



Thermochemistry of 1,3-diethylbarbituric and 1,3-diethyl-2-thiobarbituric acids: Experimental and computational study



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ABSTRACT

This paper reports an experimental and computational thermochemical study on two barbituric acid derivatives, viz. 1,3-diethylbarbituric acid and 1,3-diethyl-2-thiobarbituric acid. Values of standard molar enthalpies of formation in the gas phase at $T = 298.15$ K have been derived from experiment. Energies of combustion were measured by the static bomb combustion calorimetry in the case of 1,3-diethylbarbituric acid, and the rotating-bomb combustion calorimetry in the case of 1,3-diethyl-2-thiobarbituric acid. From the combustion energies, standard molar enthalpies of formation in the crystalline state at $T = 298.15$ K were calculated. The enthalpy of vaporization of 1,3-diethylbarbituric acid and enthalpy of sublimation of 1,3-diethyl-2-thiobarbituric acid were determined using the transpiration method. Combining calorimetric and transpiration results, values of $-(611.9 \pm 2.0)$ kJ·mol⁻¹ and $-(343.8 \pm 2.2)$ kJ·mol⁻¹ for the gas-phase enthalpies of formation at $T = 298.15$ K of 1,3-diethylbarbituric and 1,3-diethyl-2-thiobarbituric acids, respectively, were derived. Theoretical calculations at the G3 and G4 levels were performed, and a study of the molecular structure of the compounds has been carried out. Calculated enthalpies of formation were in very good agreement with the experimental values.

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1. Introduction

Over the past years, we have been involved in the study of the thermochemistry of barbituric acid (2,4,6(1*H*,3*H*,5*H*)-pyrimidine-trione) and its derivatives, with the aim of understanding the structural effects on their thermodynamic stabilities as reflected in the gas-phase enthalpy of formation. We have published thermochemical studies of the parent compound barbituric acid [1], its 5,5-dimethyl [2], 1,3-dimethyl [3], 5,5-diethyl (barbital) [4,5], 1,3,5-trimethyl, 1,5,5-trimethyl, and 1,3,5,5-tetramethyl [6] derivatives, and also of a sulfur-containing barbituric acid, 2-thiobarbituric acid [7]. We have also reported thermophysical studies of some methyl and ethyl derivatives of barbituric acid [8], and of 2-thiobarbituric acid [9]. Finishing these series of studies, in the present work we have carried out an experimental and computational study on the energy-structure relationships for two ethyl derivatives: 1,3-diethylbarbituric acid (1,3-diethyl-2,4,6(1*H*,3*H*,5*H*)pyrimidinetrione) [CAS 32479-73-5], and 1,3-diethyl-2-thiobarbituric acid

(1,3-diethyl-2-thioxodihydro-4,6(1*H*,5*H*)-pyrimidinedione) [CAS 5217-47-0], whose structures are presented in figure 1.

2. Experimental

2.1. Materials and purity control

The preparation and purification of 1,3-diethylbarbituric acid was described in detail in our previous publication [8]. It was re-crystallized from the mixture of chloroform and heptane with a volume ratio of 1.4:1. The 1,3-diethyl-2-thiobarbituric acid was commercially available from Aldrich. This sample was purified by the fractional sublimation. Provenance, purification, and analysis details of the samples under study are given in table 1.

2.2. Static bomb combustion calorimetry

The energy of combustion of 1,3-diethylbarbituric acid was measured in the isoperibol calorimeter equipped with the static bomb. The detailed procedure has been described previously [11]. The solid sample was pressed into a pellet and weighed using

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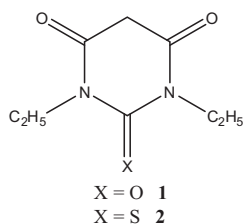


FIGURE 1. Schematic structures of 1,3-diethylbarbituric acid **1**, and 1,3-diethyl-2-thiobarbituric acid **2**.

a microbalance with 10^{-6} g resolution. We used small polyethylene pieces as an auxiliary material (table 2) in order to reach completeness of combustion. The energy equivalent of the calorimeter $\varepsilon_{\text{calor}} = 14886.0 \pm 0.9 \text{ J} \cdot \text{K}^{-1}$ (see table 3) was determined with a standard reference sample of benzoic acid (sample SRM 39j, N.I.S.T.). Correction for nitric acid formation was based on the titration with $0.1 \text{ mol} \cdot \text{dm}^{-3}$ NaOH (aq.).

2.3. Rotating-bomb combustion calorimetry

The energy of combustion of 1,3-diethyl-2-thiobarbituric acid was measured in a rotating-bomb combustion calorimeter [12]. The bomb can be rotated simultaneously axially and end-over-end in order to smooth the temperature rise during the main period of the combustion experiment. The stainless-steel combustion bomb of internal volume 0.2511 dm^3 was completely lined with platinum. All internal fittings, electrodes, and crucible were fabricated from platinum. The bomb was filled with 10.00 g of water, assembled and charged with oxygen to a total pressure of $p = 3.0 \text{ MPa}$ at $T = 293.15 \text{ K}$ without preliminary flushing according to a common procedure specific for the combustion experiments with sulfur containing compounds [13].

The solid sample of 1,3-diethyl-2-thiobarbituric acid was made into a pellet before combustion and weighed with a microbalance with 10^{-6} g resolution. The initial temperature of the combustion experiment was chosen so as to reach a final temperature close to $T = 298.15 \text{ K}$. Combustion was initiated by an electrical device connected to the computer which automatically fired the ignition

TABLE 1
Provenance, purification, and analysis details for the studied compounds.

Chemical name	CAS	Provenance	Purification method	Final mass fraction purity ^a
1,3-Diethylbarbituric acid	32479-73-5	This work ^b	Crystallization	0.9995
1,3-Diethyl-2-thiobarbituric acid	5217-47-0	Aldrich	Sublimation	0.9996

^a Assessed by HPLC and DSC.

^b Prepared from malonic acid and *N,N'*-diethylurea according to a literature procedure [8,10].

TABLE 2
Formula, density ρ , massic heat capacity c_p , and expansion coefficients $(\delta V/\delta T)_p$ of the materials at $p^\circ = 0.1 \text{ MPa}$ used in the present study.

Compounds	Formula	$\rho_{293 \text{ K}}^a / \text{g} \cdot \text{cm}^{-3}$	$c_{p298 \text{ K}}^b / \text{J} \cdot \text{K}^{-1} \cdot \text{g}^{-1}$	$10^{-6}(\delta V/\delta T)_p^c \text{ dm}^3 \cdot \text{K}^{-1}$
1,3-Diethylbarbituric acid (cr)	$\text{C}_8\text{H}_{12}\text{O}_3\text{N}_2$	1.32	1.35	0.1
1,3-Diethyl-2-thiobarbituric acid (cr)	$\text{C}_8\text{H}_{12}\text{SO}_2\text{N}_2$	1.61	1.08	0.1
Polyethylene ^d	$\text{CH}_{1.93}$	0.92	2.53	0.1
Cotton ^e	$\text{CH}_{1.774}\text{O}_{0.887}$	1.50	1.67	0.1

^a Measured with a pycnometer with $u(\rho) = 0.01 \text{ g} \cdot \text{cm}^{-3}$.

^b From [9].

^c Estimated.

^d From 10 combustion experiments, $\Delta_c u^\circ = -46357.3 \text{ J} \cdot \text{g}^{-1}$ with uncertainty $u(\Delta_c u^\circ) = 3.5 \text{ J} \cdot \text{g}^{-1}$.

^e From 10 combustion experiments, $\Delta_c u^\circ = -16945.2 \text{ J} \cdot \text{g}^{-1}$ with uncertainty $u(\Delta_c u^\circ) = 4.2 \text{ J} \cdot \text{g}^{-1}$.

TABLE 3
Results of typical combustion experiments at $T = 298.15 \text{ K}$ ($p^\circ = 0.1 \text{ MPa}$) for 1,3-diethylbarbituric acid.^a

m (Substance)/g	0.334258	0.222654	0.32035	0.43877	0.794593
m' (Cotton)/g	0.001031	0.000838	0.000919	0.001053	0.001007
m'' (Polyethylene)/g	0.340335	0.450731	0.398753	0.30103	0.11417
$\Delta T_c / \text{K}$	1.56913	1.74371	1.73008	1.60567	1.56414
$(\varepsilon_{\text{calor}}) \cdot (-\Delta T_c) / \text{J}$	-23358	-25956.8	-25754	-23902	-23283.8
$(\varepsilon_{\text{cont}}) \cdot (-\Delta T_c) / \text{J}$	-25.4	-28.69	-28.48	-26.32	-25.52
$\Delta U_{\text{decomp}} \text{HNO}_3 / \text{J}$	49.87	48.38	53.16	60.92	73.46
$\Delta U_{\text{corr}} / \text{J}$	9.7	9.69	10.44	10.76	13.56
$-m' \cdot \Delta_c u' / \text{J}$	17.47	14.2	15.57	17.84	17.06
$-m'' \cdot \Delta_c u'' / \text{J}$	15777.01	20894.67	18485.11	13954.94	5292.61
$\Delta_c u^\circ$ (cr) / ($\text{J} \cdot \text{g}^{-1}$)	-22525.4	-22539.5	-22532.1	-22526.3	-22543.1
	-(22533.3 ± 3.5)				

^a The definition of the symbols assigned according to reference [13] as follows: m (substance); m' (cotton), and m'' (polyethylene) are, respectively, the mass of compound burnt, the mass of fuse (cotton) and the mass of polyethylene pieces used as the auxiliary material, used in each experiment, masses were corrected for buoyancy; $V(\text{bomb}) = 0.320 \text{ dm}^3$ is the internal volume of the calorimetric bomb; $p(\text{gas}) = 3.00 \text{ MPa}$ is the initial oxygen pressure in the bomb; $m(\text{H}_2\text{O}) = 1.00 \text{ g}$ is the mass of water added to the bomb for dissolution of combustion gases; $\varepsilon_{\text{calor}} = (14886.0 \pm 0.9) \text{ J} \cdot \text{K}^{-1}$ is the energy equivalent of the calorimeter; $\Delta T_c = T^f - T_i + \Delta T_{\text{corr}}$ is the corrected temperature rise from initial temperature T_i to final temperature T^f , with the correction ΔT_{corr} for heat exchange during the experiment; $\varepsilon_{\text{cont}}$ is the energy equivalents of the bomb contents in their initial $\varepsilon_{\text{cont}}^i$ and final states $\varepsilon_{\text{cont}}^f$, the contribution for the bomb content is calculated with $(\varepsilon_{\text{cont}}) \cdot (-\Delta T_c) = (\varepsilon_{\text{cont}}^i) \cdot (T_i - 298.15) + (\varepsilon_{\text{cont}}^f) \cdot (298.15 - T^f + \Delta T_{\text{corr}})$; $\Delta U_{\text{decomp}} \text{HNO}_3$ is the energy correction for the nitric acid formation. ΔU_{corr} is the correction to standard states. $\Delta_c u^\circ$ is the standard massic energy of combustion, uncertainty is expressed as the standard deviation.

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