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Standard Sublimation Enthalpies of Some Dichlorophenoxy Acids and Their Methyl Esters

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The standard sublimation enthalpies of 2,4-dichlorophenoxy acetic acid, 2,4-dichlorophenoxy propionic acid, and 2,4-dichlorophenoxy butyric acid and their methyl esters 2,4-dichlorophenoxy acetic methyl ester and 2,4-dichlorophenoxy butyric methyl ester were determined by direct differential scanning calorimetry (DSC) measurements along with the Langmuir and torsion effusion methods. For 2,4-dichlorophenoxy acetic acid, 2,4-dichlorophenoxy propionic acid, and 2,4-dichlorophenoxy butyric acid, the values $\Delta_{\text{sub}}H°(298\text{ K}) = \{(122 \pm 5), (127 \pm 8), \text{and } (137 \pm 10)\}\text{ kJ}\cdot\text{mol}^{-1}$, respectively, were selected. For 2,4-dichlorophenoxy acetic acid methyl ester and 2,4-dichlorophenoxy butyric acid methyl ester, the $\Delta_{\text{sub}}H°(298\text{ K})$ final values 89 $\text{kJ}\cdot\text{mol}^{-1}$ and 100 $\text{kJ}\cdot\text{mol}^{-1}$, respectively, were selected with an estimated error of $\pm 10\text{ kJ}\cdot\text{mol}^{-1}$. From torsion data, the standard sublimation entropies for 2,4-dichlorophenoxy acetic acid, 2,4-dichlorophenoxy propionic acid, and 2,4-dichlorophenoxy butyric acid equal to $\Delta_{\text{sub}}S°(298\text{ K}) = (239, 263, \text{and } 294)\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$, respectively, were derived, with an error of $\pm 4\text{ J}\cdot\text{K}^{-1}\cdot\text{mol}^{-1}$ for all compounds.

Introduction

The physicochemical properties of pesticides are important for their application. In particular, their use at room temperature is conditioned by the vapor pressure of these compounds and their vaporization enthalpies. When the amount of a vaporized compound is small, the corresponding vaporization enthalpy can be obtained by the Clausius−Clapeyron equation, $\Delta_{\text{vap}}H°(T) = -R\ \text{d}\ln p/\text{d}(1/T)$, measuring the temperature dependence of the vapor pressure of the compound. There are several strategies for determining the vapor pressure. The mass-spectrometric, vacuum-Knudsen effusion, Langmuir, torsion, transpiration, and boiling point methods are the main methods[1] usually employed for these measurements.

In the present work, the standard sublimation enthalpies of some phenoxy-herbicides, in particular, of 2,4-dichlorophenoxy acetic acid (2,4-D), 2,4-dichlorophenoxy propionic acid (2,4-DP), and 2,4-dichlorophenoxy butyric acid (2,4-DB) and their methyl esters 2,4-dichlorophenoxy acetic methyl ester (2,4-DMe) and 2,4-dichlorophenoxy butyric methyl ester (2,4-DBMe), were determined at high temperatures, from direct differential scanning calorimetry (DSC) measurements and from the temperature dependence of the mass loss rate of the sample (through the Langmuir method[2]), and at lower temperatures, from the temperature dependence of the torsion data (through the torsion effusion method[3]). Both methods measure parameters proportional to the vapor pressures. No thermodynamic data for these compounds were found in the literature.

Experimental Section

The 2,4-D, 2,4-DB, 2,4-DP, 2,4-DMe, and 2,4-DBMe samples were supplied by Polyscience. Their purity is over 99%, as certified by the supplier; therefore, they were used without further purification.

The TG/DSC measurements were carried out on a Stanton-Redcroft 625 simultaneous TG/DSC connected to a 386 IBM-compatible personal computer. The instrument calibration was performed by using several very pure standards (indium,[4] gallium,[4] lead,[4] tin,[4] and benzoic acid[5,6]) having well-known temperatures and enthalpies of melting. Rising temperature experiments were carried out on the samples, and the experimental data were collected at every 1 K to give accuracy to the results. The uncertainty in the temperature measurements was estimated to be between (0.2 and 0.5) K, depending on the heating rate used. For each compound, some vaporization runs were carried out under a stream of argon in the temperature range from ambient to 620 K using three different heating rates of (2.5, 5, and 10) $\text{K}\cdot\text{min}^{-1}$. An open aluminum crucible, with a cross-sectional area of $2.0 \times 10^{-5}\text{ m}^2$, was used to contain the sample, while an empty one of equivalent mass was used as a reference. A sample size of about 3 mg to 5 mg of the studied compound was placed in an argon-filled drybox in the crucible. The surface area of the molten compounds was considered equal to the area of the crucible bottom and practically constant during the vaporization of the samples. The simultaneous TG/DSC system was flushed with a pure gas stream both below (flow rate 50 $\text{mL}\cdot\text{min}^{-1}$) and above (flow rate 80 $\text{mL}\cdot\text{min}^{-1}$) the open pans, to remove the vapor during the vaporization of the sample. Because of the sensitivity of the equipment, the vaporization kinetics could not be performed for mass loss rates (per unit area) below $5 \times 10^{-5}\text{ kg}\cdot\text{s}^{-1}\cdot\text{m}^{-2}$, so that all the vaporization measurements were carried out above the molten compounds at temperatures where the rate of mass loss was detectable.

The absolute vapor pressures of some compounds were measured by a torsion assembly described in detail in a

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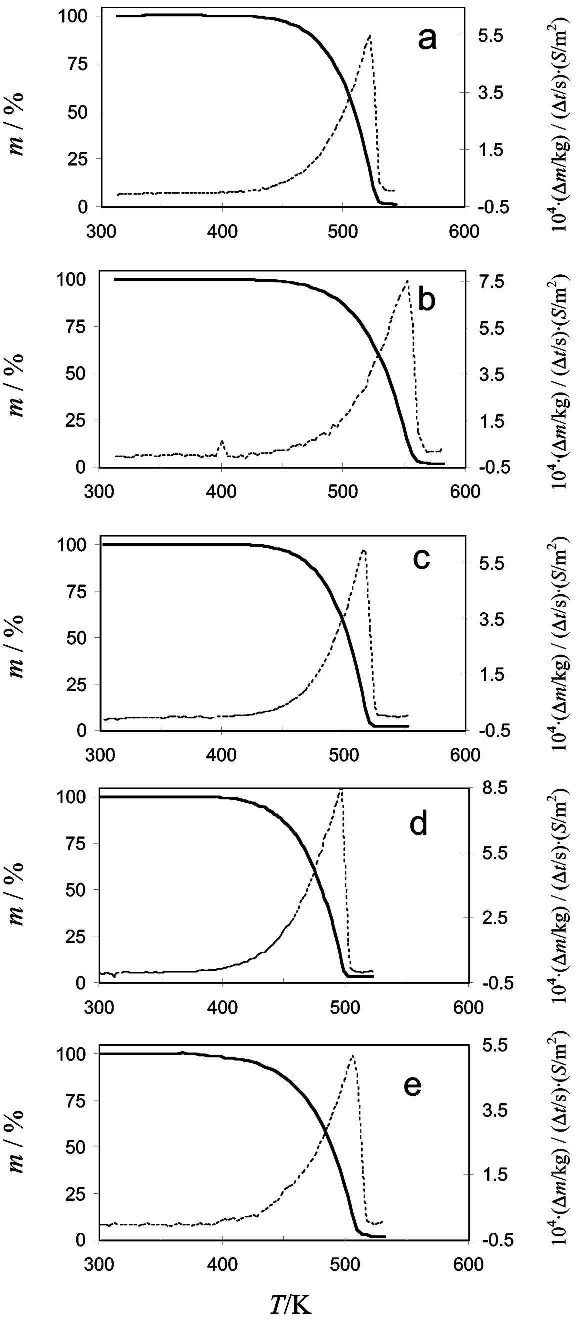

Figure 1. TG and DTG curves under a stream of argon at 10 K·min^{-1}: a, 2,4-D; b, 2,4-DB; c, 2,4-DP; d, 2,4-DMe; e, 2,4-DBMe.

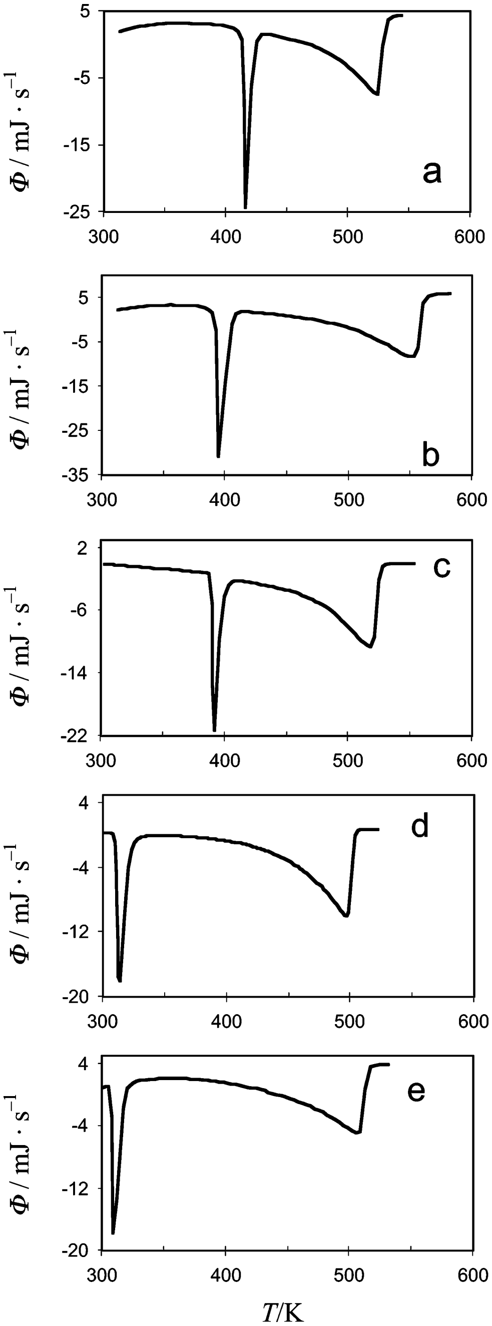

Figure 2. DSC curves under a stream of argon at 10 K·min^{-1}: a, 2,4-D; b, 2,4-DB; c, 2,4-DP; d, 2,4-DMe; e, 2,4-DBMe.

Table 1. Onset Temperatures and Mass Loss Percentages Obtained from TG Data and Onset, Peak Temperatures Obtained from DSC Data at 10 K·min^{-1} ^{a}

	from TG measurements		from DSC measurements			
			melting		vaporization	
	T_{onset}	Δm	T_{onset}	T_{peak}	T_{onset}	T_{peak}
compound	K	%	K	K	K	K
2,4-D	493.6	98.8	414.5 (411−415)	416.2	435.5	523.8
2,4-DP	476.4	97.8	389.7	391.3	473.4	518.2
2,4-DB	516.9	98.4	393.2 (391)	395.5	418.5	551.7
2,4-DMe	466.7	97.5	310.7	313.4	447.8	497.5
2,4-DBMe	482.5	100.0	308.1 (305−307)	309.7	356.9	506.4

[a] Melting temperatures (K) taken from the literature[10] are reported in parentheses.

previous work.[7] The vapor pressure (p) is related to the torsion angle of the assembly (α) by the simple equation $p = K_\alpha \alpha$, where K_α is the torsion constant of the assembly used. A conventional pyrophyllite cell having effusion holes of ~1.0 mm in diameter was used. The cell was opportunely suspended from a tungsten wire (30 μm in diameter and ≈30 cm long) from an arm of a vacuum balance (Chan 1000). K_α was determined by vaporizing standards (in this work, benzoic acid[6] and cadmium[4]) having well-known vapor pressures. The torsion constant values checked in some runs (carried out before and/or after the vaporization experiments) were found to be reproducible within ~ ±5% of their average values. This uncertainty and the error associated with the measurements of the torsion angles produce a displacement of the final ln p values of ~ ±0.10. The uncertainty in the temperature measurements was estimated as ±0.5 K. During the vaporization of the standard compounds, some second-law values of their sublimation enthalpies were calculated from the slopes of

Table 2. Standard Molar Vaporization Enthalpy Determined on Melted Compounds from DSC Measurements[a]

compound	run	ΔT K	$\Delta_{vap}H°(T)$ $kJ \cdot mol^{-1}$
2,4-D	1	431.6−526.5	76 ± 3
	2	440.4−538.5	76 ± 6
	3	442.3−564.3	77 ± 5
2,4-DP	1	415.1−518.3	76 ± 6
	2	422.7−525.2	76 ± 5
	3	426.8−529.0	76 ± 5
2,4-DB	1	421.4−550.0	81 ± 9
	2	429.6−560.5	81 ± 10
	3	435.9−566.4	81 ± 9
2,4-DMe	1	342.2−488.3	59 ± 3
	2	348.5−500.2	60 ± 3
	3	352.0−508.9	60 ± 3
2,4-DBMe	1	400.9−511.1	66 ± 6
	2	411.4−515.3	68 ± 7
	3	420.6−518.9	68 ± 6

[a] Runs 1, 2, and 3 were carried out at heating rates of (2.5, 5, and 10) $K \cdot min^{-1}$, respectively. The given errors are evaluated as semidispersion as well as initial and final temperature uncertainties.

the log α versus $1/T$ lines (where α are the experimental torsion angles). The very good agreement of the obtained enthalpies with those selected in the literature was taken as a check element of the reliability of the employed procedure and of the final torsion results obtained in the present work.

Results and Discussion

A. Thermal Analysis and Enthalpy of Fusion. The TG/DTG and corresponding DSC curves of 2,4-D, 2,4-DB, 2,4-DP, 2,4-DMe, and 2,4-DBMe are reported in Figures 1 and 2, respectively. The TG plots in Figure 1 show only one step of mass loss for the studied compounds, while the DSC signals reported in Figure 2 show two distinct endothermic effects connected with the melting of the sample and its vaporization at higher temperatures. The DSC peak temperatures for 2,4-D, 2,4-DP, 2,4-DB, 2,4-DMe, and 2,4-DBMe were found to be 416.2, 391.3, 395.5, 313.4, and 309.7, respectively, with an associated uncertainty of ±0.2 for all the compounds (see Table 1). The corresponding molar enthalpies of fusion were found to be {(32 ± 2), (32 ± 2), (35 ± 2), (20 ± 1), and (22 ± 1)} $kJ \cdot mol^{-1}$, respectively, where the given uncertainties were estimated. Practically the vaporization for each compound begins to be detectable after its melting. The melting and vaporization temperatures along with the corresponding mass loss percentages are summarized in Table 1 for each compound. In accordance with the International Confederation for Thermal Analysis and Calorimetry (ICTAC) recommendation, the onset temperature is used as the reaction temperature. The onset temperatures of melting extrapolated from the DSC curves are in close agreement with those found from the literature for 2,4-D, 2,4-DB, and 2,4-DBMe[5] (see Table 1). As expected, the melting temperatures of dichlorophenoxy methyl esters are noticeably lower (80 K to 100 K) than those of the corresponding acids. The onset temperatures of vaporization from the TG curves lie in the range from (466.7 to 516.9) K.

B. Vaporization Enthalpy from DSC Measurements. The vaporization enthalpies of the studied compounds were directly determined from the areas enclosed by the corresponding DSC peaks.[8] Calibration substances (i.e., sapphire[9] in the present work) were used in order to determine the heat flow values (in millijoules per second) as a function of temperature. For each compound, three runs at different heating rates were carried out at (2.5, 5, and 10) $K \cdot min^{-1}$ (runs 1, 2, and 3, respectively). Approximated initial and final temperatures of the DSC vaporization were estimated for each sample at a mass loss rate (per unit area) of 10^{-4} $kg \cdot s^{-1} \cdot m^{-2}$ (twice as much as the sensitivity of the equipment; see the Experimental Section). The corresponding molar vaporization enthalpies at the average temperature are also reported in Table 2. Although the errors of the results (evaluated as semidispersion as well as initial and final temperature uncertainties) are large, the vaporization enthalpies obtained at different heating rates are decidedly in good agreement. The corresponding average enthalpy values were reported in Table 3 with an estimated associated error of 2 $kJ \cdot mol^{-1}$ for all the compounds.

These enthalpies were reported at 298 K by using the difference in the heat capacity of vapor and solid and of vapor and liquid, as suggested by Chickos et al.,[10] $\Delta c_p(v,s) = 32\ kJ \cdot K^{-1} \cdot mol^{-1}$ and $\Delta c_p(v,l) = 54\ kJ \cdot K^{-1} \cdot mol^{-1}$. For this purpose, the molar heats of fusion measured in the present study were considered. The obtained values are reported in Table 3. The associated errors were estimated only as the sum of those associated with $\Delta_{vap}H°(T)$ and $\Delta_{fus}H°$.

C. Vaporization Enthalpy from Vapor Pressure Measurements. The second-law vaporization enthalpy of a compound can be determined by the temperature dependence on its vapor pressure by means of the abovementioned relation $\Delta_{vap}H°(T) = -R\, d \ln p/d(1/T)$. The vapor pressure ($p$) of a compound at a temperature, T, is related to its mass loss rate (dm/dt) measured by the thermal analysis, using the Langmuir equation:[2]

$$p = \frac{dm}{dt}\sqrt{\frac{T}{M}}\frac{\alpha'}{S\sqrt{2}\pi R} \qquad (1)$$

where R is the gas constant, M is the molecular weight of

Table 3. Second-Law Molar Vaporization Enthalpies at the Average of the Experimental Temperature Ranges and Standard Molar Vaporization Enthalpies at 298.15 K Obtained from DSC and Calculated from the Temperature Dependence on Vapor Pressure

	DSC			Langmuir			torsion		
	T	$\Delta_{vap}H°(T)$	$\Delta_{sub}H°(298\ K)$	T	$\Delta_{vap}H°(T)$	$\Delta_{sub}H°(298\ K)$	T	$\Delta_{sub}H°(T)$	$\Delta_{sub}H°(298\ K)$
compound	K	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	K	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$	K	$kJ \cdot mol^{-1}$	$kJ \cdot mol^{-1}$
2,4-D	498.0	77 ± 3	115 ± 6	502.5	76 ± 2	116 ± 4	360.5	123 ± 2	125 ± 3
					82 ± 3[a]	121 ± 5			
2,4-DP	479.1	76 ± 3	116 ± 6	530.0	76 ± 2	117 ± 4	358.5	128 ± 2	130 ± 3
2,4-DB	493.9	81 ± 3	124 ± 6	525.0	78 ± 2	123 ± 4	374.0	146 ± 1	149 ± 2
2,4-DMe	425.6	60 ± 3	88 ± 5	482.5	60 ± 2	89 ± 3			
2,4-DBMe	459.9	67 ± 3	97 ± 5	457.5	65 ± 2	96 ± 3			
					72 ± 2[a]	102 ± 3			

[a] Obtained by isothermal experiments (see text).

Table 4. Q Values Evaluated at ~5.0 K Intervals in the Experimental Temperature Ranges for Melted Compounds[a]

run 1		run 2		run 3	
T	$-\ln(Q)$	T	$-\ln(Q)$	T	$-\ln(Q)$
K	$\mathrm{kg \cdot K^{1/2} \cdot m^{-2} \cdot s^{-1}}$	K	$\mathrm{kg \cdot K^{1/2} \cdot m^{-2} \cdot s^{-1}}$	K	$\mathrm{kg \cdot K^{1/2} \cdot m^{-2} \cdot s^{-1}}$
2,4-Dichlorophenoxy Acetic Acid					
470.0	8.707	474.9	8.739	505.0	7.737
475.1	8.496	480.3	8.538	510.3	7.537
480.1	8.300	484.9	8.352	514.8	7.381
485.0	8.111	490.7	8.117	519.9	7.228
490.1	7.882	495.0	7.974	524.8	7.080
495.1	7.693	500.1	7.786	530.1	6.864
500.0	7.520	504.9	7.581	535.1	6.716
504.9	7.374	510.2	7.415		
509.9	7.176	514.6	7.255		
		520.0	7.073		
2,4-Dichlorophenoxy Propionic Acid					
490.1	7.604	495.0	7.627	500.0	7.585
494.9	7.404	500.1	7.466	505.1	7.420
500.1	7.166	505.0	7.308	509.9	7.234
505.0	6.980	509.9	7.110	515.0	7.076
510.1	6.817	515.1	6.915	520.0	6.883
515.0	6.629	520.0	6.742	525.1	6.722
519.9	6.514	525.0	6.573	530.1	6.547
525.0	6.344	530.1	6.425	535.1	6.400
530.1	6.176	535.0	6.303		
535.1	6.023				
2,4-Dichlorophenoxy Butyric Acid					
505.0	7.447	510.0	8.014	515.0	8.144
510.1	7.256	515.0	7.846	520.0	7.975
515.2	7.097	520.2	7.656	525.0	7.778
520.1	6.896	525.0	7.481	530.0	7.622
525.0	6.753	530.0	7.317	535.2	7.459
530.0	6.565	535.4	7.173	540.1	7.276
535.0	6.402	540.0	6.984	545.1	7.136
		545.0	6.822		
2,4-Dichlorophenoxy Acetic Methyl Ester					
455.0	7.308	475.0	6.984	480.1	7.115
460.0	7.112	480.0	6.823	485.1	6.948
465.0	6.946	485.0	6.694	490.0	6.802
470.0	6.794	490.1	6.533	495.0	6.671
475.0	6.644	495.0	6.367	500.0	6.532
480.1	6.484	500.0	6.255	505.1	6.343
485.0	6.303	505.1	6.112	510.0	6.248
490.1	6.167	510.0	5.935		
2,4-Dichlorophenoxy Butyric Methyl Ester					
440.0	8.783	440.2	9.457	445.1	9.355
445.1	8.548	445.0	9.258	450.1	9.172
450.2	8.373	450.0	9.040	454.9	8.998
455.0	8.199	455.1	8.794	459.9	8.766
459.9	7.967	460.0	8.647	465.0	8.599
465.0	7.786	465.0	8.457	470.0	8.403
470.2	7.593	470.0	8.309	474.9	8.248
475.1	7.448	475.0	8.149	480.0	8.122
480.0	7.335	480.0	7.940		
		485.1	7.801		
		490.0	7.684		
		495.1	7.502		
		499.9	7.345		
		505.1	7.113		

[a] Runs 1, 2, and 3 were carried out at heating rates of (2.5, 5, and 10) K·min^{-1}, respectively.

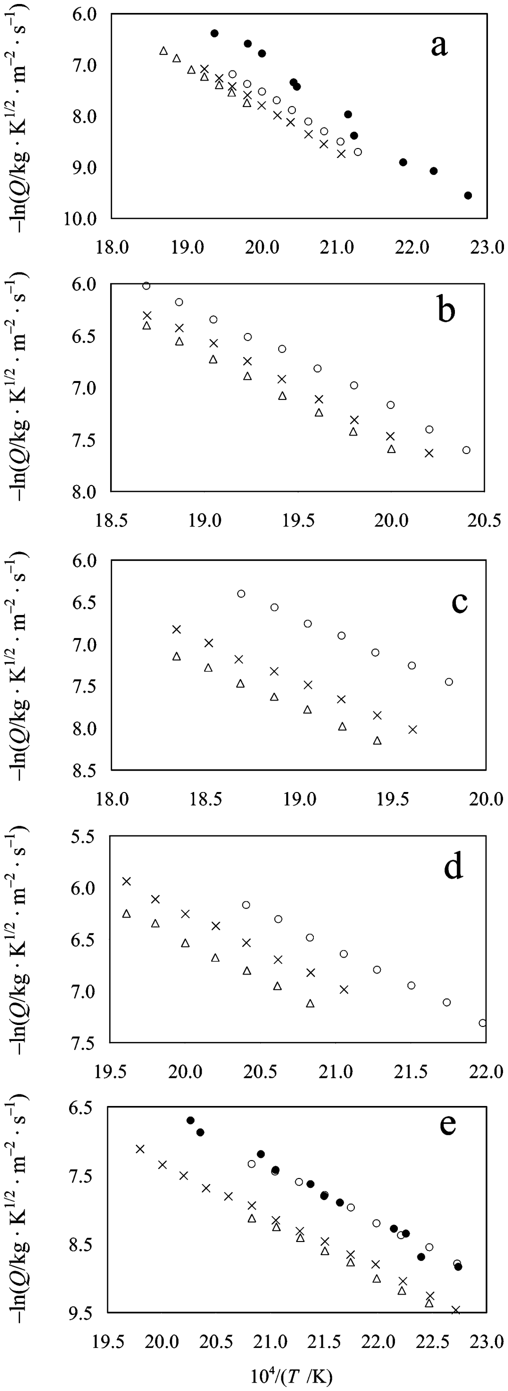

Figure 3. Temperature dependence of Q values: a, 2,4-D; b, 2,4-DP; c, 2,4-DB; d, 2,4-DMe; e, 2,4-DBMe. ●, isothermal experiments; ○, run 1; ×, run 2; △, run 3.

the compound, α′ is the vaporization constant, and S is the surface of the sample considered equal to the area of the bottom of the crucible. In this way, the $\Delta_{\mathrm{vap}}H°(T)$ value of the compound can be evaluated from the slope of the line obtained by plotting ln Q versus 1/T, where

$$Q = \frac{\mathrm{d}m}{\mathrm{d}t}\frac{1}{S}\sqrt{\frac{T}{M}}$$

The Q values for molten compounds, evaluated at ~5 K intervals in the experimental temperature ranges, are given in Table 4 and Figure 3. The slopes and intercepts of the linear ln Q versus 1/T equations obtained by least-squares treatment of the results of each run are reported in Table 5. Whereas for each compound the slopes of these equations are decidedly in agreement, the corresponding intercepts, which depend on the selected heating rate, are different, so that it is not possible to select a final ln Q versus 1/T equation. A final value was selected by weighting the slopes of the equation reported in Table 5 proportionally to the experimental points. From this value, the second-law vaporization enthalpy of the studied compounds at the middle experimental temperature was derived. The

Table 5. Temperature Dependence of Q and Vaporization Enthalpies of the Studied Compounds

compound	run	no. of points	ΔT	$\ln(Q/\mathrm{kg{\cdot}K^{1/2}{\cdot}m^{-2}{\cdot}s^{-1}}) = A - B/(T/\mathrm{K})$		$\Delta H(T)$
			K	A^a	B^a	$\mathrm{kJ{\cdot}mol^{-1}}$
2,4-D	1	9	470.0−509.9	10.88 ± 0.20	9204 ± 98	76.5 ± 0.8
2,4-D	2	10	474.9−520.0	10.58 ± 0.11	9178 ± 54	76.3 ± 0.5
2,4-D	3	7	505.0−535.1	10.27 ± 0.32	9092 ± 166	75.6 ± 1.4
2,4-DP	1	10	490.1−535.1	10.95 ± 0.33	9075 ± 167	75.5 ± 1.4
2,4-DP	2	9	495.0−535.0	10.65 ± 0.28	9054 ± 145	75.3 ± 1.2
2,4-DP	3	8	500.0−535.1	10.69 ± 0.17	9140 ± 87	76.0 ± 0.7
2,4-DB	1	7	505.0−535.0	11.18 ± 0.25	9407 ± 128	78.2 ± 1.1
2,4-DB	2	8	510.0−545.0	10.45 ± 0.23	9418 ± 123	78.3 ± 1.0
2,4-DB	3	7	515.0−545.1	10.24 ± 0.21	9469 ± 113	78.7 ± 0.9
2,4-DMe	1	8	455.0−490.1	8.50 ± 0.19	7189 ± 89	59.8 ± 0.7
2,4-DMe	2	8	475.0−510.0	8.06 ± 0.26	7150 ± 129	59.5 ± 1.1
2,4-DMe	3	7	480.1−510.0	7.81 ± 0.33	7161 ± 164	59.5 ± 1.4
2,4-DBMe	1	9	440.0−480.0	8.97 ± 0.35	7802 ± 161	64.9 ± 1.3
2,4-DBMe	2	14	440.2−505.1	8.18 ± 0.20	7748 ± 95	64.4 ± 0.8
2,4-DBMe	3	8	445.1−480.0	8.08 ± 0.35	7758 ± 160	64.5 ± 1.3

[a] The quoted errors are standard deviations.

Table 6. Q Langmuir Values Calculated by Experimental Data Obtained in Separate Isothermal Experiments (See Text)

compound	T	$\Delta m/S \pm 2$	$\Delta t \pm 5$	$-\ln(Q)$
	K	$\mathrm{g{\cdot}m^{-2}}$	s	$\mathrm{kg{\cdot}K^{1/2}{\cdot}s^{-1}{\cdot}m^{-2}}$ ^{a}
2,4-D	439.6 ± 0.2	29	519	9.43 ± 0.06
		7	140	9.61 ± 0.26
		8	160	9.61 ± 0.23
			average	9.6 ± 0.2
	448.7 ± 0.2	36	440	9.05 ± 0.05
		9	121	9.10 ± 0.20
			average	9.1 ± 0.1
	457.0 ± 0.2	51	538	8.91 ± 0.04
	471.0 ± 0.2	90	536	8.33 ± 0.03
		31	202	8.43 ± 0.08
			average	8.4 ± 0.1
	472.8 ± 0.5	34	140	7.94 ± 0.08
		41	180	8.00 ± 0.06
			average	8.0 ± 0.1
	488.5 ± 0.5	72	166	7.35 ± 0.05
		54	143	7.49 ± 0.06
			average	7.4 ± 0.1
	489.6 ± 0.2	54	122	7.32 ± 0.07
		36	84	7.35 ± 0.10
			average	7.3 ± 0.1
	500.0 ± 0.2	429	505	6.66 ± 0.01
		122	180	6.89 ± 0.04
			average	6.8 ± 0.1
	504.7 ± 0.2	132	140	6.56 ± 0.05
		108	121	6.61 ± 0.06
			average	6.6 ± 0.1
	516.2 ± 0.2	388	285	6.18 ± 0.02
		54	61	6.60 ± 0.11
			average	6.4 ± 0.2
2,4-DBMe	439.8 ± 0.2	17	148	8.84 ± 0.12
	446.5 ± 0.2	71	529	8.65 ± 0.03
		31	240	8.71 ± 0.07
		28	220	8.71 ± 0.08
			average	8.7 ± 0.1
	449.3 ± 0.4	36	206	8.37 ± 0.07
		33	180	8.35 ± 0.07
		26	141	8.33 ± 0.09
			average	8.3 ± 0.1
	451.6 ± 0.2	32	160	8.24 ± 0.08
		17	89	8.32 ± 0.15
			average	8.3 ± 0.1
	462.0 ± 0.2	42	151	7.90 ± 0.07
		44	158	7.91 ± 0.07
		64	238	7.94 ± 0.04
			average	8.0 ± 0.1
	465.2 ± 0.2	130	418	7.79 ± 0.02
		44	140	7.79 ± 0.07
		43	141	7.81 ± 0.07
			average	7.8 ± 0.1
	467.9 ± 0.2	67	181	7.61 ± 0.05
		43	121	7.65 ± 0.08
			average	7.6 ± 0.1
	475.0 ± 0.3	98	220	7.43 ± 0.04
		91	204	7.42 ± 0.04
		80	180	7.42 ± 0.05
			average	7.4 ± 0.1
	478.2 ± 0.4	80	142	7.18 ± 0.05
		56	101	7.20 ± 0.08
			average	7.2 ± 0.1
	491.2 ± 0.6	24	32	6.89 ± 0.22
		32	41	6.86 ± 0.17
			average	6.9 ± 0.1
	493.5 ± 0.2	267	259	6.56 ± 0.03
		64	81	6.83 ± 0.09
			average	6.7 ± 0.2

[a] The errors are calculated by the error propagation.

vaporization enthalpies, with an error estimated for all compounds equal to ±2 $\mathrm{kJ{\cdot}mol^{-1}}$, are summarized in Table 3 along with the corresponding $\Delta_{\mathrm{sub}}H°(298\ \mathrm{K})$ values obtained by using the same procedure of the DSC data. The final $\Delta_{\mathrm{sub}}H°(298\ \mathrm{K})$ values are decidedly in good agreement with the ones obtained by calorimetric measurements.

The Langmuir Q values for 2,4-D and 2,4-DBMe were also determined by isothermal experiments, and the experimental data are reported in Table 6 and plotted in Figure 3a and e. It is interesting to note that the isothermal results are in better agreement with those obtained from non-isothermal experiments carried out under low heating rates. The vaporization constant (α') depends on the selected heating rate. As a consequence, at a given pressure and temperature, the rate of mass loss changes with the heating rate according to the Langmuir equation.[2] However, for fixed heating rates, the α' value could be considered constant in the temperature range covered during the complete vaporization of the sample. In any case, eventual

Table 7. Torsion Data Measured above Solid Compounds

run 1		run 2		run 3		run 4	
T	$-\ln(\alpha)$	T	$-\ln(\alpha)$	T	$-\ln(\alpha)$	T	$-\ln(\alpha)$
K	rad	K	rad	K	rad	K	rad
2,4-Dichlorophenoxy Acetic Acid							
358.5	3.64	346.0	5.15	351.5	4.74	348.0	4.23
361.5	3.24	348.5	4.74	354.5	4.23	535.0	3.54
363.0	3.01	351.0	4.45	358.0	3.83	357.0	3.13
366.0	2.70	352.0	4.23	360.0	3.49	360.0	2.84
369.0	2.41	353.0	4.05	362.5	3.24	365.5	2.15
371.0	2.15	354.5	3.97	366.0	2.84	370.0	1.67
375.0	1.75	357.5	3.64	369.0	2.58	374.0	1.45
377.0	1.59	360.5	3.40	370.0	2.37	378.0	0.81
379.0	1.40	361.0	3.28	373.0	2.13	384.5	0.17
		363.0	3.07	375.0	1.93		
		364.5	2.90	375.5	1.85		
		365.5	2.75	378.0	1.61		
		369.0	2.34	379.5	1.45		
		370.5	2.26	380.5	1.33		
				383.5	1.05		
				385.0	0.90		
				386.0	0.84		
				387.0	0.78		
2,4-Dichlorophenoxy Propionic Acid							
357.5	2.54	343.0	4.23	347.0	3.89		
360.0	2.15	347.0	3.70	352.0	3.28		
364.0	1.58	353.0	3.07	355.5	2.95		
366.0	1.46	356.0	2.73	360.5	2.26		
372.0	0.83	358.5	2.47	366.0	1.46		
375.0	0.45	360.5	2.15	367.0	1.40		
		364.0	1.65	370.0	1.19		
		371.0	0.81	374.0	0.70		
2,4-Dichlorophenoxy Butyric Acid							
361.0	4.59	356.5	5.15	358.0	4.92	360.0	4.23
362.5	4.34	359.5	4.74	360.0	4.59	363.0	3.76
363.5	4.23	361.5	4.45	363.0	4.23	367.0	3.36
365.5	4.05	363.5	4.14	367.0	3.76	373.0	2.62
369.5	3.49	366.5	3.89	369.0	3.44	377.0	2.18
370.0	3.40	368.0	3.64	372.0	3.01	383.0	1.34
372.5	3.07	370.0	3.44	375.0	2.62	386.0	0.90
373.0	2.95	372.5	3.13	378.0	2.15		
375.0	2.75	374.0	2.90	381.0	1.85		
377.5	2.47	377.0	2.62	383.0	1.59		
		378.0	2.36	386.5	1.39		
		380.0	2.20	389.0	1.00		
		382.0	1.89	391.0	0.78		
		384.0	1.59				
		386.0	1.37				
		387.0	1.16				
		389.5	1.02				
		391.0	0.78				

changes are comparable with the error associated in the slope of the ln Q versus $1/T$ equation.

The isothermal results were treated by the usual linear regression by the least-squares method, and the following equations were obtained.

2,4-D(l)
$$\ln(Q/\mathrm{kg{\cdot}K^{1/2}{\cdot}m^{-2}{\cdot}s^{-1}}) = (12.93 \pm 0.90) - (9918 \pm 420)/(T/\mathrm{K}) \text{ (from 439.6 to 516.2 K)} \quad (2)$$

2,4-DBMe(l)
$$\ln(Q/\mathrm{kg{\cdot}K^{1/2}{\cdot}m^{-2}{\cdot}s^{-1}}) = (10.70 \pm 0.60) - (8596 \pm 270)/(T/\mathrm{K}) \text{ (from 439.8 to 493.5 K)} \quad (3)$$

The associated errors are standard deviations.

The slopes of these equations were higher than those obtained with the previous experiments (see Table 5).

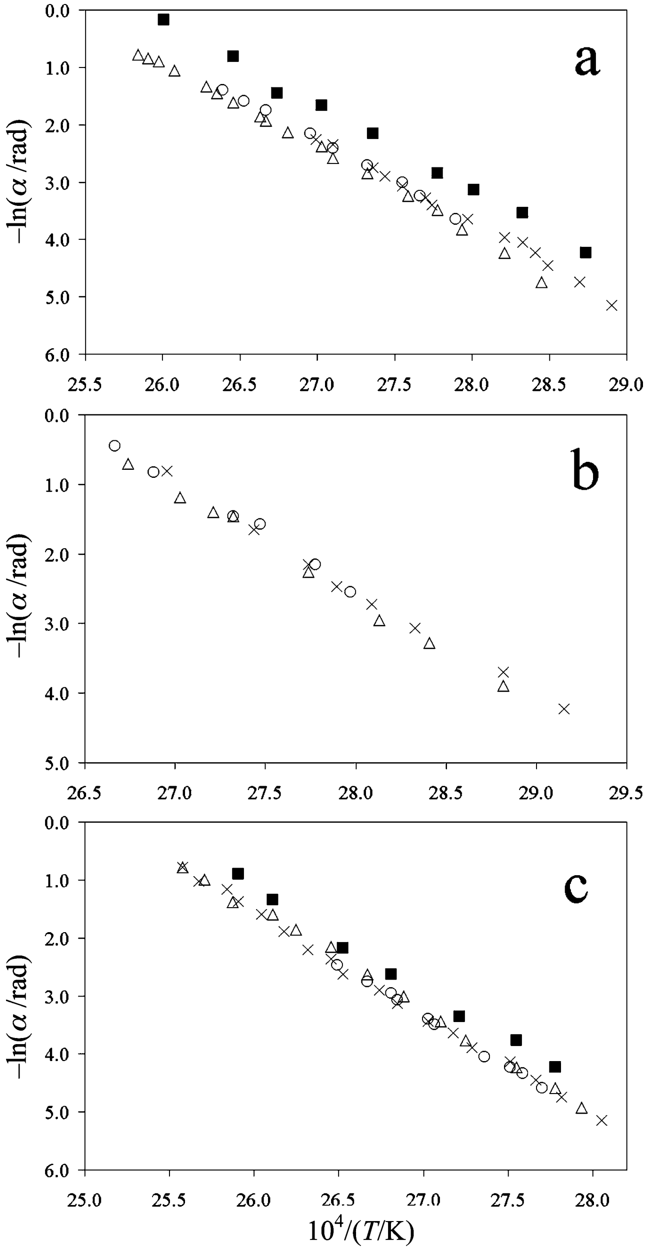

Figure 4. Torsion data: a, 2,4-D; b, 2,4-DP; c, 2,4-DB. ○, run 1; ×, run 2; △, run 3; ■, run 4.

Table 8. Temperature Dependence of the Torsion Results for 2,4-D, 2,4-DP, and 2,4-DB

		no. of	ΔT	$\ln(\alpha/\mathrm{rad}) = A - B/(T/\mathrm{K})$	
compound	run	points	K	A^a	B^a
2,4-D	1	9	358.5−379.0	35.52 ± 0.81	14673 ± 298
2,4-D	2	14	346.0−370.5	35.65 ± 0.85	14712 ± 305
2,4-D	3	18	351.5−387.0	35.95 ± 0.49	14594 ± 181
2,4-D	4	9	348.0−384.5	35.70 ± 0.84	14629 ± 305
2,4-DP	1	6	357.5−372.0	38.78 ± 1.81	15510 ± 661
2,4-DP	2	8	343.0−371.0	38.13 ± 1.23	15285 ± 438
2,4-DP	3	8	347.0−374.0	39.19 ± 1.07	15599 ± 386
2,4-DB	1	10	361.0−377.5	42.41 ± 0.85	17630 ± 314
2,4-DB	2	18	356.5−391.0	42.43 ± 0.57	17631 ± 212
2,4-DB	3	13	358.0−391.0	42.49 ± 0.72	17622 ± 270
2,4-DB	4	7	360.0−386.0	42.04 ± 1.38	17439 ± 515

[a] The errors are standard deviations.

The torsion data for solid 2,4-D, 2,4-DP, and 2,4-DB are reported in Table 7 and Figure 4. The linear ln α versus $1/T$ equations obtained by least-squares treatment of the data of each run are reported in Table 8. Both the slopes and intercepts of the equations for each compound are decidedly in good agreement. By weighting the slope and intercept of each equation proportionally to the experimen-

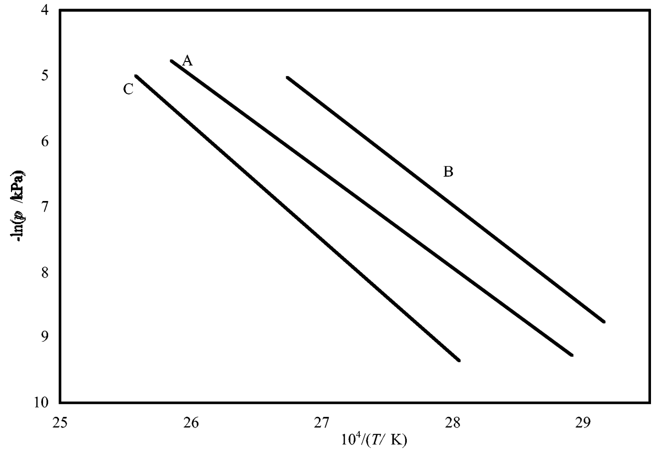

Figure 5. Vapor pressures above the following: A, 2,4-D; B, 2,4-DP; C, 2,4-DB.

tal points, we selected the following equations:

$$\text{2,4-D(s)} \qquad \ln(\alpha/\text{rad}) = (35.74 \pm 0.20) - (14\,756 \pm 150)/(T/\text{K}) \text{ (from 346.0 to 387.0 K)} \quad (4)$$

$$\text{2,4-DP(s)} \qquad \ln(\alpha/\text{rad}) = (38.69 \pm 0.50) - (15\,460 \pm 200)/(T/\text{K}) \text{ (from 343.0 to 374.0 K)} \quad (5)$$

$$\text{2,4-DB(s)} \qquad \ln(\alpha/\text{rad}) = (42.39 \pm 0.10) - (17\,600 \pm 100)/(T/\text{K}) \text{ (from 356.5 to 391.0 K)} \quad (6)$$

The associated errors were estimated. The second-law sublimation enthalpies, calculated from the slopes of these equations, are reported in Table 3 with the corresponding $\Delta_{\text{sub}}H°(298\text{ K})$ values obtained using the difference in the heat capacity of solid and vapor proposed by Chickos et al.[10]

The torsion data were used to obtain the absolute vapor pressures of these compounds, employing as K_α the value 14.6 Pa·rad^{-1}. The corresponding $\ln p$ versus $1/T$ lines thus obtained are plotted in Figure 5. From the absolute vapor pressures, the sublimation entropies for 2,4-D, 2,4-DB, and 2,4-DP, $\Delta_{\text{sub}}S°(T) \approx \Delta_{\text{sub}}S°(298\text{ K}) = (239, 263, \text{and } 294)$ J·K^{-1}·mol^{-1}, respectively, were derived. An estimated error of ±4 J·K^{-1}·mol^{-1} was associated with all of these compounds.

Conclusion

The calorimetric vaporization enthalpies obtained from DSC as well as those obtained from non-isothermal Langmuir data are in excellent agreement. The isothermal Langmuir results are quite higher than the other ones. The derived standard sublimation enthalpy ($\Delta_{\text{sub}}H°(298\text{ K})$) values are lower than those obtained by the torsion method for 2,4-D, 2,4-DP, and 2,4-DB. Taking into account that the torsion measurements were carried out above the solid phases and at experimental temperatures near 298 K, the obtained final $\Delta_{\text{sub}}H°(298\text{ K})$ values seem to be more reliable than the other final values obtained at higher temperatures above the liquid phases, because they are influenced by the uncertainty decidedly higher due to both the correction at 298 K, because of the estimated Δc_p values, and the error associated with the values of the heat of fusions. On this basis, giving more weight to the final torsion results, for 2,4-D, 2,4-DP, and 2,4-DB, the values $\Delta_{\text{sub}}H°(298\text{ K}) = \{(122 \pm 5), (127 \pm 8), \text{and } (137 \pm 10)\}$ kJ·mol^{-1}, respectively, were selected. For 2,4-DMe and 2,4-DBMe, the $\Delta_{\text{sub}}H°(298\text{ K})$ final values 89 kJ·mol^{-1} and 100 kJ·mol^{-1}, respectively, were selected, but we are convinced that these values should be considered decidedly as lower limits for the above-mentioned reason. Thus, an estimated error of ~ ±10 kJ·mol^{-1} for both values is proposed.

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