Enthalpy of Formation of Trifluoroacetonitrile

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Abstract: At temperatures above 830°K, the thermally initiated reaction of CF_3CN reversibly yields C_2F_6 and C_2N_2. Equilibrium constants were determined in the temperature range 865–925°K and a reaction enthalpy of −10.54 kcal/mol derived by third-law analysis. When combined with heats of formation of C_2F_6 and C_2N_2, this result gave the enthalpy of formation of CF_3CN as −118.4 kcal/mol. Calorimetric measurements of the enthalpy of reaction of nitrogen trifluoride with CF_3CN to give CF_4 and N_2 gave the enthalpy of formation of CF_3CN as −118.9 kcal/mol in good agreement with the equilibrium study. The stability of CF_3CN is from 10 to 20 kcal less than predicted by empirical estimation methods. Stabilization of about 5 kcal/mol postulated for CF_3 groups adjacent to sp^2 carbons does not appear in CF_3CN.

Interpretation of the energetics and kinetics of free radical addition reactions of trifluoroacetonitrile at high temperatures has been hindered by lack of an experimental enthalpy of formation of $CF_3CN(g)$.[2] The low-temperature heat capacity has been measured[3] and a third-law entropy derived, in good agreement with calculations[4] based on molecular structure[5] and the vibrational assignment.[6,7]

For the enthalpy of formation, however, only estimates[2b] have been published, ranging from −127 to −139 kcal/mol. We have now determined the enthalpy of formation by two independent methods. The equilibrium constant of the reaction

$$2CF_3CN(g) \rightleftharpoons C_2F_6(g) + C_2N_2(g) \quad (1)$$

in the range 865–925°K was measured and the enthalpy of reaction calculated by third-law[8] analysis. Second, the energy of reaction of CF_3CN with NF_3 was directly measured in a bomb calorimeter. Combined with well-established enthalpies of formation[9] of C_2F_6, C_2N_2, and NF_3, these two approaches yield enthalpies of formation of $CF_3CN(g)$ in good agreement.

Experimental Section

A. Equilibrium Measurements. Hexafluoroethane and CF_3CN samples were purchased from Peninsular Chemresearch, Inc. and cyanogen from Columbia Organic Chemicals, Inc. Small amounts were degassed and triply distilled under vacuum prior to use. The experimental procedure involved charging 60-cc Vycor reaction tubes with C_2F_6 and C_2N_2 to a total pressure of approximately 200 mm at 25°. These sealed tubes were placed in an electrically heated furnace (controlled to ±3°) and sampled at 18-hr intervals until equilibrium was established. Chromatographic analysis of the products indicated that equilibrium was reached in 72 hr. Twofold variations in the concentration of C_2F_6 over C_2N_2 (and *vice versa*) did not affect the equilibrium. Equilibrium constants for reaction 1 are defined by

$$K_{eq} = \frac{[C_2F_6(g)][C_2N_2(g)]}{[CF_3CN(g)]^2} \quad (2)$$

The experimental equilibrium constants are given in Table I. A third-law[8] average reaction enthalpy at 298.15°K of −10.54 ± 0.14 kcal was calculated by means of free-energy functions for CF_3CN,[4] C_2N_2,[9] and C_2F_6.[9] The essential independence of the calculated $\Delta H_r°_{298}$ on temperature is good evidence that equilibrium was established. Combined with enthalpies of formation[9] of −321.2 ± 1.2 kcal/mol for $C_2F_6(g)$ and +73.87 ± 0.43 kcal/mol for $C_2N_2(g)$, the enthalpy of reaction yields $\Delta H_f°_{298}(CF_3CN, g)$ = −118.4 ± 1.0 kcal/mol.

Table I. Equilibrium Constants for the Reaction $2CF_3CN \rightleftharpoons C_2F_6 + C_2N_2$

Run	Temp, °K	K_{eq}	$\Delta H_r°_{298}$
V-3-1	865	41.3	−10.63
-3-2		40.0	−10.58
-4-1		36.0	−10.40
-4-2		36.9	−10.44
I-3-1	885	35.5	−10.61
-3-2		36.5	−10.66
-4-1		31.8	−10.42
III-5-1	925	27.1	−10.60
-5-2		26.0	−10.52
			−10.54 ±0.14 kcal/mol

B. Bomb Calorimetry Measurements. Materials. Low-temperature distillation was employed to purify CF_3CN for the calorimetric study. This technique removed impurities of 0.2% of ethylene and carbon dioxide as identified by infrared and mass spectrometry. The infrared spectrum of the purified material agreed with that published by Edgell and Potter[6] and the sample purity was taken as 99.9+%.

A Research grade sample of NF_3 was purchased from Air Products and Chemicals, Inc. Infrared and mass spectrometry indicated the only impurity was 0.15% CF_4. Since this impurity was "inert" under the conditions of the experiment it was not necessary to remove it. Previous experience suggested and preliminary experiments confirmed that mixtures of CF_3CN and NF_3 are stable at room temperature, but detonate when ignited by electrical fusion of a fine nickel wire. The NF_3 must be present in slight excess to

$$CF_3CN(g) + {}^5/_3NF_3(g) \longrightarrow 2CF_4(g) + {}^4/_3N_2(g) \quad (3)$$

ensure complete conversion and the excess NF_3 is decomposed to N_2 and F_2.

(1) (a) Dow Chemical Co., Thermal Research Laboratory; (b) Dow Chemical Co., Physical Research Laboratory; (c) Rensselaer Polytechnic Institute.

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Table II. Calorimetric Data for Reaction 3

Run no.	CF_3CN, g	$\Delta\theta$, deg	q_v, cal	Corrections, cal: NF_3	NiF_2	I^b	$\Delta E_r/M$, cal/g
1	0.5449	0.4918	−1,573.6	−8.7	1.4	0.4	−2,900.5
2	0.5430	0.4896	−1,567.5	−5.4	0.8	0.4	−2,894.5
3	0.5446	0.4898	−1,567.2	−8.6	0.3	0.4	−2,892.2
4	0.5426	0.4892	−1,565.2	−8.2	0.7	0.4	−2,897.7
5	0.5446	0.4906	−1,569.7	−10.5	1.2	0.4	−2,898.6
6[a]	0.5430	0.4883	−1,562.4	−9.9	1.2	0.3	−2,892.8
						Av	−2,896.0₅
						σ (std dev of mean) =	± 1.2 cal/g

[a] The reactants in run no. 6 were allowed to remain mixed for 24 hr before firing to determine any prereaction. [b] I = electrical ignition energy.

Calorimetric System. A conventional Dickinson-type isothermal shield combustion calorimeter was used. A data acquisition system consisting of a Hewlett-Packard Model 2801A Quartz Thermometer and an IBM 1800 computer automatically monitored the temperature as a function of time. The temperature rise was corrected for heat exchange with the surroundings by means of a Burroughs 5500 digital computer, according to the standard mathematical procedures.[10]

A nickel combustion bomb of 0.352-l. volume was conditioned by several explosions with excess NF_3 in order to produce a coating of nickel fluoride on the bomb walls. After this conditioning the bomb was opened only in an inert atmosphere. The calorimeter system was calibrated from 24 to 25° by addition of electrical energy. Fourteen experiments gave a value of $\mathcal{E}$(calor) = −3199.6 cal/deg with a standard deviation of 0.3 cal/deg.

Procedure. A heat determination first involved fitting a weighed nickel fuse between the electrodes of the bomb. The bomb was then evacuated to 1-μ pressure. A weighed amount of trifluoroacetonitrile contained in a 10-ml stainless steel cylinder was then metered into the bomb to a pressure of 300 mm. In a similar manner, NF_3 was then admitted to the bomb to a total pressure of 815 mm. The bomb was then placed in the calorimeter and the reaction initiated by discharging a standardized capacitor across the nickel fuse wire. There was an audible "click" as the instantaneous reaction took place.

After each heat measurement the bomb was attached to a vacuum system for gas sampling. The F_2 due to excess NF_3 was removed by reaction with mercury and the CF_4 and N_2 checked by mass and infrared spectral analysis. In all determinations CF_4 and N_2 were found in the correct ratio as predicted by the amounts of starting materials. No other products of reaction were detected. The bomb was finally opened in a dry nitrogen glove box and the unburned pieces of nickel fuse recovered. These were cleaned and weighed to determine the net amount burned to NiF_2. Data for this correction were available.[11]

Results

Table II lists the results of six experiments including a test run (no. 6) which indicates that the gases CF_3CN and NF_3 do not react within limits of detection on standing for 24 hr. $\Delta\theta$ is the temperature rise corrected for heat exchange and q_v is equal to the product of $\mathcal{E}$(calor) and $\Delta\theta$. The next three columns are corrections for dissociation of excess NF_3, combustion of the nickel fuse, and electrical ignition energy. $\Delta E_r/M$ is the internal energy change in cal/g of CF_3CN.

The average value of $\Delta E_r/M$ and a molecular weight of 95.024 for CF_3CN yield $\Delta E_{r298} = -275.19 \pm 0.22$ kcal/mol. For constant pressure conditions we calculate $\Delta H_{r298} = -274.80 \pm 0.22$ kcal/mol. With enthalpies of formation[9] of -223.05 ± 0.10 kcal/mol for CF_4(g) and -31.43 ± 0.20 kcal/mol for NF_3(g) we derive $\Delta H_f{}^\circ{}_{298}(CF_3CN\ (g)) = -118.9 \pm 0.5$ kcal/mol, in excellent agreement with the equilibrium data. An average of -118.7 ± 0.5 kcal/mol is selected as a "best" value.

(10) W. N. Hubbard, D. W. Scott, and G. Waddington, "Experimental Thermochemistry," Vol. I, F. D. Rossini, Ed., Interscience, New York, N. Y., 1956, Chapter 5.

(11) E. Rudzitis, E. H. Van Deventer, and W. N. Hubbard, *J. Chem. Eng. Data*, **12**, 133 (1967).

Discussion

The published estimates[2b] are too negative by 10–20 kcal/mol. The stability of CF_3CN is thus much less than predicted by the usual methods. The relation of CF_3CN to other compounds containing the CF_3 or CN group is perhaps most easily demonstrated by calculating the enthalpies of various "redistribution" reactions. For this purpose all enthalpy of formation data are taken from a recent compilation[12] to ensure consistency. Results presented in Table III are uniformly exothermic.

Table III. Enthalpies of Redistribution Reactions (298°K)

Reaction	ΔH_r, kcal
$2CF_3CN \rightarrow CF_3CF_3 + C_2N_2$	−9.8
$CF_3CN + CH_3CH_3 \rightarrow CF_3CH_3 + CH_3CN$	−18.3
$CF_3CN + C_6H_5CH_3 \rightarrow C_6H_5CN + CF_3CH_3$	−19.2
$CF_3CN + C_6H_5CH_3 \rightarrow C_6H_5CF_3 + CH_3CN$	−15.7
$CF_3CN + C_6H_5C_6H_5 \rightarrow C_6H_5CF_3 + C_6H_5CN$	−15.7

Another view of the stability of CF_3CN is provided by the "bond energy comparison" discussed by Flannery and Janz.[2b] For the reaction

$$XCF_3 + 3H \longrightarrow XCH_3 + 3F \qquad (4)$$

they calculate an average of 48.3 kcal from several examples with varying X, with some evidence that CF_3 groups adjacent to sp^2 carbon give a more endothermic result. Recent revisions to fluorine thermochemistry[12] raise the average to about 53 kcal. The present study gives a value for X = CN of 40 kcal, much *less* endothermic than the average. Speculation by Flannery and Janz[2b] that reaction of CF_3CN would be more endothermic than the average is not supported.

Recent "best" values for enthalpies of formation[9] of CF_3 radical of −112.4 kcal/mol and of CN radical of 104 kcal/mol can be used with the present work to calculate the CF_3–CN bond dissociation energy as 110.5 kcal/mol. Data for CH_3 and CH_3CN[12] yield the CH_3–CN bond dissociation energy as 117.8 kcal/mol. Whereas CF_3 appears to interact more strongly than CH_3 with some atoms (F, H, Cl),[2b] the opposite is true for the CN group.

(12) D. R. Stull, E. F. Westrum, Jr., and G. C. Sinke, "Chemical Thermodynamics of Organic Compounds," John Wiley, New York, N. Y., 1969.