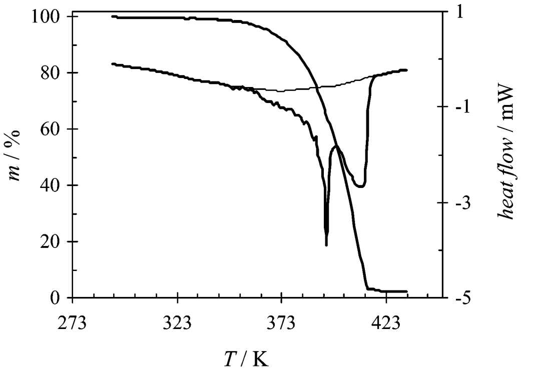

Figure 2. Simultaneous NI-TG and NI-DSC curves of benzoic acid at 1 $K\cdot min^{-1}$ under a stream of argon at 0.83 $cm^3\cdot s^{-1}$.

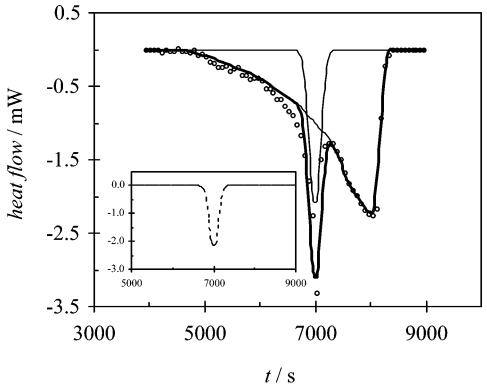

Figure 3. Deconvolution of melting and vaporization DSC peaks of benzoic acid after the DSC baseline correction: ○, experimental data; thin line, deconvoluted DSC peaks; bold line, sum of deconvoluted DSC peaks. The single deconvoluted melting DSC peak is framed inside the figure.

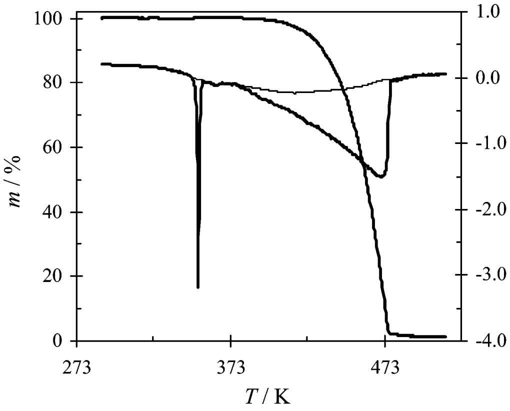

Figure 4. Simultaneous NI-TG and NI-DSC curves of simetryn at 1 $K\cdot min^{-1}$ under a stream of argon at 0.83 $cm^3\cdot s^{-1}$.

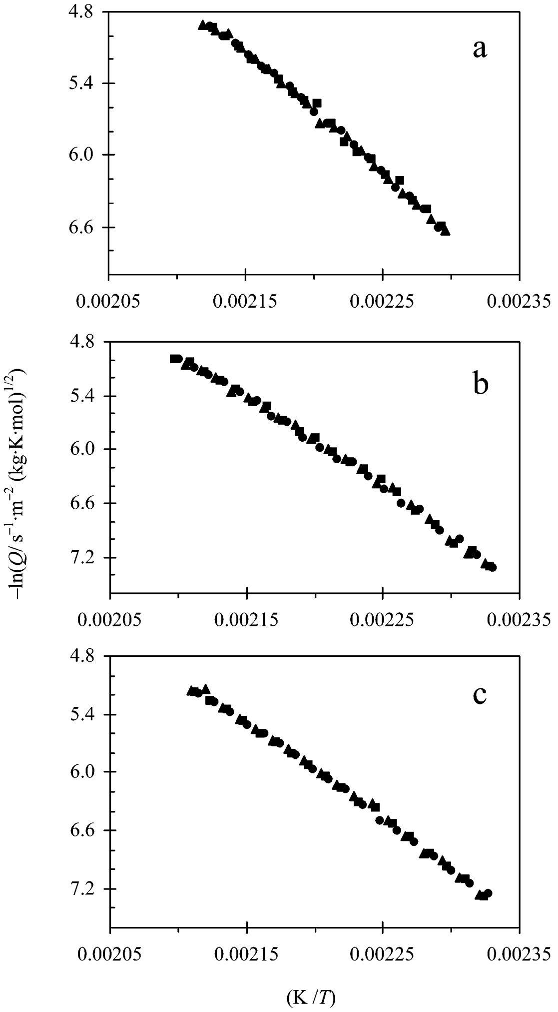

Figure 5. Temperature dependence of −ln Q values from NI-TG experiments: a, simetryn; b, ametryn; c, terbutryn. ●, run 1; ■, run 2; ▲, run 3.

Table 3. Standard Molar Vaporization Enthalpy Determined on Melted Compounds from NI-DSC Measurements at 1 $K\cdot min^{-1}$

compd	run	ΔT / K	$T_{1/2}$ / K	$\Delta_{vap}H°(T)$ / $kJ\cdot mol^{-1}$
simetryn	1	381 − 483	461	88 ± 3
	2	380 − 483	460	87 ± 4
	3	381 − 484	461	88 ± 4
ametryn	1	398 − 487	465	89 ± 4
	2	399 − 488	466	91 ± 4
	3	398 − 488	466	92 ± 5
terbutryn	1	400 − 488	467	88 ± 4
	2	401 − 488	467	86 ± 5
	3	401 − 488	467	86 ± 4

of the experiment. Using this procedure, the sample is kept at this temperature for 1500 s, and from the linear portion of the TG curve, three Δm mass loss values and their corresponding time intervals Δt are recorded. Therefore, for each isothermal experiment, from the three $\Delta m/\Delta t$ ratios obtained, three corresponding Q values were derived at selected temperatures, and the final average Q value was determined at the average temperature. In this way, the $\Delta_{vap}H(T)$ values for the studied compounds were evaluated in each experiment from the slope of the line obtained by plotting $-\ln Q$ vs $1/T$. The sensitivity of the experimental TG equipment, under both isothermal and nonisothermal conditions, enables us to carry out reliable vaporization measurements on the three triazine derivatives examined only above the molten compounds, where the mass loss rates (per unit area) are higher than $5\cdot 10^{-5}$ $kg\cdot s^{-1}\cdot m^{-2}$.

To make a check of the reliability of this procedure, the sublimation enthalpies of benzoic acid and ferrocene, which have well-known sublimation enthalpies,[15−21] were calculated from I-TG and NI-TG experiments. The NI-TG and DSC curves of benzoic acid under a stream of argon are shown in Figure 2 up to about 460 K. The temperature dependence of ln Q values of benzoic acid and ferrocene obtained from NI-TG measurements is reported in Table 1. The temperature dependence of ln Q values of benzoic acid and ferrocene obtained from I-TG measurements is also reported in Table 1. Concerning the vaporization of molten benzoic acid and sublimation of solid ferrocene, all the regression

Table 4. Molar Vaporization Enthalpies at the Average of the Experimental Temperature Ranges (T) and Standard Molar Vaporization Enthalpies at 298.15 K Obtained from NI-DSC, NI-TG, and I-TG Measurements and Calculated from the Temperature Dependence on Vapor Pressure

	NI-DSC			NI-TG			I-TG		
	$T_{1/2}$	$\Delta_{\text{vap}}H°(T_{1/2})$	$\Delta_{\text{sub}}H°(298\text{ K})$	T	$\Delta_{\text{vap}}H°(T)$	$\Delta_{\text{sub}}H°(298\text{ K})$	T	$\Delta_{\text{vap}}H°(T)$	$\Delta_{\text{sub}}H°(298\text{ K})$
compd	K	kJ·mol^{-1}	kJ·mol^{-1}	K	kJ·mol^{-1}	kJ·mol^{-1}	K	kJ·mol^{-1}	kJ·mol^{-1}
simetryn	461	88 ± 4	120 ± 6	453.0	83.7 ± 1.3	115 ± 4	423.7	86.6 ± 1.3	116 ± 4
ametryn	466	91 ± 4	125 ± 6	453.0	84.9 ± 1.3	118 ± 4	435.4	87.0 ± 1.6	119 ± 5
terbutryn	467	87 ± 5	115 ± 7	451.9	83.2 ± 1.0	111 ± 4	433.6	83.0 ± 1.5	110 ± 5

parameters of the $-\ln Q$ vs $1/T$ lines derived by both the I-TG and NI-TG methods are in good agreement. Therefore, weighing their slopes and intercepts proportionally to the experimental points, we selected the following final equations.

Benzoic acid(s):

$$\ln(Q/\text{kg}^{1/2}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{K}^{1/2}\cdot\text{mol}^{1/2}) = (20.73 \pm 0.54) - (10287 \pm 184)/(T/\text{K}) \text{ (from 333 K to 356 K)} \quad (2a)$$

$$\ln(Q/\text{kg}^{1/2}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{K}^{1/2}\cdot\text{mol}^{1/2}) = (20.68 \pm 0.27) - (10263 \pm 103)/(T/\text{K}) \text{ (from 361 K to 393 K)} \quad (2b)$$

Benzoic acid(l):

$$\ln(Q/\text{kg}^{1/2}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{K}^{1/2}\cdot\text{mol}^{1/2}) = (15.41 \pm 0.23) - (8130 \pm 98)/(T/\text{K}) \text{ (from 396 K to 458 K)} \quad (3)$$

Ferrocene(s):

$$\ln(Q/\text{kg}^{1/2}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{K}^{1/2}\cdot\text{mol}^{1/2}) = (17.00 \pm 0.54) - (8702 \pm 179)/(T/\text{K}) \text{ (from 313 K to 353 K)} \quad (4a)$$

$$\ln(Q/\text{kg}^{1/2}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{K}^{1/2}\cdot\text{mol}^{1/2}) = (16.37 \pm 0.48) - (8392 \pm 198)/(T/\text{K}) \text{ (from 396 K to 436 K)} \quad (4b)$$

$$\ln(Q/\text{kg}^{1/2}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{K}^{1/2}\cdot\text{mol}^{1/2}) = (14.11 \pm 0.22) - (8501 \pm 86)/(T/\text{K}) \text{ (from 357 K to 403 K)} \quad (4c)$$

The associated errors are standard deviations. These findings enable us to conclude that both the proposed methods provide comparable results even if the experimental temperature ranges are quite different. From the slopes of these equations, the sublimation and vaporization enthalpies were obtained at the average of the experimental temperature ranges. No significant differences are found between the sublimation enthalpy values of benzoic acid derived by eqs 2a and 2b, whose average value is $\Delta_{\text{sub}}H(T) = (85.4 \pm 1.0)$ kJ·mol^{-1}, whereas the vaporization enthalpy $\Delta_{\text{vap}}H(T) = (67.6 \pm 0.8)$ kJ·mol^{-1} was selected from the slope of eq 3. From the slope of eqs 4a, 4b, and 4c, the sublimation enthalpies of ferrocene $\Delta_{\text{sub}}H(T) = \{(72.4 \pm 1.3), (69.8 \pm 1.6), \text{and } (70.7 \pm 0.7)\}$ kJ·mol^{-1}, respectively, were derived.

The values of the standard molar enthalpy of sublimation of benzoic acid, at $T = 298$ K, presented in Table 1 were derived from the values for $\Delta_{\text{sub}}H(T)$ considering the difference in the molar heat capacity, $\Delta C_p(\text{g,s}) = C_p(\text{g}) - C_p(\text{s}) = -(48 \pm 5)$ J·K^{-1}·mol^{-1}, taken from the literature.[15] From the vaporization experiments, the values of $\Delta_{\text{sub}}H(298\text{ K})$ were also calculated adjusting the $\Delta_{\text{vap}}H(T)$ values to $T = 298$ K, considering the difference in the molar heat capacity, $\Delta C_p(\text{g,l}) = C_p(\text{g}) - C_p(\text{l}) = -(63 \pm 5)$ J·K^{-1}·mol^{-1}, and $\Delta C_p(\text{g,s})$ taken from the literature[15] and using the molar enthalpy of fusion, derived in this work from DSC measurements. To obtain the $\Delta_{\text{fus}}H(T_{\text{fus}})$, a deconvolution of the superimposed sublimation−vaporization and fusion DSC peaks was performed. The corresponding DCS curves are presented in Figure 3. Inside this figure, the obtained single melting DSC peak is framed. From the area of this peak, the molar enthalpy of fusion, $\Delta_{\text{fus}}H(T_{\text{fus}}) = (16.1 \pm 1.0)$ kJ·mol^{-1} ($T_{\text{fus}} = 395.2$ K),[17] was obtained. The associated uncertainty was estimated taking into account the error in the determination of the DSC peak area. In this way, we have obtained the value $\Delta_{\text{sub}}H°(298\text{ K}) = (90.3 \pm 2.0)$. Therefore, for benzoic acid, the mean value $\Delta_{\text{sub}}H°(298\text{ K}) = (89.4 \pm 1.9)$ kJ·mol^{-1} was obtained in excellent agreement with the recommended value (89.7 ± 1.0) kJ·mol^{-1}.[21] For ferrocene, the difference $\Delta C_p(\text{g,s}) = C_p(\text{g}) - C_p(\text{s}) = -(37 \pm 5)$ J·K^{-1}·mol^{-1} was used to derive the values of $\Delta_{\text{sub}}H°(298\text{ K})$ presented in Table 1. From these values, the mean value $\Delta_{\text{sub}}H°(298\text{ K}) = (73.8 \pm 0.8)$ kJ·mol^{-1} was derived. This value is in excellent agreement with the recommended value (73.4 ± 1.1) kJ·mol^{-1} and with the recently published value (74.5 ± 0.1) kJ·mol^{-1}.[18]

Results and Discussion

Enthalpy of Fusion. Simultaneous TG and DSC curves of simetryn are given in Figure 4 as an example. The shapes of the corresponding TG and DSC curves for the other two studied compounds are similar. The TG curve shows only one step of mass loss, and two distinct endothermic DSC peaks are observed in the DSC curve due to melting and vaporization, respectively. As observed in a previous study,[9] no additional thermal effects due to decomposition were found up to 550 K in the DSC curves of the herbicides studied. The melting and vaporization temperatures along with the corresponding mass loss percentage are summarized in Table 2 for each compound. The melting DSC peak temperatures for simetryn, ametryn, and terbutryn were found to be (352.2, 359.1, and 376.0) K, respectively, with an associated uncertainty of ± 0.5 K for all the compounds. The DSC peak melting temperatures substantially agree with those taken from the literature[22,23] for all the compounds tested. An expected increasing trend is observed with increasing molecular weight of the examined compounds (from simetryn to terbutryn). It was not necessary to make a deconvolution of the melting and vaporization DSC peaks. The molar enthalpies of fusion, {(24 ± 1), (26 ± 2), and (21 ± 2)} kJ·mol^{-1}, were found, respectively, for simetryn, ametryn, and terbutryn, whereas the associated uncertainties were estimated as twice the standard deviation of the mean of the three experiments performed. An excellent agreement was found with the molar enthalpies of fusion taken from the literature[9] for simetryn, ametryn, and terbutryn, which were equal to (24.11, 26.13, and 21.16) kJ·mol^{-1}, respectively. Vaporization of each compound begins to be detectable after its melting.

Vaporization Enthalpy from DSC Measurements. The vaporization enthalpies of the studied compounds were directly determined from the areas enclosed by the corresponding DSC peaks[24] opportunely evaluated. Calibration substances (sapphire[21] in the present work) were used to determine

Table 5. Values of ln Q Evaluated at about (2 to 3) K Intervals in the Experimental Temperature Ranges for Melted Compounds[a]

run 1		run 2		run 3		run 4	
T/K	$-\ln Q$	T/K	$-\ln Q$	T/K	$-\ln Q$	T/K	$-\ln Q$
N,N′-Diethyl-6-(methylthio)-2,4-diamine-1,3,5-triazine							
436.6	6.608	435.6	6.628	436.1	6.595	435.1	6.673
438.6	6.452	437.6	6.531	438.1	6.447	437.1	6.480
440.7	6.342	439.7	6.417	440.2	6.375	439.2	6.499
442.5	6.265	441.6	6.315	442.1	6.217	441.1	6.325
444.6	6.128	443.6	6.196	444.1	6.158	443.1	6.236
446.6	6.024	445.6	6.088	446.1	6.029	445.1	6.109
448.6	5.913	447.6	5.956	448.1	5.974	447.1	5.995
450.6	5.791	449.6	5.841	450.1	5.890	449.1	5.882
452.6	5.729	451.5	5.764	452.0	5.734	451.0	5.697
454.6	5.634	453.6	5.734	454.1	5.570	453.1	5.677
456.5	5.523	455.6	5.560	456.1	5.540	455.1	5.579
458.3	5.423	457.3	5.478	457.8	5.465	456.9	5.519
460.6	5.317	459.5	5.392	460.1	5.362	458.9	5.415
462.6	5.254	461.6	5.279	462.1	5.282	461.1	5.312
464.7	5.161	463.6	5.197	464.2	5.191	463.1	5.203
466.7	5.063	465.7	5.100	466.2	5.090	465.2	5.130
468.8	5.004	467.7	4.974	468.2	5.003	467.2	5.047
470.9	4.924	469.9	4.952	470.4	4.931	469.3	4.975
		471.9	4.903			471.4	4.902
N-Ethyl-*N′*-(1-methylethyl)-6-(methylthio)-2,4-diamine-1,3,5-triazine							
429.1	7.307	430.2	7.259	429.6	7.304	430.8	7.138
431.3	7.169	432.4	7.152	431.9	7.125	433.0	7.106
433.7	7.001	435.0	7.011	434.3	7.038	435.6	6.980
436.3	6.893	437.8	6.780	437.1	6.832	438.5	6.861
439.2	6.666	440.5	6.616	439.9	6.680	441.2	6.631
441.9	6.590	443.1	6.430	442.5	6.472	443.7	6.469
444.3	6.440	445.4	6.378	444.8	6.326	446.0	6.382
446.6	6.288	447.7	6.209	447.1	6.224	448.2	6.201
448.8	6.143	449.9	6.102	449.3	6.130	450.6	6.097
451.2	6.109	452.4	5.992	451.8	6.031	453.0	5.990
453.7	5.977	455.1	5.889	454.4	5.871	455.8	5.805
456.4	5.862	457.5	5.731	456.9	5.796	458.1	5.765
458.7	5.697	460.0	5.641	459.4	5.669	460.6	5.597
461.3	5.620	462.4	5.526	461.8	5.522	462.8	5.503
463.5	5.455	464.8	5.425	464.1	5.475	465.4	5.390
466.1	5.361	467.5	5.350	466.8	5.318	468.1	5.233
468.8	5.244	470.1	5.203	469.5	5.233	470.7	5.165
471.3	5.163	472.4	5.112	471.8	5.130	473.1	5.069
473.6	5.083	474.9	5.060	474.2	5.023	475.5	4.991
476.2	4.994			476.8	4.983		
N-(1,1-Dimethylethyl)-*N′*-ethyl-6-(methylthio)-2,4-diamine-1,3,5-triazine							
429.8	7.251	431.0	7.265	430.4	7.273	431.6	7.179
432.3	7.149	433.6	7.077	432.9	7.106	434.1	7.051
434.7	7.017	436.0	6.914	435.4	6.967	436.6	6.907
437.2	6.857	438.6	6.840	437.9	6.836	439.3	6.729
440.0	6.716	441.3	6.651	440.7	6.657	441.9	6.605
442.4	6.603	443.7	6.500	443.0	6.531	444.3	6.456
444.9	6.492	446.1	6.322	445.5	6.356	446.7	6.339
447.4	6.334	448.7	6.246	448.1	6.307	449.3	6.214
449.9	6.176	451.2	6.120	450.6	6.157	451.8	6.098
452.4	6.070	453.6	6.014	453.0	6.042	454.3	5.970
454.9	5.970	456.2	5.874	455.5	5.925	456.8	5.859
457.5	5.819	458.7	5.754	458.1	5.806	459.2	5.750
459.8	5.699	461.1	5.672	460.5	5.681	461.7	5.624
462.3	5.599	463.6	5.557	462.9	5.590	464.3	5.511
465.0	5.503	466.2	5.444	465.6	5.456	467.0	5.392
467.7	5.378	469.0	5.332	468.3	5.348	469.6	5.300
470.3	5.278	471.6	5.139	471.0	5.260	472.3	5.207
472.9	5.183	474.1	5.148	473.5	5.167		

[a] Q is expressed in $\mathrm{kg^{1/2} \cdot s^{-1} \cdot m^{-2} \cdot K^{1/2} \cdot mol^{1/2}}$.

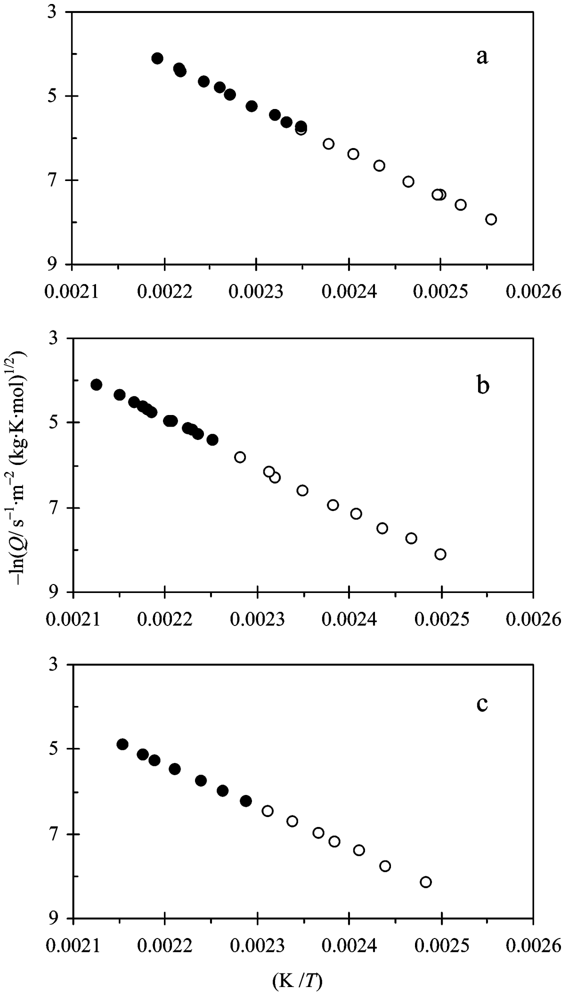

Figure 6. Temperature dependence of −ln Q values from I-TG experiments: a, simetryn; b, ametryn; c, terbutryn. ●, run 1; ○, run 2.

Table 6. Temperature Dependence of ln Q and Vaporization Enthalpies of the Studied Compounds from NI-TG Data

compd	run	no. of points	ΔT/K	A [a,b]	B/K[a,b]	$\Delta H_{\mathrm{vap}}(T)$/kJ·mol^{-1}
simetryn	1	18	436.6 − 470.9	16.54 ± 0.30	10083 ± 135	83.8 ± 1.1
simetryn	2	19	435.6 − 469.9	16.64 ± 0.32	10129 ± 146	84.2 ± 1.2
simetryn	3	18	436.1 − 470.4	16.25 ± 0.32	9949 ± 145	82.7 ± 1.2
simetryn	4	19	435.1 − 469.3	16.55 ± 0.41	10086 ± 188	83.9 ± 1.6
ametryn	1	20	429.1 − 476.1	16.29 ± 0.28	10102 ± 125	84.0 ± 1.0
ametryn	2	19	430.2 − 474.9	16.49 ± 0.40	10188 ± 181	84.7 ± 1.5
ametryn	3	20	429.6 − 476.8	16.39 ± 0.38	10141 ± 174	84.3 ± 1.4
ametryn	4	19	430.8 − 475.5	16.98 ± 0.34	10413 ± 155	86.6 ± 1.3
terbutryn	1	18	429.8 − 472.9	16.01 ± 0.20	9999 ± 90	83.1 ± 0.8
terbutryn	2	18	431.0 − 474.1	16.22 ± 0.34	10090 ± 154	83.9 ± 1.3
terbutryn	3	18	430.4 − 473.5	15.90 ± 0.27	9948 ± 122	82.7 ± 1.0
terbutryn	4	17	431.6 − 472.3	16.01 ± 0.23	9994 ± 102	83.1 ± 0.9

[a] $\ln Q = A - B/(T/\mathrm{K})$. [b] The quoted errors are standard deviations.

the temperature dependence of the heat flow values (in mJ·s^{-1}). Initial and final temperatures of the DSC vaporization were estimated for each sample when the mass loss rate (per unit area) was at least equal to 10^{-4} kg·s^{-1}·m^{-2} (about twice as much as the instrument sensitivity). The molar vaporization enthalpies, referring to the temperatures $T = T_{1/2}$ where half of the sample was vaporized, are also reported in Table 3. The $T_{1/2}$ values, derived using, in each run, comparable amounts of sample at 1 K·min^{-1}, are practically the same for each compound. The averages of the corresponding enthalpy values were reported in Table 4 with an estimated associated error of ± 4 kJ·mol^{-1} for simetryn and ametryn of and ± 5 kJ·mol^{-1} for terbutryn. These enthalpies were reported at 298 K using the difference in heat capacity for vapor and solid, $\Delta C_p(\mathrm{v,s}) = -32$ J·K^{-1}·mol^{-1}, and for vapor and liquid, $\Delta C_p(\mathrm{v,l}) = -54$ J·K^{-1}·mol^{-1}, along with the molar enthalpies of fusion evaluated in the present work from the DSC curves. These differences were evaluated from the assumptions made by Chickos et al.[25] The $\Delta_{\mathrm{sub}}H°(298\ \mathrm{K})$ values so obtained are

Table 7. Langmuir Values of ln Q Calculated by Experimental Data Obtained in Separate I-TG Experiments for Simetryn, Ametryn, and Terbutryn

run 1				run 2			
$T \pm 0.2$ K	$\Delta m/S \pm 2$ g·m^{-2}	$\Delta t \pm 5$ s	$-\ln Q^b$	$T \pm 0.2$ K	$\Delta m/S \pm 2$ g·m^{-2}	$\Delta t \pm 5$ s	$-\ln Q^b$
N,*N*′-Diethyl-6-(methylthio)-2,4-diamine-1,3,5-triazine							
391.4	1.087	131	7.9 ± 2.1	425.7	11.325	158	5.7 ± 0.6
	1.100	129	7.9 ± 1.7		11.319	155	5.7 ± 0.7
	1.140	134	7.9 ± 2.2		11.368	151	5.7 ± 0.5
		average	7.9 ± 2.0			average	5.7 ± 0.6
396.5	1.302	111	7.6 ± 3.1	428.7	14.025	177	5.6 ± 0.6
	1.308	115	7.6 ± 2.2		14.017	173	5.6 ± 0.6
	1.298	109	7.6 ± 2.6		14.013	172	5.6 ± 0.6
		average	7.6 ± 3.0			average	5.6 ± 0.6
400.2	1.956	130	7.3 ± 1.7	430.9	14.760	165	5.5 ± 0.6
	1.927	131	7.4 ± 2.0		14.630	164	5.5 ± 0.7
	1.939	124	7.3 ± 2.1		14.667	134	5.3 ± 0.5
		average	7.3 ± 2.0			average	5.4 ± 0.6
400.7	1.834	124	7.4 ± 1.4	435.8	12.811	108	5.2 ± 0.5
	1.884	134	7.4 ± 1.1		12.691	106	5.2 ± 0.6
	1.809	112	7.3 ± 1.5		12.709	109	5.2 ± 0.5
		average	7.3 ± 1.5			average	5.2 ± 0.5
405.7	2.884	146	7.1 ± 0.8	440.2	15.572	94	4.9 ± 0.4
	2.944	147	7.0 ± 0.8		15.545	104	5.0 ± 0.5
	2.525	126	7.0 ± 1.3		15.201	100	5.0 ± 0.4
		average	7.0 ± 1.0			average	5.0 ± 0.4
410.9	3.294	103	6.6 ± 0.5	442.5	15.443	105	5.0 ± 0.4
	3.650	130	6.7 ± 0.4		14.804	74	4.7 ± 0.4
	3.422	124	6.7 ± 0.5		14.786	74	4.7 ± 0.4
		average	6.7 ± 0.5			average	4.8 ± 0.4
415.8	7.148	184	6.4 ± 0.2	445.8	15.100	72	4.6 ±0.4
	8.376	215	6.4 ± 0.2		15.600	67	4.5 ± 0.3
	9.221	245	6.4 ± 0.2		14.815	79	4.8 ± 0.3
		average	6.4 ± 0.2			average	4.6 ± 0.3
420.5	3.998	82	6.1 ± 0.5	450.9	25.924	101	4.4 ± 0.3
	3.961	81	6.1 ± 0.5		23.366	83	4.3 ± 0.2
	3.966	81	6.1 ± 0.5		22.419	91	4.5 ± 0.2
		average	6.1 ± 0.5			average	4.4 ± 0.2
425.8	6.165	90	5.8 ± 0.5	451.3	27.421	100	4.4 ± 0.2
	5.999	89	5.8 ± 0.5		28.215	101	4.4 ± 0.2
	6.203	87	5.7 ± 0.5		30.405	104	4.3 ± 0.2
		average	5.8 ± 0.2			average	4.3 ± 0.1
				456.0	33.878	105	4.2 ± 0.2
					33.951	93	4.1 ± 0.2
					33.728	89	4.0 ± 0.2
						average	4.1 ± 0.2
N-Ethyl-*N*′-(1-methylethyl)-6-(methylthio)-2,4-diamine-1,3,5-triazine							
400.1	1.058	144	8.1 ± 2.1	444.2	14.193	140	5.4 ± 0.9
	1.105	140	8.0 ± 2.0		14.202	143	5.4 ± 0.8
	1.099	142	8.0 ± 2.2		14.228	139	5.4 ± 0.9
		average	8.0 ± 2.0			average	5.4 ± 0.9
405.3	1.322	112	7.6 ± 2.4	447.3	16.229	136	5.2 ± 0.9
	1.344	116	7.6 ± 2.3		16.442	142	5.3 ± 0.8
	1.339	120	7.7 ± 2.2		16.044	138	5.3 ± 0.9
		average	7.6± 2.0			average	5.3 ± 0.9
410.4	1.856	131	7.4 ± 2.0	448.7	16.843	128	5.1 ± 0.8
	1.827	132	7.4 ± 1.9		16.345	137	5.2 ± 0.7
	1.839	125	7.4 ± 1.9		17.977	137	5.1 ± 0.8
		average	7.4 ± 2.0			average	5.2 ± 0.8
415.3	2.287	115	7.1 ± 1.8	449.5	17.711	132	5.1 ± 0.8
	2.281	125	7.2 ± 1.7		17.591	130	5.1 ± 0.7
	2.267	103	7.0 ± 1.8		17.609	133	5.1 ± 0.8
		average	7.1 ± 2.0			average	5.1 ± 0.8
419.6	2.924	117	6.8 ± 1.5	453.1	17.572	111	5.0 ± 0.7
	2.921	118	6.8 ± 1.4		17.545	104	4.9 ± 0.7
	2.525	110	6.9 ± 1.3		17.201	110	5.0 ±0.6
		average	6.9 ± 1.4			average	4.9 ± 0.7
425.7	3.494	94	6.4 ± 1.1	453.7	15.643	98	4.9 ± 0.5
	3.850	114	6.5 ± 1.1		14.804	94	5.0 ± 0.7
	3.722	112	6.5 ± 1.2		14.786	94	5.0 ± 0.7
		average	6.5 ± 1.1			average	5.0 ± 0.6
N-Ethyl-*N*′-(1-methylethyl)-6-(methylthio)-2,4-diamine-1,3,5-triazine							
431.1	8.748	180	6.2 ± 1.1	457.6	19.100	99	4.8 ± 0.6
	8.676	206	6.3 ± 1.0		19.159	98	4.7 ± 0.5
	8.991	210	6.3 ± 1.0		19.261	101	4.8 ± 0.5
		average	6.2 ± 1.0			average	4.8 ± 0.5
432.4	3.998	73	6.0 ± 1.1	458.6	25.924	123	4.7 ± 0.5
	3.961	72	6.0 ± 1.0		23.366	105	4.6 ±0.6
	3.966	72	6.0 ± 1.0		22.419	113	4.7 ± 0.5
		average	6.0 ± 1.0			average	4.7 ± 0.5

Table 7 (Continued)

run 1				run 2			
$T \pm 0.2$ K	$\Delta m/S \pm 2$ $g \cdot m^{-2}$	$\Delta t \pm 5$ s	$-\ln Q^{b}$	$T \pm 0.2$ K	$\Delta m/S \pm 2$ $g \cdot m^{-2}$	$\Delta t \pm 5$ s	$-\ln Q^{b}$
438.2	6.165	83	5.7 ± 0.9	459.7	26.421	122	4.6 ± 0.4
	5.999	82	5.7 ± 0.8		26.215	123	4.6 ± 0.5
	6.203	80	5.7 ±0.8		28.405	124	4.6 ± 0.4
		average	5.7 ± 0.8			average	4.6 ± 0.4
				461.6	32.878	134	4.5 ± 0.3
					32.251	140	4.6 ± 0.4
					33.728	136	4.5 ± 0.4
						average	4.5 ± 0.4
				465.1	37.921	129	4.3 ± 0.3
					37.715	132	4.4 ± 0.3
					37.905	134	4.4 ± 0.4
						average	4.3 ± 0.3
				470.6	40.878	110	4.1 ± 0.3
					43.951	118	4.1 ± 0.2
					43.728	119	4.1 ± 0.3
						average	4.1 ± 0.3
N-(1,1-Dimethylethyl)-*N′*-ethyl-6-(methylthio)-2,4-diamine-1,3,5-triazine							
402.8	1.035	153	8.2 ± 3.3	437.2	4.623	97	6.2 ± 3.8
	1.085	149	8.1 ± 3.0		4.892	105	6.2 ± 1.9
	1.087	151	8.1 ± 3.5		4.821	103	6.2 ± 4.3
		average	8.1 ± 3.3			average	6.2 ± 2
410.0	1.302	121	7.7 ± 2.6	441.9	6.027	102	6.0 ± 1.4
	1.308	125	7.7 ± 2.5		6.040	103	6.0 ± 1.8
	1.298	129	7.8 ± 2.7		6.045	102	6.0 ± 1.6
		average	7.8 ± 2.5			average	6.0 ± 0.8
414.7	1.856	123	7.4 ± 2.5	446.8	7.143	96	5.7 ± 1
	1.827	122	7.4 ± 2.6		7.545	105	5.8 ± 0.7
	1.839	128	7.4 ± 2.3		8.077	105	5.7 ± 1.3
		average	7.4 ± 2.5			average	5.7 ±0.5
419.5	2.287	124	7.2 ± 2.3	452.4	9.311	96	5.5 ± 0.5
	2.281	134	7.3 ± 2.1		9.291	94	5.5 ± 0.3
	2.267	112	7.1 ± 2.1		9.309	97	5.5 ± 1
		average	7.2 ± 2.1			average	5.5 ± 0.5
422.6	2.924	126	6.9 ± 1.9	457.0	8.972	75	5.3 ± 0.4
	2.921	127	6.9 ± 2.0		8.945	73	5.2 ± 0.3
	2.525	119	7.0 ± 2.0		8.891	78	5.3 ± 0.3
		average	7.0 ± 2.0			average	5.3 ± 0.2
427.8	3.394	103	6.6 ± 0.2	459.5	9.943	75	5.2 ± 0.4
	3.350	123	6.8 ± 0.3		10.104	72	5.1 ± 0.5
	3.422	121	6.7 ± 0.2		9.986	71	5.1 ± 0.5
		average	6.7 ± 0.1			average	5.1 ± 0.2
432.6	4.348	118	6.5 ± 0.2	464.3	14.852	84	4.9 ± 0.2
	4.276	115	6.5 ± 0.2		14.859	85	4.9 ± 0.2
	4.291	118	6.5 ± 0.1		14.861	86	4.9 ± 0.2
	4.291	average	6.5 ± 0.1			average	4.9 ± 0.1

[a] Q is expressed in $kg^{1/2} \cdot s^{-1} \cdot m^{-2} \cdot K^{1/2} \cdot mol^{1/2}$. [b] Associated errors are due to the errors' propagation.

reported in Table 4 with their errors, estimated considering also the uncertainties associated with ΔC_p and $\Delta_{fus}H°$.

Vaporization Enthalpy from TG Measurements. From the TG experiments, the Q values for the molten compounds evaluated from NI-TG measurements, at about (2 to 3) K temperature intervals, are given in Figure 5 and in Table 5. Slopes and intercepts of the linear ln Q vs $1/T$ equations obtained by least-squares treatment of the results of each run are reported in Table 6. A final value was selected by weighing the slopes and intercepts of the equations reported in Table 6 proportionally to the experimental points.

Simetryn(l):

$$\ln(Q/kg^{1/2} \cdot s^{-1} \cdot m^{-2} \cdot K^{1/2} \cdot mol^{1/2}) = (16.50 \pm 0.34) - (10063 \pm 154)/(T/K) \text{ (from (435.1 to 470.9)K)} \quad (5)$$

Ametryn(l):

$$\ln(Q/kg^{1/2} \cdot s^{-1} \cdot m^{-2} \cdot K^{1/2} \cdot mol^{1/2}) = (16.53 \pm 0.35) - (10209 \pm 158)/(T/K) \text{ (from (429.1 to 476.8) K)} \quad (6)$$

Terbutryn(l):

$$\ln(Q/kg^{1/2} \cdot s^{-1} \cdot m^{-2} \cdot K^{1/2} \cdot mol^{1/2}) = (16.03 \pm 0.26) - (10008 \pm 117)/(T/K) \text{ (from (429.8 to 474.1) K)} \quad (7)$$

The associated errors are estimated by weighting the standard deviations of the four runs proportionally to the experimental points.

From the slopes of these selected equations, the second-law vaporization enthalpies of the studied compounds at the middle experimental temperature were derived and reported in Table 4 with an estimated error equal to ± 1 $kJ \cdot mol^{-1}$. In Table 4, the corresponding $\Delta_{sub}H°(298\ K)$ values are also obtained by using the same procedure of the DSC data. The associated errors were estimated considering the uncertainties associated with ΔC_p, $\Delta_{fus}H°$, and $\Delta_{vap}H°(T)$.

The −ln Q values as well as the values used in eq 1 (T, $\Delta m/S$, and Δt) obtained by I-TG experiments are reported in Table 7 and plotted in Figures 6a to 6c. Taking into account that higher uncertainties are associated with lower mass loss rates, which are measured at lower temperatures, the corresponding errors

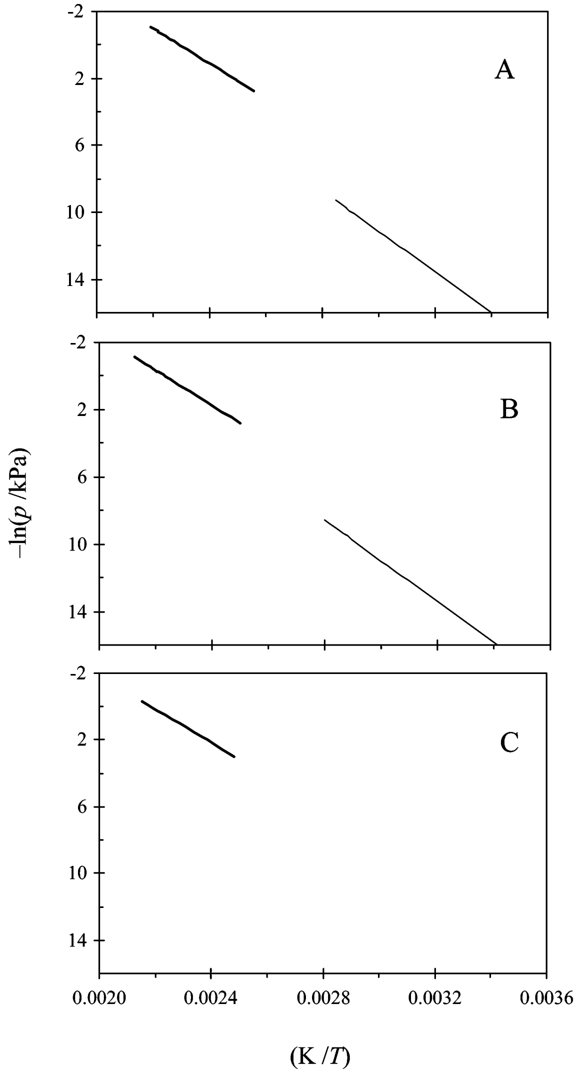

Figure 7. Vapor pressures of: A, simetryn; B, ametryn; C, terbutryn. Bold line, our data; thin line, ref 10.

associated with $-\ln Q$ values are higher than those measured at higher temperatures. Conversely, the $-\ln Q$ values for each run are so close that the errors due to semidispersion are too low. Therefore, these uncertainties are estimated taking into account both the standard deviations and the semidispersions. However, Figure 6 shows the plot of $-\ln Q$ as a function of $1/T$, whereas the slopes and intercepts of the linear $\ln Q$ vs $1/T$ equations obtained by the least-squares treatment of the results of the two runs are reported in Table 8. For each compound, by weighting the slopes and intercepts listed in Table 8 proportionally to the experimental points, the following final regression equations were selected.

Simetryn(l):

$$\ln(Q/\text{kg}^{1/2}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{K}^{1/2}\cdot\text{mol}^{1/2}) = (18.67 \pm 0.38) - (10410 \pm 160)/(T/\text{K}) \text{ (from (391.4 to 456.0) K)} \quad (8)$$

Ametryn(l):

$$\ln(Q/\text{kg}^{1/2}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{K}^{1/2}\cdot\text{mol}^{1/2}) = (18.11 \pm 0.44) - (10458 \pm 189)/(T/\text{K}) \text{ (from (400.1 to 470.6) K)} \quad (9)$$

Terbutryn(l):

$$\ln(Q/\text{kg}^{1/2}\cdot\text{s}^{-1}\cdot\text{m}^{-2}\cdot\text{K}^{1/2}\cdot\text{mol}^{1/2}) = (16.61 \pm 0.41) - (9978 \pm 178)/(T/\text{K}) \text{ (from (402.8 to 464.3) K)} \quad (10)$$

The associated errors are selected by weighting the standard deviations of the two runs proportionally to the experimental points.

The second-law vaporization enthalpies, calculated from the slopes of these equations, are reported in Table 4 with the corresponding $\Delta_{\text{sub}}H°(298\text{ K})$ values employing the same enthalpic increments and fusion enthalpies previously used. Despite the larger uncertainty in the values of enthalpies from DSC data, ascribed either to the evaluation of the initial temperature of the DSC peak or to the standard deviation of the repeated measurements, the vaporization enthalpies obtained with the three proposed methods are in appreciable agreement. Therefore, from the mean of the $\Delta_{\text{sub}}H°(298\text{ K})$ values calculated using the three methods, the final standard sublimation enthalpies, $\Delta_{\text{sub}}H°(298\text{ K}) = \{(117 \pm 5), (121 \pm 5), \text{and } (112 \pm 5)\}\text{ kJ}\cdot\text{mol}^{-1}$, respectively, were derived for simetryn, ametryn, and terbutryn. The selected uncertainties proposed were estimated from the mean of the uncertainties associated to all the $\Delta_{\text{sub}}H°(298\text{ K})$ values listed in Table 4.

The vapor pressure values of the studied compounds are derived from the $\ln Q$ data obtained by the I-TG measurements according to the equation $\ln P = \ln Q + \ln k_{\alpha'}$. The instrumental constant, $k_{\alpha'}$, values were evaluated by vaporizing in separate experiments pure benzoic acid and ferrocene having reliable vapor pressures[15−20,26] in the same temperatures ranges as those covered with the compounds. The obtained $k_{\alpha'}$ values listed in Table 9 do not depend on the standard used and agree to within about 4 % of their average value, $\ln(k_{\alpha}/\text{Pa}\cdot\text{s}\cdot\text{m}^{2}\cdot\text{kg}^{-1/2}\cdot\text{K}^{-1/2}\cdot\text{mol}^{-1/2}) = (12.1 \pm 0.5)$. Using this value, the temperature dependence of the vapor pressures follows the following Clausius−Clapeyron equations

Simetryn(1):

$$\ln(P/\text{kPa}) = (23.86 \pm 0.38) - (10410 \pm 160)/(T/\text{K}) \text{ (from (391.4 to 456.0) K)} \quad (11)$$

Ametryn(1):

$$\ln(P/\text{kPa}) = (23.30 \pm 0.44) - (10458 \pm 189)/(T/\text{K}) \text{ (from (400.1 to 470.6) K)} \quad (12)$$

Terbutryn(1):

$$\ln(P/\text{kPa}) = (21.80 \pm 0.41) - (9978 \pm 178)/(T/\text{K}) \text{ (from (402.8 to 464.3) K)} \quad (13)$$

because of the negligible temperature dependence of the vaporization enthalpies for the three herbicides examined over the examined temperature range. The associated errors are standard deviations. Moreover, the vapor pressures calculated in this work for the herbicides tested are reported in Figure 7 in comparison with the temperature dependence of the vapor pressure of simetryn and ametryn only as selected from the literature.[10] The agreement between the pressure data calculated in this work at relatively high temperatures over the liquid and those selected from the linear equations reported in the literature at lower temperatures over the solid is almost satisfactory. This poor result is probably due to the relatively low number of experimental literature data (six points for each sample) and to the fact that in the experimental temperature range mentioned in the literature[10] (from (323 to 403) K) both sublimation and

Table 8. Temperature Dependence of ln *Q* and Vaporization Enthalpies of the Studied Compounds from I-TG Data

compd	run	no. of points	ΔT K	$A^{a,b}$	$B/\mathrm{K}^{a,b}$	$\Delta H_{\mathrm{vap}}(T)$ $\mathrm{kJ \cdot mol^{-1}}$
simetryn	1	9	391.4 − 425.8	18.45 ± 0.32	10326 ± 132	85.9 ± 1.1
simetryn	2	10	425.7 − 456.0	18.87 ± 0.42	10485 ± 186	87.2 ± 1.5
ametryn	1	9	400.1 − 438.2	17.95 ± 0.65	10397 ± 272	86.4 ± 2.3
ametryn	2	12	444.2 − 470.6	18.23 ± 0.28	10504 ± 126	87.3 ± 1.0
terbutryn	1	7	402.8 − 432.6	16.62 ± 0.48	9977 ± 199	83.0 ± 1.7
terbutryn	2	7	437.2 − 464.3	16.60 ± 0.35	9980 ± 157	83.0 ± 1.3

[a] $\ln Q = A - B/(T/\mathrm{K})$. [b] The quoted errors are standard deviations.

Table 9. Instrumental Constants of the I-TG Assembly

compd	process	$\Delta T/\mathrm{K}$	$\ln(k_\alpha/\mathrm{Pa \cdot s \cdot m^2 \cdot kg^{-1/2} \cdot K^{-1/2} \cdot mol^{-1/2}})^a$
benzoic acid	sub	333 − 390	12.6 ± 0.2
	vap	415 − 458	11.61 ± 0.03
ferrocene	sub	313 − 436	12.2 ± 0.1
		average	12.1 ± 0.5

[a] The quoted errors are standard deviations.

vaporization of simetryn and ametryn occur. However, the excellent agreement found among the molar sublimation enthalpies for each herbicide studied demonstrates the reliability of the proposed methods. In addition, from the intercepts of these equations, the vaporization entropies, $\Delta_{\mathrm{vap}}S°(T) = (160, 155, \text{and } 143)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, respectively, were derived. These entropies were reported at 298 K by using the difference in heat capacity for vapor and solid, $\Delta C_p(\mathrm{v,s}) = -32\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, and for vapor and liquid, $\Delta C_p(\mathrm{v,l}) = -54\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, reported by Chickos et al.[23] along with the molar entropy of fusion. The $\Delta_{\mathrm{sub}}S°(298\ \mathrm{K})$ is (243, 244, and 214) $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ for simetryn, ametryn, and terbutryn, respectively. An estimated error of ± 5 $\mathrm{J \cdot K^{-1} \cdot mol^{-1}}$ was found to be equal for all these compounds.

Conclusion

The standard sublimation enthalpies of simetryn, ametryn, and terbutryn were obtained using three methods, and the results show a good agreement. The final standard sublimation enthalpies, $\Delta_{\mathrm{sub}}H(298\ \mathrm{K}) = \{(117 \pm 5), (121 \pm 5) \text{ and } (112 \pm 5)\}\ \mathrm{kJ \cdot mol^{-1}}$, respectively, were selected from the average values obtained by the three different techniques.

The vapor pressure values of the compounds studied are suitably derived and described by the following linear equations

Simetryn(1):

$$\ln(P/\mathrm{kPa}) = (23.86 \pm 0.38) - (10410 \pm 160)/(T/\mathrm{K}) \quad \text{(from (391.4 to 456.0) K)}$$

Ametryn(1):

$$\ln(P/\mathrm{kPa}) = (23.30 \pm 0.44) - (10458 \pm 189)/(T/\mathrm{K}) \quad \text{(from (400.1 to 470.6) K)}$$

Terbutryn(1):

$$\ln(P/\mathrm{kPa}) = (21.80 \pm 0.41) - (9978 \pm 178)/(T/\mathrm{K}) \quad \text{(from (402.8 to 464.3) K)}$$

A substantial linear trend was found among the vapor pressures calculated in this work, and the reasons for the almost satisfactory agreement between the pressure data determined in this work and that selected from the literature are probably due to the low reliability of literature data. From the intercepts of these equations, the sublimation entropies, corrected at 298 K, $\Delta_{\mathrm{sub}}S°(298\ \mathrm{K}) = (243, 244, \text{and } 214)\ \mathrm{J \cdot K^{-1} \cdot mol^{-1}}$, for simetryn, ametryn, and terbutryn, respectively, were derived.

From the results reported in this work, the reliability of sublimation and vaporization enthalpies as well as vapor pressures calculated by TG and DSC methods under isothermal and nonisothermal modes was confirmed. The advantages of the thermal analysis techniques are represented by the small sample weighing (from (4 to 6) mg, enough to uniformly cover the base of the crucible) and the short time needed to carry out a TG or a DSC experiment.

Literature Cited

(1) Smolin, E. M.; Rapoport, L. *s-Triazines and Derivatives*; Interscience Publishers: New York, 1959.

(2) Bowman, M. C.; Schechter, M. S.; Carter, R. L. *J. Agric. Food Chem.* **1965**, *13*, 360−365.

(3) Richardson, M. L. *Chemistry, Agriculture and the Environment*; The Royal Society of Chemistry: Cambridge, 1991.

(4) Wania, F.; Shiu, W.-Y.; Mackay, D. Measurement of the vapor pressure of several low-volatility organochlorine chemicals at low temperatures with a gas saturation method. *J. Chem. Eng. Data* **1994**, *39*, 572−577.

(5) Ribeiro da Silva, M. A. V.; Fonseca, J. M. S.; Carvalho, R. P. B. M.; Monte, M. J. S. Thermodynamic study of the sublimation of six halobenzoic acids. *J. Chem. Thermodyn.* **2005**, *37*, 271−279.

(6) Brunetti, B.; Portalone, G.; Piacente, V. Sublimation Thermodynamic Parameters for 5-Fluorouracil and Its 1-Methyl and 1,3-Dimethyl Derivatives from Vapor Pressure Measurements. *J. Chem. Eng. Data* **2002**, *47*, 17−19.

(7) Vecchio, S.; Brunetti, B. Standard sublimation enthalpies of some dichlorophenoxy acids and their methyl esters. *J. Chem. Eng. Data* **2005**, *50*, 666−672.

(8) Vecchio, S. Standard sublimation enthalpies and entropies of vaporization for two low-melting trichlorophenoxy herbicides. *J. Therm. Anal. Cal.* **2006**, *84*, 271−278.

(9) Rodante, F.; Catalani, G.; Guidotti, M. Thermal analysis and kinetic study of decomposition processes of some commercial pesticides. I. Triazine derivatives. *J. Therm. Anal.* **1998**, *53*, 937−956.

(10) Friedrich, K.; Stammach, K. Gas chromatographic determination of small vapour pressures of some triazine herbicides. *J. Chromatogr.* **1964**, *16*, 22−28.

(11) Boehncke, A.; Martin, K.; Muller, G. M.; Cammenga, H. K. The vapor pressure of lindane (γ-1,2,3,4,5,6-Hexachlorocyclohexane)-A comparison of Knudsen effusion measurements with data from other techniques. *J. Chem. Eng. Data* **1996**, *41*, 543−545.

(12) Jones, H. A.; Langmuir, I.; Mackay, G. M. J. The rates of evaporation and the vapor pressures of tungsten, molybdenum, platinum, nickel, iron, copper and silver. *Phys. Rev.* **1927**, *30*, 201−214.

(13) Hultgren, R.; Desai, P. D.; Hawkins, D. T.; Gleiser, M.; Kelley, K. K.; Wagman, D. D. *Selected Values of the Thermodynamic Properties of the Elements*; American Society for Metals: Metals Park, OH, 1973.

(14) Acree, W. E. Thermodynamic properties of organic compounds: enthalpy of fusion and melting point temperature compilation. *Thermochim. Acta* **1991**, *189*, 37−56.

(15) De Kruif, C. G.; Blok, J. G. The Vapor Pressure of Benzoic Acid. *J. Chem. Thermodyn.* **1982**, *14*, 201−206.

(16) Rojas-Aguilar, A.; Orozco-Guareño, E.; Martínez-Herrera, M. An experimental system for measurement of enthalpies of sublimation by d.s.c. *J. Chem. Thermodyn.* **2001**, *33*, 1405−1418.

(17) Marsh, K. N. *Recommended reference materials for the realization of physicochemical properties*; Blackwell Sci. Pub.: Oxford, 1987.

(18) Monte, M. J. S.; Santos, L. M. N. B. F.; Fulem, M.; Fonseca, J. M. S.; Sousa, C. A. D. New static apparatus and vapor pressure of reference materials: Naphtalene, Benzoic Acid, Benzophenone, and Ferrocene. *J. Chem. Eng. Data* **2006**, *51*, 757−766.

(19) Lippincott, E. R.; Nelson, R. D. The thermodynamic functions of bis-cyclopentadienyl iron, bis-cyclopentadienylnickel and bis-cyclopentadienylruthenium. *J. Am. Chem. Soc.* **1955**, *77*, 4990−4993.

(20) Edwards, J. W.; Kington, G. L. Thermodynamic properties of ferrocene. *Trans. Faraday Soc.* **1962**, *58*, 1334−1340.

(21) Sabbah, R.; Xu-wu, A.; Chickos, J. S.; Leitão, M. L. Planas; Roux, M. V.; Torres, L. A. Reference materials for calorimetry and differential thermal analysis. *Thermochim. Acta* **1999**, *331*, 93−204.

(22) O'Neil, M. J.; Smith, A.; Heckelman, P. E.; Obenchain, J. R.; Gallipeau, J. A. R.; D'Arecca, M. A. *The Merck Index*, 13th ed.; Merck & Co., Inc.: Whitehouse Station, NJ, 2001.

(23) Donnely, J. R.; Drewes, L. A.; Johnson, R. L.; Munslow, W. D.; Knapp, K. K.; Sovocool, G. W. Purity and heat of fusion data for environmental standards as determined by differential scanning calorimetry. *Thermochim. Acta* **1990**, *167*, 155−187.

(24) Wendlandt, W. W. *Thermal Methods of Analysis*; Wiley: New York, 1964.

(25) Chickos, J. S.; Hosseini, S.; Hesse, D. G.; Liebman, J. F. Heat Capacity Corrections to a Standard State: A Comparison of New and Some Literature Methods for Organic Liquids and Solids. *Struct. Chem.* **1993**, *4*, 271−278.

(26) Pelino, M.; Tomassetti, M.; Piacente, V.; D'Ascenzo, G. Vapor pressure measurements of ferrocene, mono- and 1,1′-di-acetyl ferrocene. *Thermochim. Acta* **1981**, *44*, 89−99.

Received for review December 21, 2006. Accepted June 26, 2007.

JE600580R