Heat of Formation and Other Properties of Trinitrofluoromethane

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The energy of reaction of liquid trinitrofluoromethane with diethyl oxalate as fuel was determined in a rotating bomb calorimeter. The standard heat of formation, which is −51.99 ± 0.48 kcal. per mole (±0.48 is estimated standard deviation of the mean), at °C. was calculated using a computer program which has been developed for compounds containing C, H, O, N(F, Cl, Br). The effect of temperature on density, vapor pressure, and surface tension of the compound was determined for a given temperature range. The equations relating these properties to the temperature are given. For better characterization, several other properties, such as freezing and boiling point, refractive index, and heat capacity were also measured and are reported.

THE REACTION of liquid trinitrofluoromethane with diethyl oxalate was carried out in an oxygen atmosphere using diethyl oxalate as the fuel. The equation of the idealized heat of reaction from which the heat of formation is determined is:

$$\text{F—C(NO}_2)_3\text{(liq.)} + \text{C}_6\text{H}_{10}\text{O}_4\text{(liq.)} + 4.25\ \text{O}_2\ \text{(gas)} + 115.5\text{H}_2\text{O(liq.)} \rightarrow 7\text{CO}_2\text{(gas)} + \text{HF}\cdot120\text{H}_2\text{O(liq.)} + 3/2\text{N}_2\text{(gas)} \quad (1)$$

To obtain clean combustion without explosion, the proper ratio of fluorotrinitromethane (FNF) to diethyl oxalate was determined in separate combustion runs and was found to be 35% FNF to 65% oxalate.

EXPERIMENTAL

Material. FNF was synthesized (*1*) and then purified by fractional distillation at atmospheric pressure (b.p.—84.2° C., 760.1 mm. of Hg), using a 6-inch column. Analysis by vapor-phase chromatography indicated a purity of better than 99.6%.

The benzoic acid used for calibration of the calorimeter was a standard sample 39h of the National Bureau of Standards, having a certified heat of combustion of −6318.3 cal. per gram mass in vacuum. The fuse was an unmercerized cotton thread ($\Delta E_i/M = -4050$ cal. per gram). The bag to contain the sample was made from a polypropylene film whose value of $\Delta E_i/M = -11059$ cal. per gram was determined by a series of combustion experiments in this laboratory.

Diethyl oxalate was distilled, using a Todd column, and the 11th fraction (boiling point of 106° C. at 52 mm.) was used. A check on a VPC indicated that the material had a purity of better than 99.5% and its E_i/M value, as determined in this laboratory, was −4882.83 cal. per gram.

Apparatus and Procedures. COMBUSTION EXPERIMENT. The combustion experiments were carried out in a rotating bomb calorimeter built after a design of the Bureau of Mines, Bartlesville, Okla. (*6*). The modification to the original instrumentation and the accuracy of the measurements have been reported (*10*). Since the seams of the Mylar bags used in previous measurements were brittle and caused trouble when the bags were folded and placed in the crucible, this material was replaced with polypropylene. The quantities of reactants were chosen to give a temperature rise in the calorimeter of approximately 2° C. Otherwise, the same procedure was used as was reported for chlorotrinitromethane (*10*).

The complete combustion of the FNF was evidenced by infrared analysis, titration of the water solution, and absorption of carbon dioxide on Ascarite. Thus, incomplete combustion, according to Equation 1 was easily noted by the presence of nitrogen oxides, carbon monoxide, carbon tetrafluoride, fluorine in the gas phase, or unburned carbon inside the calorimeter bomb, and these runs 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 IR 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 IR.

MEASUREMENTS OF OTHER PROPERTIES. Density measurements were made with a 2-ml. pycnometer (calibrated at 20° C.) over a temperature range from 20° to 65° C. The changes in the volume of the bottle were corrected (*7*).

The freezing point was obtained from freezing curves and determined within ±0.05° C. by a method developed by the National Bureau of Standards (*4*). The refractive index was measured with a Baush and Lomb refractometer with an accuracy of ±0.0003.

Surface tension was measured by the maximum bubble pressure method using a Cassel surface tensiometer (*3*) with an accuracy of ±0.1 dyne per cm. The tensiometer was calibrated with purified water, toluene, benzene, cyclohexane, and acetone. A brief description of the apparatus has been presented (*11*).

Vapor pressure measurements were made in a static tensimeter which was immersed in a controlled temperature bath. The temperature of the bath was uniform to ± 0.01° C. Basically, the apparatus is comprised of two manometer limbs. One was connected to the high-vacuum line and the other was in contact with the vapor in equilibrium with the liquid sample. The heights of the mercury columns in the manometer were measured with a cathetometer. (Second digits were estimated.) To introduce the sample into the sample bulb of the tensimeter, the mercury could be withdrawn into a reservoir. After thoroughly degassing the apparatus at pressures down to 10^{-4} torr or less, a previously dried and distilled sample was distilled into the sample bulb of the tensimeter.

Approximately 30% of the sample was then removed by distillation, and the remaining material was trapped by introducing mercury into the two arms of the manometer. A series of readings of vapor pressure at different temperatures was taken. The vapor pressure measurements were made approaching the test temperature from the lower side. To check for possible decomposition of the sample during the measurements, a few readings were taken on the same material, approaching from the higher temperature side. The results were in good agreement, thus indicating no decomposition of material. The mercury was withdrawn again and approximately 50% of the sample was removed. Then, after introducing the mercury into the manometers, another series of readings was taken for the remaining sample. The readings obtained by this procedure were in good agreement, indicating that there was no impurity of sufficient volatility to give false measurements of the vapor pressure. The temperatures were varied from 0.77° to 69.90° C. and measured with calibrated thermometers.

The heat capacity was determined in a calorimeter with an uncertainty of ±0.01 cal. per gram degree C. All uncertainties are estimated standard deviations of the mean.

RESULTS

Table I lists the average (five measurements) heat of formation of FNF, which were calculated from the heat of reaction at 25° C. for FNF and diethyl oxalate. The heats of reaction according to Equation 1 were measured as −799.987 ± 0.48 kcal. per mole at constant volume and −797.470 ±0.48 kcal. per mole constant pressure. To calculate the heat of formation of FNF, the following heats of formation were used: −94051.8 cal. per mole for CO_2 and −68317.5 cal. per mole for H_2O. The calculations were performed on a digital computer for which a special program was developed (*2*).

Several other measured properties of FNF are summarized in Table I. The density changes, with the temperature determined at 20°, 25°, 35°, 45°, 55°, and 65° C. are listed in the first column of Table I. The plot of density, ρ, *vs.* temperature, T, results in a straight line with the equation:

$$\rho = 1.8459 - 0.002415T \qquad (2)$$

The surface tension values were fitted to the Ramsey-Shields equation, which gave a straight-line relation over the measured temperature range. The equation for this relation is:

$$\gamma\left(\frac{169.03}{\rho}\right)^{2/3} = -2.083t + 561.44 \qquad (3)$$

γ = surface tension in dynes/cm.
ρ = density of the liquid
t = temperature in ° C.

From the Ramsey-Shields equation, the critical temperature was estimated to be 275° C. This value, however, is subject to considerable error since the high volatility of the compound prohibited measurements above 50° C., and its lack of stability prohibited a direct determination.

The vapor pressure values are listed in Table I as a function of the temperature, and the equation of this correlation is:

$$\log P = 6.8187 - \frac{1785.71}{T} \qquad (4)$$

The calculated heat of vaporization (Clausius-Clapeyron) is $\Delta H_t = 8.171$ kcal. per mole.

Using Equation 5, the heat of formation of FNF was estimated to be −53.4 kcal. per mole.

$$\Delta H_f = \sum_i n_i q_i + \sum_j (\Delta Ha)_j \qquad (5)$$

Where n_i and q_i are the numbers and bond energies of the *i*th bond in the molecule and $(\Delta Ha)_j$ the heat of formation of the *j*th gaseous atoms produced by complete decomposition of the compound.

The following bond energies were used: $E(C - F)$ = 101.7(*9*), $E(C - N)$ = 67.4(*3*), $E(NO_2)$ = 212 kcal. per mole.

The bond energies of NO_2 were determined from the heats of formation of seven different nitro compounds.

Table I. Summary of Measured Properties of FNF at Different Temperatures

Melting point: −29° ± 0.05° C.

T, ° C.	ρ, G./ Ml. ± 0.001[b]	γ, Dynes/ Cm. ± 0.1[b]	P[a], Mm. Hg ± 0.1	n, ± 0.0003[b]	C_p, Cal./ G. ° C. ±0.01[b]	ΔH_f, Kcal./ Mole ± 0.48[b]
1.65			20.6			
5.56			25.6			
10		26.42	32.2			
15		25.70	42.5			
20	1.795	25.18	55.8			
25	1.785			1.3944	0.21	−51.99
25.1			71.6			
35	1.762					
35.9			119.3			
40		22.60				
45	1.737					
49.9			195.0			
50		21.57				
55	1.717					
60.1			290.5			
65	1.689					
69.9			410.4			
84.2			760.1			

[a] Average pressure from three to four readings which were taken before and after parts of the sample were distilled over as described in vapor pressure measurements under apparatus and procedures. The mean was corrected to the mercury pressure at 0° C. [b] Estimated standard deviation.

Ketelaar (*8*) reports a value of 214 kcal. per mole. The dissociation energies were obtained from Wilkins (*9*). Agreement between calculated and measured heat of formation is good.

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Heats of Formation and Bond Energies of *N*-Fluoro-*N*-nitrobutylamine Isomers

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The heats of formation of the three isomers—normal, secondary, and tertiary—of butyl-*N*-fluoronitramine are calculated from the heats of combustion as determined with a high precision platinum-lined rotating bomb calorimeter and found to be −38.5 ± 0.4, −37.3 ± 1.0, and −29.9 ± 0.3 kcal. per mole, respectively. The bond energy for N—F in primary $N<^{F}_{NO^2}$ is calculated and found to be 67.04 kcal. per mole. The influence of the molecular structure on the heats of formation and bond energies is discussed.

THE INVESTIGATION of the heat of formation and the N—F bond energy was carried out as a part of a program to evaluate *N*-fluoro-*N*-nitro compounds.

The reactions of the liquid *N*-fluoro-*N*-nitrobutylamines with either diethyloxalate or diethylphthalate as diluents were carried out in an oxygen atmosphere (30 atm.).

The equation of the idealized heat of combustion from which the heat of formation at 298.1° K. and 1 atm. is determined is: $C_4H_9O_2N_2F(l) + 5O_2(g) + 146H_2O(l) \rightarrow 4C_2(g) + HF \cdot 150H_2O(1) + N_2(g)$. To obtain clean combustion without explosion, the proper ratio of the fluoronitramine compounds to the diluting compounds was determined in a series of preliminary combustions. Best results were obtained with the ratio 35:65 for fluoronitramine to diluting compound.

EXPERIMENTAL

Material. The *N*-fluoro-*N*-nitro-*n*-butylamine (*3*), and the *N*-fluoro-*N*-nitro-(*sec*- and *tert*-) butylamine (7) were synthesized and then purified by distillation. The purification of these materials was difficult since all three isomers are unstable at room temperature, with the *tert* compound being the least stable. Because of this instability and the high volatility of the material, none of the usual chromatographic methods could be applied to check the purity of the material.

The samples were distilled several times in high vacuum at low temperature (0° C.) and checked by IR spectrophotometer and refractive index measurements. When no changes in the IR curves and refractive indices were detected between subsequent distillations, the samples were used for combustion measurements. Table II lists some properties of the three isomers.

The high instability and volatility of these fluoronitramines made the measurements extremely difficult. Sometimes the material had to be purified between subsequent combustion runs (especially the tertiary compound).

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. (*5*). The modifications to the original instrumentation have been described earlier (*18*).

Procedure. Essentially, the standard procedure was used as reported previously (*18*). Both the butylfluoronitramine and the diluting agent were sealed in a polypropylene bag, and the bag was placed in the platinum crucible of the bomb. The quantities of the material were chosen to give a temperature rise in the calorimeter of approximately 1.5° C.

Heats of Combustion and Formation. The auxiliary data used in the combustion energy calculations are listed in Table I.

The heats of combustion and formation are summarized in Table II. The average deviation from the mean in these measurements was 0.0%. Data reduction was performed on a digital computer for which a special program had