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Heats of Dissociation of Cyanogen

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Some arguments are presented which would indicate that the heat of dissociation of C_2N_2 into two CN radicals ($D(C_2N_2 \text{ into } 2CN)$) is 5.52 ev and the heat of dissociation of CN radicals into atoms ($D(CN)$) is 6.52 ev.

THE heat of dissociation of the cyanogen molecule into two cyanogen radicals ($D(C_2N_2 \text{ to } 2CN)$) and the heat of dissociation of the radical ($D(CN)$) are connected with the heat of formation from atoms of the cyanogen molecule (Q_a):

$$\begin{aligned} CN(^2\Sigma^+) &\rightarrow C(^3P) + N(^4S) - D(CN), \\ \frac{1}{2}C_2N_2 &\rightarrow CN(^2\Sigma^+) - D(C_2N_2), \\ \frac{1}{2}C_2N_2 &\rightarrow C(^3P) + N(^4S) - Q_a \end{aligned}$$

The calculations of $D(CN)$ made earlier¹ are shown in Table I. They depend on the heat of sublimation of carbon ($L(C)$) or the atomic heat of formation of carbon monoxide ($D(CO)$) and the heat of dissociation of nitrogen ($D(N_2)$). In cases *a*, *b*, and *c*, the values used at that time are indicated, while in cases *d* and *e* the value 9.608 ev for $D(CO)$, suggested by Hagstrum,¹ is employed along with two different values for $D(N_2)$. In case *d*, the current value for $D(N_2)$ ($=7.384$ ev) is tried, and in case *e* the value of 9.764 ev suggested by Gaydon² is accepted. In case *f* Herzberg's value for $D(CO)=9.144$ ev is used. The object of this note is to suggest that the higher value for $D(N_2)$ is preferable since cases *e* and *f* are the only ones to which no objection can be raised. The reasons are:

1. Cases *a* and *b*.—They can be excluded because $D(C_2N_2)$ from Kistiakowsky and Gershonowitz¹ is too low to account for the rate experiments of Robertson and Pease¹ and the results of a Born-Haber cycle discussed below.

2. Case *c*.—Here $D(CN)$ ($=6.37$ ev), being nearly equal to $D(C_2N_2)$ ($=6.34$ ev), is unlikely on chemical grounds as mentioned by Herzberg.³ It would be expected that the breaking of a carbon-carbon bond, even if it were almost a

double bond since it is located between two triple bonds, would require less energy than the breaking of a triple bond between carbon and nitrogen as in the radical. However, the difference between bond energies and heats of dissociation in molecules more complicated than diatomic structures must not be lost sight of.

3. Case *d*.—Now $D(CN)$ ($=5.34$ ev) is even less than $D(C_2N_2)$ ($=5.52$). Hence it can be excluded for the reason given under case *c*. Furthermore, $D(CN)$ would be less than 5.5 ev, which can hardly be the case since any sort of Birge-Sponer extrapolation should yield a value greater than 5.5 ev, as mentioned by White.¹

4. Case *e*.—It is based on the work of Robertson and Pease¹ and Hogness and Lui-Sheng.¹ $D(CN)$ is greater than $D(C_2N_2)$, and the latter is also greater than 5.5 ev (see case *d*). The value of $D(C_2N_2)$ used agrees with the result of a Born-Haber cycle calculation shown below.

5. Case *f*.—It is also acceptable since it differs only from Case *e* by a somewhat lower $D(CO)$ value.

Hence the present considerations point toward the higher value of the heat of dissociation of nitrogen ($D(N_2)=9.764$ ev).

Further evidence for the value of 127 kcal. for $D(C_2N_2 \text{ to } 2CN)$ can be obtained from a Born-Haber cycle involving potassium and sodium cyanides (Table II). While some of the energy values entering the calculation, such as the electron affinity of CN radical and the lattice energies of KCN and NaCN, are not well known, still the calculation suffices to show that values of 77 kcal. and 146 kcal. of Kistiakowsky and Gershonowitz¹ and White,¹ respectively, cannot be correct. The electron affinity of the CN radical is taken to be equal to the value for the bromine atom since both have very closely the same ionic radius. It is assumed that the CN radical is in

¹ See references, Table I.

² A. G. Gaydon, *Nature* **153**, 407 (1944).

³ G. Herzberg, *J. Chem. Phys.* **10**, 306 (1942).

TABLE I. Heats of dissociation of cyanogen (ev).

	a	b	c	d	e	f
$\frac{1}{2}\text{C}_2\text{N}_2 \rightarrow \text{CN}$	-1.67	-1.67	-3.17	-2.76	-2.76	-2.76
$\text{C} + \text{O} \rightarrow \text{CO}$	9.14	9.61	11.05	9.61	9.61	9.14
$\text{N} \rightarrow \frac{1}{2}\text{N}_2$	3.69	3.69	3.69	3.69	4.88	4.88
$\frac{1}{2}\text{N}_2 + \text{CO} \rightarrow \frac{1}{2}\text{C}_2\text{N}_2 + \text{O}$	-5.20	-5.20	-5.20	-5.20	-5.20	-5.20 ^{g, h, i}
$\text{C} + \text{N} \rightarrow \text{CN}$	5.96	6.42	6.37	5.34	6.53	6.06

^a G. Herzberg, Chem. Rev. 20, 145 (1937); $D(\text{C}_2\text{N}_2)$ from G. B. Kistiakowsky and H. Gershinowitz, J. Chem. Phys. 1, 432 (1933) as 77 kcal. or 3.384 ev.

^b H. D. Hagstrum, Phys. Rev. 72, 947 (1947); same as a except $D(\text{CO}) = 9.608$ ev.

^c J. U. White, J. Chem. Phys. 8, 459 (1940) finds $D(\text{C}_2\text{N}_2) = 146$ kcal. or 6.384 ev and uses $D(\text{CO}) = 11.054$ ev.

^d T. R. Hogness and Lui-Sheng, J. Am. Chem. Soc. 54, 123 (1932) give $D(\text{C}_2\text{N}_2) = 127$ kcal. or 5.522 ev; accepted by N. R. Robertson and R. N. Pease, J. Chem. Phys. 10, 490 (1942).

^e Same as d but $D(\text{N}_2) = 9.764$ ev.

^f Same as e but $D(\text{CO}) = 9.144$ ev.

^g From $D(\text{O}_2) = 5.082$ ev; heat of combustion of $\text{C}_2\text{N}_2 = 256.4 \pm 5$ kcal. (reference h) and heat of combustion of $\text{CO} = 2.902$ ev (reference i).

^h F. R. Bichowsky and F. D. Rossini, *The Thermochemistry of the Chemical Substances* (Reinhold Publishing Corporation, New York, 1936).

ⁱ E. J. Prosen, R. S. Jessup, and F. D. Rossini, Bur. Stand. J. Research 33, 447 (1944).

every respect halogen-like. Similarly, the lattice energy is obtained from a plot of lattice energies of halides of sodium and potassium as a function of their crystal spacing⁴ and from the same quantity of CN radical. Other cyanides have also been considered, but their lattice energies are not known as accurately as the ones of the two alkali metals. It seems, therefore, that the value $D(\text{C}_2\text{N}_2 \text{ into } 2\text{CN}) = 127$ kcal. mentioned by Robertson and Pease¹ and first determined by Hogness and Lui-Sheng,¹ is the correct heat

⁴ R. W. G. Wyckoff, *The Structure of Crystals* (The Chemical Catalog Company, Inc., New York, 1931).

TABLE II. Heat of dissociation of cyanogen into cyanogen radicals $D(\text{C}_2\text{N}_2 \text{ into } 2\text{CN}) = 120 \pm 8$ kcal.

Reaction	Na kcal.	K kcal.
$[\text{M}] + [\text{C}] + \frac{1}{2}\text{N}_2 \rightarrow [\text{MCN}]$	23.0 ^a	28.5 ^a
$\text{E}^- + \text{M}^+ \rightarrow [\text{M}]$	143.4 ^a	120.9 ^a
$\text{CN}^- \rightarrow \text{CN} + \text{E}^-$	-84.3 \pm 3	-84.3 \pm 3 ^b
$[\text{MCN}] \rightarrow \text{M}^+ + \text{CN}^-$	-175.0 \pm 5	-159.0 \pm 5 ^a
$\frac{1}{2}\text{C}_2\text{N}_2 + \text{O}_2 \rightarrow \text{CO}_2 + \frac{1}{2}\text{N}_2$	128.2 \pm 3	128.2 \pm 3 ^a
$\text{CO}_2 \rightarrow [\text{C}] + \text{O}_2$	-94.1	-94.1 ^c
$\text{C}_2\text{N}_2 \rightarrow 2\text{CN}$	-117.6	-119.6

^a See reference 4.

^b J. Sherman, Chem. Rev. 11, 93 (1932); L. Helmholz and J. E. Mayer, J. Chem. Phys. 2, 245 (1934); see reference 6.

^c Reference 5.

of dissociation of the cyanogen molecule into cyanide radicals.

The high value of $D(\text{CO}) = 11.04$ ev is excluded on the basis of another study⁵ concerning carbon-carbon and carbon-hydrogen bond energies. No choice can be made in the present case between $D(\text{CO}) = 9.14$ ev and 9.61 ev, but $D(\text{N}_2) = 9.764$ ev seems indicated.

Appearance potentials⁶⁻⁸ of C^+ and N^+ ions in HCN and C_2N_2 do not help in deciding between the two values of $D(\text{N}_2)$ discussed above. It simply means that the ions would have different amounts of kinetic energy, depending on the value of $D(\text{N}_2)$ used.

⁵ Unpublished results.

⁶ P. Kusch, A. Hustrulid, and J. T. Tate, Phys. Rev. 52, 843 (1937).

⁷ J. T. Tate, P. T. Smith, and A. L. Vaughan, Phys. Rev. 48, 525 (1935).

⁸ K. E. Dorsch and H. Kallman, Zeits. f. Physik 60, 376 (1930).