Heats of Formation of 1,1,1-Trinitro-4,4-bisdifluoroaminopentane and 2-Fluoro-2,2-dinitroethanol by Combustion Calorimetry

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The energies of combustion of 1,1,1-trinitro-4,4-bisdifluoroaminopentane and 2-fluoro-2,2-dinitroethanol with diethyloxalate and diethylphthalate, respectively, as desensitizers were determined in a rotating bomb calorimeter. The standard heats of formation at 25° C. and 1 atm. were calculated to be −60.89 ± 0.37 kcal. per mole for 1,1,1-trinitro-4,4-bisdifluoroaminopentane and −114.15 ± 0.29 kcal. per mole for 2-fluoro-2,2-dinitroethanol. (±0.37 and ±0.29 kcal. per mole are the estimated standard deviations of the mean.)

THE combustions of 1,1,1-trinitro-4,4-bisdifluoroaminopentane (TDP) and 2-fluoro-2,2-dinitroethanol (FDE) were carried out in an oxygen atmosphere (at a pressure of 30 atm.) using diethyloxalate and diethylphthalate, respectively, as desensitizers. The heats of formation were calculated in their standard state at 25° C. and 1 atm. from the following equations of the idealized reactions:

$$C_5H_7O_6N_5F_4(s) + 2.75\ O_2(g) + 278.5\ H_2O\ (l) \rightarrow 5\ CO_2(g) + 4\ (HF \cdot 70\ H_2O)(l) + 2.5\ N_2(g) \text{ for TDP} \quad (1)$$

and

$$C_2H_3O_5N_2F + 49\ H_2O(l) \rightarrow 2CO_2(g) + HF \cdot 50\ H_2O(l) + N_2(g)\ (2) \text{ for FDE} \quad (2)$$

Since FDE contains enough oxygen and fluorine in its molecule to ensure complete combustion according to Equation 2, no oxygen gas appears in this equation. As the two compounds are sensitive explosives, they had to be desensitized by adding inert materials. To achieve clean combustion without explosion, approximately 70 wt. % of diethyloxalate was added to TDP and 25 wt. % of diethylphthalate to FDE. The ratios were determined in separate experiments.

EXPERIMENTAL

Materials. TDP was prepared (*8*), recrystallized several times, and checked for purity by melting point determination (39–40° C.). No impurity was detected by gas chromatography. FDE was prepared (*1*), vacuum distilled (2 mm. of Hg, b.p. 56° C.), crystallized from a solution of methylene chloride and pentane (1 to 1, by volume), and dried for 1 hour at 40° C. and 10 mm. of Hg. The final purity was estimated from the freezing curve (f.p. 10.5° C.) by a method developed by the National Bureau of Standards (*4*) and was better than 99.6%.

The vapor pressures of FDE were determined to ±0.1 mm. of Hg by the static method in the range of 40° to 100° C. The plot of log P cm. *vs.* $1/T_0K$ gave a straight line with the equation log $P = -2911/T + 8.320$. The heat of vaporization, calculated from the slope, is 13.30 kcal. per mole.

Diethyloxalate was distilled several times on a Todd Column and the purity estimated in the same way as FDE. The energies of combustion and formation, determined at this laboratory, were $\Delta E_c^\circ/M = -4882.83 \pm 0.47$ cal. per gram and $\Delta H_f^\circ = -192.03 \pm 0.07$ kcal. per mole, respectively. Diethylphthalate was distilled on a Todd Column and the 11th fraction was used for the combustion experiments (boiling point of 106° C. at 52 mm. of Hg). The energy of combustion and heat of formation were $\Delta E_c^\circ/M = -6416.58 \pm 0.84$ cal. per gram and $\Delta H_f^\circ = -179.99 \pm 0.19$ kcal. per mole, respectively. Benzoic acid was National Bureau of Standards standard sample 39h, with a certified energy of combustion of $\Delta E_c/M = 6317.88 \pm 0.72$ cal. per gram. Conversion from certified conditions to standard conditions gives $\Delta E_c^\circ/M = -6312.96 \pm 0.72$ cal. per gram.

Polypropylene film (Kordite Corp., Macedon, N. Y.) was used to hold the samples for combustion. The energy of combustion and heat of formation were $\Delta E_c^\circ/M = -11059.8 \pm 0.71$ cal. per gram and $\Delta H_f^\circ = -20.81 \pm 0.25$ kcal. per mole, respectively. The fuse was an unmercerized cotton thread with $\Delta E_c^\circ/M = -4050$ cal. per gram.

APPARATUS AND PROCEDURE

The combustion experiments were carried out in a rotating bomb calorimeter, laboratory designation BMR2 (*5*). The modifications to the bomb have been reported (*11*). The bomb was platinum lined, and the temperature of the jacket was held constant within ±0.002° C.

The average deviations from the mean in these measurements were 0.044 and 0.095% for TDP and FDE, respectively. The procedure was essentially the same as that reported previously (*12*).

ANALYTICAL

The combustion products were analyzed for carbon tetrafluoride, carbon monoxide, carbon dioxide, water, nitrous acids, and total acids. Neither carbon monoxide nor carbon tetrafluoride were detected. Recovery of carbon dioxide was better than 99%. No comparison experiments were conducted, since the heats of solution of CO_2 in HF nH_2O as reported by Cox and Head (*3*) were used for the data reduction to standard state.

Complete combustion of the fluorine compounds was evidenced by infrared analysis, titration of the water solution in the bomb, and absorption of CO_2 on Ascarite. Incomplete combustion runs, according to Equation 1, were rejected. The gaseous reaction products were passed through a train of Ascarite to absorb carbon dioxide and through magnesium perchlorate to absorb water. Then the remaining gases were condensed in a trap cooled with liquid nitrogen. Any

CF_4, CO, or oxides of nitrogen present were concentrated by distilling off the oxygen and could easily be detected after being transferred to an infrared cell. In all runs reported here, no fluorine gas was detected by the KI-starch solution, and no CF_4, CO, or oxides of nitrogen were found by infrared analysis.

RESULTS

Table I gives the energies of combustion and formation with other calorimetric data of TDP and FDE. To calculate the heats of formation of TDP and FDE, the heats of formation for $CO_2 = -94051.8$ cal. per mole, $H_2O = -68317.5$ cal. per mole, $HF \cdot 70H_2O = -76327$, and $HF \cdot 50H_2O = -76317$ cal. per mole were used. Calculations were made on a RCA digital computer for which a special program has been developed (2). The values of density, heat capacity, and $(\partial E/\partial P)_T$ used in the computations are listed in Table II.

As the heat evolution on mixing of the compounds with the desensitizing agents is very small, it was assumed to be zero. No quantitative measurements were made.

The heats of formation of TDP and FDE were estimated from the bond energies using the equation:

$$\Delta H_f = \Sigma_i n_i q_i + \Sigma_j (\Delta H_A)_j$$

Table I. Calorimetric Data

1,1,1-Trinitro-4,4-bisdifluoroaminopentane

Run No.	89229	89236	89248	89251	89254	89257
m'(cpd), g.	0.601310	0.596294	0.596765	0.604426	0.604033	0.602276
m''(diethyl oxalate), g.	1.246554	1.253476	1.169889	1.166598	1.212294	1.17619
m'''(propylene film), g.	0.040816	0.03462	0.042833	0.035469	0.034531	0.035917
m''''(fuse), g.	0.011059	0.009592	0.012945	0.01261	0.011083	0.010971
$n^i(H_2O)$, moles	0.55860	0.55549	0.55878	0.557348	0.55667	0.55549
$\Delta tc(t_fO - t_i - \Delta t_{corr})$, deg.	1.976787	1.963104	1.888628	1.870548	1.920701	1.880392
Δt_{corr}	0.025072	0.24250	0.024344	0.024173	0.023908	0.024248
ω(calor)($-\Delta tc$), cal.	−8177.87	−8121.26	−7813.16	−7738.36	−7945.84	−7779.09
ΔE_{ign}, cal.	0.953	0.993	1.03	0.910	1.03	1.11
ΔE, corr st. states, cal.	10.92	10.88	10.51	10.39	10.64	10.40
ΔE_{dec} (HNO_3), cal.	13.05	10.59	5.95	8.82	11.28	9.64
$n'' \Delta E°c$(d.oxalate), cal.	−6086.71	−6120.51	−5712.37	−5696.30	−5919.42	−5743.13
$n''' \Delta E°c$(poly. film), cal.	−451.41	−382.89	−473.72	−392.28	−381.90	−397.23
$n'''' \Delta E°c$(fuse), cal.	−44.79	−38.85	−52.43	−51.07	−44.89	−44.43
$n' \Delta E°c$(cpd.), cal.	−1597.57	−1582.12	−1581.80	1602.96	−1601.71	−1597.57
$\Delta E°c$(cpd)/M, cal./g.	−2652.56	−2653.26	−2650.63	−2652.04	−2651.69	−2652.56
ωi(cont)$(t_i - t_h)$	−24.77	−25.96	−24.98	−24.70	−25.38	−24.77
ωf(cont)$(t_h - t_f + \Delta t_{corr})$	0.34	0.38	0.33	0.33	0.35	0.34
$\Delta E°c$(cpd), kcal./mole	−820.03	−820.25	−819.43	−819.87	−819.76	−820.03
$\Delta H°c$, (cpd), kcal./mole	−817.21	−817.43	−816.62	−817.05	−816.94	−817.21
$\Delta H°f$(cpd), kcal./mole	−60.83	−60.61	−61.42	−60.99	−61.10	−60.83
Av.						
$\Delta E°c$(cpd)/M, cal./g.	−2652.36	±1.19[a]				
$\Delta E°c$(cpd), kcal./mole	−819.97	±0.36[a]				
$\Delta H°c$(cpd), kcal./mole	−817.15	±0.37[a]				
$\Delta H°f$(cpd), kcal./mole	−60.89	±0.37[a]				

2-Fluoro-2,2-dinitroethanol

	95520	95523	96126	96132	96147
m'(cpd), g.	1.916708	1.837016	1.859105	1.836885	1.842008
m''(diethyl phthalate), g.	0.570438	0.568510	0.562688	0.570759	0.575871
m'''(polypropylene film), g.	0.072229	0.076884	0.060116	0.082697	0.068302
m''''(fuse), g.	0.009092	0.008757	0.008668	0.008892	0.009422
$n^i(H_2O)$, moles	0.55435	0.55954	0.55398	0.55515	0.55713
$\Delta tc(t_f - t_i - \Delta t$ corr.), deg.	1.750647	1.732592	1.686822	1.750898	1.723036
Δt corr	0.023199	0.023435	0.022594	0.023283	0.023376
ω(calor.)($-\Delta tc$), cal.	−7243.13	−7168.43	−6979.06	−7244.16	−7128.89
ΔE_{ign}, cal.	1.23	1.27	1.15	1.19	1.23
ΔE, corr. st. states, cal.	12.95	12.72	12.56	12.73	12.67
ΔE_{dec}(HNO_3), cal.	14.92	13.88	14.07	15.06	15.90
$n'' \Delta E°c$(d.phthalate), cal.	−3660.26	−3647.89	−3610.53	−3662.32	−3695.12
$n''' \Delta E°c$(poly. film), cal.	−798.83	−850.32	−664.87	−914.61	−755.40
$n'''' \Delta E°c$(fuse), cal.	−36.82	−35.46	−35.10	−36.01	−38.16
$n' \Delta E°c$(cpd), cal.	−2740.81	−2629.50	−2662.63	−2624.96	−2632.82
ωf(cont)$(t_i - t_h)$	−23.67	−23.00	−22.17	−23.03	−22.72
ωf(cont)$(t_h - t_f + \Delta t_{corr})$	0.96	0.39	0.33	0.30	0.30
$\Delta E°c$(cpd)/M, cal./g.	−1429.96	−1431.40	−1432.21	−1429.03	−1429.32
$\Delta E°c$(cpd), kcal./mole	−220.30	−220.52	−220.65	−220.16	−220.20
$\Delta H°c$(cpd), kcal./mole	−218.52	−218.74	−218.87	−218.38	−218.42
$\Delta H°f$(cpd), kcal./mole	−114.22	−114.00	−113.87	−114.36	−114.31
Av.					
$\Delta E°c$(cpd)/M, cal./g.	−1430.38	±1.37[a]			
$\Delta E°c$(cpd), kcal./mole	−220.37	±0.295[a]			
$\Delta H°c$(cpd), kcal./mole	−218.59	±0.295[a]			
$\Delta H°f$(cpd), kcal./mole	−114.15	±0.295[a]			

[a] Mean standard deviation.

Table II. Values of Density, Heat Capacity, and $(\partial E/\partial P)_T$ of TDP, FDE and Auxiliary Materials

Compound	Density, Gram/Cc.	Heat Capacity, C_P Cal./G./° C.	$(\partial E/\partial P)_T$, Cal./Atm.-G.
TDFP	1.687	0.21 est.[a]	–0.006 est.
FDNOL	1.60	0.21 est.	–0.006 est.
Diethyl oxalate	1.079 (7)	0.43 est.	–0.006 est.
Diethyl phthalate	1.123 (7)	0.43 est.	–0.006 est.
Benzoic acid	1.32 (5)	0.289 (5)	–0.0028 (5)
Fuse	1.5 (9)	0.40 (9)	. . .
Polypropylene film	0.9	0.135	–0.008 est.

[a] Estimated.

where n_i and q_i are the n numbers and the bond energy of the ith bond in the molecule and $(\Delta H_A)_j$ the heat of formation of the jth gaseous atom produced by complete decomposition of the compound. The following bond energies: E(C—C)(*10*) = 85.5 kcal. per mole, E(C—N)(*6*) = 67.4 kcal. per mole, $E(NO_2)$ = 212 kcal. per mole (*12*), E(N—F) = 67.0 kcal. per mole (*6*), E(C—H)(*6*) = 99.29 kcal. per mole, E(C—F) = 107.0 kcal. per mole, E(C—O)(*10*) = 85.8 kcal. per mole, and E(O—H)(*10*) = 110.6 kcal. per mole and the dissociation energy values reported by Wilkins (*10*) were used in the calculations. The value for C—F was calculated from the measured heat of formation of fluorotrinitromethane (*12*) assuming that the C—F bond in the two molecules, fluorotrinitromethane and FDE, are the same. The calculated heat of formation of TDP is –59.37 kcal. per mole and is in agreement with the measured value of –60.89 kcal. per mole. The calculated heat of formation of FDE is –106.3 kcal. per mole and not in as good an agreement with the measured value of –114.15 kcal. per mole. The observed discrepancy between the calculated and measured values of FDE may be accounted for by the gem position of the fluoro and nitro groups.

NOMENCLATURE

m = mass of compound, gram
n = number of moles of compound
n^i = initial number of moles
t_f = final temperature of calorimeter in degrees Celsius
t_i = initial temperature of calorimeter
t_h = reference temperature to which the combustion reaction is referred
Δt_{corr} = rise in temperature of the calorimeter due to thermal leakage of the outer jacket
Δtc = $t_f - t_i - t_{\text{corr}}$
ω^i(cont) = sum of heat capacities of contents in the bomb due to initial conditions of the bomb before ignition
ω^f(cont) = sum of heat capacities of contents in the bomb due to final conditions of the bomb
ΔE, corr. st. states = Washburn corrections
Σ(calor) = calibration of the calorimeter or heat capacity, cal. per deg.
ΔE_{dec} (HNO_3) = energy released from the formation of nitric acid, cal.
ΔE_{dec} (AS_2O_5) = energy released from the formation of AS_2O_5, cal.
ΔE_{ign} = energy released due to ignition, cal.
ΔEc = energy of combustion of compound at constant volume, kcal. per mole
ΔHc = heat of combustion of compound at constant pressure, kcal. per mole
ΔH_f = heat of formation of compound, kcal. per mole
$n''\Delta Ec$(d.oxalate) = energy released from the diethyl oxalate burned in experiment. Similar notations represents energy released for other materials burned in experiments

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