Mass-spectrometric Determination of the Heat of Atomization of the Molecule BCN or BNC

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GASEOUS triatomic molecules containing carbon, nitrogen, and a third light element have recently received considerable attention because of their interesting structural, electronic, and bonding properties. In these previous investigations several methods have been used, such as Knudsen-cell mass spectrometry[1] (NaCN and AlCN or AlNC), photoionization mass spectrometry[2] (HCN and the cyanogen halides), optical spectroscopy[3] (HCN, HNC, FCN, FNC, NCO, and NCS) and *ab initio* calculations[4] (LiNC and LiCN).

The BCN (or BNC) molecule, for which previously no observations have been reported, appeared of particular interest because of its similarity in electronic structure to the recently detected AlCN (or AlNC) molecule[1b] and because of its being isoelectronic with the well known molecule C_3.[3a,5] By analogy with these two molecules, BCN was expected to be of high stability. The mass spectrometric identification and the determination of the heat of atomization of gaseous BCN is reported here. The molecule BCN was identified in the vapour effusing from a titanium nitride-coated graphite Knudsen cell which was enveloped by a tungsten Knudsen cell. The presence of titanium nitride provided a convenient source of nitrogen at the high temperatures which were most favourable for the observation of gaseous BCN. The principles of the mass spectrometric method and the experimental procedure used have been described elsewhere.[6]

The atomization energy, D_0^0, of the BCN molecule was calculated by the third-law method from the experimentally determined enthalpy, ΔH_0^0, of the isomolecular reactions:

$$BCN(g) + CN(g) = BC_2(g) + N_2(g) \quad (1)$$

and

$$2BCN(g) + C(g) = B_2C(g) + 2CN(g) \quad (2)$$

according to the relation

$$\Delta H_0^0 = -\boldsymbol{R}T\ln K_p - T\Delta[(G_T^0 - H_0^0)/T]$$

The equilibrium constant, K_p, was calculated from the ion currents, which were measured with 25 ev electrons and corrected for the isotopic abundance, for the energy dependence of the relative ionization cross sections, and, where necessary, for fragment contributions. Here the assumption was made that the relative maximum ionization cross-sections and the relative multiplier gains of the reactant and product ions compensate each other. The free-energy functions, $-(G_T^0 - H_0^0)/T$, were taken from the literature for $CN(g)$,[7] $N_2(g)$,[7] $C(g)$,[7], $BC_2(g)$,[8] and $B_2C(g)$.[8] The free-energy functions for $BCN(g)$ were assumed to be the same as have been calculated for the isoelectronic molecule C_3.[9]

Enthalpy change for the reactions (1): $BCN(g) + CN(g) = BC_2(g) + N_2(g)$ *and* (2): $2BCN(g) + C(g) + B_2C(g) + 2CN(g)$

Reaction	T(°K)	log K^a_p	$-\Delta[(G^0_T-H^0_0)/T]$ (cal. deg.$^{-1}$ mol.$^{-1}$)	$-\Delta H^0_0$ (kcal. mol.$^{-1}$)	D^0_0 (BCN)[b] (kcal. mol.$^{-1}$)
$BCN(g) + CN(g) = BC_2(g) + N_2(g)$ ..	2311	2·983	3·07	38·7	303
	2181	3·324	3·15	40·1	302
	2199	3·459	3·14	41·9	300
	2234	2·574	3·12	33·3	309
$2BCN(g) + C(g) = B_2C(g) + 2CN(g)$ ..	2181	1·274	0·67	14·2	297
	2199	1·350	0·68	15·1	297
	2234	0·671	0·71	8·5	300
	2150	0·964	0·65	10·7	299
					average 301 ± 5

[a] A typical set of relative ion currents is that for 2234° K: BCN^+(M 37) = 1·46 × 10^{-11}; B_2C^+ (M 34) = 7·50 × 10^{-12}; BC_2^+ (M 35) = 3·60 × 10^{-11}; CN^+ (M 26) = 2·72 × 10^{-11}; C^+ (M 12) = 5·52 × 10^{-12}; N_2^+ (M 28) = 4·14 × 10^{-9}.
[b] Using the literature values for the dissociation and atomization energies of N_2, CN, B_2C, and BC_2 indicated in the text.

The results from several sets of ion currents are summarized in the Table. The enthalpy values, ΔH^0_0, for reactions (1) and (2) were combined with the appropriate literature values for the other molecular reactants to yield the heat of atomization, D^0_0, for the BCN molecule of 301 ± 5 kcal. mol.$^{-1}$. The dissociation energies or heats of atomization used were: N_2 225 ± 2,[7] BC_2 294 ± 7,[8] and B_2C 254 ± 7 kcal. mol.$^{-1}$.[8] For CN a value of 177 ± 3·5 kcal. mol.$^{-1}$ was calculated from the selected value for $\Delta H^0_{f,0}(CN)$ = 102 ± 2 kcal. mol.$^{-1}$ given by Berkowitz *et al.*[2] and the JANAF auxiliary values for C and N_2.[7]

Considering possible systematic errors in the measurements and in the parameters estimated in this investigation and the uncertainties in the literature thermodynamic data used, a value of $D^0_0(BCN)$ = 301 ± 10 kcal. mol.$^{-1}$ is selected. This value is only slightly less than that for the isoelectronic molecule C_3 [with $D^0_0(C_3)$ = 321 kcal. mol.$^{-1}$][5] and similar to that of AlCN or AlNC.[2b] The present investigation does not permit any conclusion as to which of the possible isomers, BCN or BNC, is thermodynamically more stable. Optical spectroscopic measurements and *ab initio* calculations are expected to permit such conclusions and to determine details of the molecular and electronic structural properties of this molecule. In this connection it is interesting to note that *ab initio* calculations predict LiNC to be thermodynamically more stable than LiCN.[4]

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