

Enthalpy of Formation of Trifluoroacetonitrile

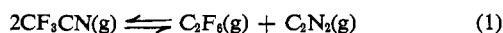
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Abstract: At temperatures above 830°K, the thermally initiated reaction of CF₃CN reversibly yields C₂F₆ and C₂N₂. Equilibrium constants were determined in the temperature range 865–925°K and a reaction enthalpy of –10.54 kcal/mol derived by third-law analysis. When combined with heats of formation of C₂F₆ and C₂N₂, this result gave the enthalpy of formation of CF₃CN as –118.4 kcal/mol. Calorimetric measurements of the enthalpy of reaction of nitrogen trifluoride with CF₃CN to give CF₄ and N₂ gave the enthalpy of formation of CF₃CN as –118.9 kcal/mol in good agreement with the equilibrium study. The stability of CF₃CN is from 10 to 20 kcal less than predicted by empirical estimation methods. Stabilization of about 5 kcal/mol postulated for CF₃ groups adjacent to sp² carbons does not appear in CF₃CN.

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 CF₃CN(g).² The low-temperature heat capacity has been measured³ and a third-law entropy derived, in good agreement with calculations⁴ based on molecular structure⁵ 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



in the range 865–925°K was measured and the enthalpy of reaction calculated by third-law⁸ analysis. Second, the energy of reaction of CF₃CN with NF₃ was directly measured in a bomb calorimeter. Combined with well-established enthalpies of formation⁹ of C₂F₆, C₂N₂, and NF₃, these two approaches yield enthalpies of formation of CF₃CN(g) in good agreement.

Experimental Section

A. Equilibrium Measurements. Hexafluoroethane and CF₃CN 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 C₂F₆ and C₂N₂ 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 C₂F₆ over C₂N₂ (and *vice versa*)

did not affect the equilibrium. Equilibrium constants for reaction 1 are defined by

$$K_{\text{eq}} = \frac{[\text{C}_2\text{F}_6(\text{g})][\text{C}_2\text{N}_2(\text{g})]}{[\text{CF}_3\text{CN}(\text{g})]^2} \quad (2)$$

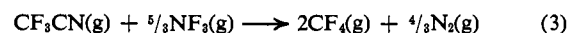
The experimental equilibrium constants are given in Table I. A third-law⁸ average reaction enthalpy at 298.15°K of –10.54 ± 0.14 kcal was calculated by means of free-energy functions for CF₃CN,⁴ C₂N₂,⁹ and C₂F₆.⁹ The essential independence of the calculated Δ*H*_{*r*,298} on temperature is good evidence that equilibrium was established. Combined with enthalpies of formation⁹ of –321.2 ± 1.2 kcal/mol for C₂F₆(g) and +73.87 ± 0.43 kcal/mol for C₂N₂(g), the enthalpy of reaction yields Δ*H*_{*r*,298}(CF₃CN, g) = –118.4 ± 1.0 kcal/mol.

Table I. Equilibrium Constants for the Reaction 2CF₃CN ⇌ C₂F₆ + C₂N₂

Run	Temp, °K	K _{eq}	Δ <i>H</i> _{<i>r</i>,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 CF₃CN 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 Potter⁶ and the sample purity was taken as 99.9+ %.

A Research grade sample of NF₃ was purchased from Air Products and Chemicals, Inc. Infrared and mass spectrometry indicated the only impurity was 0.15% CF₄. 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 CF₃CN and NF₃ are stable at room temperature, but detonate when ignited by electrical fusion of a fine nickel wire. The NF₃ must be present in slight excess to



ensure complete conversion and the excess NF₃ is decomposed to N₂ and F₂.

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

(2) (a) B. Hardman and G. J. Janz, *J. Amer. Chem. Soc.*, **90**, 6272 (1968); (b) J. B. Flannery and G. J. Janz, *ibid.*, **88**, 5097 (1966).

(3) E. L. Pace and R. J. Bobka, *J. Chem. Phys.*, **35**, 454 (1961).

(4) G. J. Janz and S. C. Wait, *ibid.*, **26**, 1766 (1957).

(5) M. D. Danford and R. L. Livingston, *J. Amer. Chem. Soc.*, **77**, 2944 (1955).

(6) W. F. Edgell and R. M. Potter, *J. Chem. Phys.*, **24**, 80 (1956).

(7) S. C. Wait and G. J. Janz, *ibid.*, **26**, 1554 (1957).

(8) G. N. Lewis and M. Randall, "Thermodynamics," revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, N. Y., 1961, p 178.

(9) "JANAF Thermochemical Tables," D. R. Stull, Ed., The Dow Chemical Co., Midland, Mich., 1969.

Table II. Calorimetric Data for Reaction 3

Run no.	CF ₃ CN, g	Δθ, deg	q _v , cal	Corrections, cal			ΔE _r /M, cal/g
				NF ₃	NiF ₂	I ^b	
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 NF₃ 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 ε(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, NF₃ 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 F₂ due to excess NF₃ was removed by reaction with mercury and the CF₄ and N₂ checked by mass and infrared spectral analysis. In all determinations CF₄ and N₂ 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 NiF₂. 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 CF₃CN and NF₃ do not react within limits of detection on standing for 24 hr. Δθ is the temperature rise corrected for heat exchange and q_v is equal to the product of ε(calor) and Δθ. The next three columns are corrections for dissociation of excess NF₃, combustion of the nickel fuse, and electrical ignition energy. ΔE_r/M is the internal energy change in cal/g of CF₃CN.

The average value of ΔE_r/M and a molecular weight of 95.024 for CF₃CN yield ΔE_{r298} = -275.19 ± 0.22 kcal/mol. For constant pressure conditions we calculate ΔH_{r298} = -274.80 ± 0.22 kcal/mol. With enthalpies of formation⁹ of -223.05 ± 0.10 kcal/mol for CF₃(g) and -31.43 ± 0.20 kcal/mol for NF₃(g) we derive ΔH_{f°298}(CF₃CN (g)) = -118.9 ± 0.5 kcal/

(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).

mol, in excellent agreement with the equilibrium data. An average of -118.7 ± 0.5 kcal/mol is selected as a "best" value.

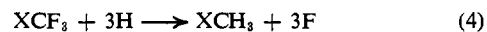
Discussion

The published estimates^{2b} are too negative by 10-20 kcal/mol. The stability of CF₃CN is thus much less than predicted by the usual methods. The relation of CF₃CN to other compounds containing the CF₃ 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 compilation¹² to ensure consistency. Results presented in Table III are uniformly exothermic.

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

Reaction	ΔH _r , kcal
2CF ₃ CN → CF ₃ CF ₃ + C ₂ N ₂	-9.8
CF ₃ CN + CH ₃ CH ₃ → CF ₃ CH ₃ + CH ₃ CN	-18.3
CF ₃ CN + C ₆ H ₅ CH ₃ → C ₆ H ₅ CN + CF ₃ CH ₃	-19.2
CF ₃ CN + C ₆ H ₅ CH ₂ → C ₆ H ₅ CF ₃ + CH ₃ CN	-15.7
CF ₃ CN + C ₆ H ₅ C ₆ H ₅ → C ₆ H ₅ CF ₃ + C ₆ H ₅ CN	-15.7

Another view of the stability of CF₃CN is provided by the "bond energy comparison" discussed by Flannery and Janz.^{2b} For the reaction



they calculate an average of 48.3 kcal from several examples with varying X, with some evidence that CF₃ groups adjacent to sp² carbon give a more endothermic result. Recent revisions to fluorine thermochemistry¹² 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 CF₃CN would be more endothermic than the average is not supported.

Recent "best" values for enthalpies of formation⁹ of CF₃ radical of -112.4 kcal/mol and of CN radical of 104 kcal/mol can be used with the present work to calculate the CF₃-CN bond dissociation energy as 110.5 kcal/mol. Data for CH₃ and CH₃CN¹² yield the CH₃-CN bond dissociation energy as 117.8 kcal/mol. Whereas CF₃ appears to interact more strongly than CH₃ 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.