Enthalpies of Combustion and Formation of 1,1-Bis(difluoroamino)heptane

N—F Thermochemical Bond Energy

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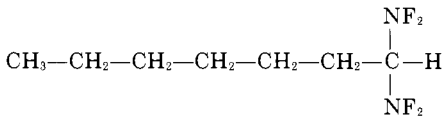
The enthalpy of combustion of liquid 1,1-bis(difluoroamino)heptane was measured in a rotating-bomb calorimeter. The enthalpy of vaporization was estimated. The experimental enthalpy of combustion and the estimated enthalpy of vaporization were used to calculate the following values, in kcal. per mole at 298.15° K., for this compound: standard enthalpy of formation of the liquid from graphite and gaseous hydrogen, fluorine, and nitrogen, -64.8_2; standard enthalpy of formation of the gas (estimated), −52.8. The N—F thermochemical bond energy in 1,1-bis(difluoroamino)heptane was estimated to $67._3$ kcal., about the same as the N—F thermochemical bond energy in NF_3, N_2F_4, and 1,2-bis(difluoroamino)-4-methylpentane, but several kilocalories less than the N—F thermochemical bond energy in perfluoropiperidine.

IN A CONTINUING study of compounds of interest in propellant thermochemistry, the enthalpy of combustion of 1,1-bis(difluoroamino)heptane (I)



$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\underset{\underset{NF_2}{|}}{\overset{\overset{NF_2}{|}}{C}}{-}H \qquad (1)$$

was measured, and the enthalpy of formation was derived. Another similar molecule, 1,2-bis(difluoroamino)-4-methylpentane, was studied by the Bureau (*4*); however, the two $—NF_2$ groups were bonded to adjacent carbon atoms in the hydrocarbon chain. The two $—NF_2$ groups in 1,1-bis(difluoroamino)heptane are bonded to the same (primary) carbon atom. Although ordinary amines having the two $—NH_2$ groups bonded to adjacent carbon atoms are stable, those having the two $—NH_2$ groups bonded to the same carbon atom are unstable. Thus, it was of interest to determine whether the N—F thermochemical bond energy in 1,1-bis(difluoroamino)heptane was similar to that in 1,2-bis(difluoroamino)-4-methylpentane and several other molecules, such as NF_3, N_2F_4, and perfluoropiperidine (*8*), whose bonds exist in a different molecular environment.

The enthalpy of combustion of 1,1-bis(difluoroamino)heptane was measured in a rotating-bomb calorimeter (*4*, *7*). The enthalpy of formation of the liquid at 298.15° K. was computed from the experimental enthalpy of combustion. Because of experience with decomposition of similar compounds during vapor pressure measurements and because 1,1-bis(difluoroamino)heptane decomposed noticeably during attempts at preparative-scale, gas-liquid chromatographic (GLC) purification, the vapor pressure was not measured. The enthalpy of vaporization was estimated in order to estimate the enthalpy of formation in the gaseous state at 298.15° K. The N—F thermochemical bond energy was derived and compared to that in several other molecules.

EXPERIMENTAL

Material and Purification. Two samples of 1,1-bis(difluoroamino)heptane were supplied by the Thiokol Chemical Corp. through the courtesy of Harry F. Smith. The first sample contained significant carbonyl impurity and decomposed during attempted preparative-scale GLC purification. Thermochemical measurements were made on a second sample that appeared to be more pure. The infrared absorption spectrum showed no evidence of carbonyls or water. The boiling point of this sample was 48° C. at 4.5 mm. Duplicate elemental analyses were reported by Thiokol. Anal. Calcd. for $C_7H_{14}N_2F_4$: C, 41.58; H, 6.98; N, 13.85; F, 37.59. Found: C, 41.27, 41.44; H, 7.26, 7.23; N, 13.97, 14.10; F, 37.36, 37.53. Analysis of the nuclear magnetic resonance spectrum contributed by the Basic Production Research Group of this Center revealed that the compound had the desired substitution on the terminal carbon atom. Another good indication of purity was the comparison of the amounts of combustion products from the bomb calorimetry to those expected from the stoichiometry of the combustion reaction. Gravimetric carbon dioxide analysis yields results of high accuracy, and the carbon dioxide recovery was $100.06_0 \pm 0.01_3\%$ of that expected. HF recovery by the ordinary, acid-base, volumetric procedure gave $99.8_4 \pm 0.1_4\%$ of the HF expected.

Calorimetric Technique. The rotating-bomb calorimeter BMR II (*7*), platinum-lined bomb Pt 3b (*5*), internal volume 0.349_4 liter, and experimental techniques for organic fluorine compounds (*6*, *7*) have been described. Modification of these techniques for studying a compound that is likely to detonate or react violently upon ignition has also been described (*4*), and was used for 1,1-bis(difluoroamino)heptane. The bomb initially contained 10 ml. of distilled water, and the initial pressure of purified oxygen was 30 atm. A solution of paraffin oil and 1,1-bis(difluoroamino)heptane was prepared in a polyester bag for each combustion experiment. About 40 to 45% of the energy in an experiment came from combustion of the 1,1-bis(difluoroamino)-

heptane; the remainder came from combustion of the paraffin oil and polyester bag.

Comparison experiments were done (*6*) in which paraffin oil was burned to produce the same amount of carbon dioxide as the corresponding experiment with 1,1-bis(difluoroamino)heptane. Also, the bomb initially contained a solution of aqueous HF such that dilution by the water formed in the combustion reaction produced the same final amount and concentration of aqueous HF. The comparison experiment minimizes possible errors in the reduction to standard states (*6*).

RESULTS

Units of Measurements and Auxiliary Quantities. The results reported are based on the 1961 International Atomic Weights (*2*) and fundamental constants (*10*), and the definitions: 0° C. = 273.15° K. and 1 cal. = 4.184 (exactly) joules. The laboratory standards of mass and resistance had been calibrated by the National Bureau of Standards.

For reducing weights in air to in vacuo, converting the energy of the actual bomb process to that of the isothermal process, and reducing to standard states (*6*), the following estimated values, all for 298.15° K., were used for 1,1-bis(difluoroamino)heptane: density, 1.18 gram per ml.; specific heat, 0.4 cal. per deg. per gram; and $(\partial E/\partial P)_T$, -0.007 cal. per atm. per gram.

The paraffin oil used as a diluent and the cotton thread fuse have been described (*5, 7*). Obtained in experiments performed concurrently with the 1,2-bis(difluoroamino)-heptane experiments, the value of $\Delta Ec°/M$ for the paraffin oil was $-10{,}984.2_9 \pm 0.1_5$ cal. per gram (mean and standard deviation). The value of $\Delta Ec°/M$ for the polyester film obtained in experiments chronologically near these reported here was $-5473.8_9 \pm 0.2_8$ cal. per gram (mean and standard deviation of the mean) for the dry polyester.

Computation of the enthalpy of formation of 1,1-bis-(difluoroamino)heptane utilized the following values, expressed in kcal. per mole, of enthalpy of formation from reference (*12*): CO_2(g), -94.051; H_2O(1), -68.315; and HF (in 50 H_2O), -76.316. This computational procedure incorporates one significant change from the data previously used from reference (*11*), the change in the enthalpy of formation of aqueous HF. This change is reflected in the enthalpy of formation of 1,1-bis(difluoroamino)heptane and the derived N—F thermochemical bond energies.

Calorimetric Results. Six combustion experiments were attempted with 1,1-bis(difluoroamino)heptane, and all were successful. These experiments and their corresponding comparison experiments (*6, 7*) are summarized in Table I. The comparison experiments are treated as *bona fide* calibration experiments and used to obtain an apparent energy equivalent of the calorimetric system, $\varepsilon_{\text{app.}}$ (calor.). The value of $\varepsilon_{\text{app.}}$ (calor.) is then used to compute the standard enthalpy of combustion. The value of $\Delta Ec°/M$ (compound) refers to the reaction

$$C_7H_{14}N_2F_4(\text{soln., in oil}) + 19/2\ O_2(g) + 195\ H_2O\ (l) = 7\ CO_2(g) + N_2(g) + 4\ HF\cdot 50\ H_2O\ (l) \qquad (1)$$

Derived Results. The derivation of the thermochemical data of Table II necessarily neglected the enthalpy of solu-

Table I. Summary of Calorimetric Experiments[a]

	Combustion Experiments					
	1	2	3	4	5	6
m'(compound), g.	0.564549	0.554400	0.554159	0.543348	0.561757	0.568619
m''(oil), g.	0.443859	0.393956	0.323095	0.331976	0.363597	0.329341
m'''(polyester), g. (dry)	0.076941	0.075235	0.158323	0.074619	0.076341	0.074446
m''''(fuse)	0.001054	0.000959	0.001882	0.001196	0.001136	0.001224
$n^i(H_2O)$, mole	0.5523	0.5523	0.5523	0.5523	0.5523	0.5523
Δt_c(deg.)	2.18295	2.02874	1.94891	1.84143	1.95916	1.87269
$\varepsilon_{\text{app.}}$ (calor.)($-\Delta t_c$), cal.	−8750.51	−8132.12	−7810.49	−7380.75	−7852.20	−7506.17
ε(cont.)($-\Delta t_c$), cal.[b]	−30.27	−28.06	−26.93	−25.42	−27.08	−25.87
$\Delta E_{\text{ign.}}$, cal.	0.41	0.47	0.57	0.29	0.46	0.59
$\Delta E_{\text{cor. to std. states}}$, cal.	7.17	6.64	6.75	6.04	6.41	6.13
$\Delta E^f_{\text{dec.}}$ (HNO_3), cal.	11.02	11.77	10.63	9.48	11.10	10.12
$-m''''\Delta Ec°/M$(fuse), cal.	4.27	3.88	7.62	4.84	4.60	4.96
$-m'''\Delta Ec°/M$(polyester), cal.	421.17	411.83	866.64	408.46	417.88	407.51
$-m''\Delta Ec°/M$(oil), cal.	4875.48	4327.33	3548.97	3646.52	3993.85	3617.58
$m'\Delta Ec°/M$(compound), cal.	−3461.26	−3398.26	−3396.24	−3330.54	−3444.98	−3485.15
$\Delta Ec°/M$(compound), cal.	−6131.02	−6129.63	−6128.64	−6129.66	−6132.51	−6129.15

Mean value and standard deviation: −6130.10 ± 0.58 cal. per gram

	Comparison Experiments					
m'(oil), g.	0.771546	0.715542	0.704511	0.647688	0.689592	0.657121
m''(fuse), g.	0.000899	0.001114	0.001130	0.001167	0.001176	0.000992
$n^i(H_2O)$, mole	0.5456	0.5457	0.5434	0.5458	0.5456	0.5456
n^i(HF), mole	0.01117	0.01097	0.01096	0.01075	0.01111	0.01125
Δt_c, (deg.)	2.10991	1.95735	1.92716	1.77174	1.88650	1.79748
$m'\Delta Ec°/M$(oil), cal.	−8474.88	−7859.72	−7738.55	−7114.39	−7574.68	−7218.01
$m''\Delta Ec°/M$(fuse), cal.	−3.64	−4.51	−4.58	−4.73	−4.76	−4.02
$-\Delta E^f_{\text{dec.}}$ (HNO_3), cal.	−1.37	−2.63	−1.35	−1.43	−1.58	−1.79
$-\Delta E_{\text{cor. to std. states}}$, cal.	−6.54	−6.03	−5.90	−5.40	−5.79	−5.51
$\Delta E_{\text{ign.}}$, cal.	−0.57	−0.32	−0.58	−0.27	−0.43	−0.41
ε(cont.)($-\Delta t_c$), cal.[b]	29.28	27.24	27.63	24.81	26.26	25.02
$\varepsilon_{\text{app.}}$ (calor.)($-\Delta t_c$), cal.	−8457.72	−7845.97	−7723.33	−7101.41	−7560.98	−7204.72
$\varepsilon_{\text{app.}}$ (calor.), cal./deg.	4008.57	4008.46	4007.62	4008.16	4007.94	4008.23

[a] The symbols and abbreviations of this table are those of reference (6), except as noted. [b] ε^i(cont.)($t_i - 25°$) + ε^f(cont.)($25° - t_f + \Delta t_{\text{cor.}}$).

Table II. Derived Data at 298.15° K., Kcal./Mole

$\Delta Ec°$	(Liquid)	$-1239.4_9 \pm 0.2_8$[a]
$\Delta Hc°$	(Liquid)	-1240.3_8 [illegible] 0.2_8
$\Delta Hf°$	(Liquid)	-64.8_2
$\Delta Hf°$	(Gas)	-52.7_6

[a] Uncertainties expressed are the "uncertainty interval," equal to twice the over-all standard deviation of the mean.

Table III. The N—F Thermochemical Bond Energy at 298.15° K., Kcal./Bond

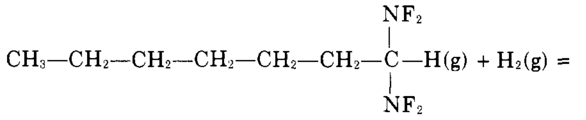
NF_3	66.5
N_2F_4	66.3
1,1-Bis(difluoroamino)heptane	67.3
1,2-Bis(difluoroamino)-4-methylpentane	67.9
Perfluoropiperidine	73.9

tion of the compound with oil, possibly a few tenths kcal. mole^{-1}. Quantities of compound necessary for measuring the enthalpy of solution were not available. The molal values for $\Delta Ec°$ (the energy of the idealized combustion reaction at 298.15° K.) and $\Delta Hc°$ (the standard enthalpy of combustion at 298.15° K.) refer to Reaction 1, and the value of $\Delta Hf°$ (the standard enthalpy of formation at 298.15° K.) refers to the following reaction.

$$7\ C(c,\ graphite) + 7\ H_2(g) + N_2(g) + 2\ F_2(g) = C_7H_{14}N_2F_4\ (l\ or\ g) \qquad (2)$$

The enthalpy of vaporization of the compound, $\Delta Hv°_{298.15}$, was estimated as 12.06 kcal. per mole in order to estimate the enthalpy of formation of the gas. The enthalpy of vaporization was estimated from that of 1,2-bis(difluoroamino)-4-methylpentane (*4*) and increments from those of the hydrocarbons (*1*). Because the value of the enthalpy of formation of aqueous HF is still uncertain, no uncertainty was assigned to the enthalpy of formation of 1,1-bis(difluoroamino)heptane.

The N—F Thermochemical Bond Energy. The N—F thermochemical bond energy was calculated with a procedure analogous to that of reference (*4*). Consider the hypothetical reaction



$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}\overset{\displaystyle NF_2}{\underset{\displaystyle NF_2}{C}}{-}H(g) + H_2(g) =$$

$$CH_3{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_2{-}CH_3(g) + N_2(g) + 2\ F_2(g) \qquad (3)$$

for which $\Delta H_{298.15} = \Delta Hf°_{298.15}\ [C_7H_{16}(g)] - \Delta Hf°_{298.15}\ [C_7H_{14}N_2F_4(g)] = 4E(N{-}F) + 2E(C{-}N) + E(H{-}H) - E(N{\equiv}N) - 2E(F{-}F) - 2E(C{-}H)$, and the E's are thermochemical bond energies. The enthalpy of Reaction 3 can be evaluated from the enthalpies of formation of gaseous 1,1-bis(difluoroamino)heptane from this research and gaseous *n*-heptane (*1*). A consistent set of bond energies was used as follows: $E(H{-}H) = 104.19$ kcal. (*12*), $E(F{-}F) = 37.76$ kcal. (*12*), $E(N{\equiv}N) = 225.958$ kcal. (*12*), $E(C{-}H) = 99.388$ kcal. from the enthalpy of formation of methane (*12*) and the enthalpy of atomization of carbon (*12*), $E(C{-}N) = 67.48$ kcal. from the enthalpy of formation of dimethylamine (*9*), and $E(N{-}H) = 93.43$ kcal. from the enthalpy of formation of ammonia (*12*). When these values were substituted in Equation 1, the N—F thermochemical bond energy in 1,1-bis(difluoroamino)heptane was $E(N{-}F) = 67.3$ kcal.

The derived value of the N—F thermochemical bond energy is compared with other recent bond energy calculations in Table III. Placing these results on an internally consistent basis was attempted with 1961 atomic weights (*2*) and the revised enthalpy-of-formation data of reference (*12*). One conclusion from Table III is that the N—F thermochemical bond energies in the two $—NF_2$ substituted compounds are about the same and nearly equal to those in NF_3 and N_2F_4. Since the N—F bond in perfluoropiperidine is in a considerably different molecular environment, the considerable difference of this bond energy to that in the other compounds is not surprising.

Increasing evidence (*3*) indicates that the enthalpy of formation of aqueous HF solutions is 0.5 to 1.0 kcal. mole^{-1} more negative than the values used in the calculations of this paper. Use of such a value would increase all the N—F thermochemical bond energy values by the same 0.5 to 1.0 kcal.

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NOMENCLATURE

∂ = differential operator
P = pressure, atm.
T = temperature, ° K.
m = mass, grams
n = number of moles
$\varepsilon_{app.}$ (calor.) = apparent energy equivalent of calorimeter, cal. per deg., as obtained from a comparison experiment rather than a standard benzoic acid calibration
ε(cont.) = energy equivalent of contents, cal. per deg.
$\Delta E_{dec.}$ = energy of decomposition, calories
$\Delta E_{cor.\ to\ std.\ states}$ = energy for reduction to standard states, calories
$\Delta E_{ign.}$ = electrical ignition energy, calories
Δt_c = corrected temperature rise, degrees
$\Delta Ec°/M$ = standard energy of idealized combustion reaction, cal. per gram
$\Delta Ec°$ = standard energy of idealized combustion reaction, kilocalories per mole
$\Delta Hc°$ = standard enthalpy of combustion, kilocalories per mole
$\Delta Hf°(g)$ = standard enthalpy of formation of gas, kilocalories per mole
$\Delta Hv°$ = standard enthalpy of vaporization, kilocalories per mole
i = superscript indicating initial state
f = superscript indicating final state
E = bond energy, kilocalories

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Enthalpies of Formation of Ethylenediamine, 1,2,-Propanediamine, 1,2,-Butanediamine, 2-Methyl-1,2-propanediamine, and Isobutylamine

C—N and N—F Thermochemical Bond Energies

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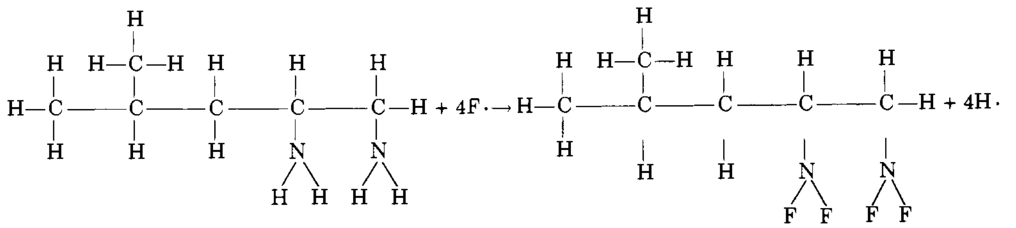
The enthalpies of combustion of ethylenediamine, 1,2-propanediamine, 1,2-butanediamine, 2-methyl-1,2-propanediamine, and isobutylamine, as determined by oxygen-bomb combustion calorimetry, were used to derive the following values, in kcal. per mole, for the enthalpies of formation of the liquid, $\Delta Hf^{\circ}_{298.15}$, from graphite and gaseous hydrogen and nitrogen: ethylenediamine, −15.06 ± 0.13; 1,2-propanediamine, −23.38 ± 0.10; 1,2-butanediamine, −28.74 ± 0.19; 2-methyl-1,2-propanediamine, −32.00 ± 0.16; and isobutylamine, −31.68 ± 0.12. These values were combined with enthalpies of vaporization derived from vapor pressure measurements to obtain values of the enthalpies of formation in the gaseous state. For these molecules, the C—N thermochemical bond energy was derived and compared to that in the simple alkyl amines. The N—H thermochemical bond energy in a 1,2-diamine was compared to the N—F thermochemical bond energy in a 1,2-bis(difluoroamino)alkane.

IN 1962 the difluoroamino compound, 1,2-bis(difluoroamino)-4-methylpentane, was studied in this laboratory (7), and a value of the N—F thermochemical bond energy was derived. This derivation required selections of values of C—H, N—H, and C—N thermochemical bond energies from other molecules. Pure samples of 1,2-diamines were not available then, but if thermochemical studies could have been made on such compounds, then obviously the N—F thermochemical bond energy in a 1,2-bis(difluoroamino)alkane could have been compared directly to the N—H thermochemical bond energy in a 1,2-diamine by consideration of reactions such as Reaction 1. It is assumed that all bond energies other than N—H and N—F are fixed during the reaction. However, this assumption is not entirely valid, because bond energies in complex molecules are rather labile. This treatment and its comparison to earlier bond energy calculations (7) are instructive, nevertheless.

In this laboratory and others, enthalpies of formation of most of the alkyl amines having four or less carbon atoms in the molecule have been measured. The present study adds values of the enthalpy of formation of isobutylamine and the 1,2-diamines with four or less carbon atoms. The carbon-nitrogen bond energies in the alkyl amines were compared to those in the 1,2-diamines.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