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Determination of the Enthalpies of Combustion and Formation of Substituted Triazines in an Adiabatic Rotating Bomb Calorimeter

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To obtain reliable thermodynamic data on substituted triazines, *it is necessary to use a calorimeter that* is capable of high precision with small quantities of sample and in which a homogeneous solution of the corrosive combustion products can be maintained. The enthalpies of combustion of six substituted triazines have been determined in a platinum-lined adiabatic rotating bomb calorimeter. These are the first determinations of enthalpies of combustion or formation to have been reported for these compounds. The values *derived for the enthalpies of formation in kJ/mol at 25 °C* are as follows: 2,4,6-trimethoxy-1,3,5-triazine, −478.60±0.87; 2,4,6-triethoxy-1,3,5-triazine, −584.99±1.50; 2,4,6-tris(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine, −1109.80±1.53; 2,4-dimethoxy-6-(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine, −697.08±1.15; 2-methoxy- 4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine, −907.71±2.40; 2-amino-4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine, −773.12±1.50.

Key words: adiabatic calorimeter; aneroid calorimeter; combustion; enthalpy; fluorine compounds; formation; heat; rotating bomb calorimeter; thermochemistry; triazines.

1. Introduction

The triazines comprise an interesting group of compounds for which few data on the enthalpies of combustion and formation exist in the available literature. This is probably due to the difficulty of preparation and purification of these materials.

The parent compound, symmetrical triazine ($s-C_3H_3N_3$), which is unstable in the presence of moisture,has been studied previously. Preliminary values for the enthalpy of combustion were reported by Berets [1][1] who obtained −424.8±0.5 and 12.2 kcal/mol[2] for the enthalpies of combustion and vaporization, respectively, at 25 °C. A more recent determination by K. Arvidsson of the University of Lund, Sweden [2] yielded values of −426.06±0.22 and 13.20±0.03 kcal/mol and K. Bystrom, also of the University of Lund [3] obtained values of −425.66 and 12.95±0.05 kcal/mol, respectively, for these quantities.

About the Authors, Paper: Walter H. Johnson, a chemist, and Edward J. Prosen, a chemical physicist, are both retired from NBS but continue an active association with the Bureau's Division of Chemical Thermodynamics on an as-needed basis. The work they describe was sponsored by the Department of Defense (Picatinny Arsenal).

Some calorimetric measurements on substituted triazine derivatives have been carried out. For example, Berets [1], Lemoult [4] and Selivanov et al. [5] determined the heat of combustion of cyanuric acid, $C_3N_3(OH)_3$, at 25 °C. Melamine, 2,4,6-

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[1] Figures in brackets indicate literature references.

[2] 1 thermochemical calorie= 4.184 joules.

amino-1,3,5-triazine, ($C_3N_3(NH_2)_3$), has also been studied by Tauernier and Lameroux [6], Salley and Gray [7], and Lemoult [8], respectively. Other related compounds for which calorimetric determinations of thermochemical properties have been reported are 1,3,5-triphenyl-1,3,5-triazine-2,4,6-trione [9], 2,4,6-triphenoxy-1,3,5-triazine [9], 2,4,6-trichloro-1,3,5-triazine [10], 6-amino-1,3,5-triazine [9], 4,6-diamino-1,3,5-triazine-2-one [9], hexahydro-1,3,5-trinitroso-1,3,5-triazine [11,12], 1,3,5-trinitro-1,3,5-triazine [11,12], 2,4-dichloro-6-ethylamine-1,3,5-triazine [13], 2-chloro-4,6-bis(ethylamine)-1,3,5-triazine [13], 2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine [13], and 2-chloro-4,6-bis(isopropyl-amino)-1,3,5-tri-azine [13].

This investigation reports the values for the enthalpies of formation of symmetrical triazines substituted with fluorine, nitro and alkyl or alkoxy groups, determined using an adiabatic rotating bomb calorimeter. These substituted derivatives of symmetrical triazine present certain problems for calorimetric measurements. First, they are difficult to prepare and to purify except in very small quantities, which means that the calorimeter used in the measurements must be capable of making high precision measurements on very small quantities of sample. Second, the combustion products of the compounds studied in this investigation are carbon dioxide, nitrogen, water, hydrofluoric acid, and nitric acid. Therefore, in order to obtain reliable calorimetric data for these compounds, the bomb must be rotated to obtain a homogeneous solution of the aqueous acids, and the interior of the bomb must be lined with platinum to prevent corrosion.

2. Materials

The triazine samples were obtained from Picatinny Arsenal through the courtesy of V. I. Siele. All were colorless crystalline materials, had very low vapor pressure, were nonhygroscopic and stable in moist air. Because of the rather long chemical names, the materials have been designated as Triazine I, Triazine II, etc., in the sections of this paper that follow:

- 2,4,6-Trimethoxy-1,3,5-triazine **Triazine I**

The Picatinny label was: 762-50-77, mp 135–137 °C. No further purification was attempted.

- 2,4,6-Triethoxy-1,3,5-triazine **Triazine II**

The Picatinny label was: 762-50-78, bp 101 °C at 0.6 mm. The melting point was found to be 27.5 °C. No purification was attempted.

- 2,4,6-Tris(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine **Triazine III**

The Picatinny label was: 51-55, mp 76–77 °C. An attempt was made to further purify a portion of this material by a zone-melting technnique; however, no difference was observed in the energy of combustion or in the stoichiometry of the combustion products between the treated and untreated portions.

- 2,4-Dimethoxy-6-(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine **Triazine IV**

The Picatinny label was: 762-50-59-1, mp 54–56 °C. No purification was attempted.

- 2-Methoxy-4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine **Triazine V**

The Picatinny label was: 51-54, mp 98.5–100 °C. No purification was attempted.

- 2-Amino-4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine **Triazine VI**

The Picatinny label was: 762-50-57-1, mp 91–92.5 °C. No purification was attempted.

Benzoic Acid—The benzoic acid used for the calibration experiments was Standard Reference Material 39i, obtained from the National Bureau of Standards' Office of Standard Reference Materials. The purity was given as 99.997 mol%.

Oxygen—Commercial oxygen was purified by passing successively through an oxidizer containing copper oxide at 450 °C, a carbon dioxide absorber, and a drier containing magnesium perchlorate. In some experiments a cylinder of high purity oxygen was used; analysis showed the following maximum concentrations of impurities in ppm: N_2, 3.0; H_2O, 2.0; and N_2O, 0.8. The presence of these impurities in the given concentrations would not significantly affect the results of this investigation. There was no apparent difference between the results obtained using the two samples of oxygen.

3. Calorimetric Apparatus

An adiabatic rotating bomb calorimeter, designed and constructed by the present authors at this laboratory and described in ref. [14], was used for all measurements in this investigation. The bomb is completely lined with platinum to prevent reaction with corrosive solutions, and can be rotated to insure a homogeneous solution of the bomb liquid. The adiabatic feature results in a low heat capacity, approximately 2500 J/K, to permit high precision with relatively small quantities of sample. The bomb is surrounded by an adiabatic shield, automatically maintained at the temperature of the bomb; the calorimeter is enclosed within a jacket and is operated under high vacuum. The volume of the bomb is 98 cm^3.

Temperatures are determined by means of a capsule-type platinum resistance-thermometer located within the bomb wall. A heater, also located within the bomb wall, serves to preheat the bomb to the desired initial temperature. The thermometer is connected in series with a 27.5 Ω standard resistor, a variable resistor and a 2 V storage cell. The standard resistor is enclosed in a thermostat which is controlled at 30.6 °C. The thermometer current is 5 mA. The potential leads of the resistor are connected to the standard cell terminals of an L&N microvolt potentiometer which had been altered to tap off 1.000 V instead of 1.018 V. The potential leads of the thermometer are connected to the emf terminals of the potentiometer. The working current of the potentiometer was adjusted such that the potential reading across the 27.5 Ω resistor was 1.000 with a current of 5 mA. The actual voltage corresponding to a dial reading of 1.0000 is, therefore, 0.1375 V. The emf reading is, therefore, the ratio of the resistance of the thermometer to that of the standard resistor. A nanovoltmeter used as a detector permits the measurement of temperature within $\pm 15 \times 10^{-6}$ °C.

Ignition of the sample is accomplished by discharging an 18,000 μF condenser, previously charged to about 23 V, through a platinum wire fuse in contact with the sample. From the drop in potential across the condenser, the quantity of electrical energy can be calculated. By means of separate experiments it was found that 67% of the calculated energy was actually dissipated within the calorimeter; this factor was used to determine the actual quantity of ignition energy.

Since this is a dry (aneroid) bomb (not surrounded by water), the rotation which is carried out to produce uniform product concentrations inside the bomb does not produce enough energy to require any corrections to be made for this rotation.

4. Procedure

The approximate quantity of sample required was pressed into a pellet and weighed in a small platinum crucible using a microbalance. All weights were corrected to weights in vacuum by means of buoyancy corrections derived from the density of the sample and air-density measurements at the time of weighing. The crucible was supported in the bomb so that the sample was in contact with a 2 cm length of 0.075 mm diameter platinum wire connected between the bomb electrodes. The quantity of water initially placed in the bomb was 0.3 cm^3 for the benzoic acid calibration experiments and for those materials which did not contain fluorine; 3.00 cm^3 of water was used for the fluorine-containing compounds.

The bomb was then closed, flushed with 1 liter of oxygen and filled to 3.204 MPa (31.62 atm) with purified oxygen. The bomb was placed in the calorimeter, the filling temperature was observed and the calorimeter jacket was evacuated. The adiabatic temperature controls were placed in operation and the calorimeter was heated to approximately 24.98 °C. The calorimeter was left overnight with the vacuum pumps and the temperature controls in operation. While this period of time was much longer than required for thermal equilibrium to be established, the experiments were performed in this manner so that the calorimetric experiment, the analyses of the combustion products, and the preparation for the next experiment could be completed during the working day.

On the following morning the calorimeter temperatures were observed at intervals of a few minutes during a 45 min initial rating period. The sample was then ignited and rotation of the bomb was initiated approximately 2 min after firing. After about 20 min, thermal equilibrium was approached and temperatures were observed at intervals of a few minutes during a final rating period. Rotation of the bomb was omitted for the benzoic acid calibration experiments. Because of the heating effect of the 5 mA current through the platinum resistance thermometer, there was a constant rise in temperature of approximately 1 K/h. The initial and final calorimeter temperatures were obtained by extrapolation of the initial and final time-vs-temperature curves to the actual time of ignition.

The bomb was removed from the calorimeter and the gaseous contents released slowly through a weighed carbon dioxide absorption tube [15]; a stream of CO_2-free air was passed through the bomb at 100 cm^3/min for approximately 1 h to complete transfer of carbon dioxide. The absorption tube was flushed with dry hydrogen before weighing to reduce the effect of displacement of oxygen by the sodium carbonate formed.

The bomb was opened and the liquid contents transferred to a weighed polyethylene bottle taking care that the liquid made no contact with anything other than platinum and polyethylene. The bottle, together with the solution and washings, was weighed. A weighed aliquot was placed in a polyethylene titration flask which contained a plastic-coated stirring bar. A stream of CO_2-free air was passed through the stirred solution for 1 h to remove the dissolved carbon dioxide. Slightly less than the theoretical quantity of standard alkali was added from a buret, a combination calomel-glass electrode was introduced, and the titration was completed using a pH meter.

A second aliquot was taken for the determination of nitric acid by a micro-Kjeldahl procedure in which the acid was converted to ammonia and collected in an excess of standard sulfuric acid. Back titration with standard alkali gave the quantity of nitric acid in the aliquot. The quantity of hydrofluoric acid should be given by the difference between the total acidity and the acidity of the nitric acid, determined as described above, if no other acids are present. In order to verify the quantity of hydrofluoric acid, a few of the aliquots were titrated using a fluoride selective electrode. The results obtained by repetitions of the Kjeldahl procedure for nitric acid determination varied by as much as 10%, probably because the acid concentrations were very low. The quantity of nitric acid was, therefore, taken as the difference between the total acidity and the theoretical quantity of hydrofluoric acid.

5. Results and Discussion

The certified calorific value for the benzoic acid used for calibration of the calorimeter was 26434±3 J/g under certificate conditions. This reduces to $\Delta U\,°C = -26412.35 \pm 3.0$ at 26 °C and -26410.36 ± 3.0 at 28 °C for the change in internal energy under standard conditions.

The densities of the materials, when not given with the other sample data, were determined by an approximate flotation procedure. Values for the heat capacity were estimated. The compressibility coefficients for the triazines were taken as 0. The values used in the calculations are given in table 1.

All calculations are based upon the 1971 Table of Atomic Weights [16].

All computations of Washburn corrections were by computer using a program originally prepared by C. H. Shomate of the Naval Ordinance Test Station, China Lake, CA, and modified to include compounds containing fluorine by G. T. Armstrong and E. J. Prosen of the National Bureau of Standards according to the method of Hubbard, Scott, and Waddington [17].

The results of the CO_2 analyses are given in table 2.

The results of the benzoic acid calibration experiments are given in tables 3, 4, and 5. The terms used in the tables are described as follows:

EEE-std, the effective energy equivalent of the standard, empty calorimeter at the standard mean temperatue of the experiment;

Table 1. Values taken for density, heat capacity, and compressibility coefficient.

	Density $g{\cdot}cm^{-3}$	Cp $J{\cdot}g^{-1}{\cdot}K^{-1}$	$\left(\frac{\partial V}{\delta P}\right)$ $cm^3{\cdot}g^{-1}{\cdot}K^{-1}$
Benzoic acid	1.320	1.21	4.4×10^{-4}
Triazine I	1.316	2.32	0
Triazine II	1.150	2.26	0
Triazine III	1.795	1.17	0
Triazine IV	1.700	1.64	0
Triazine V	1.720	1.31	0
Triazine IV	1.771	1.17	0

Table 2. Results of the carbon dioxide analyses.

	No. of Expts.	$CO_{2(found)}/CO_{2(theor.)}$
Triazine I	5	0.9982±0.0009
Triazine II	5	.9979±0.0008
Triazine III	7	1.0028±0.0004
Triazine IV	6	0.9999±0.0002
Triazine V	5	1.0005±0.0004
Triazine VI	6	1.0000±0.0004

Table 3. Results of the benzoic acid calibration experiments for Triazine I.

Expt. No.	**91**	**92**	**93**	**104**	**107**	**110**
EEE-Std, $J{\cdot}K^{-1}$	2512.90	2513.28	2513.28	2513.25	2513.32	2513.20
Cv-cont (i), $J{\cdot}K^{-1}$	4.79	4.79	4.77	4.88	4.87	4.88
Corr to tm, $J{\cdot}K^{-1}$	0.12	0.16	0.12	0.18	0.06	0.12
Corr-parts, $J{\cdot}K^{-1}$	0.00	0.00	0.00	−0.36	−0.36	−0.36
EEE-actual, $J{\cdot}K^{-1}$	2517.81	2518.22	2518.27	2517.95	2517.89	2517.84
Temp rise, K	3.150904	3.164264	3.167566	3.206961	3.086207	3.170323
Q-total, J	−7933.37	−7968.32	−7976.78	−8704.95	−7770.73	−7982.35
q-ign, J	1.02	1.05	0.90	1.06	1.19	1.16
q-decomp HNO_3, J	0.33	1.62	0.45	0.45	0.63	0.82
q-WC, J	6.13	6.16	6.13	6.39	6.14	6.32
q-corr to 28 °C, J	−0.05	−0.06	−0.05	−0.07	−0.03	−0.05
Q-std react, J	−7925.93	−7959.55	−7969.35	−8067.12	−7762.80	−7974.11
M_s, g	.300107	.301380	.301751	.305453	.293930	.301931
$\Delta U°C$ (28 °C), $J{\cdot}g^{-1}$	−26410.36	−26410.36	−26410.36	−26410.36	−26410.36	−26410.36
Mean EEE-std, $J{\cdot}K^{-1}$	2513.22					
sdm	±.12					

Table 4. Results of the benzoic acid calibration experiments for Triazine II.

Expt. No.	253	255	265	281	282	283
EEE-Std, J·K^{-1}	2514.17	2514.10	2514.08	2514.48	2514.26	2514.04
Cv-cont (i), J·K^{-1}	4.56	4.56	4.58	4.45	4.44	4.59
Corr to tm, J·K^{-1}	.07	.08	.10	.09	.09	.13
Corr-parts, J·K^{-1}	0.00	0.00	0.00	.00	.00	.00
EEE-actual, J·K^{-1}	2518.81	2518.74	2518.76	2519.02	2518.79	2517.76
Temp rise, K	1.077327	1.084430	1.103032	1.088817	1.075373	1.146946
Q-total, J	−2713.58	−2731.39	−2778.27	−2742.75	−2708.63	−2888.88
q-ign, J	.97	.97	.88	.83	1.01	.90
q-decomp HNO$_3$, J	.31	.08	.07	.22	.02	.15
q-WC, J	1.95	1.96	2.01	1.98	1.95	2.10
q-corr to 26°C, J	−.01	−.01	−.01	−.02	−.02	−.02
Q-std react, J	−2710.39	−2728.39	−2775.32	−2739.75	−2705.67	−2885.75
M$_s$, g	.102618	.103300	.105077	.103730	.102440	.109257
ΔU°C (26°C), J·g^{-1}	−26412.35	−26412.35	−26412.35	−26412.35	−26412.35	−26412.35
Mean EEE-std, J·K^{-1}	2514.19					
sdm	±.07					

Table 5. Results of the benzoic acid calibration experiments for Triazine III, IV, V, and VI.

Expt. No.	160	162	165	172	184	188	200
EEE-Std, J·K^{-1}	2514.80	2514.78	2514.72	2515.05	2514.85	2514.75	2515.00
Cv-cont (i), J·K^{-1}	4.48	4.48	4.48	4.48	4.60	4.57	4.57
Corr to tm, J·K^{-1}	.10	.06	.07	.10	.28	.12	.07
Corr-parts, J·K^{-1}	0.00	0.00	0.00	.00	.00	.00	.00
EEE-actual, J·K^{-1}	2519.38	2519.32	2519.27	2519.63	2519.73	2519.45	2519.64
Temp rise, K	1.046650	1.060647	1.071820	1.084813	1.325942	1.117483	1.068379
Q-total, J	−2636.91	−2672.11	−2700.20	−2733.33	−3341.02	−2815.44	−2691.93
q-ign, J	.97	.94	1.02	.85	.98	.86	.90
q-decomp HNO$_3$, J	.24	.24	.31	.33	.31	.25	.27
q-WC, J	1.85	1.87	1.90	1.92	2.45	2.04	1.94
q-corr to 26°C, J	−.01	−.01	−.01	−.01	−.05	−.02	−.01
Q-std react, J	−2633.86	−2669.05	−2696.99	−2730.23	−3337.33	−2812.31	−2688.83
M$_s$, g	.099721	.101053	.102111	.103369	.126355	.106477	.101802
ΔU°C (26°C), J·g^{-1}	−26412.35	−26412.35	−26412.35	−26412.35	−26412.35	−26412.35	−26412.35
Mean EEE-std, J·K^{-1}	−2514.85						
sdm	±.05						

Cv-cont(i), the heat capacity of the initial bomb contents including the crucible, sample, water, and oxygen;

Corr to t$_m$, a correction to the heat capacity of the calorimeter for deviation of the actual mean temperature of the experiment from the standard mean temperature;

Corr-parts, a correction to the heat capacity of the calorimeter for alterations during the series of experiments;

EEE-actual, the effective energy equivalent of the actual initial calorimeter system at the actual mean temperature of the experiment;

Temp. rise, the observed increase in temperature of the calorimeter following combustion of the sample;

Q-total, the total quantity of energy evolved by the overall bomb process, obtained as the product of EEE-actual and the temperature rise;

q-ign, the electrical energy added to the calorimeter system to ignite the sample;

q-decomp HNO$_3$, the calculated quantity of energy required to decompose any nitric acid, formed in the combustion process, into nitrogen (g) and water (liq) using 59.7 kJ/mol;

q-WC, the Washburn correction [17,18] applied to convert reactants and products to their respective standard states at the actual final temperature;

q-corr to std t_f, a correction applied for deviation of the actual final temperature from the selected standard final temperature;

Q-std react, the energy evolved by the reaction with reactants and products in their respective standard states at the selected final temperature, obtained as the algebraic sum of Q-total and the energy corrections;

m_s, the mass of sample;

ΔU°C, the energy evolved by the standard reaction at the selected final temperature for the constant volume process.

The values in the tables were taken from the computer printout and have been rounded for convenience. For this reason, slight differences from the more exact computer results may result by calculation from the tabulated values. For the calibration experiments the value for EEE-std was obtained from ΔU °C using an iterative procedure. Three separate series of calibration experiments were performed because of significant changes in the calorimeter system and in the selected temperature increment.

The results of the combustion experiments on the triazines are given in tables 6, 7, 8, 9, 10, and 11.

The values given in the tables correspond to the following reactions:

(1) 2,4,6-Trimethoxy-1,3,5-triazine **Triazine I**

$C_6H_9O_3N_3(c) + 6.75\ O_2(g) \rightarrow 6\ CO_2(g) + 1.5\ N_2(g) + 4.5\ H_2O(liq)$

$\Delta U\ °C(28\ °C) = -18524.3 \pm 4.9$ J/g.

Table 6. Results of the Triazine I combustion experiments.

Expt. No.	99	100	101	102	103
EEE-Std, J·K^{-1}	2513.22	2513.22	2513.22	2513.22	2513.22
Cv-cont (i), J·K^{-1}	5.38	5.37	5.41	5.38	5.38
Corr to tm, J·K^{-1}	.07	.08	.14	.08	.07
Corr-parts, J·K^{-1}	.00	.00	.00	−.01	−.36
EEE-actual, J·K^{-1}	2518.67	2518.67	2518.71	2518.66	2518.31
Temp rise, K	3.096776	3.112201	3.175631	3.102691	3.101981
Q-total, J	−7999.76	−7838.61	−7998.68	−7814.64	−7811.74
q-ign, J	.98	.95	1.56	1.08	1.08
q-decomp HNO_3, J	37.09	37.02	38.41	37.02	36.87
q-WC, J	6.22	6.22	6.39	6.23	6.22
q-corr to 28 °C, J	.00	.00	.00	.00	.00
Q-std react, J	−7755.47	−7794.41	−7952.31	−7770.31	−7767.57
m_s, g	.418671	.420776	.429295	.419443	.419321
ΔU °C (28 °C), J·g^{-1}	−18524.01	−18523.91	−18524.12	−18525.32	−18525.14
Mean, ΔU ° (28 °C), J·g^{-1}	−18524.30				
sdm	±0.26				

Table 7. Results of the Triazine II combustion experiments.

Expt. No.	267	268	269	270	274	272[a]
EEE-Std, J·K^{-1}	2514.19	2514.19	2514.19	2514.19	2514.19	2514.19
Cv-cont (i), J·K^{-1}	4.78	4.72	4.70	4.71	4.69	4.68
Corr to tm, J·K^{-1}	.36	.10	.07	.09	.11	7.16
Corr-parts, J·K^{-1}	.00	.00	.00	.00	.00	.00
EEE-actual, J·K^{-1}	2519.33	2519.00	2518.96	2518.99	2518.98	2526.03
Temp rise, K	1.394706	1.101912	1.063056	1.092145	1.108613	1.087068
Q-total, J	−3513.73	−2775.72	−2677.80	−2751.10	−2792.58	−2745.96
q-ign, J	.95	.88	.83	.97	.90	.83
q-decomp HNO_3, J	11.53	8.65	8.70	9.41	9.72	8.45
q-WC, J	2.06	1.61	1.54	1.58	1.60	1.57
q-corr to 26 °C, J	−.03	−.01	−.00	−.01	−.01	−.26
Q-std react, J	−3499.21	−2764.59	−2666.73	−2739.14	−2780.37	−2735.36
M_s, g	.146350	.115652	.111537	.114566	.116265	.114194
ΔU°C (26 °C), J·g^{-1}	−23909.87	−23904.35	−23908.94	−23908.89	−23914.14	−23953.74
Mean E E-std, J·K^{-1}	−23909.24					
sdm	±1.56					

[a] Burned as liquid at 30 °C, not included in average.

Table 8. Results of the Triazine III combustion experiments.

Expt. No.	182	185	186	276	278	279
EEE-Std, J·K^{-1}	2514.85	2514.85	2514.85	2514.85	2514.85	2514.85
Cv-cont (i), J·K^{-1}	16.01	16.01	16.02	16.01	15.98	15.99
Corr to tm, J·K^{-1}	−0.01	0.00	0.01	0.00	−0.01	−0.01
Corr-parts, J·K^{-1}	.00	.00	.00	−0.70	−0.70	−0.70
EEE-actual, J·K^{-1}	2530.85	2530.87	2530.87	2530.16	2530.12	2530.13
Temp rise, K	.989164	.981087	.982180	1.009298	.980954	.963102
Q-total, J	−2503.43	−2483.00	−2485.77	−2553.69	−2481.93	−2436.77
q-ign, J	1.02	.88	.99	.90	.99	.94
q-decomp HNO_3, J	16.04	15.22	15.44	14.95	15.16	17.45
q-WC, J	6.92	6.89	6.89	7.10	6.88	6.74
q-corr to 26 °C, J	0.00	0.00	0.00	0.00	0.00	0.00
Q-std react, J	−2749.45	−2460.01	−2461.45	−2530.73	−2458.90	−2411.66
M_s, g	.345488	.342742	.343138	.352485	.342530	.336088
ΔU°C (26 °C), J·g^{-1}	−7176.65	−7177.43	−7176.28	−7179.68	−7178.66	−7175.67
Mean EEE-std, J·K^{-1}	−7177.40					
sdm	±.62					

Table 9. Results of the Triazine IV combustion experiments.

Expt. No.	190	191	192	193	194
EEE-Std, J·K^{-1}	2514.85	2514.85	2514.85	2514.85	2514.85
Cv-cont (i), J·K^{-1}	15.99	15.96	15.97	15.97	15.96
Corr to tm, J·K^{-1}	.11	−.12	.07	.06	.05
Corr-parts, J·K^{-1}	.00	.00	.00	.00	.00
EEE-actual, J·K^{-1}	2530.95	2530.69	2530.89	2530.87	2530.86
Temp rise, K	1.108844	1.043991	1.085806	1.063969	1.043179
Q-total, J	−2806.43	−2642.02	−2748.06	−2692.77	−2640.14
q-ign, J	.95	.97	1.06	1.06	1.01
q-decomp HNO_3, J	15.65	15.51	16.06	15.32	15.19
q-WC, J	5.40	5.07	5.27	5.17	5.06
q-corr to 26 °C, J	.01	.00	.00	.00	.00
Q-std react, J	−2784.43	−2620.48	−2725.66	−2671.22	−2618.88
m_s, g	.240709	.226561	.235644	.230945	.226476
ΔU °C (26 °C), J·g^{-1}	−11567.60	−11566.32	−11566.89	−11566.48	−11563.57
Mean, ΔU ° (28 °C), J·g^{-1}	−11566.17				
sdm	±.69				

Table 10. Results of the Triazine V combustion experiments.

Expt. No.	167	168	169	170	171	362
EEE-Std, J·K^{-1}	2514.85	2514.85	2514.85	2514.85	2514.85	2517.46
Cv-cont(i), J·K^{-1}	11.93	15.93	16.00	15.97	16.00	15.93
Corr to tm, J·K^{-1}	−.03	−.06	.01	.02	−.01	−.02
Corr-parts, J·K^{-1}	.00	.00	.00	.00	.00	−.08
EEE-actual, J·K^{-1}	2526.75	2530.77	2530.86	2530.84	2530.84	2533.30
Temp rise, K	1.180365	.941348	1.007736	1.019433	.994826	.993761
Q-total, J	−2982.49	−2382.34	−2550.44	−2580.02	−2517.74	−2517.49
q-ign, J	.86	.95	.92	.90	1.02	.61
q-decomp HNO_3, J	13.85	14.25	15.71	15.42	16.34	15.41
q-WC, J	6.29	5.70	6.06	6.11	5.99	5.97
q-corr to 26 °C, J	.01	.00	.00	.00	.00	.00
Q-std react, J	−2961.48	−2361.45	−2527.74	−2557.59	−2494.40	−2495.50
M_s, g	.339291	.270904	.290118	.293462	.286357	.286325
ΔU°C (26 °C), J·g^{-1}	−8728.45	−8716.90	−8712.79	−8710.23	−8715.23	−8715.63
Mean EEE-std, J·K^{-1}	−8716.63					
sdm	±2.53					

Table 11. Results of the Triazine VI combustion experiments.

Expt. No.	201	203	204	205	206
EEE-Std, $J \cdot K^{-1}$	2514.85	2514.85	2514.85	2514.85	2514.85
Cv-cont (i), $J \cdot K^{-1}$	15.93	15.94	15.96	15.98	15.96
Corr to tm, $J \cdot K^{-1}$	−.04	−.02	.01	.06	.04
Corr-parts, $J \cdot K^{-1}$	.00	.00	.00	.00	.00
EEE-actual, $J \cdot K^{-1}$	2530.74	2530.77	2530.82	2530.90	2530.85
Temp rise, K	.959145	.979893	1.002171	1.071997	1.027877
Q-total, J	−2427.35	−2479.88	−2536.32	−2713.12	−2601.40
q-ign, J	.88	.78	78	.90	.86
q-decomp HNO_3, J	15.12	14.27	15.34	18.37	17.49
q-WC, J	6.04	6.18	6.33	6.74	6.45
q-corr to 26 °C, J	.00	.00	.00	.00	.00
Q-std react, J	−2405.32	−2458.65	−2513.86	−2687.11	−2576.61
m_s, g	.298999	.305657	.312668	.334324	.320487
ΔU °C (26 °C), $J \cdot g^{-1}$	−8044.57	−8043.82	−8040.03	−8037.42	−8039.67
Mean, ΔU ° (28 °C), $J \cdot g^{-1}$	−8041.10				
sdm	±1.34				

(2) 2,4,6-Triethoxy-1,3,5-triazine **Triazine II**
$C_9H_{15}O_3N_3(c)+11.25\ O_2(g) \rightarrow 9\ CO_2(g)+1.5\ N_2(g)$
$+7.5\ H_2O(liq)$
ΔU °C(26 °C)=−23909.2±6.7 J/g

(3) 2,4,6-Tris(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine **Triazine III**
$C_9H_6O_{15}N_9F_3(c)+2.25\ O_2(g)+298.5\ H_2O(liq)$
$\rightarrow 9\ CO_2(g)+4.5\ N_2(g)+3[HF+100\ H_2O](liq)$
ΔU °C(26 °C)=−7177.4±2.9 J/g

(4) 2,4-dimethoxy-6-(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine **Triazine IV**
$C_7H_8O_7N_5F(c)+5.25\ O_2(g)+96.5\ H_2O(liq)$
$\rightarrow 7\ CO_2(g)+2.5\ N_2(g)+[HF+100\ H_2O](liq)$
ΔU °C(26 °C)=11566.2±4.9 J/g

(5) 2-Methoxy-4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine **Triazine V**
$C_8H_7O_{11}N_7F_2(c)+3.75\ O_2(g)+197.5\ H_2O(liq)$
$\rightarrow 8\ CO_2(g)+3.5\ N_2(g)+2[HF+100\ H_2O](liq)$
ΔU °C(26 °C)=−8716.6±5.6 J/g

(6) 2-Amino-4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine **Triazine VI**
$C_7H_6O_{10}N_8F_2(c)+3\ O_2(g)+198\ H_2O(liq)$
$\rightarrow 7\ CO_2(g)+4\ N_2(g)+2\ [HF+100\ H_2O](liq)$
ΔU °C(26 °C)=−8041.1±2.4 J/g

The enthalpies of combustion have been combined with the enthalpies of formation of carbon dioxide [19], water [19], and aqueous hydrofluoric acid [20] to obtain the enthalpies of formation. A summary of the experimental heats of combustion and the derived values for heats of formation is given in table 12.

Table 12. Summary of the experimental and derived values.

Convenient Name	Chemical Name	ΔU °C (26 °C) kJ/mol	ΔH °C (25 °C) kJ/mol	ΔH °F (25 °C) kJ/mol
Triazine I	2,4,6-Trimethoxy-1,3,5-triazine	−18524.30±0.26[a]	−3168.69±.83	−478.60±.87
Triazine II	2,4,6-Triethoxy-1,3,5-triazine	−23909.24±1.56	−5100.31±1..43	−584.99±1.50
Triazine III	2,4,6-Tris(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine	−7177.40±0.62	−3827.60±1.21	−1109.80±1.53
Triazine IV	2,4-dimethoxy-6-(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine	−11566.17±0.69	−3380.24±1.00	−697.08±1.15
Triazine V	2-Methoxy-4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine	−8716.63±2.53	−3599.66±2.30	−907.71±2.40
Triazine VI	2-Amino-4,6-bis(2-fluoro-2,2-dinitroethoxy)-1,3,5-triazine	−8041.10±1.34	−3197.82±1.36	−773.12±1.50

[a] Actual temperature 28 °C for Triazine I.

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