March, 1986] *Bull. Chem. Soc. Jpn.*, *59*, *839—842 (1986)*

Formation of NH($A^3\Pi$) by Electron-Impact Dissociation of Isothiocyanic Acid

Ikuo Tokue and Yoshio Ito
Department of Chemistry, Faculty of Science, Niigata University, Niigata 950-21
(Received October 7, 1985)

Emission spectra of the fragments of Isothiocyanic acid (HNCS) produced by electron impact were studied. The onset for formation of NH($A^3\Pi$) is 9.2±0.5 eV. On the basis of the excitation function of the NH(A-X) band, NH(A) is shown to be formed via a spinforbidden process HNCS$\rightarrow$NH($A^3\Pi$)+CS($X^3\Sigma^+$) near the onset. At higher energies, a spin-allowed process HNCS$\rightarrow$NH(A)+CS($a^3\Pi$) seems to be predominant. The ratio of the formation rate of NH(c) to that of NH(A) is 0.18±0.03.

Isothiocyanic acid (HNCS) has 16 valence electrons and is isoelectronic with isocyanic acid (HNCO). The ground state of both molecules is known to have trans bent structure (C_s symmetry).[1,2] Emission spectra of the fragments from isocyanic acid (HNCO) and their formation mechanisms have been extensively investigated by photolysis[3–6] and electron-impact dissociation.[7,8] It was shown in a previous paper[8] that NH(A) near its onset is produced via a spin-forbidden excitation and that NH(A) at higher energies, NH(c), NCO(A), and NCO(B) are produced via a spin-allowed excitation. On the other hand, there has been only a little amount of information[9] about the dissociation mechanism of HNCS.

In the present study, the emission spectra of the fragments produced by electron-impact on HNCS have been analyzed for the first time. Dissociation processes for formation of NH(A) are assigned on the basis of the emission spectra and the excitation function. To sssist with the assignment, we have derived the excitation energy to the singlet and triplet states of HNCS by a semiempirical calculation (CNDO/S). In addition, the vibrational and rotational distributions of the NH(A) and NH(c) states are estimated on comparing the observed spectrum of the NH emission with synthetic envelopes.

Experimental

The apparatus and the experimental conditions have been described previously.[10] The pressure of the sample vapor in the collision region during the emission measurement was controlled to 2.7—6.7 mPa by a variable leak valve.

The HNCS was prepared by heating the mixture of dry, powdered samples of KSCN and $KHSO_4$ to 70 °C under vacuum.[11] The vapor generated was dried over P_2O_5 and trapped at liquid N_2 temperature. After being pumped several times at about −30 °C to remove volatile impurities, it was stored just before use in a gas reservoir at a pressure less than 3 Torr[†] measured by Pirani gauge to avoid deposition on the Pyrex wall.

A spectral band pass of 0.32 nm fwhm was used for the measurement of the excitation function. The energy scale for the impinging electron was calibrated by using the onset and the peak of the excitation function[12] for the (1,0) band of the $N_2(C^3\Pi_u\text{-}B^3\Pi_g)$ emission from N_2 mixed together in the sample gas.

Results and Discussion

Emission Spectra. Figure 1 shows the emission spectra in the region 250—500 nm obtained by electron impact on HNCS. These specta belong to the hydrogen Balmer lines, the CN($B^2\Sigma^+\text{-}X^2\Sigma^+$),

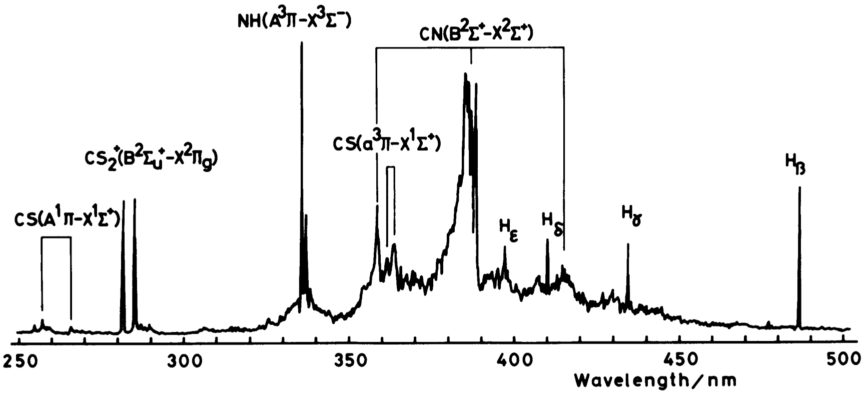

Fig. 1. Emission spectra produced by electron impact (150 V, 45 μA) on HNCS at 5.7 mPa.

[†] 1 Torr=133.322 Pa.

$CS(a^3\Pi-X^1\Sigma^+)$, $NH(A^3\Pi-X^3\Sigma^-)$, $CS(A^1\Pi-X^1\Sigma^+)$ bands.[13] The sharp emission near 280 nm is assigned to the $CS_2^+(B^2\Sigma_u^+-X^2\Pi_g)$ band from CS_2 impurity.[14] In addition, broad emission is observed between 340 and 470 nm. This is attributed to the NCS radical since the peaks observed near 370, 394, 396, 408, 430, 443 nm agree with those found in the literature.[15]

Although the CS_2^+(B–X) and $CS_2^+(A^2\Pi_u-X^2\Pi_g)$ band produced by electron impact on CS_2 are very strong,[16] the CS_2^+(A–X) band is not found between 450 and 530 nm as shown in Fig. 1. In a supplementary measurement, the CS(a–X) band is not observed by electron impact on CS_2 under the same conditions as for HNCS. It follows that the CS(a–X) band is produced from HNCS and that the CS(A–X) band includes a minor contribution from CS_2 impurity. On comparison with the emission produced from CS_2 under the same conditions, we concluded that the influence of CS_2 impurity in the emission spectrum is negligible except for the CS(A–X) band.

The ratio of the emission intensity of the NH(A–X) band to that of the CN(B–X) band was not reproducible. This indicates that the sample vapor includes HCN impurity since the CN(B–X) emission from HCN is generally known to be very strong. HCN is considered to be formed secondarily in the gas reservoir by the reaction[10] $3HNCS \rightarrow HCN + H_2C_2N_2S_3$. The influence of HCN impurity upon the CN(B–X) band is difficult to be estimated. In addition, the CS(a–X) band overlapped the CN(B–X) band. Hence, we did not measure the excitation function of the CS(a–X) band and did not attempt the population analysis about the CN(B–X) band. Neverthless, it is noteworthy that the appearance voltage of the CS(a–X) band is higher than the NH(A–X) band. This will be discussed in a later section.

Population Analysis of NH(A). The emission spectrum which covers the region 324—344 nm consists of two heavily overlapping bands corresponding to the (0,0) band of the NH(c–a) system and the (0,0) and (1,1) bands of the NH(a–X) system. The rotational structure can be resolved only partly due to the limited resolution. The observed spectrum is therefore compared with band envelopes simulated by a microcomputer. The procedure of the band-envelope analysis has been reported in detail.[17]

This analysis of the intensities of the NH emission bands provides information about the ratio of the formation rate of $NH(c^1\Pi)$ to that of $NH(A^3\Pi)$, P(c)/P(A), in the dissociative excitation. In addition, it provides the rotational distribution and the relative vibrational population, $N_v/N_{v=0}$, of the NH radical. In this analysis, the rotational distribution of the v level of the NH(A) or the NH(c) state is assumed to be represented by a Boltzmann temperature (T_v).

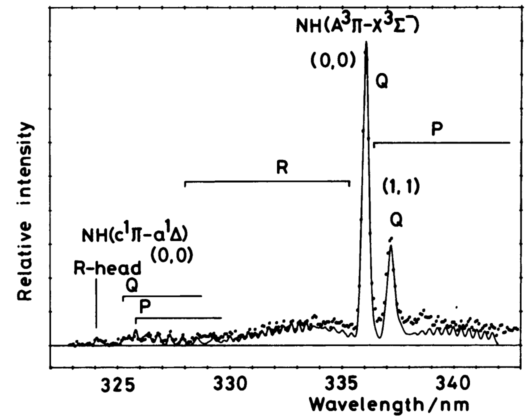

Fig. 2. The observed spectrum of NH (dots) at an impact energy of 30 eV with 0.17 nm fwhm resolution. The trace is the best-fit synthetic spectrum.

The observed spectrum at an impact energy of 30 eV is compared in Fig. 2 with synthetic envelopes. T_0 of NH(c) is fixed to be 1000 K. $P(c)/P(A)$ is derived to be 0.18±0.03 and is independent of the impact energy from the onset up to 80 eV. T_0 and N_1/N_0 of NH(A) are estimated to be ≃3000 K and 0.42±0.05, respectively. T_0 of NH(A) is nearly equal to that for HNCO, while N_1/N_0 of NH(A) is considerably larger than that for HNCO (0.24—0.30).

The disagreement between the observed spectra and the synthetic envelopes near 337 nm in Fig. 2 is attributable to the (2,2) band of the NH(A–X) transition which is not included in band envelopes. In addition, there is a tendency of synthetic envelopes to deviate from the observed spectrum at the wavelengths longer than 333 nm. This is probably caused by overlapping of the $NCS(A^2\Pi-X^2\Pi)$ and $NCS(B^2\Sigma^+-X^2\Pi)$ bands, since the NCS emission has been observed between 330 and 500 nm.[15]

Excitation Function of the NH(A–X) Band. Figure 3 shows the excitation function of the NH(A–X) band from HNCS. This is very similar in shape to that from HNCO.[8] The excitation function of the NH(c–a) band cannot be measured because of its weak intensity. The onset for formation of NH(A) is found to be 9.2±0.5 eV. In addition, the second rise in the plot appears near 20 eV.

The main dissociation processes leading to the formation of NH(A) and NH(c) from HNCS at low energy are as follows:

$$HNCS \rightarrow NH(A^3\Pi) + CS(X^1\Sigma^+), \quad \Delta H = 8.44\,\text{eV}, \quad (1)$$

$$HNCS \rightarrow NH(A^3\Pi) + CS(a^3\Pi), \quad \Delta H = 11.87\,\text{eV}, \quad (2)$$

$$HNCS \rightarrow NH(c^1\Pi) + CS(X^1\Sigma^+), \quad \Delta H = 10.17\,\text{eV}. \quad (3)$$

The ΔH values derived by using the electronic energy[13] and the enthalpy of formation[18] of HNCS and of the fragments, represent the enthalpy of

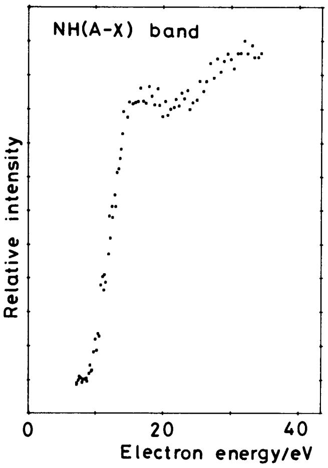

Fig. 3. NH(A-X) emission intensity at the head of the (0, 0) band versus electron energy.

dissociation. Process 1 is a spin-forbidden reaction, while Processes 2 and 3 are spin-allowed reactions. On comparing the observed onset with ΔH, it becomes evident that Process 1 is the main dissociation process leading to the formation of NH(A) near its onset. Process 2 seems to be the main dissociation process at higher energies on the following grounds. First, the excitation function of the NH(A-X) band rising linearly with the electron energy near the onset deviates from the straight line at 12 eV. This value is nearly equal to the ΔH for Process 2. Second, the excitation function above 20 eV increases monotonously with the electron energy. This implies that NH(A) is mainly produced via a spin-allowed excitation at higher energies. Third, the appearance voltage of the CS(a-X) band is higher than that of the NH(A-X) band. This indicates that CS(a) is not produced by the reaction HNCS$\rightarrow$NH(X)+CS(a) with ΔH=8.45 eV.

In order to support the foregoing conclusion, we have carried out a semiempirical calculation (CNDO/S).[19] The excitation to the singlet and triplet HNCS states is estimated on the assumption that the Franck-Condon principle is valid. The structural parameters for the ground state of HNCS (trans bend) reported by Yamada et al.[1] are used for the calculation. The electronic configuration in the ground state of HNCS is $(1-4)a'^2 1a''^2 (5,6)a'^2 2a''^2$. This configuration agrees with the result by the HF/STO-3G calculation by using the GAUSSIAN 80 system.

Considering the accuracy of CNDO/S calculation, we can attempt only qualitative discussion. By resolving the species of NH($A^3\Pi$) and CS($X^1\Sigma^+$) into that of point group C_s, we obtain $^3A'+^3A''$ and $^1A'$, respectively. The product between these species yields the $^3A'$ and $^3A''$ states for non-linear HNCS. The observed onset for formation of NH(A) indicates that the precursor for the NH(A)+CS(X) products lies in the region 8.7—9.7 eV. Moreover, the NC bond of the precursor is expected to be weakened due to the promotion of an electron from the bonding orbital. Thus, the 6-$^3A'$ (at 8.0 eV) and 6-$^3A''$ (at 8.7 eV) states are considered to be most probable as the precursor. The former corresponds to the excitation out of the 5a′ MO into the 7a′ MO (in plane $\pi_{NC}\rightarrow$in plane $\pi_{NCS}{}^*$) and the latter corresponds to the excitation out of the 5a′ MO into the 3a″ MO (in plane $\pi_{NC}\rightarrow$out-of-plane $\pi_{NCS}{}^*$). The fact that the 6-$^3A'$ and 6-$^3A''$ states lie considerably lower than the next NH($a^1\Delta$)+CS($a^3\Pi$) state (9.74 eV) which can only correlate with the triplet HNCS states gives another ground for the above inference.

The authors thank the Computer Center, Institute for Molecular Science, for the use of the HITAC M-200H computer and the Library Program GAUSSIAN 80.

References

1) K. Yamada, M. Winnewisser, G. Winnewisser, L. B. Szalanski, and M. C. L. Gerry, *J. Mol. Spectrosc.*, **79**, 295 (1980).

2) L. Fusina and I. M. Mills, *J. Mol. Spectrosc.*, **86**, 488 (1981).

3) W. D. Woolley and R. A. Back, *Can. J. Chem.*, **46**, 295 (1968).

4) H. Okabe, *J. Chem. Phys.*, **53**, 3507 (1970).

5) W. S. Drozdoski, A. P. Baronavski, and J. R. McDonald, *Chem. Phys. Lett.*, **64**, 421 (1979).

6) G. T. Fujimoto, M. E. Umstead, and M. C. Lin, *Chem. Phys.*, **65**, 197 (1982).

7) K. Fukui, I. Fujita, and K. Kuwata, *J. Phys. Chem.*, **81**, 1252 (1977).

8) I. Tokue and Y. Ito, *Chem. Phys.*, **89**, 51 (1984).

9) C. R. Boxall and J. P. Simons, *J. Photochem.*, **1**, 363 (1972/73).

10) I. Tokue and M. Ikarashi, *Bull. Chem. Soc. Jpn.*, **54**, 2565 (1981); I. Tokue, M. Ikarashi, S. Takizawa, and Y. Ito, *Bull. Chem. Soc. Jpn.*, **56**, 583 (1983).

11) R. Kewley, K. V. L. Sastry, and M. Winnewisser, *J. Mol. Spectrosc.*, **10**, 418 (1963), and Ref. 2 in this paper.

12) T. G. Finn, J. F. M. Aarts, and J. P. Doering, *J. Chem. Phys.*, **56**, 5632 (1972).

13) K. P. Huber and G. Herzberg, "Constants of diatomic molecules," Van Nostrand, Princeton, (1979), and the related references there in.

14) L. C. Lee, D. L. Judge, and M. Ogawa, *Can. J. Phys.*, **53**, 1861 (1975).

15) P. D'amario, G. Di. Stefano, M. Lenzi, and A. Mele, *J. Chem. Soc., Faraday Trans. 1*, **68**, 940 (1972).

16) M. Toyoda, T. Ogawa, and N. Ishibashi, *Bull. Chem. Soc. Jpn.*, **47**, 95 (1974).

17) I. Tokue and M. Iwai, *Chem. Phys.*, **52**, 47 (1980).

18) D. D. Wagman, W. H. Evans, V. B. Parker, R. H.

Schumm, I. Halow, S. M. Bailey, K. L. Churney, and R. L. Nuttall, *J. Phys. Chem. Ref. Data,* **11**, (1982) suppl. No. 2.

19) The values of $1/2(I_s+A_s)$ and $1/2(I_p+A_p)$ for sulfur were not given in the original program. Hence, we used the values found in the book, J. A. Pople and D. L. Beveridge, "Approximate Molecular Orbital Theory," McGraw-Hill, New York, (1970). Orbital energies for COS molecule obtained by test run were reasonable.