Heat of Formation of Viton A by Combustion Calorimetry

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BECAUSE OF recent interest in polymeric substances with good high temperature stability, the heat of formation of Viton A (empirical formula $C_5H_{3.5}F_{6.5}$) has been determined by combustion calorimetry, applying a technique similar to that used by Scott, Good, and Waddington (*6*). Nujol mineral oil was mixed with the samples to serve as a kindling agent and as a source of hydrogen to convert the fluorine quantitatively to HF.

Assuming quantitative conversion of the fluorine to HF and deducting heat of combustion of the mineral oil resulted in the net reaction,

$$C_5H_{3.5}F_{6.5}(s) + (6.5n + 1.5)\ H_2O(l) + 4.25\ O_2(g) = 5CO_2(g) + 6.5\ HF \cdot nH_2O(l) \quad (1)$$

The heat of this reaction was calculated from combustions with various mixtures of oil and fluoropolymer and found to be essentially constant for mixtures containing 75% or more mineral oil. Subsequent mass spectrographic analyses of the combustion products confirmed the assumption that no CF_4 was formed from mixtures containing 75% or more mineral oil.

APPARATUS AND PROCEDURE

The calorimeter used in the measurements is a standard Parr Adiabatic Calorimeter, Series 1200, with a Beckman thermometer substituted for the calorimeter thermometer. The bomb is a Parr platinum-lined bomb, Model 1106, with an internal volume of 0.340 liters.

The standard Parr ignition box and ignition wire were used in both the calibration and sample measurements. The bomb was flushed twice by filling to 10 atm. pressure (gage), emptying, and finally filling to 30 atm. (gage) for all runs. The water, 2000 grams, was weighed into the calorimeter pail using a torsion balance sensitive to 0.05 gram at 2500 gram load.

The Viton samples were cut up into small pieces and weighed into the platinum combustion cup; then the Nujol was weighed into the same cup. In all of the runs with Viton-oil mixtures, 1.38 grams of water was added to the bomb. All combustions were clean—with no trace of carbon deposit. Average final temperature of the measurements was 29.7° C.

Mass spectrograpic analysis of the gasous combustion products showed that mixtures containing 75% or more of mineral oil yielded no CF_4. No fluoride compounds other than HF and CF_4 were detected in any of the combustion products. No weight loss was observed in the platinum crucible used. In two comparative experiments, a pelletized mixture of equal weights of benzoic acid and Viton A produced a final gas mixture containing 0.12 ± .08 mole % CF_4 and 8.78 ± .10 mole % CO_2.

Final HF concentrations were $HF \cdot 27\ H_2O$ from the 15% Viton combustions and $HF \cdot 15\ H_2O$ from the 25% Viton combustions. The final concentration was considered as $HF \cdot 20\ H_2O$ in the calculations which follow. Correction of the actual measurements of a final concentration of $HF \cdot 20\ H_2O$ amounted to only −0.08 cal. per gram for the 25% Viton combustions and +0.05 cal. per gram for the 15% Viton combustions, and was therefore omitted.

Units of Measurement. All data reported are based on the 1956 to 57 International Atomic Weights (*7*) and on a summary of fundamental constants listed by Rossini (*4*). Standardization of the calorimeter was performed by means of combustions with benzoic acid, Bureau of Standards, Standard Sample 39 h. Four calibration measurements (2434.7, 2434.6, 2434.1, and 2435.7) resulted in a mean energy equivalent value of 2434.8 ± 1.1 cal. per ° C., with the uncertainty in the mean value assigned according to the recommendations of Rossini (*4*).

For reducing apparent masses from air to vacuum, densities of 1.320, 0.89, and 1.8 grams per cc. were used for benzoic acid, mineral oil, and Viton A, respectively. No corrections were applied for the heats of compression of Viton, Nujol, water, and aqueous HF.

MATERIALS

The Viton A sample used in the measurements is a copolymer of nominal composition: 60 weight % vinylidene fluoride and 40 weight % hexafluoropropylene or 77.8 mole % $CH_2=CF_2$ and 22.2 mole % $CF_3CF=CF_2$. This corresponds to a theoretical elemental composition of 32.10% C, 1.89% H, and 66.10% F and an empirical formula of $C_{5.00}H_{3.50}F_{6.50}$. Bomb combustion products from mixtures of 13% Viton and 87% mineral oil were analyzed for fluorine in this laboratory by the acid titration method described by Good, Scott, and Waddington (*2*). The average of three determinations (65.88, 66.20, and 65.84) was 65.97% F. compared with the theoretical, 66.10%. A portion of the sample used in the measurements was sent to the manufacturer (Du Pont) for confirmatory analysis. Their analysis indicated 32.0 and 32.1% C. and 1.9 and 2.1% H by standard analytical methods, and 61 ± 1% vinylidene fluoride and 39 ± 1% hexafluoropropylene determined by an infrared technique. (The infrared analysis corresponds to a fluorine content of 65.80%). The nominal composition of $C_5H_{3.5}F_{6.5}$ was assumed to be correct; the effect of the uncertainty in the analysis on the derived heat of formation is discussed in a paragraph below.

Nujol mineral oil was used as a kindler and source of hydrogen in the combustions. An empirical formula of $C_{12}H_{26}$ was assumed for the unit fugacity corrections. The benzoic acid used in apparatus calibrations was National Bureau of Standards Sample 39 h, having a certified heat of combustion of 26.4338 abs. kjoules per gram mass.

MEASUREMENTS AND RESULTS

The results of the measurements are shown in Table I. The heats of combustion of mixtures containing from 0 to 25.05% Viton A fit the equation,

$$-\Delta E_B = 10{,}966.5 - 8146.4 \times \text{wt. fraction Viton A (cal. per gram)} \quad (2)$$

with an average absolute deviation of 7.7 cal. per gram.

This equation fits the average of the 0% Viton combustions exactly and deviates from the average of the 15% and 25% Viton combustions by −0.8 and +0.4 cal. per gram respectively. Taking ΔE of the bomb reaction from Equation 2 and substracting the heat evolution due to the mineral oil (10,966.5 × wt. fraction oil) results in a constant value of −2820.1 cal. per gram for ΔE of Reaction 1, with an estimated over-all uncertainty of ±11.8 cal. per gram.

Table I. Heats of Combustion of Viton A–Nujol Mixtures and Deviation of Measurements from the Equation

$-\Delta E_B = 10{,}966.5 - 8146.4 \times$ Wt. Fraction Viton (cal./g.)

m(Nujol), G.	m(Viton), G.	$-\Delta E_B$, Cal./G.	d, Cal./G. [$-\Delta E_B$ (Measured) + ΔE_B (Equation)]
1.0041	...	10,944.4	−22.1
1.0015	...	10,966.4	−0.1
1.0036	...	10,976.8	+10.3
0.7428	...	10,973.2	+6.7
0.7400	...	10,971.6	+5.1
0.8504	0.1494	9,753.0	+3.6
0.8505	0.1508	9,723.2	−16.4
0.8520	0.1504	9,746.8	+2.3
0.8760	0.1547	9,751.2	+7.5
0.7508	0.2499	8,942.7	+10.4
0.7553	0.2525	8,919.7	−6.1
0.7476	0.2494	8,932.0	+3.7
0.7520	0.2504	8,925.2	−6.3
0.5060	0.5117	6,849.4	−21.1
0.5010	0.5008	6,876.3	−17.8
0.3330	0.6786	5,450.4	−51.5
0.3329	0.6804	5,464.8	−31.4
0.2068	0.8265	4,374.3	−75.9

An alternate method of calculation, deducting the heat of combustion of the oil and evaluating ΔE of Reaction 1 for each run, results in averages of −2814.6 cal. per gram for the four combustions with 15% Viton and −2822.0 cal. per gram for the four combustions with 25% Viton. Thus the final value of −2820.1 cal. per gram is weighted approximately 2.5 to 1 in favor of the 25% Viton combustions.

The correction to unit fugacity is constant at +2.6 cal. per gram for combustions with 100, 85, and 75% oil, and for Reaction 1. Application of this correction, conversion to a molal basis, and correction to a constant pressure process results in $\Delta H^0_{302.8} = -526{,}660$ cal. per mole for Reaction 1. No correction to 298.15° K. was applied. The use of Circular 500 (5) values for the heats of formation of H_2O (l), $CO_2(g)$, and $HF \cdot 20H_2O$ permits evaluation of the heat of formation of Viton A as −332,700 ± 2200 cal. per mole, or −1.779 ± 0.020 kcal. per gram.

In a comparative experiment two pelletized samples of 50% Viton and 50% benzoic acid were burned in the bomb under similar conditions with measured net heats of combustion of −2735.0 and −2736.9 cal. per gram under bomb conditions. Mass spectrographic analysis of the gaseous products from one of these combustions indicated 0.12 ± 0.8 mole % CF_4 and 8.78 ± 0.10 mole % CO_2. Using the heat of formation of CF_4 (*6*) and other necessary heats of formation from Circular 500 (*5*), separate derivations of the heat of formation of Viton A were made using the extremes in the uncertainty of the CF_4 analysis. For 0.04 mole % CF_4 the derived heat of formation was −1.840 kcal. per gram; for 0.20 mole % CF_4, the derived heat of formation was −1.776 kcal. per gram. This serves as a rough check on the value derived from the Viton-oil combustions.

The chief source of error in the final derived heat of formation is the uncertainty in the sample analysis. Assuming the analysis of 61% $CH_2{=}CF_2$ and 39% $CF_3{=}CF_2$ or $C_5H_{3.55}F_{6.45}$ would lead to a derived heat of formation of −334.9 kcal per mole or −1.799 kcal. per gram.

Data Comparisons. DuPont estimated a heat of formation of −1.79 kcal. per gram based on heats of formation of the starting materials and the process heat balance. Consideration of Viton A as a simple mixture of polyethylene (*3*) and Teflon (*6*) results in a heat of formation of −1.742 kcal. per gram.

Assuming the heat of formation of an equivalent hydrogen polymer (0.778 mole fraction polyethylene and 0.222 mole fraction polypropylene) to be −0.4634 kcal. per gram or −6.5 kcal. per CH_2 group, and utilizing the C—F bond energies derived by Good and others (*1*) results in a calculated heat of formation of −1.755 kcal. per gram for $C_5H_{3.5}F_{6.5}$. Similarly for the reaction,

$$C_5H_{10}(\text{polymer}) + 3.25\,F_2(g) = C_5H_{3.5}F_{6.5}(\text{polymer}) + 3.25\,H_2(g) \qquad (3)$$

the heat of reaction predicted from the C—F bond energy values of Good and others (*1*) is −295.83 kcal. per mole, which is in reasonable agreement with the value of −300.20 based on this work.

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LITERATURE CITED

(1) Good, W.D., Douslin, D.R., Scott, D.W., George, A., Lacina, J.J., Dawson, J.P., Waddington, G., *J. Phys. Chem.* **63**, 1133 (1959).

(2) Good, W.D., Scott, D.W., Waddington, G., *Ibid.*, **60**, 1080 (1956).

(3) Parks, G.S., Mosley, J.R., *J. Chem. Phys.* **17**, 691 (1949).

(4) Rossini, F.D., "Experimental Thermochemistry," Interscience, New York, 1956.

(5) Rossini, F.D., Wagman, D.D., Evans, W.H., Levine, S., Jaffe, I., Selected Values of Chemical Thermodynamic Properties, Natl. Bur. Standards (U. S.) Circ. **500**, 1952.

(6) Scott, D.W., Good, W.D., Waddington, G., *J. Am. Chem. Soc.* **77**, 245 (1955).

(7) Wichers, E., *Ibid.*, **80**, 4121 (1958).

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