phate system or with the value 0.3 given by Davies *(7)* for 1:1, 1:2, and 2:1 electrolytes.

The physicochemical relationships used in the computation describe a model somewhat different from the model described by the measurements. Thus, plots of log total phosphorus concentration vs. calculated values of pH for the several series of solutions form a family of sigmoid curves, whereas plots of the observed values of pH form a family of smooth parabolic arcs that approach pH 7 at infinite dilution. The difference in shapes of the curves is attributed, at least in part, to the use of an expression for the activity coefficient that contained the Debye-Hückel relationship and only one additional adjustable parameter, a form used by Davies *(7)*; Farr and Elmore *(10)* successfully used three adjustable parameters in adapting the Debye-Huckel relationship to their data. Moreover, in the single-ion activity coefficient expression used in our computer program, the ionic size, å, was fixed at 5Å for all polyphosphate species. This constant probably is not correct for all polyphosphate species, since å by definition is an adjustable parameter.

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Received for review May 12, 1972. Accepted October 13, 1972. More detailed methods for calculations including Tables VII and VIII will appear following these pages in the microfilm edition of this volume of the Journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D.C. 20036. Refer to the following code number: JCED-73-24. Remit by check or money order $4.00 for photocopy or $2.00 for microfiche.

Enthalpies of Formation of Some Fluorodinitroethyl Derivatives and 2,2′,4,4′,6,6′-Hexanitroazobenzene

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The enthalpies of formation of bis(2-fluoro-2,2-dinitroethyl)nitrosamine (BFDNO), bis(2-fluoro-2,2-dinitroethyl)nitramine (BFDNAM), *N,N′*-bis(2-fluoro-2,2-dinitroethyl)oxamide (BFDNOX), 2,2′,4,4′,6,6′-hexanitroazobenzene (HNAB), *N,N,O*-tris(2-fluoro-2,2-dinitroethyl)carbamate (TFDC) and bis(2-fluoro-2,2-dinitroethyl)oxalate (REX-17) were determined to be −102.041 ± 0.21, −120.735 ± 0.56, −232.335 ± 0.82, +61.087 ± 0.26, −266.926 ± 0.22, and −288.862 ±0.67 kcal/mol, respectively, by combustion calorimetery using a platinum-lined rotating-bomb calorimeter. The compounds were burned with either diethyl phthalate or diethyl oxalate to desensitize and to ensure complete combustion.

The enthalpies of formation of bis(2-fluoro-2,2-dinitroethyl)nitrosamine (BFDNO), bis(2-fluoro-2,2-dinitroethyl)nitramine (BFDNAM), *N,N′*-bis(2-fluoro-2,2-dinitroethyl)oxamide (BFDNOX), 2,2′,4,4′,6,6′-hexanitroazobenzene (HNAB), *N,N,O*-tris(2-fluoro-2,2-dinitroethyl)carbamate (TFDC), and bis(2-fluoro-2,2-dinitroethyl)oxalate (REX-17) were determined by combustion calorimetry using a platinum-lined rotating-bomb calorimeter. A mixture of these compounds with either diethyl phthalate (DEP) or diethyl oxalate (DEO) was burned in an oxygen atmosphere (30 atm). The ratios of the compounds to DEP or DEO were selected after a series of preliminary runs on a Parr stationary adiabatic-bomb calorimeter indicated the amounts needed to produce a smooth and clean combustion. Since these compounds were considered shock sensitive, DEP and DEO served as desensitizers. The enthalpies of formation (298.15K) were determined from the following idealized equations at 1 atm:

BFDNO:

$$C_4H_4O_9N_6F_2(c) + 179\ H_2O(l) \rightarrow 4\ CO_2(g) + 2\ (HF{\cdot}90H_2O)(l) + 3\ N_2(g) \qquad (1)$$

BFDNAM:

$$C_4H_4O_{10}N_6F_2(c) + C_6H_{10}O_4(l) + 6\ O_2(g) + 194\ H_2O(l) \rightarrow 10\ CO_2(g) + 2\ (HF{\cdot}100H_2O)(l) + 3\ N_2(g) \qquad (2)$$

BFDNOX:

$$C_6H_6O_{10}N_6F_2(c) + 2\ O_2(g) + 238\ H_2(l) \rightarrow 6\ CO_2(g) + 2\ (HF{\cdot}120H_2O)(l) + 3\ N_2(g) \qquad (3)$$

HNAB:

$$C_{12}H_4O_{12}N_8(c) + 7\ O_2(g) \rightarrow 12\ CO_2(g) + 2\ H_2O(l) + 4\ N_2(g) \qquad (4)$$

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TFDC:

$$C_7H_6O_{14}N_7F_3(c) + 0.75\ O_2(g) + 178.5\ H_2O(l) \rightarrow 7\ CO_2(g) + 3(HF{\cdot}60H_2O)(l) + 3.5\ N_2(g) \quad (5)$$

REX-17:

$$C_6H_4O_{12}N_4F_2(c) + 0.5\ O_2(g) + 179\ H_2O(l) \rightarrow 6\ CO_2(g) + 2\ (HF{\cdot}90H_2O)\ (l) + 2\ N_2(g) \quad (6)$$

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. *(10)*. The modification to the original instrumentation and the basic procedure were as previously reported *(19)* 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 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 is connected to an oscillator and its outputs are scanned and measured by a quartz thermometer. A strip chart recorder is used to verify stabilization of the baths at each temperature setting. Nine calibration temperatures were used ranging from −80° to +240°C in 40° increments. 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 drifts in a triple point cell, in a certified tin freezing-point standard, and against the freezing point of triple-distilled mercury. If excessive drift was noted, the transfer standard was 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 the NBS transfer standard at all points. The internal volume of the rotating-bomb was 0.346 liter.

The density measurements of DEP and DEO were made with a 5-ml Guy-Lussac pycnometer calibrated with distilled water. The esters were distilled through a 14-in. glass bead column and collected on a water condenser.

The heats of solution of the above compounds with DEP or DEO were determined in specially designed equipment for measuring small quantities of heat. A small 10-ml Dewar flask was the reaction vessel containing a thermocouple connected to a paper chart recorder, and its reference thermocouple in a reference Dewar containing water.

Before determining heats of solution, known weights of DEP or DEO were put into the reaction Dewar and allowed to reach the temperature of the water in the reference Dewar as evidenced by the paper chart recorder. When the compounds were added to the reaction Dewar, temperature differentials between the solutions and the reference water were recorded on the paper chart. The water temperature was determined by another thermocouple connected to a Leeds & Northrup potentiometer that read directly to 0.0001 mV. The thermocouples were calibrated against a precalibrated thermometer certified by the Bureau of Standards. The millivolt readings for the thermocouples were in agreement with literature values *(11)* for the various temperatures measured. The reference thermocouple was immersed in an ice bath and the other thermocouple in a water bath whose temperature was varied over the range of 20–40°C in 5° steps.

Procedure. BFDNAM, BFDNOX, TFDC, and REX-17 were mixed with DEO and BFDNO and HNAB with DEP individually in a polypropylene bag and sealed. Quantities of the mixtures to be burned were chosen to give a temperature rise in the calorimeter of approximately 2°C when possible, but complete combustion was not always achieved with such quantities. For example, REX-17 burned completely only when quantities of DEO and REX-17 were added to give a Δt_c rise of 1.5–1.62° (Table VI). The bags were placed in a platinum crucible in the bomb. Ten milliliters 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 in 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 for 25 min after ignition with predetermined time intervals for the rate of change in the temperature.

Materials. All the compounds investigated were obtained from H. G. Adolph, U.S. Naval Ordnance Laboratory, White Oak, Md. They were prepared in a manner similar to bis(2-fluoro-2,2-dinitroethyl)amine *(2)*. They had been recrystallized several times, chemically analyzed, checked by gas chromatography and nuclear magnetic resonance, and found to have a purity of better than 99% *(1)*.

Diethyl phthalate was of a commercial grade distilled several times until a constant boiling point of 297°C was reached. The boiling point of DEP has a reported value of 296.1°C *(11)*. The refractive index was $n_D^{20} = 1.5019$ which is in agreement with the value found in literature *(11)*. An elemental analysis of the purified material was in agreement with the theoretical formula within limits of the determination.

Anal. Calculated $C_{12}H_{14}O_4$: 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 $\Delta E_c°/M = -6411.26 \pm 1.66$ cal/gram at this laboratory (mean std dev for six runs).

Benzoic acid. NBS sample 39i was used to calibrate the calorimeter. The benzoic acid had a heat of combustion of 26.434 ± 0.003 abs kJ/gram under certified conditions. Conversion to standard conditions *(12)* gives $\Delta E_c°/M = -6312.96 \pm 0.72$ cal/gram.

Polypropylene. The film was burned in the calorimeter and its energy of combustion determined to be $\Delta E_c°/M = -11083.14 \pm 1.66$ cal/gram (mean and std dev for eight runs). Elemental analysis showed that the actual and theoretical formula were in agreement within the limits of the determination.

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

Fuse. The fuse used to ignite the materials was a commerical grade of cotton thread with an energy of *combustion* $\Delta E_c°/M = -4050$ cal/gram *(16)* with an empirical formula of $C_1H_{1.744}O_{0.884}$.

Diethyl oxalate. The ester was a commercial grade dis-

Table I. Summary of Calorimetric Data for Bis(2-fluoro-2,2-dinitroethyl)nitrosamine (BFDNO)

Run no.	23917	23918	23919	23920
m' (cpd), g	0.994116	0.697889	0.978961	0.974721
m'' (diethyl phthalate), g	0.906304	0.913504	1.032039	0.988356
m''' (polypropylene film, g	0.052165	0.48582	0.050161	0.050584
m'''' (fuse), g	0.007771	0.007646	0.008212	0.007871
$n^i(H_2O)$, moles	0.55026	0.55401	0.56159	0.56037
$\Delta t_c(t_f - t_i - \Delta t_{corr})$, deg	1.9447	1.8290	2.1253	2.0576
Δt_{corr}, deg	0.0229	0.0235	0.0237	0.0223
ξ(calor) $(-\Delta t_c)$, cal	−8003.33	−7527.18	−8746.59	−8467.97
ξ^i(cont) $(t_i - t_h)$, cal	−25.90	−24.27	−28.75	−27.75
ξ^f(cont) $(t_h - t_f + \Delta t_{corr})$	0.76	0.67	0.77	0.74
ΔE_{ign}, cal	0.95	0.87	0.87	0.87
ΔE, corr std states, cal	11.54	10.67	13.05	12.61
ΔE_{dec} (HNO_3), cal	32.79	15.55	15.48	16.24
ΔH(soln)[a]	3.2	3.2	3.2	3.2
$n''\Delta E_c^\circ$ (diethylphthalate), cal	−5810.56	−5856.72	−6616.68	−6336.61
$n'''\Delta E_c^\circ$ (polypropylene), cal	−578.16	−538.44	−555.94	−560.63
$n''''\Delta E_c^\circ$ (fuse), cal	−31.53	−31.02	−33.31	−31.93
ΔE_c° (cpd)/M, cal/g	−1568.23	−1567.99	−1569.16	−1572.45
ΔE_c° (cpd), kcal/mol	−498.868	−498.789	−499.164	−500.210
ΔH_c° (cpd), kcal/mol	−494.720	−494.641	−495.016	−496.062
ΔH_f° (cpd), kcal/mol	−102.477	−102.556	−102.181	−101.134
Average				
ΔE_c° (cpd)/M, cal/g	−1569.60 ± 0.66[b]			
ΔE_c° (cpd), kcal/mol	−499.303 ± 0.21			
ΔH_c° (cpd), kcal/mol	−495.155 ± 0.21			
ΔH_f° (cpd), kcal/mol	−102.041 ± 0.21			

[a] Heat of solution for 1 gram of cpd added to 1 gram of diethyl phthalate. [b] Mean std dev.

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

Run no.	32125	32126	32127
m' (cpd), g	0.929566	1.001772	1.066336
m'' (diethyl oxalate), g	1.180163	1.164161	1.150010
m''' (polypropylene film), g	0.056969	0.056188	0.066301
m'''' (fuse), g	0.008837	0.008456	0.008886
n^i (H_2O), moles	0.55107	0.55921	0.56238
$\Delta t_c(t_f - t_i - t_{corr})$, deg	1.8874	1.8885	1.9224
Δt_{corr}, deg	0.0215	0.0213	0.0222
ξ(calor) $(-\Delta t_c)$, cal	−7767.64	−7771.88	−7911.40
ξ^i(cont) $(t_i - t_h)$, cal	−25.12	−25.63	−26.24
ξ^f(cont) $(t_h - t_f + \Delta t_{corr})$	0.51	0.71	0.73
ΔE_{ign}, cal	0.93	0.93	0.93
ΔE, corr std states, cal	11.76	12.16	12.46
ΔE_{dec} (HNO_3), cal	18.30	11.26	11.26
ΔH(soln)[a]	2.9	2.9	2.9
$n''\Delta E_c^\circ$ (diethyl oxalate), cal	−5754.20	−5676.18	−5607.18
$n'''\Delta E_c^\circ$ (polypropylene film), cal	−631.40	−622.74	−734.82
$n''''\Delta E_c^\circ$ (fuse), cal	−35.85	−34.30	−36.05
ΔE_c°,[b] kcal/mol	−1193.080	−1191.604	−1192.342
ΔH_c°,[c] kcal/mol	−1188.932	−1187.456	−1188.194
ΔH_f° (cpd), kcal/mol	−121.134	−122.611	−121.873
Average			
ΔE_c°,[b] kcal/mol	−1193.479 ± 0.56[c]		
ΔH_c°,[d] kcal/mol	−1189.33 ± 0.56		
ΔH_f° (cpd), kcal/mol	−120.735 ± 0.56		

[a] Heat of solution for 1 gram of cpd added to 1.1 grams of diethyl oxalate. [b] Energy of combustion for 1 mole of BFDNAM and 1 mole of diethyl oxalate in the presence of oxygen and water as given in above reference equation. [c] Mean std. dev. [d] Heat of combustion for 1 mole

23921	23923	23924
0.933989	1.011802	1.076053
1.052522	1.075528	1.057354
0.052895	0.050581	0.048187
0.008437	0.008972	0.008437
0.56132	0.55668	0.56343
2.1485	2.2084	2.1973
0.0233	0.0202	0.0221
−8842.07	−9088.58	−9042.90
−29.04	−29.69	−29.90
0.76	0.75	0.80
0.87	0.87	0.87
13.03	13.48	13.62
17.31	18.86	19.84
3.2	3.2	3.2
−6748.00	−6895.50	−6778.98
−586.24	−560.60	−534.06
−34.23	−36.40	−34.23
−1571.21	−1570.22	−1567.95
−499.814	−499.501	−498.776
−495.667	−495.353	−494.629
−101.530	−101.844	−102.568

32128	32129	32130
1.000561	1.107953	1.055147
1.163756	1.187884	1.159978
0.056848	0.054156	0.056273
0.009407	0.008711	0.007861
0.55882	0.55308	0.55754
1.8934	1.9531	1.9052
0.0231	0.0227	0.0217
−7792.01	−8037.74	−7840.94
−25.57	−26.24	−25.77
0.60	0.60	0.66
0.97	0.93	0.93
12.05	12.54	12.26
16.89	19.70	15.48
2.9	2.9	2.9
−5674.21	−5791.85	−5655.78
−630.05	−600.22	−623.68
−38.16	−35.34	−31.89
−1193.990	−1195.020	−1194.839
−1189.842	−1190.872	−1190.691
−120.224	−119.194	−119.375

of BFDAM and 1 mole of diethyl oxalate in the presence of oxygen and water as given in above reference equation.

tilled several times until the boiling point became constant at 105°C at 55 mm pressure. An elemental analysis of the purified material was also performed. Results were in agreement with the theoretical formula within limits of the determination.

Anal. Calcd $C_6H_{10}O_4$: C, 49.30; H, 6.90; O, 43.79; mol wt 146.14. Found: C, 49.72; H, 7.19; O, 43.45. The energy of combustion was $\Delta E_c{}^\circ/M = -4875.78 \pm 1.13$ cal/gram (mean std dev for nine runs).

Analytical procedure. Complete combustions were evidenced by infrared analysis, titration of the acid solutions, and absorption of carbon dioxide on Ascarite. The run numbers that are missing in the sequences of numbers on Tables I–VI were rejected for incomplete combustions or mechanical problems. The gaseous reaction products were passed through a train of magnesium perchlorate and Ascarite to absorb water and carbon dioxide. Gas samples were also taken directly from the bomb without passing through any type of absorbent and were analyzed by ir spectroscopy. There were no indications of gases other than CO_2, N_2, and O_2 (N_2 and O_2 cannot be detected by ir). The $NO_3{}^-$ was reduced to ammonia by Devarda's alloy and was distilled into excess standardized HCl. After carbon dioxide had been removed by boiling, the remaining acidity of the bomb washings was determined by titration with NaOH with phenolphthalein as an indicator.

Units of measurements and auxiliary quantities. All data reported are based on the 1961 atomic weights *(6)*, and the 1963 fundamental constants and definition of the thermodynamic temperature scale and of the thermochemical calorie: 1 cal = 4.184 (exactly) abs J *(7)*.

Physical properties of the compounds and auxiliary materials are listed in Table VII.

The calorimeter was calibrated with benzoic acid, NBS sample 39i, and was 4115.45 ± 0.58 cal/deg (mean std dev for nine calibration experiments).

Results and Discussion

The determination of the enthalpies of formation of fluoronitro compounds with the combustion calorimeter has been accomplished by dissolving them in such compounds as diethyl phthalate and diethyl oxalate *(3)*. 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 improve safety in handling.

Several trial runs were conducted on each of the above compounds with DEP, DEO, and other solvents in a Parr stationary adiabatic-bomb calorimeter to determine the best auxiliary material to use with each compound, the proper weight ratios to approximate the heat released for initial temperature settings on the rotating bomb, and to test for ignitability and good combustion of these solutions. Such trial runs on a stationary bomb saved time and reduced damage in the event of a detonation.

Since all of the compounds were mixed with DEP or DEO before being put into the bomb, heats-of-solution reactions occurred outside the calorimeter. Thus heats of solution were determined for the weights of the compounds and their solvents as given in Tables I–VI. Because only limited amounts of the compounds were available and small quantities of heat were involved, it became necessary to design equipment with low heat capacity and the ability to measure heat changes very rapidly.

Table III. Summary of Calorimetric Data for Bis(2-fluoro-2,2-Dinitroethyl)oxamide (BFDNOX)

Run no.	32137	32139	32140	32141
m' (cpd), g	0.87565	1.001802	1.060662	0.995002
m'' (diethyl oxalate), g	1.349963	1.285844	1.281521	1.345589
m''' (polypropylene film), g	0.058485	0.059826	0.055442	0.063338
m'''' (fuse), g	0.008456	0.008516	0.009182	0.008501
n^i (H_2P), moles	0.55465	0.55327	0.56182	0.55855
$\Delta t_c(t_f - t_i - \Delta t_{corr})$, deg	2.1377	2.1151	2.1256	2.1931
Δt_{corr}, deg	0.0226	0.0225	0.0226	0.0230
ξ(calor) $(-\Delta t_c)$, cal	−8797.62	−8704.61	−8747.82	−9025.62
ξ^i(cont) $(t_i - t_h)$, cal	−28.31	−28.26	−28.75	−29.53
ξ^f(cont) $(t_h - t_f + \Delta t_{corr})$	0.36	0.68	0.68	0.67
ΔE_{ign}, cal	0.87	0.91	0.91	0.91
ΔE, corr std states, cal	13.25	13.43	13.71	13.90
ΔE_{dec} (HNO_3), cal	19.00	17.87	19.28	19.42
$n''\Delta E_c^\circ$ (diethyl oxalate), cal	−6582.11	−6269.48	−6248.40	−6560.78
$n'''\Delta E_c^\circ$ (polypropylene), cal	−648.20	−663.06	−614.47	−701.98
$n''''\Delta E_c^\circ$ (fuse), cal	−35.60	−35.31	−38.07	−35.25
ΔE_c° (cpd)/M, cal/g	−1734.95	−1729.02	−1735.91	−1730.92
ΔE_c° (cpd), kcal/mol	−628.077	−622.699	−625.180	−623.384
ΔH_c° (cpd), kcal/mol	−623.929	−618.551	−621.033	−619.236
ΔH_f° (cpd), kcal/mol	−229.707	−235.085	−232.604	−234.400

Average

ΔE_c° (cpd)/M, cal/g	−1735.37 ± 1.81[a]
ΔE_c° (cpd), kcal/mol	−625.449 ± 0.82
ΔH_c° (cpd), kcal/mol	−621.301 ± 0.82
ΔH_f° (cpd), kcal/mol	−232.335 ± 0.82

[a] Mean std dev.

Table IV. Summary of Calorimetric Data for 2,2′,4,4′,6,6′-Hexanitroazobenzene

Run no.	36246	36255	36257	36258
m' (cpd), g	0.635902	0.608125	0.724094	0.809109
m'' (diethyl phthalate), g	0.892938	0.936667	0.957928	0.979850
m''' (polypropylene film), g	0.050088	0.492380	0.499280	0.048362
m'''' (fuse), g	0.007071	0.006951	0.007781	0.007111
n^i (H_2O), moles	0.56430	0.55827	0.56103	0.55793
$\Delta t_c(t_f - t_i - \Delta t_{corr})$, deg	1.9886	2.0340	2.1528	2.2427
Δt_{corr}, deg	0.0221	0.0213	0.0223	0.0223
ξ(calor) $(-\Delta t_c)$, cal	−8184.00	−8370.85	−8859.76	−9229.74
ξ^i(cont) $(t_i - t_h)$, cal	−26.46	−26.88	−28.54	−29.71
ξ^f(cont) $(t_h - t_f + \Delta t_{corr})$	0.60	0.61	0.57	0.63
ΔE_{ign}, cal	0.91	0.87	0.83	0.83
ΔE, corr std states, cal	11.46	11.62	12.59	13.29
ΔE_{dec} (HNO_3), cal	16.23	14.64	16.16	16.85
$n''\Delta E_c^\circ$ (diethyl phthalate), cal	−5724.86	−6005.22	−6141.53	−6282.08
$n'''\Delta E_c^\circ$ (polypropylene), cal	−555.13	−545.71	−553.36	−536.00
$n''''\Delta E_c^\circ$ (fuse), cal	−28.64	−28.15	−31.51	−28.80
ΔE_c° (cpd)/M, cal/g	−2944.78	−2945.18	−2943.82	−2942.86
ΔE_c° (cpd), kcal/mol	−1331.665	−1331.845	−1331.231	−1330.797
ΔH_c° (cpd), kcal/mol	−1326.332	−1326.512	−1325.899	−1325.464
ΔH_f° (cpd), kcal/mol	+61.075	+61.255	+60.641	+60.207

Average

ΔE_c° (cpd)/M, cal/g	−2944.81 ± 0.57[a]
ΔE_c° (cpd), kcal/mol	−1331.677 ± 0.26
ΔH_c° (cpd), kcal/mol	−1326.344 ± 0.26
ΔH_f° (cpd), kcal/mol	+61.087 ± 0.26

[a] Mean std dev.

32142	32143	32146
1.016263	1.023103	1.163736
1.322222	1.282211	1.272889
0.05257	0.054161	0.051569
0.008616	0.008141	0.007461
0.56415	0.55793	0.55743
2.1458	2.1057	2.1491
0.0209	0.0214	0.0227
−8830.95	−8665.92	−8844.54
−28.82	−28.34	−28.95
0.38	0.71	0.71
0.95	0.87	0.91
13.87	13.50	14.07
14.78	18.01	18.01
−6446.85	−6251.77	−6206.31
−582.64	−600.27	−571.55
−35.72	−33.75	−30.93
−1736.51	−1735.20	−1745.08
−625.396	−624.925	−628.483
−621.249	−620.777	−624.335
−232.388	−232.860	−229.301

36260	36263	36264
0.880621	0.822777	0.826162
0.947053	0.956409	0.992890
0.049323	0.045305	0.049108
0.007256	0.007141	0.006981
0.55865	0.55710	0.55622
2.2468	2.2083	2.2780
0.0219	0.0226	0.0225
−9246.62	−9088.17	−9375.02
−29.79	−29.24	−30.09
0.63	0.66	0.61
0.87	0.83	0.83
13.47	13.12	13.48
17.79	17.73	18.48
−6071.81	−6131.79	−6365.68
−546.65	−502.12	−544.27
−28.39	−28.92	−28.27
−2947.58	−2943.97	−2945.46
−1332.932	−1331.298	−1331.972
−1327.599	−1325.966	−1326.639
+62.342	+60.708	+61.382

A thermocouple, connected to a paper chart recorder, was inserted into a reaction Dewar with its reference thermocouple in a reference Dewar containing water at room temperature. The solvent, DEP or DEO, was put into the reaction Dewar and allowed to reach the temperature ot the reference water as evidenced by the paper chart recorder. An average weight of the compounds used in the combustion experiments were put into the reaction Dewar, closed and shaken. The differential temperatures between the mixture and the reference Dewar were automatically recorded on the paper chart. A theoretical heat capacity of the solutions was calculated from the heat capacities of the solvent and compound and assumed constant over the small temperature range, 20–27°C, of the experiments. From the calculated heat capacities and differential temperatures, the heats of solution were determined as shown in Tables I–VI. The paper recorder recorded the differential temperature continuously to determine the maximum changes of the solutions. The maximum heat exchange of 3.9 cal (TFDC) for any one solution measured is small compared to the total heat liberated in the experimental runs. As noted in Tables I–VI, all heats of solution were endothermic. No heat of solution was recorded for BFDNOX or HNAB.

The accuracy of this method depended on the maximum change in temperature being quickly reached so that the surrounding walls of the Dewar would not absorb appreciable amounts of heat from the mixtures. These temperatures were reached in approximately 25 sec. An experiment was conducted to determine the accuracy of the equipment. The temperature of the water in the reference Dewar was measured by another thermocouple. Two milliliters of water was added to the reaction Dewar and allowed to reach the temperature of the reference Dewar. Water (1.5 ml) at a known temperature was then added to the 2 ml, and the maximum temperature differential recorded on the paper chart. The experimental temperature changes were found to be 98–99% of the theoretical value.

There were varying degrees of solubility of compounds in their solvents. It is not necessary to dissolve completely the compounds to obtain complete combustions, but the more soluble they are the better they will burn. Solubility of the compounds in their respective solvents usually determined the ratio of compound to solvent used. Best results are usually obtained with a minimum of solvent. All compounds are explosive materials, but nontoxic if not taken internally.

All data reduction was performed on a digital computer *(4)*. To correct for the heat of solution of CO_2 in the hydrofluoric acid solutions, the data of Cox and Head *(8)* were used. The following heats of formation were used: CO_2(g) = −94,051 cal/mol; H_2O(l) = −68,317.5 cal/mol *(17)*.

The uncertainties assigned to gaseous carbon dioxide and liquid water are ±0.011 and ±0.0144 cal/mol, respectively *(18)*.

Nomenclature

ΔE_{ign} = ignition energy, cal

ΔE_{corr} std states = energy reduction to standard states, cal *(10, 13)*

$\Delta E_{\text{dec}}(HNO_3)$ = energy released from formation of nitric acid, cal

ΔH (soln) = heat released due to mixing of compounds before loading bomb

$\Delta E_c{}^\circ$ = standard energy of idealized combustion reaction, cal/mol

Table V. Summary of Calorimetric Data for *N*,*N*,O-tris(2-fluoro-2,2-dinitroethyl)carbamate

Run no.	36229	36230	36231	36232	36233	36234
m' (cpd), g	1.407572	1.501704	1.507944	1.503681	1.527839	1.502023
m'' (diethyl oxalate), g	0.945408	0.942206	0.954836	0.936257	0.937272	0.948483
m''' (polypropylene film), g	0.047086	0.048837	0.052680	0.054201	0.046521	0.048252
m'''' (fuse), g	0.007821	0.007716	0.007946	0.008706	0.007931	0.007456
n^i (H_2O), moles	0.55348	0.55843	0.55471	0.56021	0.55560	0.55910
$\Delta t_c(t_f - t_i - \Delta t_{corr})$, deg	1.7896	1.8258	1.8535	1.8354	1.8225	1.8309
Δt_{corr}, deg	0.0231	0.0214	0.0220	0.0230	0.0234	0.0208
ξ(calor) $(-\Delta t_c)$, cal	−7365.03	−7514.01	−7628.00	−7553.52	−7500.42	−7535.00
ξ^i(cont) $(t_i - t_h)$, cal	−24.71	−24.88	−25.11	−25.03	−24.75	−24.99
ξ^f(cont) $(t_h - t_f + \Delta t_{corr})$	1.23	0.72	0.68	0.66	0.71	0.73
ΔE_{ign}, cal	0.91	0.87	0.95	0.87	0.87	0.91
ΔE, corr std states, cal	12.62	13.07	13.25	13.14	13.16	13.15
ΔE_{dec} (HNO_3), cal	21.11	22.52	19.70	21.11	19.70	21.11
ΔH(soln)^a	3.9	3.9	3.9	3.9	3.9	3.9
$n''\Delta E_c°$ (diethyl oxalate), cal	−4609.59	−4593.98	−4655.56	−4564.97	−4569.92	−4624.58
$n'''\Delta E_c°$ (polypropylene film), cal	−521.86	−541.27	−583.86	−600.72	−515.60	−534.78
$n''''\Delta E_c°$ (fuse), cal	−31.73	−31.30	−32.23	−35.32	−32.17	−30.25
$\Delta E_c°$ (cpd)/M, cal/g	−1553.53	−1552.31	−1553.89	−1554.80	−1550.53	−1551.65
$\Delta E_c°$ (cpd), kcal/mol	−728.854	−728.282	−729.024	−729.448	−727.446	−727.972
$\Delta H_c°$ (cpd), kcal/mol	−723.077	−722.505	−723.247	−723.671	−721.669	−722.195
$\Delta H_f°$ (cpd), kcal/mol	−266.727	−267.299	−266.556	−266.132	−268.134	−267.608

Run no.	36235	36236	36237	36238	36239
m' (cpd), g	1.592559	1.573394	1.660471	1.520634	1.543692
m'' (diethyl oxalate), g	0.947881	0.922481	0.942196	0.953564	0.942126
m''' (polypropylene film), g	0.051439	0.047697	0.048362	0.044679	0.047832
m'''' (fuse), g	0.006506	0.006885	0.007006	0.007836	0.008506
n^i (H_2O), moles	0.55649	0.56648	0.55871	0.55568	0.55771
$\Delta t_c(t_f - t_i - \Delta t_{corr})$, deg	1.8730	1.8261	1.8827	1.8352	1.8392
ξ(calor) $(-\Delta t_c)$, cal	−7708.26	−7515.24	−7748.18	−7552.69	−7569.15
Δt_{corr}, deg	0.0201	0.0220	0.0222	0.0210	0.0214
ξ^i(cont) $(t_i - t_h)$, cal	−25.50	−25.16	−25.07	−24.92	−25.04
ξ^f(cont) $(t_h - t_f + \Delta t_{corr})$	0.72	0.70	0.03	0.69	0.70
ΔE_{ign}, cal	0.91	0.91	0.91	0.91	0.91
ΔE, corr, std states, cal	13.57	13.39	13.86	13.24	13.29
ΔE_{dec} (HNO_3), cal	21.11	19.70	19.70	19.70	21.11
ΔH(soln)^a	3.9	3.9	3.9	3.9	3.9
$n''\Delta E_c°$ (diethyl oxalate), cal	−4621.65	−4497.80	−4593.93	−4649.36	−4593.59
$n'''\Delta E_c°$ (polypropylene film), cal	−570.11	−528.63	−536.00	−495.18	−530.13
$n''''\Delta E_c°$ (fuse), cal	−26.39	−27.93	−28.42	−31.79	−34.51
$\Delta E_c°$ (cpd)/M, cal/g	−1554.29	−1555.48	−1551.70	−1553.82	−1552.15

Table V. (*Continued*)

Run no.	36235	36236	36237	36238	36239
$\Delta E_c°$ (cpd), kcal/mol	−729.212	−729.769	−727.997	−728.990	−728.205
$\Delta H_c°$ (cpd), kcal/mol	−723.435	−723.992	−722.220	−723.213	−722.428
$\Delta H_f°$ (cpd), kcal/mol	−266.369	−265.812	−267.584	−266.591	−267.375
Average					
$\Delta E_c°$ (cpd)/*M*, cal/g	−1553.10 ± 0.46[b]				
$\Delta E_c°$ (cpd), kcal/mol	−728.654 ± 0.22				
$\Delta H_c°$ (cpd), kcal/mol	−722.877 ± 0.22				
$\Delta H_f°$ (cpd), kcal/mol	−266.926 ± 0.22				

[a] Heat of solution for 1.5 grams of compound mixed with 0.9 grams of diethyl oxalate. [b] Mean std dev.

Table VI. Summary of Calorimetric Data for Bis(2-fluoro-2,2-dinitroethyl)oxalate (REX-17)

Run no.	32161	32163	32267	32168	32171	32172
m' (cpd), g	0.663383	1.30195	1.31756	1.369938	1.126687	1.169325
m'' (diethyl oxalate), g	0.953094	0.872388	0.870761	0.841589	0.837636	0.828194
m''' (polypropylene), g	0.062548	0.055387	0.048567	0.052880	0.048537	0.046526
m'''' (fuse), g	0.008411	0.008281	0.008116	0.008121	0.008016	0.007931
n^i (H_2O), moles	0.56265	0.56297	0.56298	0.55357	0.55876	0.55732
$\Delta t_c(t_f - t_i - \Delta t_{corr})$, deg	1.5295	1.6296	1.6157	1.6089	1.5139	1.5109
Δt_{corr}, deg	0.0204	0.0227	0.0216	0.0217	0.0208	0.0204
ξ(calor) $(-\Delta t_c)$, cal	−6294.60	−6706.55	−6649.35	−6621.36	−6230.39	−6218.05
ξ^i(cont) $(t_i - t_h)$, cal	−20.91	−22.27	−22.06	−21.75	−20.48	−20.43
ξ^f(cont) $(t_h - t_f + \Delta t_{corr})$	0.93	0.70	0.68	0.71	0.66	0.67
ΔE_{ign}, cal	0.91	0.95	0.95	0.91	0.87	0.87
ΔE, corr std states, cal	9.75	12.17	12.20	12.22	10.99	11.07
ΔE_{dec} (HNO_3), cal	11.26	15.48	14.07	12.67	14.07	15.48
ΔH(soln)[a]	2.5	2.5	2.5	2.5	2.5	2.5
$n''\Delta E_c°$ (diethyl oxalate), cal	−4647.07	−4253.56	−4245.63	−4103.39	−4084.12	−4038.08
$n'''\Delta E_c°$ (polypropylene film), cal	−693.23	−613.86	−538.28	−586.08	−537.94	−515.65
$n''''\Delta E_c°$ (fuse), cal	−34.87	−34.33	−33.65	−33.67	−33.23	−32.88
$\Delta E_c°$ (cpd)/*M*, cal/g	−1379.38	−1378.88	−1383.83	−1380.43	−1390.20	−1386.56
$\Delta E_c°$ (cpd), kcal/mol	−499.496	−499.312	−501.107	−499.877	−503.413	−502.093
$\Delta H_c°$ (cpd), kcal/mol	−495.052	−494.868	−496.663	−495.433	−498.969	−497.649
$\Delta H_f°$ (cpd), kcal/mol	−290.249	−290.433	−288.637	−289.868	−286.331	−287.651
Average						
$\Delta E_c°$ (cpd)/*M*, cal/g	−1383.21 ± 1.84[b]					
$\Delta E_c°$ (cpd), kcal/mol	−500.883 ± 0.67					
$\Delta H_c°$ (cpd), kcal/mol	−496.439 ± 0.67					
$\Delta H_f°$ (cpd), kcal/mol	−288.862 ± 0.67					

[a] Heat of solution of 1.3 grams of REX-17 added to 0.8 gram of diethyloxalate. [b] Mean std dev.

Table VII. Density, Heat Capacity, and $(\partial E/\partial P)T$

	Density, g/ml	C_p,cal/ deg g	$(\partial E/\partial P)T$, cal/atm g
BFDNO	1.8[a]	0.3[b]	−0.006[b]
BFDNAM	1.8[a]	0.3[b]	−0.006[b]
BFDNOX	1.9[a]	0.3[b]	−0.006[b]
HNAB	1.7[c]	0.3[b]	−0.006[b]
TFDC	1.89[c]	0.3[b]	−0.006[b]
REX-17	1.87[a]	0.3[b]	−0.006[b]
DEP	1.123[d]	0.393[e]	−0.006[b]
DEO	1.08[d]	0.466[f]	−0.006[b]
Polypropylene	0.9[g]	0.315[b]	−0.008[b]
Thread	1.5[h]	0.4[i]	−0.007[j]

[a] Estimated by Naval Ordnance Laboratory, White Oak, Md. [b] Estimated. [c] Determined by Naval Ordnance Laboratory, White Oak, Md. [d] See ref. *11*. [e] See ref. *5*. [f] See ref. *9*. [g] Determined by authors. [h] See ref. *14* [i] See ref. *15*. [j] See ref. *13*.

ΔH_c° = standard heat of combustion of compound at constant pressure, kcal

ΔH_f° = enthalpy of formation, kcal/mol

m', m'', m''', m'''' = mass in grams of compound, auxiliary material, polypropylene film, and fuse, respectively

n', n'', n''', n'''' = number of moles of compound, auxiliary material, propylene film, and fuse, respectively

n^i = initial number of moles of water in bomb

t_i = initial temperature of calorimeter, °C

t_f = final temperature of calorimeter, °C

t_h = reference temperature to which combustion reaction is referred (25°C)

Δt_{corr} = rise in temperature of calorimeter due to thermal leakage of outer jacket

ξ(Calor) = energy equivalent of calorimeter, cal/deg

ξ(cont) = energy equivalent of contents, cal/deg [ξ^i(cont) $(t_i - 25)$ + ξ^f(cont) $(25 - t_f + \Delta t_{\text{corr}})$ where ξ^i(cont) and ξ^f(cont) are energy equivalents of contents before and after combustion, respectively]

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Heat of Combustion of 5-Amino-3,4-dimethylisoxazole

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The heat of combustion of crystalline 5-amino-3,4-dimethylisoxazole in the standard state at 25°C, ΔHc° (c) is −723.46 ± 0.30 kcal mol^{-1}. With the use of appropriate auxiliary data, this gives ΔHf° (c) = −19.76 ± 0.31 kcal mol^{-1} and ΔHf° (g) = 1.24 ± 0.68 kcal mol^{-1}.

5-Amino-3,4-dimethylisoxazole is the precursor for Gantrisin, the most important of the isoxazole sulfa drugs. Despite its pharmacological importance, no thermochemical data has been reported for this compound. Such data will be necessary if quantitative studies of the energetics of biochemical reactions are made. We have measured the heat of combustion and other physical properties necessary to derive the enthalpy of formation in the condensed state (c) and the gaseous state (g).

Experimental

Apparatus and procedure. The apparatus and experimental procedure were similar to those described previously (*3*), except a heater was added to the calorimeter vessel so that all experiments could be started at about the same temperature. The temperature rise of about 2.7°C was measured with a Hewlett-Packard Model 2801A quartz thermometer. The internal volume of the bomb was 0.344 liter. The sample pellets were weighed to an accuracy of 0.01 mg, and corrections for air buoyancy were applied. Ignition was accomplished by fusing a 10-cm length of 44 standard wire gage (swg) platinum wire wrapped around a small piece (~4 mg) of Whatman No. 1 filter paper. This is placed in close contact with the pellet and acts as a fuse. Its heat of combustion has been found to be 4118 ± 10 cal g^{-1} *(9)*. The

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