Statistical Thermodynamic Functions of Cyanogen, Dicyanoacetylene, and Dicyanodiacetylene

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A statistical thermodynamic study of C_2N_2, C_4N_2, and C_6N_2 is presented. Calculated values are given for the following thermodynamic quantities: $S°$, $C_v°$, $E°$, $A°$, $H°$, $G°$, $(H° - E_0°)/T$, and $-[(G° - E_0)/T]$, where the dissociation energy values have been estimated from available heat of formation data. The present data have been satisfactorily correlated with previous results on nitriles.

A SATISFACTORY CORRELATION of heats of formation and absolute entropies of nitriles was obtained earlier (*16*) by using partitioned group contributions which included the possibility of perturbations of portions of the molecule by neighboring groups. Because of the lack of accurate thermodynamic data on nitriles in the literature, a statistical thermodynamic study was undertaken on the first three members of the polycyanoacetylene series: cyanogen, N≡C—C≡N, dicyanoacetylene (DCA), N≡C—C≡C—C≡N, and dicyanodiacetylene (DCDA), N≡C—C≡C—C≡C—C≡N. Although some statistical thermodynamic data are available for cyanogen and for DCA, further calculations are reported here for a number of reasons. Our calculations include thermodynamic functions which are dependent on the dissociation energy and such functions are involved in our work on the correlation of thermodynamic functions of nitriles. In addition, however, a discrepancy exists between the results for DCA obtained by two different workers. Hence, it appeared worthwhile to repeat the DCA calculations, as well as the cyanogen work, in an attempt to determine the cause of this discrepancy.

Although necessary vibrational and structural data are available, it soon became apparent that there is an acute lack of definitive dissociation energy values, even for some of the more common gases. In view of this, it was necessary to calculate the dissociation energies through use of experimental heats of formation, or where such latter values are not available, by approximation methods. In the context of this paper, dissociation energy is taken to mean that energy required to effect the following reaction: $A_aB_bC_c$---(gas) = aA(gas) + bB(gas) + cC(gas) + ------ where A, B, C and a, b, c, ------refer to the atoms and their numbers, respectively.

METHOD

The vibrational spectra of cyanogen (*2, 5, 10, 15, 21*), DCA (*12-14*), and DCDA (*14*) have been analyzed for the fundamental vibrational frequencies and corresponding species assignments. All three molecules are of $D_{\infty h}$ symmetry. The internuclear distances for DCDA are estimated from the DCA values and the close symmetry similarities of the molecules involved should readily justify such an approximation. A referee has suggested further support by comparing the C—C bond lengths in H_3—C—C≡C—H and H_3—C—C≡N, which are 1.462 A. (*11*) and 1.458 A. (*4*), respectively. All of the physical constants used in the calculations are taken from the extensive study of Cohen and DuMond (*3*). Table I contains all the pertinent physical property data used in the calculations.

Table I. Physical Properties Pertinent to Calculations

	Cyanogen	DCA	DCDA
Fundamentals, cm.$^{-1}$	2328.5 (*10*)	2290 (*14*), 504^a	2235 (*14*), 2097, 490.5^a
	850.6 (*10*)	2119, 263^a	2183, 717, 276^a
	2157.6 (*5*)	692, 472^a	1287.5, 501^a, 61.5^a
	507.2^a (*10*)	2241, 107^a	571, 455^a
	235.0^a (*15*)	1154	2266, 156^a
r(C≡N), A.	1.157 (*17*)	1.14 (*7*)	1.14 (estd.)
r(C–C), A.	1.380 (*17*)	1.37 (*7*)	1.37 (estd.)
r(C≡C), A.		1.19 (*7*)	1.19 (estd.)
$\Delta H°_{f_{298.16}}$, kcal./mole	73.60 (*19*)	126.5 (*1*)	179.4 (estd.)
De, kcal./mole	494.8 (estd.)	785.3 (estd.)	1075.8 (estd.)
$I_{xx} = I_{yy}$ $I_{zz} = 0$, g.-sq. cm.	177.67×10^{-40}	616.58×10^{-40}	1473.4×10^{-40}
$E_0°$ kcal./mole	−485.0	−769.3	−1054.0

^{a} Doubly degenerate.

To calculate the molar thermodynamic functions a rigid rotator, harmonic oscillator model for a gas in the thermodynamic standard state at 1-atm. pressure was assumed. These functions for a linear polyatomic ideal gas are outlined by Hill (*8*). Effects such as nuclear spins, centrifugal distortion, and isotopic mixing have been neglected.

From the vibrational and structural data of a molecule, the entropy and heat capacity may be calculated at any desired temperature. However, to calculate the free energy, internal energy, and enthalpy, a reliable value for De, the dissociation energy, must be evaluated by some independent method. To date the knowledge of accurate dissociation energies is limited, even for the most common molecules. An excellent analysis of existing data on the energy required for the following reaction is given by Tsang *et al.* (*25*).

$$C_2N_2(g) \rightleftharpoons 2CN(g)$$

A range of values from 77 to 146 kcal. per mole indicates the relative uncertainty in the energy required to break the C—C bond of cyanogen. No data were found for the dissociation energy of cyanogen according to the following reaction:

$$C_2N_2(g) = 2C(g) + 2N(g)$$

In view of this situation, available heats of combustion and formation have been used to estimate a De value for each of the three molecules. The following reactions have been used in the calculations:

$C(s) = C(g)$ $\Delta H^\circ_{298.16} = 171.698$ kcal. per mole (*19*)

$N_2(g) = 2N(g)$ $\Delta H^\circ_{298.16} = 224.98$ kcal. per mole (*6*)

Although the heats of formation of both cyanogen and DCA have been determined experimentally, it was necessary to estimate the corresponding value for DCDA. The method of group equations developed by Rossini and coworkers and described by Janz (*9*) has been used. The standard heats of formation and the corresponding calculated dissociation energy values are given in Table I along with the calculated moments of inertia and the respective E°_0 values, where E°_0 is the internal energy of one mole of perfect gas at the absolute zero of temperature.

Calculated results for the thermodynamic properties of cyanogen, DCA, and DCDA for $T = 298.16°$ K. are contained in Table II.

DISCUSSION OF THERMODYNAMIC DATA

There have been a number of publications on the thermodynamic properties of cyanogen (*15, 20, 24*), but in each case no value of the dissociation energy was required, since entropy, heat capacity, the free energy function, $-[(G^\circ - E^\circ_0)/T]$, and the enthalpy function, $(H^\circ - E^\circ_0)/T$, were the only thermodynamic functions examined. No thermodynamic data for DCDA were found in the literature. The study by Miyazawa (*15*) contains data for the accepted vibrational and structural parameters of cyanogen and there is complete agreement between his work and this one in the places where comparisons can be made.

Stull (*22, 23*) and Nagarajan *et al.* (*18*) have both calculated thermodynamic values for DCA, but Nagarajan *et al.* have pointed out a discrepancy between their data and those of Stull for the entropy function; the values at 298.16° K. are 64.102 cal. deg.$^{-1}$ mole^{-1} for the former and 69.314 for the latter. For DCA results of the present study are in agreement with those of Stull for the entropy function. The results of the present work are in agreement with those of Stull and of Nagarajan for Cp° and, hence, the difference cannot be attributable to different vibrational data as postulated by Nagarajan. The entropy function is, of course, dependent on the moment of inertia, and upon comparison of the respective moments of inertia from the three studies in question it is evident that the value of $I_{xx} = I_{yy} = 46.0342 \times 10^{-40}$ gram per sq. cm. for DCA quoted by Nagarajan is in error. From the results of the present study we attribute the entropy difference quoted (*18*) to this incorrect moment of inertia value, and the agreement between Stull's results and ours is excellent.

Since no thermodynamic data are available on DCDA, further comparisons are not possible. However, some comment on the value selected for the dissociation energy of DCDA is appropriate. The difference between the dissociation energy of DCA and of cyanogen is the same as the difference between that of DCDA and DCA. This is, of course, entirely expected because of the method used in estimating the heat of formation of DCDA. However, further intuitive justification for selecting a value of *De* for DCDA such that this above-mentioned identity of the differences between the *De* values is obtained, can be seen by observing that in all three of the molecules two $C \equiv N$ bonds must be broken, whereas in passing from cyanogen to DCA, one obtains an additional C—C and $C \equiv C$ bond. Further, in passing from DCA to DCDA, an additional C—C and $C \equiv C$ bond is similarly obtained. The value of *De* selected for DCDA would then appear to be an entirely reasonable one, at least to a first-order approximation.

Table II. Calculated Thermodynamic Functions at $T = 298.16°$ K.[a]

	Cyanogen	DCA	DCDA
C°_v	11.5913	18.5406	25.9465
S°	57.7840	69.3120	80.9913
$(H^\circ - E^\circ_0)/T$	10.1519	14.2162	18.5599
$[-(G^\circ - E^\circ_0)/T]$	47.6321	55.0958	62.4314
A°	−499.8179	−786.2969	−1073.1920
E°	−482.5891	−765.6309	−1049.0430
H°	−481.9966	−765.0383	−1048.4510
G°	−499.2253	−785.7043	−1072.5990

[a] C°_v, S°, $(H^\circ - E^\circ_0)/T$, $-[(G^\circ - E^\circ_0)/T]$, values in calories mole^{-1} deg.$^{-1}$ $A^\circ, E^\circ, H^\circ, G^\circ$ values in kilocalories mole^{-1} deg.$^{-1}$

Table III. Groups and Their Contributions to Thermodynamic Properties in Nitriles

	Contribution		
Group	C_v°, cal. mole^{-1} deg.$^{-1}$	S°, cal. mole^{-1} deg.$^{-1}$	ΔH_f°, kcal. mole^{-1}
C_t–$(N_t)(C_t)$	5.80	28.89	36.80
C_t–$(C_t)^2$	7.18	5.80	26.45

The internuclear distances are quoted to ±0.02 A., and the frequencies should be accurate to ±1 cm.$^{-1}$ The heats of formation of cyanogen and DCA are known to within ±0.2 kcal. per mole and hence the dissociation energy values should be accurate to ±1 kcal. per mole.

Since one of the purposes of this work was to supply further data for the previous correlation studies (*16*) on nitriles, it is of interest to examine some of the present results. In the previous work only data for 298.16° K. were considered. If the present data for the entropy and the heat capacity at constant volume and at 298.16° K. are examined, the group C_t-$(N_t)(C_t)$, of which there are two in cyanogen, contributes 28.8920 cal. mole^{-1} deg.$^{-1}$ to the entropy and 5.7957 cal. mole^{-1} deg.$^{-1}$ to the heat capacity at constant volume. Correspondingly, DCA may be considered as composed of two C_t-$(N_t)(C_t)$ groups and two C_t-$(C_t)^2$ groups. Then the C_t-$(C_t)^2$ group must contribute 11.5280 and 3.4747 cal. mole^{-1} deg.$^{-1}$ to the entropy and heat capacity, respectively. Using these values and those previously mentioned for the group C_t-$(N_t)(C_t)$, and considering that DCDA is composed of two C_t-$(N_t)(C_t)$ groups and four C_t-$(C_t)^2$ groups, values of 80.84 and 25.49 cal. mole^{-1} deg.$^{-1}$ for the entropy and heat capacity, respectively, of DCDA are obtained. These compare well with the statistical values of 80.9913 and 25.9465 cal. mole^{-1} deg.$^{-1}$

Table III records the contributions to S°, C°_v, and ΔH°_f from each of the two groups mentioned above, as found by averaging over all three compounds considered here. For ΔH°_f, the average was taken only over two compounds, cyanogen and DCA, since an experimental ΔH°_f value is not available for DCDA.

Calculated data for the thermodynamic functions at 10° K. intervals from 200° to 500° K. for all three molecules are available from the authors.

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Thermodynamic Functions for 1,1,2,2,-Tetrachloroethane and 1,1-Difluoro-2,2-Dichloroethane

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Thermodynamic functions C_p°, S°, $(H^\circ-H_0^\circ)/T$, $-(F^\circ-H_0^\circ)/T$, have been calculated for 1,1,2,2,-tetrachloroethane and 1,1-difluoro-2,2-dichloroethane in the ideal gas state from 273.15° to 1000° K. at 1 atm. pressure. The restricted internal rotational contribution has been treated, for both compounds, by employing the Lielmezs-Bondi approximate method.

1,1,2,2-TETRACHLOROETHANE

Recently published spectrographic data (*1*), combined with information from previous spectrographic (*11, 12*) and molecular structural investigations (*4, 11, 13*), has made it possible to estimate the thermodynamic functions, C_p°, S°, $(H^\circ-H_0^\circ)/T$, and $-(F^\circ-H_0^\circ)/T$, for the 1,1,2,2-tetrachloroethane equilibrium mixture of trans and skew form isomers in the ideal gas state at 1 atm. pressure. Table I (deposited with ASIS) presents the thermodynamic functions calculated by the Lielmezs-Bondi approximate method (*2, 5, 8, 9, 10*). The results presented in Table I are fitted to Equation 1

$$\Lambda = a + bT + cT^2 \qquad (1)$$

where Λ is the thermodynamic function and T is the temperature (°K.). The constants a, b, and c (Equation 1) were calculated using least-squares curve-fitting methods (*14*) and are given in Table II (deposited with ASIS).

Table III gives the values of the molecular parameters used in the calculation of the thermodynamic functions for 1,1,2,2-tetrachloroethane.

Although calorimetric data are not available, comparison of the values presented with previously calculated values (*7*) reveals a maximum difference in heat capacity of 0.6%, while for entropy the maximum difference is 1.5%. This suggests that the presented values, based on more recent spectrographic data, may well be within the bounds of experimental accuracy.

1,1,-DIFLUORO-2,2-DICHLOROETHANE

As with the symmetrical tetrachloroethane, recent spectrographic and molecular structural data (*6*) have made it possible to calculate the thermodynamic functions—Table IV; internal rotation contribution is treated by means of Lielmezs-Bondi method (*2, 5, 8, 9, 10*)—for 1,1-difluoro-2,2-dichloroethane. Table V gives the constants of Equation 1, and Table VI, the values of the molecular parameters used in the calculations. The isomerization energy was selected as 600 cal. per mole from the suggested range of 500 to 700 cal. per mole (*6*). The six lowest used frequencies (Table VI) were chosen, as proposed by Kartha, *et al.* (*6*). Calculations were then performed over the given isomerization energy range from 500 to 700 cal. per mole and with the frequencies varying ±10 wave numbers from the estimated values (*6*) in order to determine the deviation in thermodynamic functions over this range. The results of this calculation are shown, with the maximum deviation between function values (expressed as a per cent difference) in Table VII.

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