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The Sublimation Enthalpy of Dimethyl Oxalate

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The sublimation enthalpy of dimethyl oxalate has been measured by calorimetric and head space analysis. These results along with vaporization enthalpy measured by correlation gas chromatography and fusion enthalpy measurements are compared to results predicted by two estimation techniques. A previous experimental measurement was found to be in error. A mean value of (75.2 ± 0.5) kJ/mol was obtained which results in a corrected molar value of (-681.5 ± 0.8) kJ/mol for the enthalpy of formation of gaseous dimethyl oxalate, $\Delta_f H_m^{\circ}$ (g, 298.15 K). This new value of $\Delta_f H_m^{\circ}$ (g, 298.15 K) for dimethyl oxalate, in combination with other enthalpies of formation, suggests that the ground state of oxalates are destabilized relative to α-diketones by approximately 25 kJ/mol.

KEY WORDS: Sublimation enthalpy; dimethyl oxalate; vaporization enthalpy; correlation gas chromatography; formation enthalpy.
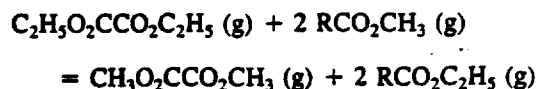
INTRODUCTION

Although physical property information ultimately depends on experimental measurement, estimation techniques can provide an important contribution to the validation of this information by identifying potentially inaccurate results. This is particularly true with reports of sublimation enthalpies based on the measurement of vapor pressure as a function of temperature. A particular apparatus or technique, used to make vapor pressure measurements on compounds whose vapor pressures differ over many orders of magnitude, may prove reliable in some pressure and/or temperature regimes and fail in others [1].

Recently Filippini and Gavezzotti have reported empirical intermolecular potentials that have been developed to evaluate sublimation enthalpies of a variety of organic crystals [2]. A large discrepancy was observed between their calculations 70.7 kJ/mol [3] and the literature value of 47.4 kJ/mol reported for the sublimation enthalpy of dimethyl oxalate at 298.15 K [4]. At their request [5], we have reexamined the sublimation enthalpy ($\Delta_{sub} H_m^{\circ}$ (298.15 K)) of this compound by various approximation techniques and by experimental calorimetric and head space analysis. The results of our investigations are reported below.

Estimation of the sublimation enthalpy by additivity of estimated values of enthalpies of vaporization and fusion, shown to work well for hydrocarbons [6], is not applicable here, mainly because of the unique structure of dimethyl oxalate. A group value for adjacent carbonyl groups is not available and this precludes the use of standard group methods [7] to estimate the vaporization enthalpy of dimethyl oxalate. An alternative method of arriving at an estimate of $\Delta_{sub} H_m^{\circ}$ (298.15 K) is to compare experimental heats of formation of solid dimethyl oxalate ($\Delta_f H_m^{\circ}$ (s, 298.15 K), -756.3 kJ/mol) [4] with an estimated value for its formation in the gas phase, ($\Delta_f H_m^{\circ}$ (298.15 K)). The difference between these two enthalpies is the sublimation enthalpy.

Assuming the following reaction (where R=CH$_3$ and n-C$_4$H$_9$) to be thermoneutral, using

$$C_2H_5O_2CCO_2C_2H_5 \text{ (g)} + 2\ RCO_2CH_3 \text{ (g)}$$

$$= CH_3O_2CCO_2CH_3 \text{ (g)} + 2\ RCO_2C_2H_5 \text{ (g)}$$

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available experimental heat of formation data in the gas phase, $\Delta_f H_m^\circ$ (g, 298.15 K) [8], for methyl acetate, diethyl oxalate, ethyl acetate, methyl pentanoate, and ethyl pentanoate and solving for $\Delta_f H_m^\circ$ (g, 298.15 K) of dimethyl oxalate, results in estimations of $\Delta_f H_m^\circ$ of (-671 ± 16 (R=CH$_3$)) and (-683 ± 13 (R = n-C$_4$H$_9$)) kJ/mol, respectively. Similarly, replacing diethyl oxalate, ethyl acetate, and ethyl pentanoate in the above equation with $\Delta_f H_m^\circ$ (g, 298.15 K) for oxalic acid and acetic and pentanoic acids and again assuming thermoneutrality, results in a $\Delta_f H_m^\circ$ (g, 298.15 K) for dimethyl oxalate of (-682 ± 11) and (-682 ± 13) kJ/mol, respectively. The sublimation enthalpy of dimethyl oxalate by these approximations is estimated to lie between 74 and 86 kJ/mol.

An alternative experimental estimate of $\Delta_{sub} H_m^\circ$ (298.15 K) can be obtained from the sum of the vaporization and fusion enthalpies. Using the vapor pressure (p) data of Askonas and Daubert [9] from 347–421 K, a ln p vs. $1/T$ plot results in a vaporization enthalpy of (49.4 ± 0.2) kJ/mol (384 K). Correcting the vaporization enthalpy to 298.15 K [10] and combining it with the experimental fusion enthalpy of 21.1 kJ/mol [11] results in an approximate value of 75.7 kJ/mol.

We have also measured the sublimation enthalpy of dimethyl oxalate directly. Experimental measurements were obtained calorimetrically in Marseille, France, and by head space analysis in St. Louis, MO. The vaporization enthalpy of dimethyl oxalate was also measured in St. Louis by correlation gas chromatography. All experimental methods have been described in detail, previously [1, 12, 13].

EXPERIMENTAL

A sample of dimethyl oxalate (99%, Aldrich Chemical Co.) was sublimed and analyzed by gas chromatography on a 30 m × 0.32 mm DB-5 0.25 μm film thickness capillary column. Gas chromatographic analysis of a carbon tetrachloride solution of dimethyl oxalate suggested a purity of 99.9+ mol%. The same sample source was used in both the calorimetric and head space analysis experiments.

Calorimetric measurements were conducted in a Knudsen cell with orifices of 0.1 and 0.3 mm at 298.15 K. Measurements with a 0.1 mm orifice was performed close to equilibrium. The peak shape observed was that of a plateau with the intensity of the signal first increasing and then maintaining a constant value until most of the sample was exhausted. The peak shape observed with larger orifices was more Gaussian in shape and effusion was far from equilibrium. The sublimation enthalpies were calculated from the area under the curves. The results from both sets of experiments are within experimental error. The response of the instrument was calibrated from the Joule effect. The mean of 17 independent measurements was used in the calibration.

The mass of sample transferred in the head space experiments was determined by infrared spectroscopy on a Perkin Elmer Model 1600 series FTIR in chloroform using a 0.2 mm solution cell. Net absorbance measurements were measured by subtracting the absorbance of the carbonyl at 1747.7 cm^{-1} and the baseline at 1900 cm^{-1}. A series of five standard solutions were used to determine the relationship between concentration and absorbance. A good linear relationship was observed (correlation coefficient, 0.999).

The GC correlation experiments of Table III were performed on an HP5890 Series II g.c. run isothermally on a DB-5MS capillary column at a head pressure of 69 kPa using He as the carrier gas as previously described [13]. Acetone was used as the nonretained reference. Corrected retention times, t_r, were calculated for each compound at each temperature by subtracting the corresponding retention time of acetone from each value.

The fusion enthalpy of dimethyl oxalate was also measured in triplicate on a Perkin Elmer DSC-2 using indium metal (28.6 J/g) [14] as the standard. A result of (21.3 ± 0.4) kJ/mol is in good agreement with the value of 21.1 kJ/mol reported earlier [11].

The vaporization enthalpies for dimethyl malonate, diethyl succinate and diethyl adipate, cited in column 5 of Table IV, were obtained from vapor pressures calculated as a function of temperature from the Antoine constants over a 30 K span and corrected to 298.15 K. Temperature ranges were chosen as close to 298.15 K as possible but within the range of applicability of the constants: dimethyl malonate, 53.68 (323 K); diethyl succinate, 56.48 (342 K); diethyl adipate, 57.49 kJ/mol (362 K) [15]. The following equation was used to correct the vaporization enthalpies from T to 298.15 K:

$$\Delta_{lg} Cp(T - 298.15) = (10.58 + 0.26 Cp_{1,calc})$$
$$\cdot (T - 298.15\ K),\quad J/mol$$

In this equation, $Cp_{1,calc}$ is the heat capacity of the liquid calculated for each ester by group additivity. See Ref. 10 for additional details.

RESULTS

Table I summarizes the results of the calorimetric measurements. A mean value of (74.6 ± 0.7) kJ/mol at

Table I. Sublimation Enthalpy of Dimethyl Oxalate by Calorimetry

Sample size $m/(\text{mg})$	kJ/mol	Orifice diameter d/mm
14.4655	74.61	0.3
15.8154	73.88	0.3
18.0749	74.37	0.3
11.0963	73.80	0.3
8.6211	74.75	0.3
9.8260	73.89	0.3
20.8540	75.36	0.1
19.2417	75.95	0.1
25.0528	74.58	0.1
mean		
74.5 ± 0.7		

$\Delta_{sub}H^\circ_m(298.15\ \text{K})$

Table II. Vapor Pressure p Measurements by Head Space Analysis[a]

T/K	T_{bulb}/K	m/mg	p/Pa
298.4	377.2	34.37	73.75
298.4	377.2	29.0	62.24
298.4	377.2	31.97	68.61
294.8	371.2	22.29	47.08
295.2	371.2	23.15	48.88
293.6	371.2	19.66	41.51
393.7	373.2	19.67	41.76
293.7	373.2	19.98	42.42
288.0	373.2	10.7	22.71
288.2	373.2	10.2	21.65
288.2	373.2	10.54	22.38
287.5	373.2	11.87	25.20
287.5	373.2	12.05	25.59
287.5	373.2	12.05	25.58
287.6	374.2	12.42	26.43
280.7	374.2	5.03	10.71
281.0	374.2	4.72	10.05
281.0	374.2	4.46	9.50
278.7	379.2	3.74	8.07
278.7	379.2	3.06	6.59
278.6	379.2	3.21	6.92
272.8	379.2	2.39	5.16
272.8	379.2	1.81	3.91
272.9	377.2	2.08	4.46
268.3	381.2	1.00	2.17
268.4	381.2	0.99	2.15

[a]The temperature of the sample is denoted by T and of the bulb by T_{bulb}, and m denotes the mass of sample collected.

298.15 K was obtained. The uncertainty represents the standard deviation.

The results obtained from head space analysis of dimethyl oxalate are summarized in Table II. A plot of $\ln p$ vs. $1/T$ resulted in the following straight line and was characterized by a correlation

$$\ln p/\text{Pa} = (-9089 \pm 188)/T + (23.18 \pm 0.11)$$

coefficient of 0.9948. Multiplying by the gas constant, $R = 8.314$ J/(mol K), results in a sublimation enthalpy of (75.6 ± 1.6) kJ/mol at a mean temperature of 283.4 K. Correcting to 298.15 K [10] affords an enthalpy of sublimation of (75.3 ± 1.6) kJ/mol. The uncertainty of ±1.6 was derived from the uncertainty in the slope.

Table III lists the observed retention times (rt) for a series of simple linear diesters as a function of temperature. A plot of $\ln(1/(\text{corrected retention time}, t_r)$ vs. $1/T$ for each compound resulted in a straight line characterized by the slope and correlation coefficient listed in columns 2 and 4, respectively, of Table IV. Multiplication by R, the gas constant, affords the enthalpy of transfer from solution to vapor, $\Delta^g_{sln}H_m$ at the mean tem-

perature of 408 K. Correlation of the literature vaporization enthalpies at 298.15 K of column 5 with $\Delta^g_{sln}H_m$ (408 K), results in the following equation:

$$\Delta_{vap}H^\circ_m (298.15\ \text{K}) = (0.512 \pm 0.01)\Delta^g_{sln}H_m (408\ \text{K})$$

$$+ (37160 \pm 120)\ \text{J/mol}$$

This relationship was used to obtain the vaporization enthalpies listed in the last column of Table IV. The correlation between experimental vaporization enthalpy and

Table III. Retention Time Measurements for a Series of Diesters[a]

T/K	383.2	393.2	403.2	413.2	423.2	433.2
Compound			rt/s			
acetone	138.9	140.5	142.7	144.4	146.6	148.4
dimethyl oxalate	169.0	163.5	160.4	158.5	158.1	157.9
dimethyl malonate	196.7	183.5	175.0	169.4	166.4	164.3
diethyl malonate	287.6	245.9	218.8	200.8	189.5	181.5
diethyl succinate	447.4	351.9	290.7	250.8	225.1	207.4
dimethyl adipate	603.8	453.7	358.4	297.1	257.6	230.6

[a]Temperature is denoted by T and retention times in seconds by rt. Acetone is the nonretained reference.

Table IV. Summary of Vaporization Enthalpy Results by Correlation Gas Chromatography

Compound	$-sl$	$\Delta_{trn}^g H_m$	r	$\Delta_{vap} H_m^o$	$\Delta_{vap} H_m^o$
dimethyl oxalate	3853.93	32.04	0.9995		53.6 ± 0.5
dimethyl malonate	4303.64	35.78	0.9997	53.6	55.5 ± 0.6
diethyl malonate	4993.58	41.51	0.9998		58.4 ± 0.6
diethyl succinate	5498.44	45.71	0.9998	60.08	60.6 ± 0.6
dimethyl adipate	5757.99	47.87	0.9998		61.7 ± 0.6
diethyl adipate	6468.21	53.77	0.9998	64.64	64.7 ± 0.7

^{a}The slope of the line obtained by plotting $\ln(1/t_r)$ vs. $1/T$ is denoted by sl and the correlation coefficient characterizing the fit by r. Literature values [15] are listed in column 5 and calculated vaporization enthalpies are given in column 6. All enthalpies are in kJ/mol. Values of $\Delta_{trn}^g H_m$ are reported at 408 K and those of $\Delta_{vap} H_m^o$ are for 298.15 K.

enthalpy of transfer was characterized by a coefficient r = 0.9998. Vaporization enthalpies for diethyl malonate and dimethyl adipate are also reported.

The vaporization enthalpy of (53.6 ± 0.5) kJ/mole (298.15 K) obtained by correlation gas chromatography combined with the fusion enthalpy of (21.3 ± 0.4) kJ/mol reported in the experimental section results in a sublimation enthalpy of (74.9 ± 0.6) kJ/mol. This value can be compared to (75.3 ± 1.6) kJ/mol obtained from head space analysis, (74.6 ± 0.7) kJ/mol obtained calorimetrically and (75.9 ± 0.5) kJ/mol obtained from the combined data of Askonas and Daubert [9] and our fusion enthalpy measurements. All four values agree within the precision of the measurements and result in a mean value of (75.2 ± 0.5) kJ/mol. The uncertainty represents the standard deviation associated with the four independent assessments. The comparison between experimental values, the value estimated by Filippini and Gavezzotti, and the value obtained from heat of formation data are all in good agreement with each other and illustrate the usefulness of such estimations in identifying unreliable experimental measurements. Combining this sublimation enthalpy of (75.2 ± 0.5) kJ/mol with the molar enthalpy of formation of the solid, ($\Delta_f H_m^o$ (s, 298.15 K), (−756.5 ± 0.3) kJ/mol) [4], results in a value of (−681.3 ± 0.6) kJ/mol for $\Delta_f H_m^o$ (g, 298.15 K) of dimethyl oxalate.

Simple esters and simple aldehydes and ketones are generally colorless, as are oxalate esters. That many α-diketones are yellow is suggestive of differences between α-diketones and esters. Consider the formal gas phase carbon-carbon coupling reactions of the following two aldehydes:

$$2\ CH_3CHO \longrightarrow CH_3COCOCH_3 + H_2$$

$$\Delta H_r(g, 298.15\ K) = 5.1 \pm 1.6\ kJ/mol$$

$$2\ HCHO \longrightarrow OHCCHO + H_2$$
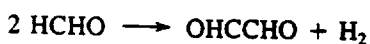
$$\Delta H_r(g, 298.15\ K) = 5.2 \pm 1.3\ kJ/mol$$

As noted previously [16], such reactions (and the formal coupling of terminal olefins to form conjugated dienes) are essentially thermoneutral. Indeed, both reactions are found to be approximately 5 kJ/mol endothermic. By contrast, for the enthalpy of formation of oxalic acid and dimethyl oxalate from formic acid and methyl formate:

$$2\ HCO_2H \longrightarrow HOCOCO_2H + H_2$$

$$\Delta H_r(g, 298.15\ K) = 33.7 \pm 5.0\ kJ/mol$$

$$2\ HCO_2CH_3 \longrightarrow CH_3OCOCO_2CH_3 + H_2$$

$$\Delta H_r(g, 298.15\ K) = 29.7 \pm 1.7\ kJ/mol$$

we find these related reactions endothermic by ca. 25 kJ/mol. This suggests considerable ground state destabilization of oxalic acid and its derivatives, i.e. they are less "conjugated" than α-diketones. In that the color of monoolefins, dienes, etc., is increasingly red shifted toward the visible as the conjugation increases, it is perhaps not surprising, based on these thermochemical calculations, that oxalates should be blue shifted relative to diketones.

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