1088 *J. Chem. Eng. Data* **2000,** *45,* 1088−1092

Thermodynamic Study on the Sublimation of Six Substituted Quinoxalines

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The Knudsen mass-loss effusion technique was used to measure the vapor pressures at different temperatures of the following substituted quinoxalines: 2-hydroxyquinoxaline, between 383.17 K and 399.15 K; 2-hydroxy-3-methylquinoxaline, between 375.16 K and 391.15K; 2,3-dichloroquinoxaline, between 313.15 K and 329.15 K; 2,3,6,7-tetrachloroquinoxaline, between 347.16 K and 361.17 K; 2,3-dimethylquinoxaline between 294.14 K and 308.14 K; 2,3-bis(bromomethyl)quinoxaline, between 351.14 K and 365.14 K. From the temperature dependence of the vapor pressure, the standard molar enthalpies of sublimation at the mean temperature of the experimental range were derived by the Clausius−Clapeyron equation. From these results the standard molar enthalpies, entropies, and Gibbs functions of sublimation at $T = 298.15$ K were calculated. An empirical equation for estimating vapor pressure−temperature data from enthalpies of sublimation values is presented.

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1. Introduction

Enthalpies of sublimation can be experimentally determined using a calorimetric method or from the temperature dependence of the vapor pressure. A few estimation methods are also available: Bondi[1] has developed a general method based on structural information, and for compounds with structural affinities more accurate methods have also been derived.[2−5]

Vapor pressures of liquid and solid substances are key thermodynamic parameters not only to derive enthalpies of vaporization or sublimation but also in several important studies such as the determination of the Henry's constant characterizing the solubility of solids in water and developing models to simulate the behavior of chemical substances in the environment. Despite the large amount of vapor pressure data published in the literature, there is still need for more data for numerous compounds, mainly for low volatile solids. For these compounds, literature results are scarce and often inaccurate. Some estimation methods can be used to predict vapor pressures of liquids,[6] but predictive methods for sublimation vapor pressures are usually based on the entropy of fusion and on the boiling temperature of the respective liquid.[7]

This work is part of a thermodynamic study on the sublimation of several organic solids with a goal of establishing correlations between enthalpies of sublimation and temperatures of sublimation at a reference pressure.[8]

Using the Knudsen effusion method, vapor pressures of crystalline samples of six substituted quinoxalines were measured over a temperature range in order to derive their standard molar enthalpies and entropies of sublimation. The present results were used together with literature results of other heterocyclic aromatic compounds to yield a linear correlation between the enthalpy of sublimation and the temperature of sublimation at $p = 0.5$ Pa.

Table 1. Temperatures of Fusion, T_{fus}/K, Enthalpies of Fusion, $\Delta_{cr}^{l}H_{m}^{\circ}(T_{fus})$, and Mass Fraction of Impurities, *w*, of the Studied Compounds

	T_{fus} / K	$\Delta_{cr}^{l}H_{m}^{\circ}(T_{fus})$ / kJ·mol^{-1}	10^3w
2-hydroxyquinoxaline	542.51 ± 0.05	32.45 ± 0.38	1.6
2-hydroxy-3-methylquinoxaline	522.91 ± 0.09	33.43 ± 0.36	1.3
2,3-dichloroquinoxaline	424.37 ± 0.16	24.36 ± 0.12	2.5
2,3,6,7-tetrachloroquinoxaline	446.04 ± 0.07	29.63 ± 0.18	3.9
2,3-dimethylquinoxaline	379.49 ± 0.10	22.35 ± 0.03	1.4
2,3-bis(bromomethyl)quinoxaline	423.64 ± 0.05	32.43 ± 0.13	4.9

2. Experimental Section

All the compounds used were commercially obtained from Aldrich Chemical Co. with the following assessed purities (mass fraction): 2-hydroxyquinoxaline, 0.99; 2-hydroxy-3-methylquinoxaline, 0.99; 2,3-bis(bromomethyl)quinoxaline, 0.98; 2,3,6,7-tetrachloroquinoxaline, 0.98; 2,3-dichloroquinoxaline, 0.98; 2,3-dimethylquinoxaline, 0.97.

The compounds were purified by repeated sublimation under reduced pressure, and their final purity was assessed by DSC using a fractional fusion technique.[9] Since the use of this technique requires that the enthalpies and temperatures of fusion be computed from the DSC thermograms, we present these results together with the mass fraction of impurities of the purified samples in Table 1. The uncertainties assigned to the results are twice the standard deviation of the mean of at least five independent runs. DSC experiments were performed on a Setaram DSC 141 calorimeter using a heating rate of 3.33×10^{-2} K·s^{-1}. The temperature scale of the calorimeter was calibrated by measuring the melting temperatures of three high-purity reference materials (naphthalene, benzoic acid, and indium),[10] and its power scale was calibrated with high-purity indium (mass fraction > 0.99999). The recorded thermograms did not show any phase transitions between 298 K and the melting temperature of the samples contained in sealed stainless steel crucibles.

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10.1021/je0001577 CCC: $19.00

A mass-loss Knudsen effusion apparatus enabling the simultaneous operation of three Knudsen cells, with three different effusion holes, was used to measure the vapor pressures of the purified crystalline samples at several temperatures. A detailed description of the apparatus, procedure, and technique, and the results obtained with two test substances (benzoic acid and ferrocene) have been reported.[11] The consistency of the measured vapor pressure was checked, comparing the results obtained for benzoic acid and for copper(II) β-diketonates using this apparatus with the results obtained for these compounds using different experimental apparatuses and different techniques.[12]

In a typical effusion experiment the loss of mass Δm of the samples during a convenient effusion time period t is determined by weighing the effusion cells to ± 0.01 mg before and after the effusion period in a system evacuated to a pressure near 1×10^{-4} Pa. The samples are assumed to be in thermal equilibrium with a thermostatically controlled (to ± 0.001 K) silicone oil bath where the effusion cells are immersed. At the temperature T of the experiment, the vapor pressure p is calculated by eq 1:

$$p = (\Delta m / A_0 w_0 t)(2\pi R T/M)^{1/2} \qquad (1)$$

where M is the molar mass of the effusing vapor, R is the gas constant, A_0 is the area of the effusion hole, and w_0 is the respective Clausing factor calculated by eq 2, where l is the thickness of the effusion hole and r its radius:

$$w_0 = \{1 + (3l/8r)\}^{-1} \qquad (2)$$

For all the compounds studied the thickness of the effusion holes was 0.049 mm, and their areas and Clausing factors were as follows: hole 1, $A_0/\mathrm{mm}^2 = 0.596$, $w_0 = 0.959$; hole 2, $A_0/\mathrm{mm}^2 = 0.754$, $w_0 = 0.964$; hole 3, $A_0/\mathrm{mm}^2 = 0.862$, $w_0 = 0.966$.

Usually the measurements were extended through a chosen temperature interval corresponding to measured vapor pressures in the range 0.1 to 1.0 Pa.

3. Results and Discussion

The standard molar enthalpies of sublimation at the mean temperature of the experimental temperature range were derived using the integrated form of the Clausius−Clapeyron equation, $\ln(p/\mathrm{Pa}) = a - b(T/\mathrm{K})^{-1}$, where a is a constant and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}(\langle T \rangle)/R$. The experimental results obtained from each effusion cell for each studied compound, together with the residuals of the Clausius−Clapeyron equation, derived from least squares adjustment, are presented in Table 2. For all the compounds studied the calculated enthalpies of sublimation obtained from each individual hole are in agreement within experimental error and no systematic dependence of the results on the areas of the effusion holes could be detected. The entropies of sublimation at equilibrium conditions were calculated as

$$\Delta_{\mathrm{cr}}^{\mathrm{g}} S_{\mathrm{m}}\{\langle T \rangle, p(T{=}\langle T \rangle)\} = \Delta_{\mathrm{cr}}^{\mathrm{g}} H_{\mathrm{m}}^{\circ}(\langle T \rangle)/\langle T \rangle$$

Table 3 presents the parameters of the Clausius−Clapeyron equation together with the calculated standard deviations and the standard molar enthalpies of sublimation at the mean temperature of the experiments $T = \langle T \rangle$ for each hole used and for the global results. The equilibrium pressure at this temperature $p(T = \langle T \rangle)$ and the entropies of sublimation at equilibrium conditions are also presented.

Table 2. Knudsen Effusion Results for the Compounds Studied with the Vapor Pressures Obtained from Each Hole Denoted by p and the Deviations of the Experimental Results from Those Given by the Clausius−Clapeyron Equations Denoted by $\Delta \ln(p/\mathrm{Pa})$

	p/Pa			$100\Delta \ln(p/\mathrm{Pa})$		
T/K	hole 1	hole 2	hole 3	hole 1	hole 2	hole 3
		2-Hydroxyquinoxaline				
383.17	0.2139	0.2110	0.2107	0.96	−0.23	−0.83
385.20	0.2581	0.2584	0.2624	0.38	0.85	2.01
387.14	0.3097	0.3074	0.3053	0.31	0.05	−0.91
389.25	0.3742	0.3713	0.3776	−0.47	−0.59	0.91
391.22	0.4409	0.4435	0.4432	−2.26	−0.87	−1.03
393.15	0.5354	0.5351	0.5291	−0.49	0.40	−0.73
395.21	0.6434	0.6382	0.6464	−0.77	−0.48	0.88
397.13	0.7618	0.7469	0.7505	−1.09	−1.82	−1.17
399.15	0.9467	0.9256	0.9159	2.71	1.84	1.05
		2-Hydroxy-3-methylquinoxaline				
375.16	0.1630	0.1598	0.1604	0.80	0.38	−0.54
377.17	0.1957	0.1913	0.1979	−0.88	−1.70	0.44
379.06	0.2357	0.2345	0.2366	−0.86	−0.01	−0.34
381.09	0.2907	0.2895	0.2892	0.37	1.21	−0.08
383.16	0.3537	0.3511	0.3557	0.07	0.48	0.64
385.12	0.4241	0.4182	0.4218	−0.45	−0.79	−1.04
387.17	0.5206	0.5158	0.5211	0.74	0.76	0.71
389.36	0.6339	0.6288	0.6335	0.01	0.05	−0.24
391.15	0.7442	0.7358	0.7470	−0.46	−0.83	−0.33
		2,3-Dichloroquinoxaline				
313.148	0.1902	0.1853	0.1908	0.05	−0.50	0.14
315.139	0.2376	0.2333	0.2372	−0.16	−0.06	−0.54
317.154	0.2987	0.2918	0.3020	0.38	−0.03	1.17
319.150	0.3640	0.3612	0.3663	−1.70	−0.67	−1.47
321.151	0.4584	0.4561	0.4640	−0.28	0.90	0.45
323.143	0.5781	0.5634	0.5781	1.65	0.64	1.08
325.147	0.7012	0.6959	0.7057	−0.18	0.51	−0.21
327.161	0.8716	0.8459	0.8737	0.59	−1.07	0.08
329.151	1.051	1.048	1.069	−1.16	−0.27	−0.29
		2,3,6,7-Tetrachloroquinoxaline				
347.158	0.2097	0.2083	0.2098	-0.69	-0.70	-0.61
349.160	0.2629	0.2631	0.2606	0.79	1.60	-0.05
351.165	0.3224	0.3189	0.3213	0.28	-0.02	-0.04
353.153	0.3934	0.3898	0.3952	-0.32	-0.38	0.16
355.149	0.4801	0.4738	0.4836	-0.75	-1.15	-0.02
357.156	0.5904	0.5829	0.5902	-0.31	-0.61	-0.34
359.157	0.7262	0.7131	0.7203	0.45	-0.33	-0.38
361.170	0.8806	0.8814	0.8799	-0.12	1.07	-0.22
		2,3-Dimethylquinoxaline				
294.140	0.2043	0.2022	0.2042	-0.45	-0.58	-1.00
296.158	0.2641	0.2657	0.2658	0.95	2.25	0.80
298.150	0.3314	0.3280	0.3323	0.00	-0.52	-0.80
300.132	0.4139	0.4144	0.4266	-0.98	-0.54	0.69
302.145	0.5234	0.5234	0.5358	-0.78	-0.64	-0.06
304.133	0.6685	0.6627	0.6756	1.02	0.09	0.18
306.140	0.8275	0.8398	0.8485	-0.24	1.00	0.10
308.139	1.035	1.041	1.052	-0.05	0.06	-0.83
		2,3-Bis(bromomethyl)quinoxaline				
351.143	0.2268	0.2261	0.2257	0.28	1.28	-0.24
353.154	0.2778	0.2745	0.2800	−1.21	−1.01	−0.59
355.142	0.3468	0.3417	0.3493	−0.32	−0.32	0.12
357.157	0.4310	0.4223	0.4309	0.09	−0.39	−0.34
359.150	0.5383	0.5280	0.5383	1.45	1.16	0.93
361.140	0.6500	0.6408	0.6563	−0.30	0.00	0.03
363.148	0.7969	0.7847	0.7959	−0.49	-0.22	−1.36
365.143	0.9758	0.9653	0.9902	−0.44	0.36	0.17

The plots of $\ln p = f(1/T)$ for the global results obtained for each compound are presented in Figure 2. Table 4 lists the (p,T) values calculated from the (p,T) equations for the crystalline compounds within the experimental range of pressures: 0.1 to 1 Pa.

Sublimation enthalpies at the temperature 298.15 K were derived from the sublimation enthalpies calculated at the mean temperature $\langle T \rangle$ of the experiments, by the equation

Table 3. Experimental Results for the Studied Compounds Where *a* and *b* Are from the Clausius−Clapeyron Equation $\ln(p/\mathrm{Pa}) = a - b(\mathrm{K}/T)$ and $b = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\langle T\rangle)/R$ with $R = 8.314\,51\ \mathrm{J{\cdot}K^{-1}{\cdot}mol^{-1}}$

hole number	a	b	$\langle T\rangle$ / K	$p(T=\langle T\rangle)$ / Pa	$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\langle T\rangle)$ / kJ·mol^{-1}	$\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}\{\langle T\rangle,p(T=\langle T\rangle)\}$ / J·K^{-1}·mol^{-1}
			2-Hydroxyquinoxaline			
1	35.163 ± 0.380	14068 ± 149			117.0 ± 1.2	
2	34.861 ± 0.286	13953 ± 112			116.0 ± 0.9	
3	34.683 ± 0.321	13883 ± 125			115.4 ± 1.0	
global	34.903 ± 0.187	13968 ± 73	391.16	0.447	116.1 ± 0.6	297 ± 2
			2-Hydroxy-3-methylquinoxaline			
1	35.634 ± 0.166	14052 ± 63			116.8 ± 0.5	
2	35.813 ± 0.238	14125 ± 91			117.4 ± 0.7	
3	35.754 ± 0.153	14098 ± 58			117.2 ± 0.5	
global	35.734 ± 0.128	14092 ± 49	383.16	0.351	117.2 ± 0.4	306 ± 1
			2,3-Dichloroquinoxaline			
1	33.733 ± 0.214	11083 ± 69			92.1 ± 0.6	
2	33.903 ± 0.144	11143 ± 46			92.6 ± 0.4	
3	33.878 ± 0.181	11128 ± 58			92.5 ± 0.5	
global	33.838 ± 0.154	11118 ± 49	321.15	0.458	92.4 ± 0.4	288 ± 1
			2,3,6,7-Tetrachloroquinoxaline			
1	35.284 ± 0.162	12789 ± 57			106.3 ± 0.5	
2	35.165 ± 0.276	12750 ± 97			106.0 ± 0.8	
3	35.298 ± 0.073	12794 ± 26			106.4 ± 0.2	
global	35.249 ± 0.118	12778 ± 42	354.16	0.436	106.2 ± 0.3	300 ± 1
			2,3-Dimethylquinoxaline			
1	34.049 ± 0.183	10481 ± 55			87.1 ± 0.4	
2	34.329 ± 0.255	10566 ± 77			87.8 ± 0.6	
3	34.479 ±0.174	10606 ± 52			88.2 ± 0.4	
global	34.286 ±0.149	10551 ± 45	301.14	0.472	87.7 ± 0.4	291 ± 1
			2,3-Bis(bromomethyl)quinoxaline			
1	36.760 ± 0.230	13430 ± 82			111.7 ± 0.7	
2	36.596 ± 0.236	13377 ± 84			111.2 ± 0.7	
3	36.974 ± 0.198	13505 ± 71			112.3 ± 0.6	
global	36.777 ± 0.175	13437 ± 63	358.14	0.476	111.7 ± 0.5	312 ± 1

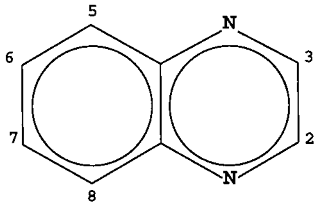

Figure 1. Quinoxaline.

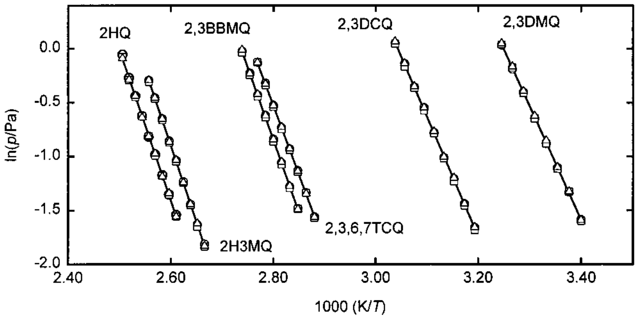

Figure 2. Plots of ln *p* against 1/*T* for 2-hydroxyquinoxaline (2HQ), 2-hydroxy-3-methylquinoxaline (2H3MQ), 2,3-bis(bromomethyl)quinoxaline (2,3BBMQ), 2,3,6,7-tetrachloroquinoxaline (2,3,6,7TCQ), 2,3-dichloroquinoxaline (2,3DCQ), and 2,3-dimethylquinoxaline (2,3DMQ): ○, hole 1; □, hole 2; Δ, hole 3.

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(T = 298.15\ \mathrm{K}) = \Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{m}}^{\circ}(\langle T\rangle) + \Delta_{\mathrm{cr}}^{\mathrm{g}}C_{\mathrm{p,m}}^{\circ}(298.15\ \mathrm{K} - \langle T\rangle) \quad (3)$$

For each compound, the value of $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{\mathrm{p,m}}^{\circ}$ was estimated within an uncertainty of ±33 J·K^{-1}·mol^{-1} using eq 4 derived by Chickos et al.[13] after comparing experimental values of $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{\mathrm{p,m}}^{\circ}$ with calculated values of $C_{\mathrm{p,m}}^{\circ}(\mathrm{cr})$ for 114 organic solids. The heat capacities of the crystals were calculated using a group additivity method developed by Chickos et al.[14] which resembles the Benson method[15] for estimating heat capacities of gases. However, in this method, the ring corrections used by Benson for estimating heat capacities of cyclic systems have been eliminated by using group values designed for cyclic compounds.

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{\mathrm{p,m}}^{\circ} = -\{0.75 + 0.15C_{\mathrm{p,m}}^{\circ}(\mathrm{cr})\} \quad (4)$$

The calculated values for $C_{\mathrm{p,m}}^{\circ}(\mathrm{cr})$ and for $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{\mathrm{p,m}}^{\circ}$ are presented in Table 5. This table also includes the calculated values, at the temperature $T = 298.15$ K, of the standard molar enthalpies of sublimation, the standard molar entropies of sublimation calculated by eq 5, where $p^{\circ} = 10^5$ Pa, and the standard molar Gibbs energies of sublimation.

$$\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{\circ}(T = 298.15\ \mathrm{K}) = \Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}\{\langle T\rangle, p(T = \langle T\rangle)\} + \Delta_{\mathrm{cr}}^{\mathrm{g}}C_{\mathrm{p,m}}^{\circ}\ln(298.15\ \mathrm{K}/\langle T\rangle) - R\ln\{p^{\circ}/p(T = \langle T\rangle)\} \quad (5)$$

The uncertainties assigned to $\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}^{\circ}(T = 298.15\ \mathrm{K})$ were obtained by considering the uncertainties of $\Delta_{\mathrm{cr}}^{\mathrm{g}}S_{\mathrm{m}}\{\langle T\rangle, p(T = \langle T\rangle)\}$ and of $\Delta_{\mathrm{cr}}^{\mathrm{g}}C_{\mathrm{p,m}}^{\circ}$ as well as the uncertainties of ln $p(T = \langle T\rangle)$ calculated from the standard deviations of the parameters of the Clausius−Clapeyron equations presented in Table 3.

There are no published vapor pressure data for the crystalline compounds studied. For dimethylquinoxaline, Ribeiro da Silva et al.[16] reported the calorimetric value $\Delta_{\mathrm{cr}}^{\mathrm{g}}H_{\mathrm{p,m}}^{\circ}(T = 298.15\ \mathrm{K})/\mathrm{kJ{\cdot}mol^{-1}} = (85.8 \pm 1.8)$, which agrees within the associated uncertainties with our result for this compound.

Table 4. (p, T) Values from the Vapor Pressure Equations

	T/K									
	p = 0.1 Pa	p = 0.2 Pa	p = 0.3 Pa	p = 0.4 Pa	p = 0.5 Pa	p = 0.6 Pa	p = 0.7 Pa	p = 0.8 Pa	p = 0.9 Pa	p = 1.0 Pa
2-hydroxyquinoxaline	375.4	382.6	386.8	390.0	392.4	394.4	396.2	397.6	399.0	400.2
2-hydroxy-3-methylquinoxaline	370.5	377.4	381.5	384.5	386.8	388.8	390.5	391.9	393.2	394.4
2,3-dichloroquinoxaline	307.6	313.6	317.3	319.9	322.0	323.7	325.1	326.4	327.6	328.6
2,3,6,7-tetrachloroquinoxaline	340.3	346.7	350.5	353.3	355.5	357.3	358.9	360.2	361.4	362.5
2,3-dimethylquinoxaline	288.4	293.9	297.3	299.7	301.6	303.2	304.6	305.8	306.8	307.7
2,3-bis(bromomethyl)quinoxaline	343.8	350.0	353.8	356.5	358.6	360.4	361.8	363.2	364.3	365.4

Table 5. Calculated Values of the Heat Capacity, $C^{\circ}_{p,m}$(cr), of the Crystalline Compounds, the Heat Capacity Differences between the Gaseous and the Crystalline Phases, $\Delta^{g}_{cr}C^{\circ}_{p,m}$, and the Standard ($p^{\circ}$ = 0.1 MPa) Molar Enthalpies, $\Delta^{g}_{cr}H^{\circ}_{m}$, Entropies, $\Delta^{g}_{cr}S^{\circ}_{m}$, and Gibbs Functions, $\Delta^{g}_{cr}G^{\circ}_{m}$, of Sublimation at T = 298.15 K

compound	$C^{\circ}_{p,m}$(cr) / $J\cdot K^{-1}\cdot mol^{-1}$	$\Delta^{g}_{cr}C^{\circ}_{p,m}$ / $J\cdot K^{-1}\cdot mol^{-1}$	$\Delta^{g}_{cr}H^{\circ}_{m}$ / $kJ\cdot mol^{-1}$	$\Delta^{g}_{cr}S^{\circ}_{m}$ / $J\cdot K^{-1}\cdot mol^{-1}$	$\Delta^{g}_{cr}G^{\circ}_{m}$ / $kJ\cdot mol^{-1}$
2-hydroxyquinoxaline	164	−25 ± 33	118.5 ± 3.1	201 ± 12	58.5 ± 4.8
2-hydroxy-3-methylquinoxaline	192	−29 ± 33	119.7 ± 2.8	209 ± 11	57.4 ± 4.4
2,3-dichloroquinoxaline	189	−29 ± 33	93.1 ± 0.9	188 ± 4	37.1 ± 1.4
2,3,6,7-tetrachloroquinoxaline	228	−35 ± 33	108.2 ± 1.9	203 ± 8	47.6 ± 3.0
2,3-dimethylquinoxaline	205	−31 ± 33	87.8 ± 0.4	190 ± 1	31.3 ± 0.6
2,3-bis(bromomethyl)quinoxaline	250	−38 ± 33	114.0 ± 2.0	217 ± 8	49.3 ± 3.2

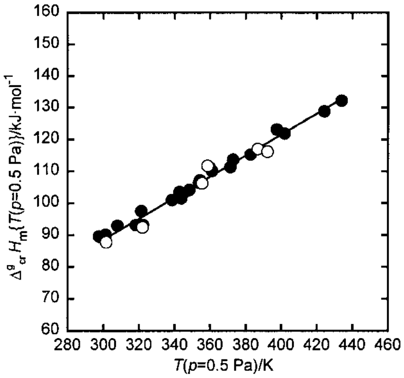

Figure 3. Dependence of the enthalpies of sublimation on the temperature of sublimation at p = 0.5 Pa: ○, substituted quinoxalines; ●, substituted quinolines.

For a series of 13 hydroxyquinolines, a linear correlation (r = 1.00), represented by eq 6, has been reported previously:[17]

$$\Delta^{g}_{cr}H^{\circ}_{p,m}\{T(p = 0.5\ \mathrm{Pa})\}/\mathrm{kJ\cdot mol^{-1}} = (0.313 \pm 0.008)\{T(p = 0.5\ \mathrm{Pa})/\mathrm{K}\} - (3.7 \pm 2.7) \quad (6)$$

where $\{T(p = 0.5\ \mathrm{Pa})\}$ is the temperature at which the vapor pressure of the crystals of those compounds is p = 0.5 Pa. The reference pressure p = 0.5 Pa was chosen since most effusion experiments are made between 0.1 and 1 Pa. Since $T(p = 0.5\ \mathrm{Pa})$ is near $\langle T\rangle$, no heat capacity corrections are needed to calculate the values of $\Delta^{g}_{cr}H^{\circ}_{m}\{T(p = 0.5\ \mathrm{Pa})\}$. The nearly zero intercept in this correlation means that equilibrium entropies of sublimation are approximately the same for all those substances. This correlation was now extended to include the present results as well as the published results for other quinolines previously reported: four aminoquinolines,[18] two cyanoquinolines,[19] four nitroquinolines,[20] and phenylquinoline.[21] The linear correlation (r = 0.989) is shown in Figure 3 and represented by eq 7:

$$\Delta^{g}_{cr}H^{\circ}_{m}\{T(p = 0.5\ \mathrm{Pa})\}/\mathrm{kJ\cdot mol^{-1}} = (0.330 \pm 0.009)\{T(p = 0.5\ \mathrm{Pa})/\mathrm{K}\} - (10.5 \pm 3.2) \quad (7)$$

For the 30 compounds considered above, the mean value of the equilibrium entropies of sublimation, at p = 0.5 Pa, and its standard deviation are $\Delta^{g}_{cr}S_m$ = (300 ± 6) $\mathrm{J\cdot K^{-1}\cdot mol^{-1}}$. For these compounds, the equilibrium entropy of sublimation may be considered nearly the same within experimental error. This empirical observation is similar to the Trouton's rule[22] for the relationship between the boiling temperatures of nonpolar liquids and their enthalpies of vaporization. For polar organic liquids, especially with hydrogen-bonded molecules such as alcohols and carboxylic acids, there is a strong tendency for association as a result of these highly directional intermolecular attractions, and therefore entropies of vaporization may deviate widely from the values predicted by Trouton. Elongated molecules also show larger entropies of vaporization due to their tendency to associate in parallel, thereby maximizing van der Waals attractions. The resulting decrease in the entropy of the liquid is reflected in a larger entropy of vaporization.

Apparently similar structural effects are also responsible for the large entropies of sublimation obtained for organic crystals with elongated or hydrogen-bonded structures, as we have observed from our results on methoxy-substituted cinnamic acids[23] and straight chain dicarboxylic acids.[24]

Using results from the literature, we have verified that eq 7 can predict, within an uncertainty of ±5 kJ·mol⁻¹, sublimation enthalpies from the experimental values of $T(p = 0.5\ \mathrm{Pa})$ for a large number of compounds. Molecules with elongated methylene chains and strong directional intermolecular attractions are exceptions. Thus, we suggest that eq 8 can be used for rough estimations of vapor pressure−temperature data from calorimetric data or estimated values of enthalpies of sublimation for a large number of organic compounds. If the temperature, T^*, at which the enthalpy of sublimation was derived is far from $T(p = 0.5\ \mathrm{Pa})$, eq 9 should be used instead of eq 8.

$$T(p = 0.5\ \mathrm{Pa})/\mathrm{K} = [\Delta^{g}_{cr}H^{\circ}_{m}\{T(p = 0.5\ \mathrm{Pa})\}/\mathrm{kJ\cdot mol^{-1}} + (10.5 \pm 3.2)]/(0.330 \pm 0.009) \quad (8)$$

$$T(p = 0.5\ \mathrm{Pa})/\mathrm{K} = \{\Delta^{g}_{cr}H^{\circ}_{m}(T^*)/\mathrm{kJ\cdot mol^{-1}} - T^*(\Delta^{g}_{cr}C^{\circ}_{p,m}/\mathrm{kJ\cdot mol^{-1}\cdot K^{-1}}) + (10.5 \pm 3.2)\}/\{(0.330 \pm 0.009) - \Delta^{g}_{cr}C^{\circ}_{p,m}/\mathrm{kJ\cdot mol^{-1}\cdot K^{-1}}\} \quad (9)$$

Temperature values at other pressures (close to the range 0.1−1 Pa) may be easily computed by using the Clausius−Clapeyron equation.

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Received for review May 24, 2000. Accepted August 1, 2000. Thanks are due to Fundação para a Ciência e Tecnologia, FCT, for financial support through Centro de Investigação em Química da Universidade do Porto (research unit no. 81) and through Faculty of Science of University of Porto (Projects PBIC/C/QUI/2193/95 and PCEX/QUI/62/96). D.M.H. thanks the PRAXIS XXI for the award of a research grant (BD/9349/96) under Programa Ciência.

JE0001577