Enthalpy of Formation of Bis(2-fluoro-2,2-dinitroethyl)amine

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The enthalpy of formation of bis(2-fluoro-2,2-dinitroethyl)amine was determined by combustion calorimetry using a platinum-lined rotating-bomb calorimeter. To desensitize and ensure complete combustion, the compound was burned with an auxiliary material, diethylphthalate. The enthalpy of formation (c,298.15°K) was determined to be −126.952 ± 0.49 kcal/mol.

The enthalpy of formation of bis(2-fluoro-2,2-dinitroethyl)-amine (BFDNA) was determined by combustion calorimetry, using a platinum-lined rotating-bomb calorimeter. A mixture of approximately 55/45 wt % of BFDNA to diethylphthalate (DEP) was burned in an oxygen atmosphere (30 atm pressure). After a series of preliminary runs on a Parr stationary adiabatic-bomb calorimeter, this ratio was selected to produce a smooth and clean combustion. Since BFDNA was considered shock sensitive, the DEP also served as a desensitizer. The enthalpy of formation (d, 298.15°K) was determined from the following idealized equation at 1 atm:

$$C_4H_5O_8N_5F_2(c) + 0.75\ O_2(g) + 118.5\ H_2O(l) \rightarrow 4\ CO_2(g) + 2\ HF\cdot 60\ H_2O(l) + 2.5\ N_2(g)$$

EXPERIMENTAL

Apparatus. The combustion experiments were carried out in a platinum-lined rotating-bomb calorimeter, built according to a design of the Bureau of Mines, Bartlesville, Okla. (*7*). The modifications to the original instrumentation, and the basic procedure were as previously reported (*16*) with the exception that the platinum resistance thermometer and Mueller bridge were replaced by a quartz crystal thermometer with a resolution of 0.0001°C coupled to a digital clock recorder. With this arrangement, time and temperature could be recorded automatically at predetermined intervals throughout the run.

The thermometer-probe was calibrated (by Dymec Division, Hewlett Packard, Palo Alto, Calif.) against a reference thermometer in a variable-temperature bath. The probe was placed in well-stirred temperature-controlled liquid baths. Use of stirred liquids as calibrating mediums with large volumes eliminated heat-transfer effects. The liquids used were alcohol at low temperatures, water at medium temperatures, and oil at high temperatures. The probe was connected to an oscillator, and its outputs were scanned and measured by a quartz thermometer. A strip chart recorder was used to verify stabilization of the baths at each temperature setting. Nine calibration temperatures were used, ranging from −80–+240°C in 40° steps. The calibration baths were monitored by a transfer standard calibrated against an NBS-certified platinum resistance thermometer and a Mueller bridge. The transfer standard was regularly checked for drift in a triple-point cell and in a certified tin freezing-point standard, and drift against the freezing point of triple-distilled mercury. If excessive drift was noted, the transfer standard could be recalibrated against the certified thermometer. These checks, plus the short-term stability of the temperature-controlled baths, achieved a calibration accuracy of 0.02°C relative to NBS at all nine points. The internal volume of the rotating bomb was 0.346 liter.

The density measurements of DEP were made with a 5-ml Guy-Lussac pycnometer calibrated with distilled water. DEP was distilled through a 14-in. glass bead column and collected on a water condenser. The complete apparatus was assembled at this station.

The heat of mixing of BFDNA and DEP was determined in a specially designed calorimeter that contained an internal volume of 4 cc surrounded by an outer water jacket which held 4.5 cc of water. The whole unit was insulated from the outside. The temperature of the water jacket was taken with an iron constantan thermocouple calibrated against a precalibrated thermometer. One thermocouple terminal was immersed in an ice bath and the other in water whose temperature was varied over the range of 20–40°C in 5° steps. The temperature change for the thermocouple calibration and heat of solution measurements were recorded by a portable-precision potentiometer that read directly to 0.02 mV.

Procedure. BFDNA and DEP were sealed in a polypropylene bag resistant to organic halides. Quantities of approximately 55/45 wt % of BFDNA to DEP gave a temperature rise of approximately 1.8°C in the calorimeter. The bag was placed in a platinum crucible in the bomb. Ten cc of distilled water was placed in the bomb that was assembled, purged, pressurized to 30 atm with oxygen, and then submerged in a weighed quantity of water into the calorimeter bucket, which, in turn, was placed in a constant-temperature jacket. When the temperature of the bucket reached a predetermined value calculated to obtain a final bucket temperature slightly below the jacket temperature of 25°C, the mixture was ignited by a thread connected to a heated wire and polypropylene bag. Following ignition, the bomb was rotated to ensure a uniform final state of the products. The temperature was recorded at 1-min intervals 10 min before ignition and 25 min after ignition with predetermined time intervals for the rate of change in the temperature.

Materials. BFDNA was obtained from H. G. Adolph, U. S. Naval Ordnance Laboratory, White Oak, Md., and prepared from 2-fluoro-2,2-dinitroethylamine, extracted from an ice solution as a solid, filtered off, and recrystallized from chloroform (*1*).

Anal. Calcd. for $C_4H_5F_2N_5O_8$: C, 16.61; H, 1.74; F, 13.14; N, 24.22; mol wt, 289. Found: C, 17.0; H, 1.70; F, 13.2; N, 24.2; mol wt, 285 (in $CHCl_3$).

Principal infrared bands (liquid film) appeared at 3400 (N—H), 1600, 1315 (NO_2), 852, 805 cm^{-1}; nmr (in $CDCl_3$, δ relative to TMS) 4.13 (double doublet, $J_{HF} = 17$ cps, $J_{NH-H} = 7.5$ cps), 2.12 (broadened quintet); area ratio 4:1.

Diethylphthalate was a commercial grade distilled several times and the distillate's boiling point determined after each distillation until a constant boiling point of 297°C was reached. DEP has a reported value of 296.1°C (*8*). The refractive index was determined to be $n^{20}{}_D = 1.5019$ which is in agreement with the value found in literature (*8*). An elemental analysis of the purified material was also determined and was in agreement with the theoretical formula within limits of the apparatus as the following shows.

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Anal. Calcd. for $C_{22}H_{14}O_4$: C, 64.85; H, 6.35; O, 28.80; mol wt, 222, 243. Found: C, 65.13; H, 6.35; O, 28.63.

The energy of combustion was determined to be $\Delta E_c°/M = -6411.26 \pm 1.66$ cal/g at this laboratory (mean and standard deviation of the mean for 6 runs).

Benzoic acid, NBS sample 39i was used to calibrate the calorimeter. The benzoic acid has a heat of combustion of 26.434 ± 0.003 abs kJ/g under certified conditions. Conversion to standard conditions (*9*) gives $\Delta E_c°/M = -63212.96 \pm 0.72$ cal/g.

Polypropylene film was burned in the calorimeter and its energy of combustion determined at this station to be $\Delta E_c°/M = -11083.14 \pm 1.66$ cal/g (mean and standard deviation for 8 runs). Elemental analysis showed that the actual and theoretical formulas were in agreement within the limits of the apparatus.

Anal. Calcd. for C_3H_6: C, 85.63; H, 14.37; mol wt, 42.081. Found: C, 85.39; H, 14.34.

The fuse used to ignite the materials was a commercial grade of cotton thread with an energy of combustion, $\Delta E_c°/M = -4040$ cal/g (*13*) with an empirical Formula of $C_1H_{1.744}O_{0.884}$.

Analytical. Complete combustions were evidenced by ir analysis, titration of the acid solution, and absorption of carbon dioxide on ascarite. Runs 23911 and 23913 were rejected owing to incomplete combustion. The gaseous reaction products were passed through a train of magnesium perchlorate and ascarite to absorb water and carbon dioxide. The carbon dioxide recovery was 99.7% or better of the theoretical value on the runs tested. Gas samples were taken directly from the bomb without passing through any type of absorbent and were analyzed by ir spectra. There was no indication of gases other than CO_2, N_2, and O_2 (N_2 and O_2 cannot be detected by ir spectra). The NO_3^- was reduced to ammonia by Devarda's alloy distilled into excess standardized HCl. The total acidity of the bomb washings was determined by titration with NaOH after carbon dioxide had been removed by boiling, using phenolphthalein as an indicator.

Units of Measurements and Auxiliary Quantities. All data reported are based on the 1961 atomic weights (*4*) and the 1963 fundamental constants and definition of the thermodynamic temperature scale and of the thermochemical calories; 1 cal = 4.184 (exactly)abs J (*5*).

Table I. Density, Heat Capacity, and $(\partial E/\partial P)T$ for Bis(2-fluoro-2,2-dinitroethyl)amine and Auxiliary Materials

	Density, g/ml	C_p, cal/deg g	$(\partial E/\partial P)T$, cal/atm g
BFDNA	1.72[a]	0.2[b]	−0.006[b]
DEP	1.123[c]	0.4[b]	−0.006[b]
Polypropylene	0.9[d]	0.315[b]	−0.008[b]
Thread	1.5[e]	0.4[f]	−0.007[g]

[a] Determined by H. G. Adolph, Naval Ordnance Laboratory, White Oak, Md. [b] Estimated. [c] (*8*). [d] Determined by authors. [e] (*11*). [f] (*12*). [g] (*10*).

The physical properties of the compound and auxiliary material are listed in Table I. The calorimeter was calibrated with benzoic acid, NBS sample 39i, and ξ(calor) was determined to be 4115.46 ± 0.58 cal/deg (mean and standard deviation for nine calibration experiments).

RESULTS AND DISCUSSION

The enthalpies of formation of fluoronitro compounds by combustion calorimeter have been determined by dissolving in such compounds as diethylphthalate and diethyl oxalate (*2*). In many cases incomplete combustion will occur when these compounds are burned alone. The desensitizing compound should completely dissolve the compound, if possible, for better combustion. Since fluoronitro compounds are considered shock sensitive, the desensitizers produce safer burns, reduce bomb damage when ignition occurs, and reduce safety problems in handling.

Several trial runs were conducted with BFDNA and DEP solutions in Parr stationary adiabatic-bomb calorimeter before conducting runs in the platinum-lined rotating-bomb calorim-

Table II. Summary of Calorimetric Data for Bis(2-fluoro-2,2-dinitroethyl)amine

Run no.	23907	23908	23909	23910	23912	23914
m'(cpd), g	0.693531	0.719120	0.732260	0.827798	1.042638	1.099686
m''(diethylphthalate), g	0.824776	0.855059	0.851760	0.930882	1.009963	0.995492
m'''(polypropylene film), g	0.050834	0.057119	0.048397	0.049238	0.043533	0.053366
m''''(fuse), g	0.008506	0.008106	0.008406	0.008261	0.008616	0.008586
$n^i(H_2O)$, moles	0.54704	0.56437	0.55465	0.55654	0.55670	0.56037
$\Delta t_c(t_f - t_i - \Delta t_{corr})$, deg	1.72846	1.80301	1.78035	1.94644	2.14694	2.17425
Δt_{corr}	0.02754	0.02459	0.02505	0.02496	0.02386	0.02555
$\xi(\text{calor})(-\Delta t_c)$, cal	−7113.41	−7420.22	−7326.96	−8010.49	−8835.64	−8948.04
ξ^i(cont), cal	−22.63	−24.30	−23.56	−25.79	−28.68	−29.18
ξ^f(cont), cal	0.71	0.84	0.70	0.63	0.77	0.75
ΔE (solution)	0.65	0.65	0.65	0.65	0.65	0.65
ΔE_{ign}, cal	0.87	0.87	0.87	0.87	0.87	0.87
ΔE_{corr} ss, cal	9.16	9.75	5.61	10.64	12.40	12.66
$\Delta E_{dec}(HNO_3)$, cal	21.18	21.18	21.11	27.84	19.55	19.48
$n''\Delta E_c°$(diethylphthalate), cal	−5287.86	−5482.01	−5460.86	−5968.13	−6475.14	−6382.36
$n'''\Delta E_c°$(propylene film), cal	−563.40	−633.06	−536.39	−545.71	−482.48	−591.46
$n''''\Delta E_c°$(fuse), cal	−34.51	−32.88	−34.10	−33.51	−34.95	−34.83
$n'\Delta E_c°$(cpd), cal	−1217.48	−1263.04	−1286.02	−1448.08	−1837.27	−1933.94
$\Delta E_c°$(cpd)/M, cal/g	−1755.48	−1756.36	−1756.23	−1749.32	−1762.14	−1758.63
$\Delta E_c°$(cpd), kcal/mol	−507.525	−507.782	−507.744	−505.745	−509.451	−508.438
$\Delta H_c°$(cpd), kcal/mol	−504.118	−504.375	−504.337	−502.338	−506.044	−505.031
$\Delta H_f°$(cpd), kcal/mol	−127.208	−126.951	−126.989	−128.988	−125.282	−126.295
Averages						
$\Delta E_c°$(cpd)/M, cal/g	−1756.34 ± 1.72[a]					
$\Delta E_c°$(cpd), kcal/mol	−507.781 ± 0.49					
$\Delta H_c°$(cpd), kcal/mol	−504.374 ± 0.49					
$\Delta H_f°$(cpd), kcal/mol	−126.952 ± 0.49					

[a] Standard deviation of the mean.

eter. These runs determine the proper ratio of compound to DEP, approximate the heat released for initial temperature settings on the rotating-bomb calorimeter, and test for ignitability and combustion of these solutions. Such trial runs could be conducted on the rotating-bomb calorimeter, but, if there is a detonation, the damage will be less severe in the stationary bomb.

Since the quantity of BFDNA was limited, small amounts were used to determine the heat of solution with DEP. One gram of BFDNA to 1 gram of DEP was mixed in the special calorimeter described under Apparatus. For the quantities used in the experiment, there was a cooling effect of approximately 0.65 calorie for the solution. This calorie change is included in the calculations shown in Table II.

All data reduction was performed on a digital computer (*3*). To correct for the heat of solution of CO_2 in the hydrofluoric acid solutions, the data of Cox and Head (*6*) were used. Heats of formation used were $CO_2(g) = -94{,}051$ cal/mol; $H_2O(l) = -68{,}317.5$ cal/mol (*14*).

The uncertainties assigned to gaseous carbon dioxide liquid water are 0.011 and 0.0144, respectively (*15*).

NOMENCLATURE

m = mass of (′) compound, (″) auxiliary material, (‴) polypropylene film, and (⁗) fuse in grams
n = number of moles of (′) compound, (″) auxiliary material, (‴) polypropylene film, and (⁗) fuse
n^i = initial number of moles of water in bomb
t_i = initial temp of calorimeter, °C
t_f = final temp of calorimeter, °C
t_h = ref temp to which combustion reaction is referred (25°C)
Δt_{corr} = rise in temperature of calorimeter because of thermal leakage of outer jacket
$\Delta t_c = t_f - t_i + \Delta t_{corr}$
ξ(calor) = energy equivalent of calorimeter, cal/deg
ξ(cont) = energy equivalent of contents, cal/deg [ξ^i (cont)$(t_i - 25) + \xi^f$ (cont)$(25 - t_f + \Delta t_{corr})$ where ξ^i (cont) and ξ^f (cont) are energy equivalents of contents before and after combustion, respectively]
ΔE_{ign} = energy released because of ignition, cal
$\Delta E_{corr\ ss}$ = energy reduction to standard states, cal (*10, 13*)
$\Delta E_{dec}(HNO_3)$ = energy released from formation of nitric acid, cal
ΔE(solution) = energy released because of mixing of BFDNA and DEP before loading bomb
$\Delta E_c°$ = standard energy of idealized combustion reaction, cal/mol
$\Delta H_c°$ = standard heat of combustion of compound at constant pressure, kcal
$\Delta H_f°$ = enthalpy of formation of BFDNA, kcal/mol

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Refractive Index of Pure Water for Wavelength of 6328 Å at High Pressure and Moderate Temperature

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The refractive index is one of the optical properties that can be used to study the short-range molecular interaction in solid, liquid, and gaseous materials at high pressure. The refractive index of liquid water at elevated pressures has been investigated and reported by Rosen (*2*) and more recently by Waxler and Weir (*5*), and Waxler et al. (*6*) who have analyzed their results in terms of molecular effects. The results reported here are absolute refractive index measurements at pressure and for a wavelength of 6328 Å, using a different experimental technique. They supplement the results of Rosen (*2*), Waxler and Weir (*5*), and Waxler et al (*6*).

EXPERIMENTAL

Instrumentation. The refractive index is measured by an interferometer of the Fabry-Pérot type (*1*) that has been modified for use in a pressure vessel. Figure 1 is a simplified diagram of the interferometer which consists of two 5-mm diameter gold-surfaced half mirrors (*B*) held rigidly in a housing of titanium (*D, E*) with the gold surfaces facing inward and separated by a hollow cylindrical spacer of titanium (*C*), 2.9566 mm length (which is also the liquid sample length or thickness). The mirror surfaces are not exactly parallel so that the inter-