believe that this reaction would not occur in experiment 7 in addition to the chlorine–bromine interchange. Because eight compounds are involved in the reaction product of this experiment, it is possible to write six equilibrium constants of the form expressed in equation 2. The values of these constants are given in Table I and are related to each other through the four equilibrium constants reported in Table II. In order to report these constants on a comparable basis, they are calculated for reaction 1 in which the compound in the reaction mixture having an isolated oxygen attached to the phosphorus and the largest amount of chlorines directly attached is put in the right side of the equation.

The value, $\Delta\Sigma\chi$, obtained by taking the total Pauling's electronegativity of X, Y and Z in equation 1 minus the total electronegativity of X', Y' and Z' ($\Delta\Sigma\chi$) is also entered in Table I. It is obvious for the six equilibria in experiment 7 that K_1 increases with $\Delta\Sigma\chi$ and, as a matter of fact, when $\log K_1$ is plotted against $\Delta\Sigma\chi$, a straight line is obtained. The values obtained from experiments 5 and 6 also fit on this plot, but the other results do not. Generally, however, it can be concluded that there seems to be a trend for K_1 to increase with $\Delta\Sigma\chi$. Furthermore, since all K_1 values are greater than unity (representing completely random reorganization), it looks as if the isolated oxygen rather than sulfur prefers to be connected to the phosphorus directly attached to the greatest number of chlorines. This rule of thumb may well fail when fluorine atoms are present in the molecules, since their electronegativity is much higher.

The isolated oxygen–sulfur interchange reaction seems to occur whenever mixtures of quadruply connected phosphorus compounds containing "isolated" oxygen and sulfur are heated to the proper temperature, generally at least 150°. Since the equilibrium favors the formation of $POCl_3$, this reaction can be used advantageously for the preparation of thionophosphonic and phosphinic deriva-

tives in good yield from the corresponding oxy derivatives by using a slight excess of thiophosphoryl chloride. This is exemplified by the preparation of chloromethylthionophosphonic dichloride in a pressure vessel as reported in the preparative section. When the reorganization is attempted in an open flask, catalysts such as PCl_3 and $AlCl_3$ are necessary to obtain a satisfactory reaction rate at the resulting lower reaction temperature (see preparation of methylchloromethylthionophosphinic chloride).

Preparative Section

Methylchloromethylphosphinic Chloride.—The procedure outlined by M. T. Kabachnik and E. S. Shepeleva[6] has been modified by operating at atmospheric pressure. To 1011 g. of CH_3PCl_2 heated in a flask to reflux temperature, 328 g. of paraformaldehyde was added in small amounts through a nitrogen-protected feeding device. The reaction is exothermic. After addition had been completed, the reaction mixture was heated to 100° for an hour. Vacuum distillation produced 884 g. (70% yield based on CH_3PCl_2) of product with an n.m.r. chemical shift of -59.2 p.p.m. Agitation during the addition of the paraformaldehyde resulted in decreased yield.

Methylchloromethylthionophosphinic Chloride.—A 147-g. quantity of $CH_3(CH_2Cl)P(O)Cl$, 339 g. of $PSCl_3$ (100% excess) and catalytic amounts of PCl_3 and $AlCl_3$ (5 g. of each) were heated at 130–140° for 30 hr. in a 500-ml. flask fitted with an efficient fractionating column. Only those reaction products which distilled under 115° were collected. The residue was distilled under vacuum and 64 g. of pure colorless $CH_3(CH_2Cl)P(S)Cl$ (39% yield (identified by n.m.r., chemical shift = -84.9 p.p.m.) could be distilled at 68–70° and 3–4 mm. Another 23 g. of 90% pure product was collected at 70–83° and 3–4 mm.

Chloromethylthionophosphonic Dichloride.—An 839-g. quantity of $CH_2ClP(O)Cl_2$ and 1735 g. of $PSCl_3$ were heated in a 3-liter stainless steel autoclave for 72 hr. at 230°. Vacuum distillation yielded 700 g. of pure product (b.p. 65–66° at 9 mm.), corresponding to about 75% yield based on $CH_2ClP(O)Cl_2$. The n.m.r. chemical shift was -72.8 p.p.m.

(6) M. T. Kabachnik and E. S. Shepeleva, *Bull. Acad. Sci. U. S. S. R., Div. Chem. Sci. S. S. R.*, 862 (1953).


Mass Spectrometric Study of Cyanogen and Cyanoacetylenes

BY VERNON H. DIBELER, ROBERT M. REESE AND J. L. FRANKLIN[1]

Relative abundances and appearance potentials are reported for the principal ions in the mass spectra of cyanogen, cyanoacetylene, dicyanoacetylene and dicyanodiacetylene. Heats of formation of radicals and radical ions are calculated and the energetically probable ionization-dissociation processes are tabulated. Carbon–carbon and carbon–nitrogen bond dissociation energies are calculated for various ionized and neutral molecular species.

Introduction

Cyanogen may be considered as the initial member of an interesting series of compounds containing only carbon and nitrogen atoms and having the general structural formula

$$N{\equiv}C{-}(C{\equiv}C)_n{-}C{\equiv}N, \text{ where } n = 0, 1, 2, 3, \ldots[2]$$
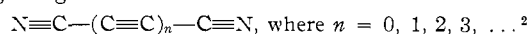
Unique bonding and structural arrangements of

these molecules result from the presence of conjugated triple bonds which are virtually unaffected by subsequent additions of triple bonds. Furthermore, their high endothermic heats of formation and very stable combustion products constitute a highly exothermic system and provide a means of achieving flame temperatures in the range of 5000 to 6000°K.[3]

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(2) A. J. Saggiomo, *J. Org. Chem.*, **22**, 1171 (1957).

(3) (a) J. B. Conway, W. F. R. Smith, W. J. Liddell and A. V. Grosse, *J. Am. Chem. Soc.*, **77**, 2026 (1955); (b) A. D. Kirshenbaum and A. V. Grosse, *ibid.*, **78**, 2020 (1956).

Mass spectra and appearance potentials of cyanogen have been reported in several papers.[4] However, there is no previous information on the behavior under electron impact of the higher members of this series. Thus the present research provides data of basic interest on ionization potentials, specific bond dissociation energies and heats of formation of radicals and ions formed from the dinitriles and from cyanoacetylene.

Experimental

Mass spectra and appearance potentials were obtained by means of a 6-inch radius Nier-type mass spectrometer. Details of the experimental techniques and apparatus have been published.[5] Briefly, however, the ion accelerating voltage was maintained constant at 2000 v. while the magnetic field was varied to focus ions of varying m/e on the collector. Data were obtained with the ion source either near ground potential or at high voltage. Ion currents were measured with a 14-stage electron multiplier followed by a d.c. amplifier and a pen recorder. The ionizing voltage scale for positive ions was calibrated by comparing the observed and spectroscopic[6] ionization potential of argon introduced simultaneously with the nitriles. The negative-ion measurements were made on a conventional 180° mass spectrometer as a matter of convenience. The ionizing voltage scale was calibrated by means of the negative molecule ion of SF_6[7] and the O^- ion of O_2.[8]

Cyanogen was of commercial origin and part of a laboratory supply. No impurities were detected in the mass spectrum and it was used without further purification. The cyanoacetylenes also were obtained from a commercial supplier. A considerable amount of hydrocarbon impurity was observed in the dicyanodiacetylene. Fortunately, this was separable to a satisfactory degree by simple low-temperature distillation in the sample-handling system of the mass spectrometer.

Results and Discussion

The experimental data are summarized in Tables I through IV. In each table, column 1 gives the mass-to-charge ratio for the principal ions observed. Column 2 gives the abundance of each positive ion relative to the most abundant ion for nominal electron energies of 70 v. The abundances of negative ions are measured at maximum cross-section and related to the most abundant positive ion at 70 v. The observed appearance potentials and mean error of at least three measurements appear in column 3. The most probable reaction, as indicated by the energetics, is shown in column 4. Column 5 gives the calculated heats of formation of the species underlined in column 4. Comparative values from the literature appear in column 6. In making the thermochemical calculations, the following heats of formation of the gaseous molecules were employed: C_2N_2, 73.6 kcal./mole[9] and C_4N_2, 128 kcal./mole.[10] The heats of formation of HC_3N and of C_6N_2 have not been determined. Accordingly, these values were esti-

(4) F. H. Field and J. L. Franklin, "Electron Impact Phenomena and the Properties of Gaseous Ions," Academic Press, Inc., New York, N. Y., 1957.

(5) J. L. Franklin, V. H. Dibeler, R. M. Reese and M. Krauss, *J. Am. Chem. Soc.*, **80**, 298 (1958).

(6) C. E. Moore, "Atomic Energy Levels," Natl. Bur. Standards Circ., 467 (1949).

(7) W. M. Hickam and R. E. Fox, *J. Chem. Phys.*, **25**, 642 (1956).

(8) H. D. Hagstrum, *Revs. Mod. Phys.*, **23**, 185 (1951).

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

(10) Calculated from heat of combustion measurements kindly communicated by Dr. G. T. Armstrong and including $\Delta H_{vap} = 6.9$ kcal./mole from ref. 1.

mated in a manner to be described, using the method of group equivalents.[11] A heat of formation of the $[-C\equiv N]$ group of 36.8 kcal./mole is obtained from $\Delta H_f(C_2N_2) = 73.6$ kcal.[9] Heats of formation of the $[\equiv CH]$ and $[-C\equiv]$ groups of 27.09 and 27.34 kcal./mole, respectively, are taken from Franklin.[11] From these values, the heats of formation of gaseous HC_3N and C_6N_2 are readily estimated to be 91 and 183 kcal./mole, respectively. As a check, the heat of formation of gaseous C_4N_2 is similarly calculated to be 128 kcal./mole, in exact agreement with the experimental value for this molecule reported above.

TABLE I

(CN)₂

m/e	Relative intensity	AP (ev.)	Probable reaction	ΔHf of boldfaced species (kcal./mole) This work	Lit.
52	100	13.6 ± 0.2	$(CN)_2 \rightarrow (CN)_2{}^+ + e$	388	387 (4)
38	1.6	19.5 ± .1	$(CN)_2 \rightarrow C_2N^+ + N$	412	421 (4)
26	7.6	21.5 ± .3	$(CN)_2 \rightarrow CN^+ + CN$	481	419 (4)
24	1.9	18.4 ± .3	$(CN)_2 \rightarrow C_2{}^+ + N_2$	498	473 (12)

Molecule Ions.—The ionization potential of cyanogen agrees well with values previously reported.[4] Ionization potentials of the various cyanoacetylenes are quite close to the ionization potential of acetylene (11.4₂) and are nearly two volts below that of cyanogen. This suggests that ionization in the cyanoacetylenes is from the $C\equiv C$ triple bond and that the electron is from a comparatively localized orbital having very little interaction with adjacent orbitals. This is rather surprising in view of the fact that all of the compounds involve systems of conjugated multiple bonds.

Ionization Potentials of Free Radicals.—The spectra of the three cyanoacetylenes apparently include several ions the appearance potentials of which can only be interpreted as the direct ionization potential of the free radical in question. For example, in dicyanoacetylene the peak at $m/e = 14$ has an appearance potential of 15 volts. This is a rather small peak and the measurement is only approximate. The appearance potential of 15 volts can only be interpreted as the ionization potential of the nitrogen atom (14.54 ev.).[4] Similarly, the mass 26 peak of cyanoacetylene gave two appearance potentials the lower of which is 14.5 volts. This corresponds rather closely to the known ionization potential of CN. Other peaks that can only be attributed to the direct ionization of free radicals present in the ion source are $C_3{}^+$ from both cyanoacetylene and dicyanoacetylene, C_2N^+ from dicyanoacetylene and CN^+, C_3N^+, C_6N^+, $C_5{}^+$ and $C_6{}^+$ from dicyanodiacetylene. Although in several instances the present values are somewhat higher than the comparative values previously reported,[4,12] in most instances the agreement is within the accuracy of the measurement and in all instances the appearance potential in question could not be accounted for by any fragmentation process. It is quite unusual to find so many free radicals present in the source in

(11) J. L. Franklin, *Ind. Eng. Chem.*, **41**, 1070 (1949).

(12) J. Drowart, R. P. Burns, G. DeMaria and M. G. Inghram, *J. Chem. Phys.*, **31**, 1131 (1959).

TABLE II

HC≡C—CN

m/e	Relative intensity	A.P. (ev.)	Probable reaction	ΔHf of boldfaced species (kcal./mole) This work	Lit.
			Positive ions		
51	100	11.6 ± 0.2	$HC_3N \rightarrow HC_3N^+ + e$	358	
50	22.6	$18.2 \pm .3$	$HC_3N \rightarrow C_3N^+ + H$	459	
38	7.3	$18.0 \pm .5$	$HC_3N \rightarrow C_2N^+ + CH$?	87	142 (13) (see text)
		$24.0 \pm .5$	$HC_3N \rightarrow C_2N^+ + C + H$	421	
37	3.9	$18.0 \pm .2$	$HC_3N \rightarrow C_3H^+ + N$	394	309 (4) (see text)
36	3.0	<14.0	$C_3 \rightarrow C_3^+ + e$	<511	479 (12)
		$17.1 \pm .5$	$C_3H \rightarrow C_3^+ + H$?	136	
		$24.5 \pm .5$	$HC_3N \rightarrow C_3^+ + N + H$	492	479 (12)
26	2.5	$14.5 \pm .5$	$CN \rightarrow CN^+ + e$	423	419 (4)
		$19.8 \pm .2$	$HC_3N \rightarrow CN^+ + C_2H$	122	Not established
25	7.9	$19.0 \pm .2$	$HC_3N \rightarrow C_2H^+ + CN$	440	414 (4)
24	7.1	$18.6 \pm .2$	$HC_3N \rightarrow C_2^+ + HCN$	489	473 (2)
13	0.4	$21.9 \pm .3$	$HC_3N \rightarrow CH^+ + C_2N$	414	360 (4) see text
12	2.7				
25.5	6.9	$32.3 \pm .2$	$HC_3N \rightarrow HC_3N^{++}$	837	
			Negative ions		
50	2.0	3.5	$HC_3N \rightarrow C_3N^- + H$	126(excess energy)	
25	1.8	6.0	$HC_3N \rightarrow CN^- + C_2H$	107	15[a]

[a] J. T. Herron and V. H. Dibeler, J. Am. Chem. Soc., 82, 1555 (1960).

TABLE III

C_4N_2

m/e	Relative intensity	A.P. (ev.)	Probable reaction	ΔHf of boldfaced species (kcal./mole) This work	Lit.
			Positive ions		
76	100	11.4 ± 0.2	$C_4N_2 \rightarrow C_4N_2^+ + e$	391	
62	1.0	$11.9 \pm .5$	$C_4N \rightarrow C_4N^+ + e$	175	
		$18.8 \pm .5$	$C_4N_2 \rightarrow C_4N^+ + N$	449	
50	17.3	$18.4 \pm .2$	$C_4N_2 \rightarrow C_3N^+ + CN$	463	
48	2.8	$17.2 \pm .2$	$C_4N_2 \rightarrow C_4^+ + N_2$	525	521 (12)
38	29.9	~ 13	$C_2N \rightarrow C_2N^+ + e$	$\Delta H_f C_2N = 123$	
		$18.1 \pm .4$	$C_4N_2 \rightarrow C_2N^+ + C_2N$	$\Delta H_f C_2N^+ = 423$	
36	7.0	<13.6	$C_3 \rightarrow C_3^+ + e$	<502	479 (21)
		$24.6 \pm .5$	$C_4N_2 \rightarrow C_3^+ + CN + N$	494	479 (12)
26	5.3	$19.2 \pm .3$	$C_4N_2 \rightarrow CN^+ + C_3N$	135	
24	5.6	$18.5 \pm .3$	$C_4N_2 \rightarrow C_2^+ + C_2N_2$	481	473 (12)
14	1.1	~ 15	$N \rightarrow N^+$	457	448 (4)
		26.0 ± 1.0	$C_4N_2 \rightarrow N^+ + C_3 + CN$?	451	448 (4)
12	6.0	24 ± 1.0	$C_4N_2 \rightarrow C^+ + $?		Several possibilities
			Negative ions		
50	2.0	1.6	$C_4N_2 \rightarrow C_3N^- + CN$	76EA(C_3N) = 55	
26	1.0	0.8	$C_4N_2 \rightarrow CN^- + C_3N$	131Using $\Delta H_i(CN^-)$ = 15 (4)	

sufficient amounts to permit measurement of their ionization potential. Consequently, it seems probable that these are characteristic of the cyanoacetylenes. However, this is rather difficult to understand as the bond strengths of these molecules (see later sections), calculated from the present data, are all rather high.

C_nN^+ Ions.—All of the compounds studied gave characteristic ions having the general formula C_nN^+, where n varies from 1 to 6. In attempting to determine the mechanism by which the various ions were formed, known heats of formation of ions or radicals and the appearance potentials of the ions were used to calculate the heat of formation of one of the products. This was compared with known values when available. The mechanisms in most instances involved product ions and neutral species in their lowest energy states. In some instances where excess energy obviously is involved, it has been possible to suggest tentatively the more extensive fragmentation that might account for the appearance potential observed. Thus, the peak at $m/e = 38$ from cyanoacetylene, (A.P. = 24 v.) is interpreted as involving the formation of carbon and H atoms as the neutral species.

In a few instances we have obtained several values for the heat of formation of a certain ion and in such cases we have either averaged the heats of formation, if they were in reasonable agreement or have chosen the lowest value if the agreement was poor. Thus, the C_2N^+ ion gave values of 412, 421 and 423 kcal./mole from cyanogen, cyanoacetylene and dicyanoacetylene. In this instance the values were averaged. On the other hand, only two values were obtained for C_4N^+. These were 449 and 488 kcal./mole from

TABLE IV

C_6N_2

m/e	Relative intensity	A.P.(ev.)	Probable reaction	ΔHf of boldfaced species (kcal./mole) This work	Lit.
			Positive ions		
100	100	11.4 ± 0.2	$C_6N_2 \rightarrow \mathbf{C_6N_2}^+ + e$	446	
86	0.3	$12.2 \pm .1$	$\mathbf{C_6N} \rightarrow C_6N^+ + e$	233	
		$19.2 \pm .3$	$C_6N_2 \rightarrow C_6N^+ + N$	514	
74	19.1	$17.3 \pm .2$	$C_6N_2 \rightarrow \mathbf{C_5N}^+ + CN$	493	
72	0.1	$12.5 \pm .3$	$C_6 \rightarrow C_6^+ + e$	? ? ?	
62	9.4	19.0 ± 1.0	$C_6N_2 \rightarrow \mathbf{C_4N}^+ + C_2N$	488 (excess energy)	
60	1.4	12.7 ± 0.5	$C_5 \rightarrow \mathbf{C_5}^+ + e$	526	521 (12)
		24.0 ± 0.5	$C_6N_2 \rightarrow C_5^+ + CN + N$	535	521 (12)
50	5.4	~ 14.4	$\mathbf{C_3N} \rightarrow C_3N^+ + e$	128	
		22.0 ± 0.5	$C_6N_2 \rightarrow C_3N^+ + \mathbf{C_3N}$	230 excited	
48	6.5	$17.8 \pm .4$	$C_6N_2 \rightarrow \mathbf{C_4}^- + C_2N_2$	520	521 (12)
38	16.7	$17.0 \pm .1$	$C_6N_2 \rightarrow C_2N^+ + \mathbf{C_4N}$	156	
		$19.7 \pm .5$	$C_6N_2 \rightarrow C_2N^+ + ?$		
36	9.7	$14.4 \pm .3$	$C_3 \rightarrow C_3^- + e$??		
		23.0 ± 2.0	$C_6N_2 \rightarrow C_3^+ + ??$		
26	0.04	14.5 ± 0.2	$CN \rightarrow \mathbf{CN}^+ + e$	423	419 (4)
		20.0 ± 1.0	$C_6N_2 \rightarrow CN^+ + C_5N$	218	
24	. .	18.4 ± 1.0	$C_6N_2 \rightarrow \mathbf{C_2}^+ + C_4N_2$	479	473 (12)
14	1.6	<19	$C_6N_2 \rightarrow N^+ + ?$		
		26.8 ± 0.3	$C_6N_2 \rightarrow N^+ + ??$		
12	7.9	23.0 ± 0.5	$C_6N_2 \rightarrow C^+ + ?$		
			Negative ions		
100	0.5	~ 0	$C_6N_2 + e \rightarrow \mathbf{C_6N_2}^-$	<183	
74	1.0	3.0	$C_6N_2 + e \rightarrow \mathbf{C_5N}^- + CN$	$163 EA(C_5N) = 53$	
50	0.5	4.0	$C_6N_2 + e \rightarrow C_3N^- + C_3N$	199(Excess energy)	
26	0.1	2.0	$C_6N_2 + e \rightarrow CN^- + C_5N$	214	

C_4N_2 and C_6N_2, respectively. In this instance the lower value was selected. In Table V, column 1, we have given the average or best value of the heat of formation of the various ions of the general formula C_nN^+.

TABLE V

AVERAGE OR BEST VALUE OF ΔH_f(KCAL./MOLE)

	Positive ion	Radical	IP (ev.)
CN	423	89^b	14.5
C_2N	419	123	12.8
C_3N	461	131	14.3
C_4N	449	166	12.3
C_5N	493^a	216^a	12.0
C_6N	514^a	233^a	12.2

^{a} May include some excess energy. ^{d} See footnote of Table II.

Heats of Formation of Radicals.—The appearance potentials of several ions from C_4N_2 and C_6N_2 can only be explained on the assumption that the neutral product is a single fragment occurring in the reaction as a free radical. For example, in considering the mass 26 peak from C_4N_2, if one employs known values for the heat of formation for C_4N_2 and CN^+, one computes the heat of formation for the neutral product of 135 kcal./mole. This is much too small a value for any possible neutral product except the free radical C_3N. Similar considerations have been employed in deducing other mechanisms.

In this way it has been possible to compute the heats of formation of several free radicals. Where several values were obtainable for the same radical by different processes, we have taken the lowest

value or have averaged several values if these were in good agreement. The heats of formation of several of the free radicals C_nN so obtained are listed in Table V. The values appear to be reasonable although we must concede that the heats of formation for C_5N and C_6N seem somewhat high and may involve excessive energy. From the heats of formation of the ions and radicals, we have computed the radical ionization potentials and these also are listed in Table V. The values for the ionization potentials seem to fall in a reasonable sequence although it does appear that the ionization potential for C_3N may be too high. The heat of formation of the positive ion may be too high, although the value given is the average of two determinations which agree well.

Similarly, we have computed heats of formation of the radicals CH, C_2H and C_3H. The value for CH (87 kcal./mole) is much smaller than the 142 kcal./mole which one computes from Herzberg's D(CH) of 80 kcal./mole.[13] As our calculated value is lower, it is rather difficult to explain the discrepancy. Errors in appearance potentials usually give results that are too high rather than too low. Our result would be explainable if the value of 419 kcal./mole employed for the heat of formation for C_2N^+ were erroneous. However, this value is an average of three different measurements which agree within about 10 kcal./mole. An alternative explanation may lie in the validity of Herzberg's D(CH) of 80 kcal./mole. The litera-

(13) G. Herzberg, "Molecular Spectra and Molecular Structure. 1. Spectra of Diatomic Molecules," D. Van Nostrand Co., New York, N. Y., 1950.

ture contains only one measurement of this important bond strength. If it is employed along with other known heats of formation of radicals, one obtains a rather extreme variation in the strength of the bonds in methane; i.e. $D(CH_3-H) = 101$, $D(CH_2-H) = 80$, $D(CH-H) = 135$ and $D(C-H) = 80$. $D(CH-H)$ appears to be much too high. This important datum should be redetermined in order to be certain of its value.

Polymeric Carbon Ions.—The presence of rather large peaks corresponding to polymeric carbon ions is a rather unusual characteristic of the mass spectra of these compounds. Thus, the C_2^+ ion from cyanoacetylene shows an abundance of 7.1%. The C_3^+, C_2^+ and C^+ ions from C_4N_2 have abundances from 5.5 to 7% and the C^+, C_3^+ and C_4^+ ions from C_6N_2 show abundances from 6.5 to 10%. This presents an unusual opportunity to obtain heats of formation of these ions for comparison with data obtained by other means. It is interesting that C_2^+ from all of the compounds studied is formed with the elimination of a neutral molecule made up of all of the remaining atoms of the original compounds. Thus, the 24 peak in cyanogen involves the formation of N_2 as the neutral species. Correspondingly, the 24 peak in cyanoacetylene is formed along with HCN; that from C_4N_2 along with C_2N_2 and that from C_6N_2 is formed along with C_4N_2 as the neutral compound.

Although there is a spread of 19 kcal./mole in the calculated heat of formation for C_2^+, the average value corresponds fairly well with that obtained by Drowart, et al.,[12] our average value being the greater by 15 kcal./mole. Considering the processes involved, this agreement is fairly good and attests once more to the small amount of activation energy that is involved in ionic processes even when they apparently must pass through cyclic or other complicated intermediates.

The C_3^+ ion was formed in all compounds except cyanogen and in each case two or three appearance potentials were distinctly measureable. The lowest appearance potentials apparently correspond to the direct ionization of C_3. These lower values could not be determined accurately. Thus, the calculated heats of formation are about a volt more than that given by Drowart, et al.[12] The higher values for the appearance potentials of C_3^+ ions result from fragmentation processes and the heats of formation obtained from these measurements agree with values of Drowart, et al., within about 15 kcal./mole.

Values for C_4^+ were obtained from C_4N_2 and C_6N_2 by fragmentation processes corresponding in the former to the elimination of N_2 and in the latter to the elimination of C_2N_2. The values agree quite closely with each other and also with that of Drowart, et al.[12] Two appearance potentials for C_5^+ were obtained from C_6N_2. The lower of these corresponds very closely with the direct ionization potential of C_5.[12] The higher value involves a fragmentation process. The agreement, however, is reasonably good for this type of measurement and the average of our two values is in fairly good agreement with that of Drowart.

It is interesting also that the formation of C_4^+

ion from C_4N_2 and C_6N_2 corresponds to the elimination of N_2 or C_2N_2 from the parent ions. Although these reactions must have occurred through cyclic intermediates, the calculated heats of formation correspond very closely to that obtained by direct ionization of C_4. This indicates once more the small activation energy involved in ionic reactions passing through four-center or even more complex intermediates. Table VI summarizes the values for the polymeric carbon ions and the comparative data by Drowart, et al.

TABLE VI

ΔH_f OF CARBON IONS (KCAL./MOLE)

	Average or best value	Drowart, et al.[12]
C_2^+	487	473
C_3^+	493	479
C_4^+	523	521
C_5^+	530	521

C_nH^+ Ions.—Cyanoacetylene gives peaks at masses 13, 25, and 37 corresponding to the ions CH^+, C_2H^+ and C_3H^+, respectively. All of these occur by fragmentation processes and all seem to involve some excess energy. The CH^+ ion occurs at an appearance potential of 21.9 volts. If we assume that the neutral species is the C_2N radical having a heat of formation of 123 kcal./mole (Table V), we calculate a heat of formation for the ion of 414 kcal./mole. Values for the heat of formation of the ion range from about 330 to 400 kcal./mole.[4] All of these values are open to question because of possible alternative mechanisms that might have been involved. The spectroscopic ionization potential of CH is 11.13 ev.,[14] and the presently accepted value for $D(CH)$ is 80 kcal./mole.[13] A heat of sublimation of carbon of 170 kcal. leads to heats of formation of CH of 142 and of CH^+ of 399 kcal./mole. This is in reasonable agreement with the 414 kcal. calculated above, particularly in view of the relatively low abundance of the CH^+ ion.

Our value for the heat of formation for C_2H^+ is 440 kcal./mole, and this is definitely higher than the value of 414 kcal./mole obtained by several workers[4] from the appearance potential of this ion from acetylene. The mass 25 peak is 7.9% of the parent and thus is large enough that the discrepancy of 26 kcal./mole is probably not attributable to errors in measurement and so excess energy is probably inherent in the process.

The appearance potential for the mass 37 ion necessarily corresponds to the elimination of an N-atom from the cyanoacetylene. It is interesting that this appearance potential is within about a volt of the appearance potentials of other N-atom elimination reactions and indeed is the lowest value for reactions of this type of the four compounds studied. However, the calculated value for the heat of formation (395 kcal./mole) is much higher than the 309 kcal./mole given as the preferred heat of formation of the ion by Field and Franklin.[4] It is our opinion that the higher value is more nearly correct for the following reason. If one computes the strength of the CH bond in

(14) A. E. Douglas and G. Herzberg, Can. J. Research, A20, 71 (1942).

CH$^+$ and C$_2$H$^+$, values of 82 and 127 kcal./mole, respectively, are obtained. Similarly, if the present value of $\Delta H_f(C_3H^+)$ = 395 kcal. is used, a CH bond strength of 137 kcal./mole is obtained for C$_3$H$^+$. This seems more reasonable than a CH bond strength of 222 kcal./mole resulting from use of $\Delta H_f(C_3H^+)$ of 309 kcal.

Negative Ions.—All negative ions observed are formed by resonance capture processes. There was no evidence for ion-pair processes. The apparent absence of negative ions in the cyanogen spectrum is surprising as all other compounds give CN$^-$ (and C$_3$N$^-$) ions of significant abundance. In addition, C$_6$N$_2$ showed a rather large peak at mass 74 corresponding to C$_5$N$^-$ and, somewhat surprisingly, a parent ion C$_6$N$_2^-$ formed by simple electron capture. Both of the negative ions formed from cyanoacetylene seem to involve a great deal of excess energy. This was also true of the C$_3$N$^-$ ion formed from C$_6$N$_2$. The appearance potential of CN$^-$ from C$_4$N$_2$ leads to a heat of formation of C$_3$N radical of 131 kcal./mole in good agreement with the heat of formation of this radical as determined from positive ion appearance potentials. Similarly, the appearance potential of CN$^-$ from C$_4$N$_2$ leads to a heat of formation of the C$_5$N radical in good agreement with that obtained from positive ion appearance potentials.

The appearance potentials of C$_3$N$^-$ from C$_4$N$_2$ lead to a heat of formation of this ion of 76 kcal./mole. This is well below values obtained for this ion from the other compounds studied. We cannot be certain that this ion is formed without excess energy, but at least this value of 76 kcal./mole is sufficiently low to yield a fairly reasonable value of 55 kcal./mole for the electron affinity of C$_3$N. We also calculate a value of 163 kcal./mole for C$_5$N$^-$ which leads to an electron affinity of C$_5$N of 53 kcal./mole. These values are in quite good agreement, as one would expect for such similar compounds. However, they are about 20 kcal./mole less than that of CN radicals. The significance of this difference is not obvious.

Bond Strengths.—The various heats of formation of radicals and ions as determined in this study permit us to calculate the strengths of several bonds in cyanogen and cyanoacetylenes. In Table VII we list the results of several of these calculations. The strengths of the first C$\equiv$N bond in the four compounds studied has been calculated for both the neutral compounds and the positive ions. In addition, the strength of the C$\equiv$N bond in the various free radicals having the formula C$_n$N and the corresponding positive ions have been calculated. In all cases it is assumed that the positive product ion is the one containing carbon atoms. It is of interest that the strength of the C$\equiv$N triple bond in all of these compounds is in the neighborhood of 160 kcal./mole with very little variation. The C$\equiv$N bond in the various radicals tends to be somewhat stronger and to vary over a wider range. In fact, there appears to be a fairly consistent decrease in bond strengths from $D(CN)$ to $D(C_5-N)$. It must be admitted that in the latter case the bond strength is sufficiently low to be of doubtful validity.

The strength of the C$\equiv$N bond in the positive

	Neutral radical	Positive ion
D(C–N)	193	133
D(C$_2$–N)	185	163
D(C$_3$–N)	169	130
D(C$_4$–N)	173	184
D(C$_5$–N)	129	140
D(NC$_2$–N)	161	146
D(HC$_3$–N)	157	148
D(NC$_4$–N)	153	170
D(NC$_6$–N)	162	180

Table VIII
STRENGTH OF CARBON–CARBON BONDS (KCAL./MOLE)

	Neutral	Positive ions[a]
D(NC–CN)	104	120
D(HC$_2$–CN)	120	145
D(NC$_3$–CN)	91	159
D(NC$_2$–C$_2$N)	118	151
D(NC$_5$–CN)	122	136
D(NC$_4$–C$_2$N)	109	123
D(NC$_3$–C$_3$N)	79	146
D(C–CN)	156	94
D(C$_2$–CN)	154	101
D(C–C$_2$N)	162	92
D(C$_3$–CN)	107	119
D(C$_2$–C$_2$N)	152	147
D(C–C$_3$N)	135	112
D(C$_5$–CN)	89	96
D(C$_4$–C$_2$N)	120	132
D(C$_3$–C$_3$N)	85	110
D(C$_2$–C$_4$N)	132	139
D(C–C$_5$N)	153	149
D(C$_4$–CN)	103	119
D(C$_3$–C$_2$N)	154	123
D(C$_2$–C$_3$N)	111	125
D(C–C$_4$N)	120	100

[a] Charge always associated with the larger fragment containing an N atom or with the fragment containing carbon atoms alone. This gives the smallest value for the bond in all cases.

ions also shows a rather wide variation. This is especially noticeable with the C$_n$N$^+$ ions which exhibit alternate high and low values with increasing values of n. This behavior tempts one to speculate as to the structure of these ions and the nature of the bonding. However, until we are more certain of the data such speculation does not seem justified.

The strengths of the various carbon–carbon bonds in both neutral molecules and positive molecular ions having the formula (C$_n$N$_2$) are listed in Table VIII. Again, no clear pattern emerges except that the bonds in the ions are all somewhat stronger than the corresponding ones in the neutral species. Table VIII also lists values for strengths of the various carbon–carbon bonds in the radicals and positive ions having the formula C$_n$N. These results show that with the radicals and with some of the ions the carbon–carbon bonds are alternately strong and weak as they are removed progressively from the N-atom. This is in accord with an alternating single and multiple bond structure. A few exceptions are noted, especially where the C$_5$N radical is involved, again suggesting that this value may be erroneously high.