Production of $CN(B^2\Sigma^+)$ Radicals in the Dissociative Excitation of BrCN and ICN by Metastable Ar and Kr Atoms in a Flowing Afterglow

Kazuhiro KANDA,* Kaoru SUZUKI,† Tamotsu KONDOW,†† Haruhiko ITO,††† and Kozo KUCHITSU†††,††††
Department of Fundamental Science, College of Science and Engineering, Iwaki Meisei University, Iwaki, Fukushima 970
† Institute for Molecular Science, Okazaki, Aichi 444
†† Department of Chemistry, School of Science, The University of Tokyo, Bunkyo-ku, Tokyo 113
††† Department of Chemistry, Nagaoka University of Technology, Nagaoka, Niigata 940-21
†††† Department of Chemistry, Josai University, Sakado, Saitama 350-02

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The dynamics of dissociative excitation of BrCN or ICN producing $CN(B^2\Sigma^+)$ radicals by $Ar(^3P_2)$ or $Kr(^3P_2)$ was investigated by using the flowing afterglow method. The observed vibrational distributions of CN(B) are consistent with the reported reaction mechanism for the CN(B) formation initiated by the transfer of the excitation energy of the metastable atom to the cyanide molecule.

An excited CN radical, $CN(B^2\Sigma^+)$, is produced efficiently by a dissociative reaction of cyanogen halide, XCN, by a heavy rare-gas atom in its metastable excited state, Rg^m,

$$Rg^m + XCN \rightarrow CN(B^2\Sigma^+) + Rg + X. \qquad (1)$$

Many studies have been made on this reaction mainly by observation of the $CN(B^2\Sigma^+-X^2\Sigma^+)$ emission.[1—6] For the reaction of Ar^m with BrCN, an analysis of polarization of the emission has shown that the dominant mechanism of the formation of CN(B) is the transfer of the excitation energy from Rg^m to BrCN followed by dissociation of $BrCN^*$.[7] This mechanism has been supported by an analysis of the vibrational distribution of CN(B) produced from reaction (1) in a low-pressure flowing afterglow.[8] A different mechanism of formation of CN(B) from the Xe^m/XCN reaction via ion-pair exciplex, Xe^+CN^-, was once proposed[5,6] with reference to the reaction of Xe^m with X_2,[9,10] but no confirming evidence seems to have since been presented, particularly for systems involving other rare-gas metastables such as Kr^m or Ar^m.

The present paper reports on our analysis of the CN(B) emissions produced from reaction (1) following Ref. 8 using a low-pressure flowing afterglow. Systems involving Kr^m, which has lower excitation energy and higher ionization potential than Ar^m, and ICN, which has higher molecular-orbital energies than BrCN, were taken to investigate whether or not there was an indication of a systematic variation in the reaction mechanism by a quantitative analysis of the vibrational or rotational energy distributions of the CN(B) produced from reaction (1).

Experimental

The details of the flowing-afterglow apparatus and the experimental procedure are described in Ref. 8. Cyanogen iodide (Aldrich, purity 95%) and cyanogen bromide (Nacalai, purity 90%) were used after degassing. The CN(B-X) emission spectra were observed by a 1-m monochromator with a spectral resolution of 0.01 nm fwhm using 10 mTorr of argon or 1 mTorr krypton (1 Torr=133.322 Pa).

Results and Discussion

The emission spectra observed for the Ar^m/XCN and Kr^m/XCN systems in the present study are both very different from those for the Ar^m/XCN system reported in previous studies at about 300 mTorr,[1,2] where collisional relaxations in long-lived excited electronic states such as $A^2\Pi_i$, $^4\Sigma^+$ and $^4\Pi$ contribute significantly to the B-X emission via the strongly perturbed rovibrational levels of the B state; we have analyzed the mechanisms of these collisional relaxations in detail in Ref. 11.

The rovibrational distributions of the CN(B) radicals obtained in the present study can be assumed to be essentially nascent by the following order estimates: The average collision time is estimated to be 6.7 μs at 10 mTorr from the cross section for rotational relaxation of CN(B) by collision with Ar, 85 Å^2.[11] This implies that the mean collision time of CN(B) radicals is about 100 times its lifetime, ca. 65 ns.[12] Furthermore, we observed that an increase in the Ar pressure from 10 to 40 mTorr caused no perceptible change in the emission spectra. For collisional relaxation of CN(B) with Kr no cross section has yet been reported, but even if its cross section is much larger than that with Ar, the effect of this relaxation can be ignored in the present case, because the ambient pressure in the Kr flow is only about 1/10 of that in the Ar flow.

Since no emission from halogen atoms was observed,[8] the halogen atoms produced in the present Rg^m/XCN reactions are essentially in the ground state. Under similar experimental conditions, the $^3P_2$ metastable atom is reported to be the dominant active species.[13] Therefore, the excitation energy of the rare-gas metastable atom is assumed to be 11.548 and 9.915 eV for $Ar(^3P_2)$ and $Kr(^3P_2)$, respectively.[14] The bond dissociation energy has been reported to be 3.77 and 3.11 eV for BrCN and ICN, respectively.[15] By the calculation described in Ref. 8, the available excess energies are estimated to be 5.31, 4.87, 3.66, and 3.23 eV for the Ar^m/ICN, Ar^m/BrCN, Kr^m/ICN, and Kr^m/BrCN systems, respectively. In the Ar^m/ICN and Ar^m/BrCN systems, the emission band from $CN(B^2\Sigma^+, v=20)$ has been identified clearly. The highest vibrational bands observed in the reaction of Kr^m with ICN and BrCN are $v=16$ and 12, respectively. These values are close to the upper limits estimated from the available energies.

The vibrational population, N_v, and the rotational energies, $E_{rot,v}$, were estimated by a computer simulation of the band envelope in the emission spectra.[3] The vibrational distributions are shown in Figs. 1 and 2. The rotational energies were estimated by assuming a Boltzmann distribution. The average vibrational and rotational energies of the $CN(B^2\Sigma^+)$ fragment calculated from N_v and $E_{rot,v}$ are summarized in Table 1. The average fractions in the total available energies channeled into the vibration and rotation are 35±10% and 10±5%, respectively. No differences were observed among the energy disposals for the four systems.

A surprisal analysis[16] on the vibrational distributions of the CN(B) fragments formed from the four systems shows that they are consistent with those constructed assuming two-body dissociation, which corresponds to the energy-transfer mechanism in the energy dispersion (See Figs. 1 and 2). The value of the vibrational surprisal parameter, λ, for CN(B) obtained in the dissociative reaction of BrCN is 0.0±1.0, and that in the dissociation of ICN is estimated to 1.5±1.0, indicating that the vibrational excitation of the product CN(B) fragment is slightly less effective than that predicted statistically. The independence of λ on the metastable atom indicates that the $CN(B^2\Sigma^+)$ fragments proceed via essentially the same reaction dynamics. This conclusion is consistent with the results of the crossed-beam study, where the CN(B) is produced from BrCN with Ar^m and Kr^m in the range of 0.7—5.2 eV collision energy.[17] The rotational surprisal parameters obtained from the analysis on the rotational distribution in each vibrational state in the present four systems are positive, indicating that the rotational excitation is less effective than that predicted statistically.

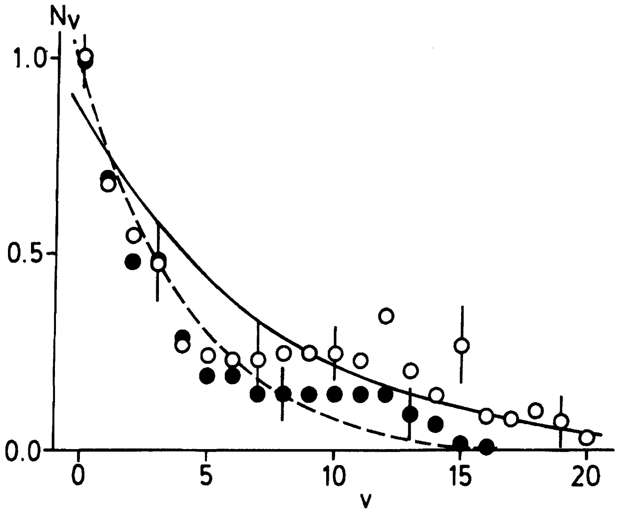

Fig. 1. The relative vibrational populations with estimated error bars plotted against the vibrational quantum number v for the $CN(B^2\Sigma^+)$ state: (○) Ar^m+ICN; (●) Kr^m+ICN. The solid and broken curves represent the best-fit predictions based on a linear surprisal analysis of the reaction of Ar^m+ICN and Kr^m+ICN, respectively, assuming two-body dissociation.

Table 1. Average Vibrational and Rotational Energies Deposited into $CN(B^2\Sigma^+)$ Fragments[a]

Reactions	Average energy	
	E_{vib}/eV	E_{rot}/eV
$Ar(^3P_2)$+ICN	2.0(2)	0.3(1)
$Ar(^3P_2)$+BrCN	1.9(2)	0.6(1)
$Kr(^3P_2)$+ICN	1.3(1)	0.4(1)
$Kr(^3P_2)$+BrCN	0.8(1)	0.4(1)

a) Numbers in parentheses represent standard errors in units of the last significant digit.

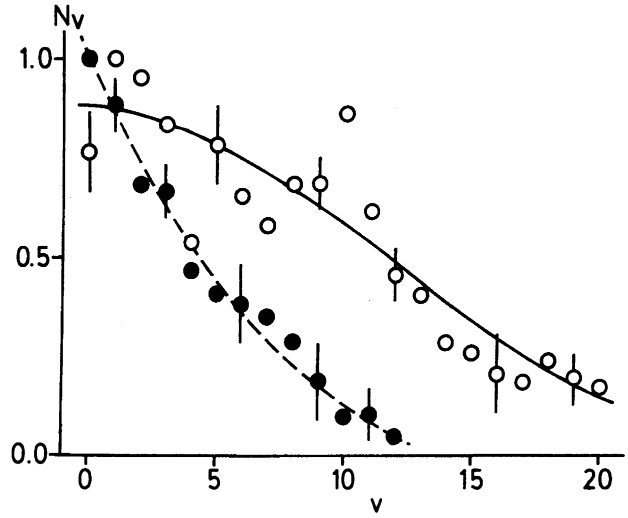

Fig. 2. The relative vibrational populations with estimated error bars plotted against the vibrational quantum number v for the $CN(B^2\Sigma^+)$ state: (○) Ar^m+BrCN; (●) Kr^m+BrCN. The solid and borken curves represent the best-fit predictions based on a linear surprisal analysis of the reaction of Ar^m+BrCN and Kr^m+BrCN, respectively, assuming two-body dissociation.

In the energy transfer mechanism, the precursor states of CN(B) are the excited states of cyanogen halide. The excitation energies of rare-gas metastables correspond to the wavelength region of vacuum ultraviolet radiation. The multiplicities of the excited states formed by photoexcitation can be different from those formed by metastable-atom excitation, but the photochemical studies of cyanogen halides give information on their electronic states. The photochemistry of these molecules in this energy region were investigated by using synchrotron radiation, by which the Rydberg transitions converging to the first and second ionization potentials were observed.[18] The absorption spectra of cyanogen halides and their photoexcitation fluorescence spectra of $CN(A^2\Pi_i)$ and $CN(B^2\Sigma^+)$ showed only the ν_1 and ν_3 bands, and no ν_2 excited vibrational bands corresponding to the bending vibration was observed.[18] Therefore, the rotational excitation of the CN(B) fragments is expected to be small. This observation is consistent with the less rotational excitation in the present low-pressure afterglow study.

The outer electronic configuration of cyanogen halides in the ground state is reported by photoelectron spectroscopy to be[19)]

$$\cdots(1\pi)^4(4\sigma)^2(2\pi)^4;\quad {}^1\Sigma^+ \tag{2}$$

considering the MO's constructed only from the valence shell atomic orbitals. The 1π and 2π orbitals arise from linear combinations of the p orbital of halogen atom with the π bonding orbital of the CN group. The 4σ orbital is essentially the lone pair of the nitrogen atom.

The excitation energy of $Ar(^3P_2)$ corresponds to the unstructured region beyond the first ionization potential in the ICN photoabsorption spectrum. In the reaction of Kr^m/ICN and Ar^m/BrCN, the excitation energies correspond to the wavelength region where the Rydberg transitions converging to the first ionization potential are congested. In the Kr^m/BrCN systems, the excitation energy corresponds to the wavelength region where some Rydberg transitions are dispersed. The $4\sigma\rightarrow 3s\sigma+\nu_3$ transition is the nearest to the excitation energy of Kr^m in the longer wavelength side.

The correlation scheme predicts that the promotion of the 4σ electron of XCN prefers the production of $CN(B^2\Sigma^+)$ to that of $CN(A^2\Pi_i)$, while the promotion of 2π electron produces $CN(A^2\Pi_i)$ rather than $CN(B^2\Sigma^+)$. However, the photoexcited fluorescence spectra of BrCN and ICN in the region of 105—155 nm show that the transitions due to excitation of 2π electron also produce $CN(B^2\Sigma^+)$ fragement.[20,21] Therefore, these states can both be the precursor states of $CN(B^2\Sigma^+)$. Since the energy gap between the ionization potential of 2π MO and the excitation energy of the metastable atom is small in the Ar^m/BrCN and Kr^m/ICN systems, the Rydberg states converging to the first ionization potential are likely to contribute dominantly to reaction (1).[8] In the Ar^m/ICN and Kr^m/BrCN systems, there is no significant difference in the values of the surprisal parameter and the energy disposal in comparison with the Ar^m/BrCN and Ar^m/ICN systems. This indicates the following possibilities for all the four systems: The product $CN(B^2\Sigma^+)$ radicals are formed through the same Rydberg manifold, or the rovibrational excitation is due to the character of the dissociative potential irrespective of the Rydberg states.

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22) A list of the rotational energies and typical CN(B-X) spectra from the four reaction systems are deposited as Document No. 67009 at the Office of the Editor of Bull. Chem. Soc. Jpn.