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Enthalpy of Formation of Dibutyl Phthalate[1]

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Standard enthalpy of formation of liquid dibutyl phthalate (DBP, $-864.67 \pm 4.77\ \mathrm{kJ \cdot mol^{-1}}$) was determined by combustion calorimetry. Using this value, the reliability of the known enthalpies of formation for alkyl phthalates was assessed.

KEY WORDS: combustion calorimetry; enthalpy of formation; dibutyl phthalate; phthalates.

1. INTRODUCTION

Knowledge accumulated on enthalpies of formation of organic compounds is vitally important for many scientific and practical applications, but often needs careful critical assessment and additional experimental validation. Aromatic esters are used as plasticizers, repellents, food preservatives, and intermediates in synthesis of plastic materials. Thermodynamics of processes with their participation, and their environmental and health impact are widely discussed. In spite of the existence of many experimental values of enthalpies of formation reported for *n*-alkyl phthalates (Table I), they are

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Table I. Literature Experimental Data on the Standard Enthalpies of Formation ($kJ \cdot mol^{-1}$) of Liquid *n*-Alkyl Phthalates at $T = 298.15$ K

Compound	$\Delta_f H°$	Source	Comment
Dimethyl phthalate	-662.3	[1]	Without Washburn corrections
	-683.8 ± 2.7	[2]	
	-684.28 ± 2.48	[3]	
Diethyl phthalate	-757.41 ± 2.22	[4]	
	-777 ± 12	[5]	Revised by Cox and Pilcher [6]
	-638	[7]	Without Washburn corrections
Dibutyl phthalate	-778	[8]	Without Washburn corrections
	-843 ± 13	[9]	Revised by Cox and Pilcher [6]
Dipentyl phthalate	-924 ± 13	[9]	Revised by Cox and Pilcher [6]
Dioctyl phthalate	-1036	[1]	Without Washburn corrections

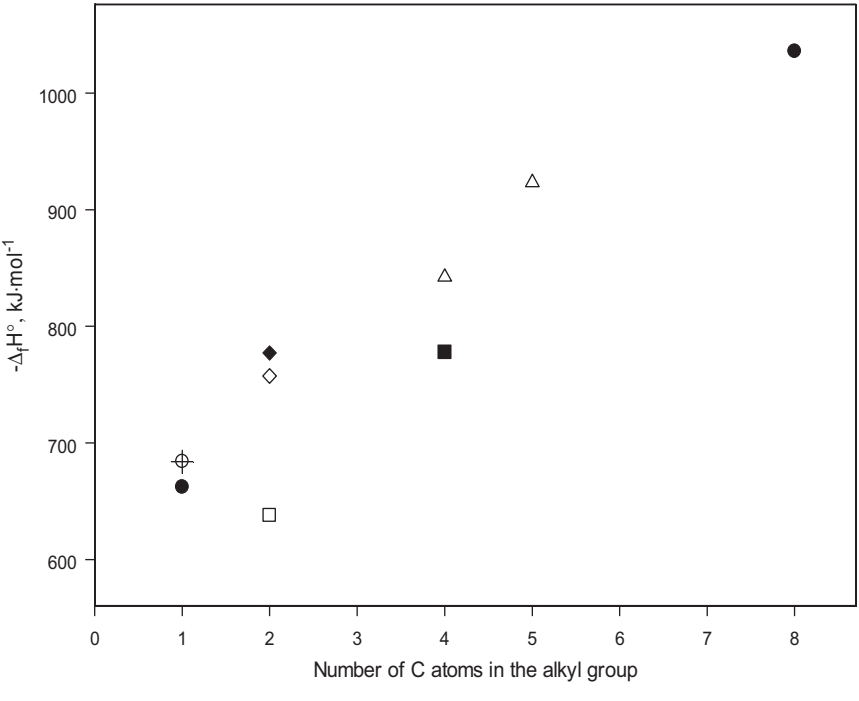

Fig. 1. Literature experimental data on the standard enthalpies of formation of liquid *n*-alkyl phthalates at 298.15 K. ●, [1]; ○, [2]; +, [3]; ◇, [4]; ◆, [5]; □, [7]; ■, [8]; △, [9].

neither reliable nor consistent (Fig. 1). Regular changes in the homologous series of phthalates are not clear, making any prediction doubtful. Even assessed recommended values [10] are not accompanied by realistic uncertainties.

Experimental measurements of the enthalpy of combustion for liquid dibutyl phthalate (DBP) should provide a reliable checkpoint in the series of the phthalates and verify an earlier evaluation [11]. From a scientific point of view, it is interesting to explore the effect of the interaction between the substituents in the 1 and 2 positions of the benzene ring on the CH_2 group increment in the enthalpy of formation in the liquid state (-25.3 ± 0.5 kJ·mol^{-1} as evaluated by us from the available data [10]), which is nearly constant for different classes of compounds (alkanes, alcohols, ketones, acids, esters, etc.).

2. MEASUREMENTS

2.1. Materials

Commercial dibutyl phthalate $C_{16}H_{22}O_4$ with a stated purity of 99 mass % was twice distilled at 800 Pa in a 1.2 m packed column and dried over 4A type molecular sieves. Prior to the combustion experiments, it was stored in a desiccator over P_2O_5 for a week. The final purity was 99.92 mass % (g.l.c., steel column 3 m × 3 mm filled with DS 550, carrier N_2, FID, sampling temperature 463 K, column temperature 433 K). The molar mass used for calculations was 278.34348 g·mol^{-1} [12]. The liquid density, d°(289.15 K) = 1049 kg·m^{-3} was calculated using a published equation [13].

2.2. Experimental Procedure

The energy of combustion was measured in two isoperibolic calorimeters described earlier [14] with static bombs A and B calibrated with a standard sample of benzoic acid (bomb energy of combustion -26434.4 ± 4.5 J·g^{-1} for mass in vacuum). Energy equivalents were W(A) = 14892.0 ± 5.4 and W(B) = 14939.4 ± 6.5 J·K^{-1} for 95% level of confidence. DBP was placed in polyethylene containers (density 946 kg·m^{-3}, bomb energy of combustion -46435.1 ± 6.8 J·g^{-1}) sealed by melting of the edges without contact with a heater. Platinum crucibles were used in all experiments. Samples were ignited by passing electrical current from a capacitor (0.01 F) through a platinum wire (diameter 0.05 mm). The energy of ignition was 2.0 J. Completeness of the combustion was determined visually as evidenced by absence of any traces of soot.

Table II. Experimental Results of Combustion of DBP[a]

m (g)	m_{aux} (g)	ΔT (K)	q_{HNO3} (J)	q_{aux} (J)	$q_{Washburn}$ (J)	Bomb	$-\Delta_c U°$ (J·g^{-1})
0.49991	0.04067	1.15741	3.3	1888.5	8.2	B	30783.5
0.39961	0.04431	0.96475	2.4	2057.5	6.5	A	30776.6
0.53113	0.04485	1.23850	3.0	2082.6	8.8	A	30780.7
0.40464	0.04055	0.96025	3.3	1882.9	6.5	B	30770.2
0.46912	0.04915	1.12021	3.6	2282.3	7.8	B	30780.4

[a] M, sample mass; m_{aux}, mass of the auxiliary substance (Polyethylene); ΔT, corrected temperature rise; q_{HNO3}, energy of formation of nitric acid; q_{aux}, energy of combustion of the auxiliary substance; $q_{Washburn}$, sum of Washburn corrections; $-\Delta_c U°$, standard energy of combustion.

3. RESULTS AND DISCUSSION

Primary experimental results are given in Table II. Uncertainties are calculated following the published recommendations [15] and are represented in accordance with the schema described recently [16]. The calibration uncertainty was propagated to the total heat effect of an experiment and divided by the sample mass, average values being 14.3 J·g^{-1}. Repeatability for 95% level of confidence was 4.6 J·g^{-1}. For calculation of the expanded uncertainty, the contribution of the auxiliary substance and impurities was also considered. It was assumed that the massic energy of combustion of the impurities differs from the main compounds by 10%. Expanded uncertainty of the enthalpy of combustion was 15.2 J·g^{-1}.

Combined expanded uncertainty for the 95% level of confidence was calculated by propagation of the uncertainty of the nominal conditions of the reactions (298.15 K and 101.325 kPa) estimated as 10% of the Washburn correction. It was 15.3 J·g^{-1}, or 4.27 kJ·mol^{-1}. Standard enthalpy of formation was calculated using the reference values $\Delta_f H°(H_2O, l) = -285.83 \pm 0.04$ kJ·mol^{-1} and $\Delta_f H°(CO_2, g) = -393.51 \pm 0.13$ kJ·mol^{-1} [17]. Thermochemical characteristics of combustion and formation of DBP are given in Table III.

Table III. Thermochemical Characteristics of Combustion and Formation of DBP (l) at $T = 298.15$ K and $P = 101.325$ kPa Along with Their Combined Expanded Uncertainties

	DBP
Standard energy of combustion (J·g^{-1})	-30778.3 ± 15.3
Standard energy of combustion (kJ·mol^{-1})	-8566.94 ± 4.27
Standard enthalpy of combustion (kJ·mol^{-1})	-8575.62 ± 4.27
Standard enthalpy of formation (kJ·mol^{-1})	-864.67 ± 4.77

The enthalpy of formation of liquid dibutyl phthalate is the third reliable reference point for the phthalates, in addition to dimethyl phthalate [2, 3] and diethyl phthalate [4]. Its value is close to the earlier recommendation [11] ($-870\ kJ \cdot mol^{-1}$) and supercedes the preceding recommendation [10] ($-842.6\ kJ \cdot mol^{-1}$), as well as the value calculated there by the group contribution method ($-900.9\ kJ \cdot mol^{-1}$).

Reliable experimental values of the standard enthalpies of formation of dimethyl, diethyl, and dibutyl phthalates are compared with the standard enthalpies of formation of 1-alkanols [10] in Fig. 2. The values for the phthalates are reduced to one alkyl group by dividing by 2. All values are relative, with values shown as differences from that for the first member in each series; dimethyl phthalate and methanol, respectively. Therefore, the plot shows successive increases in the absolute values of the enthalpy of formation with insertion of CH_2 groups. Alcohols show behavior common for many different classes of compounds with a larger initial (C_1 to C_2)

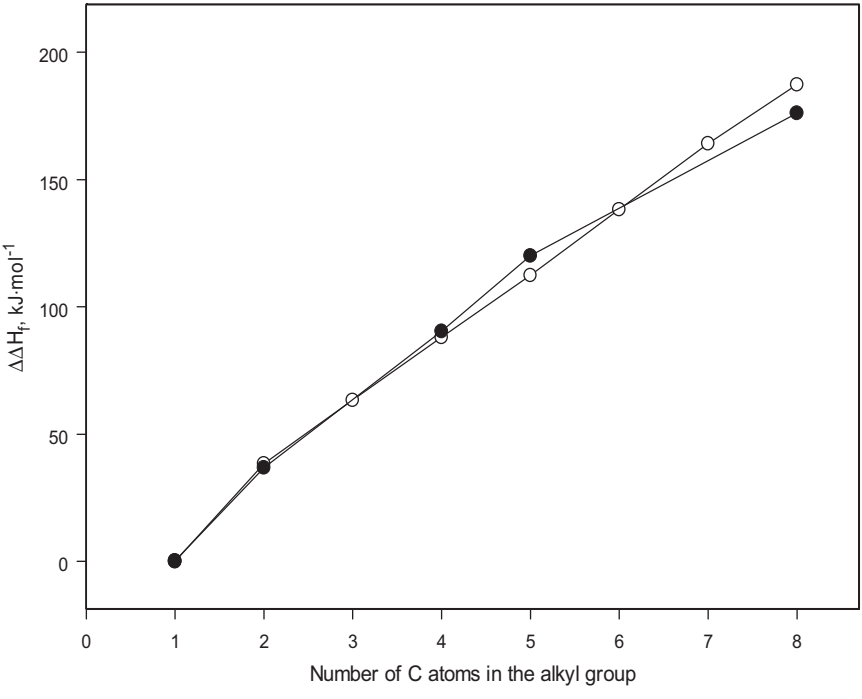

Fig. 2. Selected relative enthalpies of formation of liquid *n*-alkyl phthalates at 298.15 K reduced to 1 alkyl group $\Delta\Delta_f H = -1/2[\Delta_f H° - \Delta_f H°(\text{dimethyl phthalate})]$ compared with relative enthalpies of formation of liquid 1-alkanols [10] $\Delta\Delta_f H = -[\Delta_f H° - \Delta_f H°(\text{methanol})]$. ●, phthalates; ○, alkanols.

increment followed by a nearly constant increment. The alcohols are the closest to the phthalate class of chemical compounds R–O–X, for which accurate enthalpies of formation are known for a sufficient range of alkyl R size. The data for esters and ethers are either too few or not reliable.

In the case of liquid phthalates, insertion of the first CH_2 group (transition from methyl to ethyl phthalate) is also accompanied by a larger enthalpy effect than insertion of subsequent CH_2 groups. The average effect of insertion of the two next CH_2 groups (from ethyl to butyl phthalate), $-27.9\ kJ \cdot mol^{-1}$ per CH_2 group, is a bit larger than the generalized value ($-25.3 \pm 0.5\ kJ \cdot mol^{-1}$), which suggests the absence of additional strain in longer alkyl chains in phthalates.

The values for dipentyl and dioctyl phthalates are also shown in Fig. 2. These are much less reliable, which is indicated by their large deviations from the corresponding alcohols. Moreover, the value for dioctyl phthalate is absent in the report cited by Ref. 1. Consequently, its origin is unknown. We conclude that predicted enthalpies of formation should be preferred for phthalates higher than dibutyl phthalate. A prediction can be made by addition of the universal CH_2 group increment ($-25.3\ kJ \cdot mol^{-1}$) to the standard enthalpy of formation of dibutyl phthalate.

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