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HEAT OF COMBUSTION OF EXPLOSIVE SUBSTANCES

by
Gebhard Stegeman

Report OSRD No. 5306

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NATIONAL DEFENSE RESEARCH COMMITTEE
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HEAT OF COMBUSTION OF EXPLOSIVE SUBSTANCES

Service Project: OD-01

Endorsement (1) From Dr. Ralph Connor, Chief, Division 8 to Dr. Irvin Stewart, Executive Secretary of the National Defense Research Committee.

Forwarding report and noting:

"This report presents data on the heats of combustion of twenty-one explosive compounds and two non-explosive materials. From these data, heats of formation at constant pressure are calculated. In comparing these data with values in the literature for the same or related compounds, it should be borne in mind that the latter figures are most often given for the constant volume process.

"The quality of the experimental determinations was excellent, and in most cases the compounds studied were in a satisfactory state of purity. It is believed that the values herein reported are quite reliable."

This is the final report under Contract OEMsr-754 with the University of Pittsburgh.

HEAT OF COMBUSTION OF EXPLOSIVE SUBSTANCES^aPurpose of the Investigation:

The measurements described in this report were made to obtain satisfactory thermal data for compounds of interest in the development of high explosives.

Description of the Calorimeter:

The calorimeter used for the reported measurements was patterned after the one developed by Dickinson¹. It is described in two articles by Clarke and Stegeman². Briefly, it may be stated that an outside bath of about 30 liters capacity is used to provide constant temperature surroundings. The temperature is maintained at a constant value to within $\pm 0.002^{\circ}\text{C}$. It is provided with two stirrers which circulate the water in the bath and also pump a continuous stream of water through the hollow cover. This provides a constant temperature condition on all sides of the calorimeter itself. An inner well, made of brass holds the calorimeter container in which the combustion bomb is held and about 2,200 g. of water. A separate stirrer circulates the water continuously around the bomb.

An Emerson double-valved bomb of 516 ml. capacity constitutes the combustion chamber. It is provided with a gold lining and gold plated electrodes. The substance to be burned is placed in a platinum cup weighing about 15 grams.

a Grateful acknowledgement is made to Theodore H. Clarke for his assistance on this project.

1. Dickinson, Bull. Bur. Standards 11, 243 (1915)
2. Clarke and Stegeman, J.A.C.S. 61, 1726 (1939)
Clarke and Stegeman, J.A.C.S. 66, 457 (1944)

The temperature measurements were made by the use of a platinum resistance thermometer, standardized by the Bureau of Standards. A White double potentiometer and an H.S. galvanometer, both supplied by the Leeds and Northrup Company, were used to measure the resistances. The measuring devices were sufficiently sensitive so that a temperature change of about 0.0001°C could be detected. The precision obtained in measurements of the combustion of substances which burn readily and completely, is about $\pm 0.01\%$. Any additional details of the operation of the calorimeter may be obtained from the publications to which reference has already been made. Table I of the appendix contains the record of the standardization of the calorimeter by the use of benzoic acid furnished by the Bureau of Standards. To check the standardization, a standard sample of sucrose also furnished by the Bureau was burned in the calorimeter and a satisfactory value for the heat of combustion was obtained.

Nature of the Samples Burned:

All samples for combustion were furnished by D. P. MacDougall of the Explosives Research Laboratory at Bruceton, Pa. No attempt was made to improve the purity of the samples and it is not known that this was necessary. Densities of the various substances were supplied in most cases, and when they were lacking an approximate value was obtained in this laboratory. A precise value of the density was not essential as its only use was to make a weight correction for the sample to a vacuum basis.

Samples were prepared by grinding in a mechanically driven agate mortar. Compounds insoluble in water were ground under water to a fine state of subdivision and then dried in a desiccator.

[REDACTED]

Pellets were then made in a special press. All weighings were made on both arms of the balance to eliminate any errors due to differences in the length of the balance arms. Heat capacity values which are used in the calculations were not available in most cases and on the advice of MacDougall an approximate value of 0.30 cal. per gram was used. An error in the heat capacity has little influence on the results. Since the compounds burned contained some nitro groups, some nitric acid was always formed in the combustion and the proper correction for the extra heat developed was always made. Some of the compounds left slight residues which affected the precision of the measurements somewhat, but usually this was a negligible quantity. Table II is a record of the essential data on one of the samples showing how the derived values were obtained.

The number of combustions for each sample varied somewhat depending on the precision obtained, but in most cases a satisfactory check was obtained from three determinations.

Table III(a) contains a list of the compounds investigated.

Table III(b) contains a summary of the combustion values, and the derived values.

Summary:

This report covers the determination of the heat combustion of 23 compounds of interest in the field of high explosives. All samples were provided by the Explosives Research Laboratory at Bruceton. Some typographical and arithmetical errors found in the previously submitted reports have been corrected.

TABLE I

Standardization of Calorimeter

(40 atmospheres initial oxygen pressure)

N.B.S. Benzoic acid #39e	$S_B^* = 2762.16 \text{ cal./}^\circ\text{C}$
N.B.S. " " #39f	$S_B^* = 2762.39 \text{ cal./}^\circ\text{C}$
Heat Equivalent of Calorimeter (S_B) = $2762.28 \pm 0.12 \text{ cal./}^\circ\text{C}$ ($\pm 0.004\%$)	

Check of energy equivalent using N.B.S. sucrose sample #17

Value determined = 3939.12 cal./g.

N.B.S. listed value = 3939.35 cal./g.

*Procedure and symbols used follow those recommended by Washburn, Bureau of Standards, J. of Research 10, 525 (1933).

Density Measurements

Where necessary, the densities were measured in order to correct the weight of sample to mass in vacuum. Checks against some known substances indicate the densities are correct to within 1%.

TABLE II

Heat of Combustion of Sample: NB-251-12A (Ammonium picrate)

Deter- mina- tion number	Mass of sample in grams	Corrected tempera- ture rise	Heat evolved by iron wire in cal.	Heat evolved by nitric acid in cal.	Heat evolved by igniter in cal.	$-\Delta U_{B/M}$ in cal. at 298°K
1	2.81879	2.8465°C.	17.60	14.70	82.29	2756.63
2	2.79006	2.8174°C.	17.60	15.08	82.58	2755.95
3	2.80717	2.8329°C.	17.60	15.25	77.78	2756.02
Average				2756.20		
				$\pm .4$ cal.		
				$= \pm .015\%$		

Initial oxygen pressure = 40 atms.
 Heat equivalent of calorimeter = 2762.3 cal.
 Molecular weight of compound = 246.14
 Density of Compound = 1.717 g/me
 Heat capacity per gram, C_p = 0.30 (assumed)

$$\text{Heat evolved in the combustion} = S_B \times \Delta t + S_i(t_{25} - t_i) + S_f(t_f - t_{25})$$

S_B = Heat equivalent of the calorimeter

$$S_i = 6.889 + MC_p = 7.731$$

$$S_f = 7.915 - 34n \text{ HNO}_3 = 7.8795$$

$$(t_{25} - t_i) = 2.2357^\circ\text{C}$$

$$(t_f - t_{25}) = 0.5972^\circ\text{C}$$

S_i = Heat capacity of water, oxygen and sample in the bomb initially

S_f = Heat capacity of water, oxygen and CO_2 after combustion

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Calculation for Determination No. 3

Total heat evolved = $(2762.28 \times 2.8329) + (7.731 \times 2.2357) + (7.8795 \times 0.5972) = 7,847.25$ cal.

Heat evolved by sample = $7,847.25 - (17.60 + 15.25 + 77.78) = 7736.62$ cal. -

$\Delta U_B/M =$

$$\frac{7736.62}{2.80717} = 2,756.02 \frac{\text{cals}}{\text{gm.}}$$

Calculation of the Uncertainty in the Values of the Measurements

Calculation of the assigned errors for a series of measurements followed the procedure outlined by Rossini: (Chem. Reviews 18, 256 (1936)).

Precision error = $\pm \sqrt{e^2 + c^2 + b^2}$ where

e = error in the heat of combustion of benzoic acid

c = " " " standardization of the calorimeter

b = " " " heat of combustion of the unknown

e, c, b are calculated by the use of the relation:

$$\% \text{ error} = \pm 100 \frac{2\sqrt{e^2 + c^2 + b^2}}{\text{value of reaction energy}}$$

This gives an assigned error somewhat larger than the probable error, but is a more conservative value.

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Calculation of Derived Values

$$\begin{aligned} -\Delta U_{B/M} &= 2756.20 \pm .4 \text{ cal/g.} \\ -\Delta U_B &= 2756.20 \times 246.14 &= 678.411 \text{ K, cal./mole} \\ -\Delta U_R &= 678.411 - 1.284 \text{ (Washburn cor.} &= 677.127 \text{ " " "} \\ &\quad \text{to 1 atm.)} \\ -\Delta H_R &= 677.127 - 2.368 \text{ (}\Delta n \text{ RT cor.)} &= 674.759 \text{ " " "} \end{aligned}$$

For the reaction $C_6H_6O_7N_4 + 4O_2 = 6CO_2 + 3H_2O + 2N_2$

$$-\Delta H \text{ for } 6 CO_2 = 6(94,476) = 566,856 \text{ cal}$$

(from diamond)

$$-\Delta H \text{ for } 3H_2O = 3(68,313) = 204,939 \text{ cal}$$

Total 771,795 cal

$$-\Delta H_f = 771,795 - 674,759 = 97.04 \text{ K.cal./mole}$$

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TABLE III(a)

Compilation of Compounds Investigated

Compound Number	Code Number	Name of Compound	Date of Investigation
1*	- - - - -	Trinitrotoluene	1/3/43
2*	- - - - -	Tetryl	1/6/43
3	NB-251-12A	Ammonium Picrate	1/19/43
4	NB-251-12B	2,2-Dimethylpropane-1,3-diol dinitrate	1/22/43
5	NB-251-12C	Ethyltrimethylolmethane trinitrate Emmet	1/25/43
6	NB-251-14A	Tetramethylolcyclopentanone tetra- nitrate Fivonite	1/29/43
7	NB-251-13A	Tetramethylolcyclohexanone tetra- nitrate Sixonite	2/1/43
✓ 8	NB-251-12E	Dinitrodi(β -nitroxyethyl)oxamide NENC	2/2/43
9	NB-251-13E	Hexamethylenetetramine dinitrate	2/4/43
10	NB-251-13F	Nitroguanidine	2/5/43
11	NB-251-14B	Tetramethylolcyclohexanol penta- nitrate Sixolite	2/9/43
12	NB-251-15A	Dibentaerythritol hexanitrate DiPEHN	2/9/43
13	NB-251-14C	Dinitroethyleneurea DNEU	2/10/43
14	NB-251-12D	N-Nitro-N-methylhydroxyacetamide nitrate HYMAN	2/11/43

*Samples No. 1 and 2 were practice samples burned to ascertain the most desirable conditions for combustion.

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Table III(a) - cont'd.

Compound Number	Code Number	Name of Compound	Date of Investigation
15	R-758-A	Nitroguanidine	5/15/43
16	R-1661-B	Picric Acid	5/18/43
17	NB-251-34A	Cyclotetramethylenetetranitramine HMX	5/19/43
18	R-1710-B	Diethanolnitramine dinitrate DINA	5/21/43
19	- - - -	Diglycol distearate	2/7/44
20	- - - -	Diglycol dioleate	2/8/44
21	R-564-C	β (2,4,6-Trinitrophenylnitramino) ethyl nitrate Pentryl	2/10/44
22	CU-F-16 R-2303	N-Methyl-N- β -nitroxyethyl nitramine MeNENA	2/14/44
23	R-2175-A	Ethylenediamine dinitrate EDD	2/15/44

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TABLE III(b)

Compound Number	Mol Weight	$-\Delta U_{B/M}$	$-\Delta U_B$	$-\Delta U_R$	$-\Delta H_R$	$-\Delta H_f$
1	227.13	3598.67 ± 3.13	817.38	816.23	814.30	17.81
2	287.15	2930.39 ± 1.01	841.46	839.89	836.78	- 4.67
3	246.14	2756.20 ± .40	678.41	677.13	674.76	97.04
4	194.24	3694.24 ± 1.00	717.55	716.74	715.85	98.10
5	269.17	3078.10 ± 2.44	828.54	827.44	825.52	117.06
6	384.22	2843.99 ± 1.43	1092.71	1090.85	1087.60	172.57
7	398.24	3127.70 ± 1.33	1245.59	1243.67	1240.71	182.24
8	356.17	2003.91 ± 2.52	713.74	712.06	707.91	132.20
9	265.22	3571.93 ± 0.74	950.92	949.83	948.35	96.70
10	104.07	2005.51 ± 1.63	208.72	208.33	207.15	23.96
11	445.26	2900.94 ± 2.41	1291.67	1290.42	1286.72	170.39
12	524.28	2407.81 ± 1.38	1262.36	1259.98	1254.94	236.32
13	176.10	2202.97 ± 1.25	387.93	387.09	385.91	34.06
14	179.09	2127.22 ± 1.56	380.97	380.17	378.24	75.87
15	104.074	2011.96 ± 1.03	209.39	209.00	207.82	23.28
16	229.118	2637.21 ± 0.84	615.69	614.44	611.93	59.40
17	296.168	2254.93 ± 0.86	667.84	666.61	663.06	-11.90
18	240.136	2403.18 ± 0.38	577.09	576.06	573.69	77.46
19*	639.02	9072.99 ± 0.36				
20*	635.00	8001.74 ± 12.8				
21	362.18	2600.70 ± 1.22	941.95	940.05	935.91	24.84
22	165.11	2881.82 ± 0.76	475.82	475.17	473.84	48.68
23	186.13	2016.26 ± 0.79	375.29	374.70	373.22	117.29

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TABLE III(b) cont'd.

- $\Delta U_{B/M}$ = Heat of combustion in cal./g. for bomb process
- ΔU_B = Heat of combustion in K.cal./mole for bomb process
- ΔU_R = Heat of combustion in K.cal./mole at 1 atm. and constant volume
- ΔH_R = " " " " " " " " " " pressure
- ΔH_f = Heat of formation in K.cal./mole at standard conditions

All thermal values are calculated for 25°C. or 298.16K.

* Samples 19 and 20 did not have sufficient purity to warrant a calculation of the derived values.