Standard Molar Enthalpy of Formation and of Vaporization of Ethyl 3-Oxobutanoate

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The standard (p° = 0.1 MPa) molar enthalpy of combustion at the temperature 298.15 K of the liquid ethyl 3-oxobutanoate was determined: $\Delta_c H_m^\circ = -3149.76 \pm 0.76$ kJ·mol^{-1}, using a static-bomb calorimeter, from which its standard molar enthalpy of formation, in the liquid state, was derived as $\Delta_f H_m^\circ(\mathrm{l}) = -640.4 \pm 1.1$ kJ·mol^{-1}. The standard molar enthalpy of vaporization, at the temperature 298.15 K, determined by microcalorimetry, was found to be $\Delta_l^g H_m^\circ = 54.18 \pm 0.96$ kJ·mol^{-1}. The standard molar enthalpy of formation of ethyl 3-oxobutanoate was derived for the gaseous keto–enol equilibrium mixture and for the gaseous keto form.

Introduction

Among the 1,3-dicarbonyl compounds, the β-diketones and their coordination complexes have been the subject of intensive thermochemical studies (*1*). Ethyl 3-oxobutanoate can also act as a bidentate ligand, through the two oxygen atoms, forming a chelate ring. To derive the standard molar enthalpies of formation of ethyl 3-oxobutanoate complexes, from solution-reaction calorimetry, and the corresponding mean molar dissociation enthalpies of the metal–oxygen bonds, the standard molar enthalpy of formation of ethyl 3-oxobutanoate, in the condensed and vapor phases, is required.

Static-bomb calorimetry is the most widely used method for determining enthalpies of formation of organic compounds containing C, H, O, and N by measurement of their energies of combustion in oxygen.

The standard molar enthalpy of formation of ethyl 3-oxobutanoate, in the liquid state, has been previously reported (*2*), $\Delta_f H_m^\circ(\mathrm{l}) = -627.1$ kJ·mol^{-1}; this value was obtained from measurement of its energy of combustion, based on the mass of compound used in each combustion experiment. This paper reports the redetermination of the standard molar enthalpy of formation of liquid ethyl 3-oxobutanoate, derived from measurements of the standard molar enthalpy of combustion made by static-bomb calorimetry. The standard molar enthalpy of vaporization was measured by microcalorimetry.

Experimental Setup and Measurements

Materials. The ethyl 3-oxobutanoate (Aldrich Chemie) was dried over calcium chloride for several days and was purified (*3*) by repeated fractional distillation, under reduced pressure, through a Vigreux column, the midfraction from each one being used for further distillation. The pure fraction collected with a boiling temperature of 327.0 K at 133 Pa, lit. (*3*) 327.6 K, was stored under nitrogen and was freshly distilled prior to use. The purity of the compound was confirmed by carbon dioxide analysis (*4*); for each combustion experiment the mass of carbon dioxide produced by the combustion of the compound was determined, after correction for that formed from the combustion of auxiliary materials. The average ratio of carbon dioxide observed to that calculated from the mass of samples was 1.0000 ± 0.0001.

Static-Bomb Calorimeter. The energy of combustion of ethyl 3-oxobutanoate was measured in a static bomb calorimeter; the calorimeter, subsidiary apparatus, and technique have been described (*5, 6*). The energy equivalent of the calorimeter was determined from the combustion of benzoic acid (Bureau of Analysed Samples, Thermochemical Standard CRM-190p) having a specific energy of combustion, under standard bomb conditions of −26431.8 ± 3.7 J·g^{-1}. Combustion was carried out in oxygen at the pressure 3.04 MPa in the presence of 1.00 cm^3 of water added to the bomb. Water was added to the calorimeter can from a weighed glass vessel; as the mass of water differed slightly for each experiment, corrections were made to the energy equivalent of the calorimeter for the deviation from the average mass, 3119.6 g. From eight calibration experiments, $\epsilon(\mathrm{calor}) = 16017.0 \pm 1.3$ J·K^{-1}, where the uncertainty quoted is the standard deviation of the mean. The liquid samples of ethyl 3-oxobutanoate were contained in sealed polyester bags made from Melinex (0.025 mm thickness), using the technique described by Skinner and Snelson (*7*) who determined the specific energy of combustion of dry Melinex as $-\Delta_c u^\circ = 22902 \pm 5$ J·g^{-1}. The mass of Melinex used in each experiment was corrected for the mass fraction of water (0.0032), and the mass of carbon dioxide produced from the Melinex was calculated using the factor previously reported (*7*). These values have been confirmed by combustion of Melinex samples in our laboratory, with carbon dioxide recovery.

The amount of ethyl 3-oxobutanoate used in each experiment was determined from the mass of carbon dioxide produced. The density of ethyl 3-oxobutanoate is 1.021 (*8*), and an estimated pressure coefficient of specific energy, $(\partial u/\partial p)_T = -0.25$ J·g^{-1}·MPa^{-1}, was assumed.

The calorimeter temperature was measured to $\pm 10^{-4}$ K at intervals of 10 s using a Hewlett-Packard (HP-2804A) quartz thermometer interfaced to a Olivetti 250 E microcomputer programmed to compute the adiabatic temperature change, ΔT_{ad}; the method of calculation was based on that described by Coops *et al.* (*9*). The electrical energy for ignition was determined from the change in potential across a 1400 μF capacitor when discharged, from an initial voltage of *ca.* 41 V, through the platinum ignition wire.

All the experiments were performed under the same experimental conditions as the calibration ones. For the cotton-thread fuse, empirical formula $CH_{1.686}O_{0.843}$, $-\Delta_c u^\circ$

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Table 1. Combustion Results for Ethyl 3-Oxobutanoate

$m(\mathrm{CO_2,total})$/g	1.769 83	1.985 06	1.674 15	1.887 74	1.691 77	2.038 64
$m'(\mathrm{cpd})$/g	0.760 08	0.866 92	0.717 54	0.816 67	0.721 78	0.887 10
$m''(\mathrm{Melinex})$/g	0.097 20	0.096 34	0.092 88	0.098 22	0.096 69	0.101 61
$m'''(\mathrm{fuse})$/g	0.003 11	0.003 38	0.003 44	0.003 57	0.003 62	0.003 72
ΔT_{ad}/K	1.288 13	1.449 94	1.219 48	1.376 54	1.231 55	1.489 25
$\epsilon_i/(\mathrm{J{\cdot}K^{-1}})$	14.62	14.66	14.59	14.64	14.60	14.67
$\epsilon_f/(\mathrm{J{\cdot}K^{-1}})$	16.70	17.04	16.57	16.88	16.58	17.01
$\Delta m(\mathrm{H_2O})$/g	+3.9	+0.1	0.0	+1.1	0.0	0.0
$-\Delta U(\mathrm{IBP})$/J	20 674.23	23 248.03	19 551.78	22 077.19	19 745.40	23 877.93
$\Delta U(\mathrm{HNO_3})$/J	7.09	6.46	5.66	6.61	7.05	16.71
$\Delta U(\mathrm{ign})$/J	0.28	0.97	0.84	0.43	0.75	0.72
ΔU_Σ/J	12.55	14.26	11.79	13.49	11.94	14.71
$-\{m''\Delta_c u°(\mathrm{Melinex})\}$/J	2225.99	2206.35	2127.07	2249.52	2214.34	2327.19
$-\{m'''\Delta_c u°(\mathrm{fuse})\}$/J	50.51	54.89	55.87	57.98	58.79	60.41
$-\{\Delta_c u°(\mathrm{cpd})\}/(\mathrm{J{\cdot}g^{-1}})$	24 179.15	24 184.55	24 181.77	24 183.07	24 180.89	24 189.96

average $\langle\Delta_c u°\rangle = -24183.2 \pm 1.5\ \mathrm{J{\cdot}g^{-1}}$

Table 2. Standard Molar Enthalpy of Vaporization of Ethyl 3-Oxobutanoate at 298.15 K

m/mg	$\Delta_{\mathrm{l},298.15\,\mathrm{K}}^{\mathrm{g},372\,\mathrm{K}}H_m°/(\mathrm{kJ{\cdot}mol^{-1}})$	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_m°(298.15\ \mathrm{K})/(\mathrm{kJ{\cdot}mol^{-1}})$	m/mg	$\Delta_{\mathrm{l},298.15\,\mathrm{K}}^{\mathrm{g},372\,\mathrm{K}}H_m°/(\mathrm{kJ{\cdot}mol^{-1}})$	$\Delta_{\mathrm{l}}^{\mathrm{g}}H_m°(298.15\ \mathrm{K})/(\mathrm{kJ{\cdot}mol^{-1}})$
7.981	67.77	54.51	8.959	68.93	55.67
6.494	65.44	52.18	9.670	67.31	54.05
9.410	68.13	54.87	9.829	67.09	53.83

average $\langle\Delta_{\mathrm{l}}^{\mathrm{g}}H_m°\rangle = 54.18 \pm 0.96\ \mathrm{kJ{\cdot}mol^{-1}}$

$= 16250\ \mathrm{J{\cdot}g^{-1}}$ (*10*). The corrections for nitric acid formation were based on 59.7 kJ·mol⁻¹ for the molar energy of formation of 0.1 mol·dm⁻³ $\mathrm{HNO_3(aq)}$ from $\mathrm{N_2(g)}$, $\mathrm{O_2(g)}$, and $\mathrm{H_2O(l)}$ (*11*). The value of the specific energy, $-\Delta_c u°$, for ethyl 3-oxobutanoate refers to the combustion reaction

$$\mathrm{C_6H_{10}O_3(l)} + 7\mathrm{O_2(g)} \leftrightarrow 6\mathrm{CO_2(g)} + 5\mathrm{H_2O(l)} \qquad (1)$$

and was calculated by the procedure of Hubbard *et al.* (*10*).

Calvet Microcalorimeter. The standard molar enthalpy of vaporization of ethyl 3-oxobutanoate was measured using the microcalorimetric technique described by Skinner *et al.* (*12*) for the determination of standard enthalpies of sublimation of solid compounds, by vacuum sublimation. The liquid samples (about 8 mg), contained in a small thin glass capillary tube sealed at one end, were dropped at room temperature into the hot reaction vessel in a Calvet high-temperature microcalorimeter (Setaram, Lyon, France) held at 372 K, and were then removed from the hot zone by vacuum vaporization. At this temperature, the liquid vaporized in about 3 min. The energy equivalent of the microcalorimeter was determined from the vacuum vaporization of undecane (Aldrich Chemie, Gold Label) at the temperature 372 K, having a standard molar enthalpy of vaporization of $\Delta_{\mathrm{l}}^{\mathrm{g}}H_m° = 56.3 \pm 0.2\ \mathrm{kJ{\cdot}mol^{-1}}$ (*13*). As a check of the accuracy of the microcalorimeter for the measurement of standard enthalpies of vaporization of liquids, using the referred technique, the standard molar enthalpy of vaporization of hexadecane (Aldrich Chemie, Gold Label) was measured at the temperature 372 K; from six experiments $\Delta_{\mathrm{l}}^{\mathrm{g}}H_m° = 80.7 \pm 1.4\ \mathrm{kJ{\cdot}mol^{-1}}$ in good agreement with the value of Morawetz, $\Delta_{\mathrm{l}}^{\mathrm{g}}H_m° = 81.4 \pm 0.3\ \mathrm{kJ{\cdot}mol^{-1}}$ (*14*), determined also by a calorimetric method.

For undecane and hexadecane, literature values (*15*) were used for the correction $\Delta_{298.15\,\mathrm{K}}^{372\,\mathrm{K}}H_m°(\mathrm{g}) = 21.62$ and 31.23 kJ·mol⁻¹, respectively. For ethyl 3-oxobutanoate the correction $\Delta_{298.15\,\mathrm{K}}^{372\,\mathrm{K}}H_m°(\mathrm{g}) = 13.26\ \mathrm{kJ{\cdot}mol^{-1}}$ was estimated by group-additivity methods, *i.e.*, {2(2-pentanone) − pentane + ethyl acetate − propanone} using the data of Stull *et al.* (*15*).

The relative atomic masses were recommended by IUPAC in 1991 (*16*). All uncertainty intervals given are twice the standard deviation of the mean.

Results and Treatment of Data

The results of six combustion experiments are given in Table 1, where $\Delta m(\mathrm{H_2O})$ is the deviation of the mass of water from 3119.6 g and ΔU_Σ is the correction to the standard state. The remaining quantities are as previously descibed (*10*). As samples were ignited at 298.15 K, the energy change for the isothermal bomb process, at 298.15 K, was calculated from

$$\Delta U(\mathrm{IBP}) = -\{\epsilon(\mathrm{calor}) + \Delta m(\mathrm{H_2O})c_p(\mathrm{H_2O,\,l}) + \epsilon_f\} \times \Delta T_{\mathrm{ad}} + \Delta U_{\mathrm{ign}} \qquad (2)$$

and the specific energy of combustion from

$$\Delta_c u° = \{\Delta U(\mathrm{IBP}) + \Delta U(\mathrm{HNO_3}) - m''\Delta_c u°(\mathrm{Melinex}) - m'''\Delta_c u°(\mathrm{fuse}) + \Delta U_\Sigma\}/m'(\mathrm{cpd}) \qquad (3)$$

From Table 1, the mean value of the specific energy of combustion and its standard deviation are $\langle\Delta_c u°\rangle = -24183.2 \pm 1.5\ \mathrm{J{\cdot}g^{-1}}$. The standard molar energy of combustion, at 298.15 K, was derived as $\Delta_c U_m° = -3147.28 \pm 0.76\ \mathrm{kJ{\cdot}mol^{-1}}$; the standard molar enthalpy of combustion was then calculated as $\Delta_c H_m° = -3149.76 \pm 0.76\ \mathrm{kJ{\cdot}mol^{-1}}$.

With $\Delta_f H_m°\ (\mathrm{H_2O,\,l}) = -285.83 \pm 0.04\ \mathrm{kJ{\cdot}mol^{-1}}$ (*17*), and $\Delta_f H_m°\ (\mathrm{CO_2,\,g}) = -393.51 \pm 0.13\ \mathrm{kJ{\cdot}mol^{-1}}$ (*17*), then the standard molar enthalpy of formation of ethyl 3-oxobutanoate, in the liquid state, $\Delta_f H_m°(\mathrm{l}) = -640.4 \pm 1.1\ \mathrm{kJ{\cdot}mol^{-1}}$. In accordance with normal thermochemical practice, the uncertainties assigned to the standard molar enthalpy of combustion and formation include the uncertainties in calibration and in the values of the auxiliary quantities used.

Table 2 lists the experimental results for determining the standard molar enthalpy of vaporization of ethyl 3-oxobutanoate, the mean value, at 298.15 K, being $\langle\Delta_{\mathrm{l}}^{\mathrm{g}}H_m°\rangle = 54.18 \pm 0.96\ \mathrm{kJ{\cdot}mol^{-1}}$.

Discussion

The value of $\Delta_f H_m°(\mathrm{l}) = -640.4 \pm 1.1\ \mathrm{kJ{\cdot}mol^{-1}}$ reported in this paper is 13 kJ·mol⁻¹ more negative than that reported by Karasch (*2*), $\Delta_f H_m°(\mathrm{l}) = -627.1\ \mathrm{kJ{\cdot}mol^{-1}}$, measured a long time ago, and based on the mass of the sample.

The standard molar enthalpy of formation, in the gaseous state, is derived as $\Delta_f H_m^\circ(g) = -586.2 \pm 1.5$ kJ·mol^{-1}. The value of the standard molar enthalpy of vaporization refers to the isothermal vaporization at 298.15 K of the pure liquid (0.926 keto + 0.074 enol) *(18)* to the real gas (0.507 keto + 0.493 enol) *(18)* formed under its saturation vapor pressure. For ethyl 3-oxobutanoate there is no experimental value for the enthalpy of enolization, in the gas phase. However, an estimate can be done, based on data for other β-dicarbonyl compounds. The keto–enol tautomerism of β-dicarbonyls has been investigated *(19)* by nuclear magnetic resonance spectroscopy. The study involved a series of β-dicarbonyls, both β-diketones and β-ketoesters, in the condensed phase. For β-diketones both inductive and steric effects would appear to favor the enol form; in opposition for β-ketoesters the equilibrium is on the side of the keto tautomer.

On the other hand, Allen and Dwek *(20)* obtained, from measurements of equilibrium constants and their temperature dependence, values of the standard molar enthalpies of enolization of a series of β-diketones, in the condensed phase. For the different β-diketones, the percentage of enol ranges from 98 to 28 and there is a corresponding decrease from -20.5 to -5.4 kJ·mol^{-1} in the magnitude of the standard molar enthalpy of enolization. Assuming that the enthalpy of enolization of ethyl 3-oxobutanoate would be close to that of the β-diketone with a similar enol percentage, from the enthalpies of enolization reported by Allen and Dwek *(20)* for the different β-diketones, we estimate the value of the enthalpy of enolization of ethyl 3-oxobutanoate as $\Delta_{\text{enol}} H_m^\circ = -8 \pm 2$ kJ·mol^{-1}. Then

$$\Delta_f H_m^\circ(\text{keto, g}) = \Delta_f H_m^\circ(\text{keto/enol, g}) - 0.493\Delta_{\text{enol}} H_m^\circ = -582.2 \pm 2.5 \text{ kJ·mol}^{-1}$$

An estimate of $\Delta_f H_m^\circ(\text{keto, g}) = -598.6$ kJ·mol^{-1} can be made, calibrated against $\Delta_f H_m^\circ$(pentane-2,4-dione, keto, g), previously reported *(21)* and using the group bond-energy terms given by Cox and Pilcher *(22)*.

These calculated values differ by *ca.* 16 kJ·mol^{-1}, which, although being a large quantity (*ca.* 3% of the estimated values), seems quite acceptable in view of the different assumptions made in each of the calculation methods used here.

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