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Formation of Electronically Excited Fragments (H, CH, NH) by the Electron Impact of Pyrrole and Pyrrolidine

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In the wavelength region of 200—600 nm, photoemissions from electronically excited fragments (H, CH, NH, CN, and C_2) were observed when pyrrole and pyrrolidine were excited by electron impact (0—70 eV). Hydrogen atoms and CH and NH radicals from pyrrole and pyrrolidine are produced *via* a single collision excitation. The appearance potentials for these fragments from pyrrole are 19.4±0.8 eV for the hydrogen Balmer β (H_β), 19.7 ±0.8 eV for the CH($A^2\Delta$-$X^2\Pi$) band, and 20.0±1.0 eV for the NH($A^3\Pi$-$X^3\Sigma$) band. Those from pyrrolidine are 18.7±0.8 eV for H_β, 23.0±0.8 eV for the CH(A-X) band, and 21.8±1.0 eV for the NH(A-X) band. Dissociation processes forming these electronically excited fragments are discussed.

Fragmentation of several cyclic molecules has been studied by electron impact mass spectroscopy.[1,2] Information thus obtained has been restricted to relatively large ionic fragments. Formation of neutral species could be, only indirectly, detected by mass spectroscopy. When atoms and diatomic molecules are produced in their excited states they are easily detected by photoemission spectroscopy. Photoemissions from neutral excited fragments produced by electron impact of aromatic molecules have been investigated extensively.[3-5] However, a few papers[6,7] concerned with large heterocycles have reported emissions from fragments produced by electron impact; very little is known about the formation of neutral fragments from excited parent species.

Appearance potentials of neutral fragments in their excited states produced by electron impact[7] of pyridine and pyrazine are higher than first ionization potentials of parent molecules. In these cases, the formation of ionic fragments can compete with fragmentation to neutral excited species, or ionic fragments seem to be by-products in the formation of neutral fragments. Therefore, we expect that information obtained by mass spectroscopy is also useful for studying the fragmentation mechanism of large heterocycles by electron impact as well as by photoemission spectroscopy.

In the present paper, emission spectra of fragments produced by electron impact of pyrrole and pyrrolidine are identified and appearance potentials for the H_β, CH($A^2\Delta$-$X^2\Pi$), and NH($A^3\Pi$-$X^3\Sigma$) bands are determined. Possible dissociation processes forming H(n=4), CH($A^2\Delta$), and NH($A^3\Pi$) from pyrrole and pyrrolidine are discussed in consideration of thermochemical data.

Experimental

The apparatus and experimental details have been described in the previous paper.[7] The apparatus consists of an electron source, a collision chamber, and an optical detection system. Sample pressures during emission measurements, as measured by an ionization gauge, were 5—40 mPa. Negative potentials from the threshold to 70 eV were applied to a tungsten filament and the maximum beam current measured at Faraday cage was about 0.8 mA for 70 eV. Electron-beam currents of 10 μA at thresholds and 40—50 μA at higher energies were used for the measurement of excitation functions.

In preliminary measurements, the photoemission in the region of 200—600 nm modulated at 225 Hz by a mechanical chopper was detected by a combination of a 30 cm Czerny-Turner monochromator and an HTV R374 photomultiplier connected to a lock-in amplifier. For the measurement of excitation function, an HTV R585 photomultiplier cooled at about −20 °C and an HTV C1230 photon-counter were used with spectral resolution of 0.6 nm ((FWHM).

Pyrrole and pyrrolidine (Nakarai Chemicals, guaranteed grade) were degassed by several freeze-pump-thaw cycles just before use.

Results

Emission Spectra. Figure 1 shows emission spectra produced by electron impact on pyrrole and pyrrolidine in the region of 260—510 nm. The observed spectra were assigned to the hydrogen Balmer series (n= 4—13→2), the NH($A^3\Pi$-$X^3\Sigma$) band around 336 nm, the CN($B^2\Sigma$-$X^2\Sigma$) band around 385 nm, the CH($A^2\Delta$-$X^2\Pi$) band around 431 nm, and the C_2($A^3\Pi$-$X^3\Pi$) band around 470 nm. The NH($c^1\Pi$-$a^1\Delta$) band from neither pyrrole nor pyrrolidine was detected.

The photoemission intensities of the H_β, CH(A-X), and NH(A-X) bands from pyrrole and pyrrolidine were found to be proportional to the electron-beam current up to 0.5 mA and to the sample pressure up to 40 mPa in the collision chamber. The excitation functions for

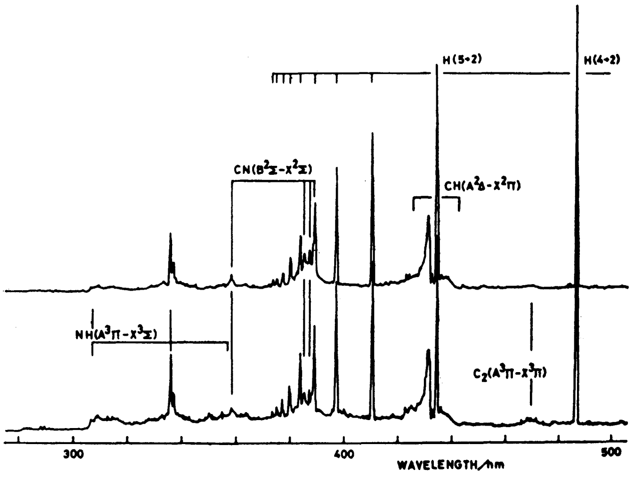

Fig. 1. Emission spectra by electron impact (70 eV, 0.5 mA).
Top view: pyrrolidine at 11 mPa, bottom view: pyrrole at 12 mPa.

these fragment species were observed at sample pressures of 5—11 mPa and the appearance potentials were found to be independent of the sample pressure. Therefore, the excited fragments, H atoms and CH and NH radicals, from pyrrole and pyrrolidine, seem to be formed from fragmentation *via* a single collision excitation by electrons. The two-step collision with another electron seems to be negligible.

Appearance Potentials for Fragment Species. The energy for the impinging electron was calibrated on the basis of both the peak of the excitation function for the (1,0) band of the $N_2(C^3\Pi\text{-}B^3\Pi)$ emission reported by Finn *et al.*8) and the appearance potential for the (0,0) band of the $N_2^+(B^2\Sigma\text{-}X^2\Sigma)$ emission reported by Borst and Zipf.9) Nitrogen was mixed with the sample vapor and their emission intensities were measured simultaneously. Slight discrepancies were observed in the steepness of the excitation function for the (1,0) band of the N_2(C-B) emission in the threshold region, probably because of the energy spread of about 2 eV in the present experiment.7)

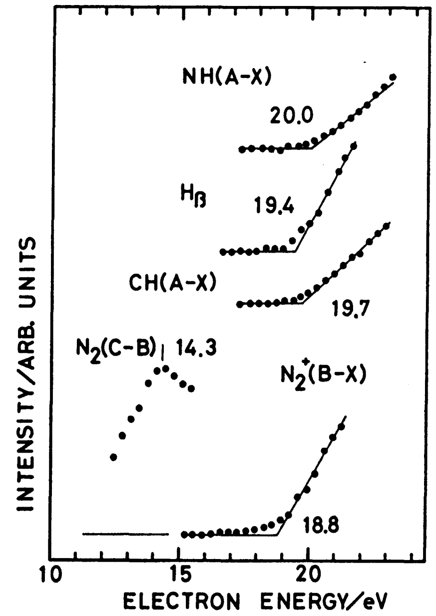

Fig. 2. The excitation functions for the H_β, the CH(A-X) and the NH(A-X) emissions from pyrrole, and those for the N_2(C-B) and N_2^+(B-X) emissions from nitrogen molecule. Typical data are presented and the standard deviation is as large as the diameter of the circles.

The excitation function for the NH(A-X) band could not be measured simultaneously from the gaseous mixture of the sample and nitrogen because the head of the (0,0) band of the N_2(C-B) emission, 337.1 nm,10) is accidentally overlapped with the head of the (0,0) band of the NH(A-X) emission, 336.0 nm.11) Therefore, the excitation function for the NH(A-X) band was measured with those for the H_β and CH(A-X) bands from the pure sample vapor, and the appearance potential for NH(A) was calibrated indirectly from those for H(n=4) and CH(A).

Figure 2 shows the excitation functions for the H_β, CH(A-X), and NH(A-X) emissions from pyrrole near their thresholds, together with those for the (1,0) band of the N_2(C-B) emission and the (0,0) band of the N_2^+(A-X) emission measured simultaneously. Figure 3 shows the excitation functions for the same fragments from pyrrolidine. The appearance potentials thus obtained for H(n=4), CH(A), and NH(A) from pyrrole are listed in the third column of Table 1, and those from pyrrolidine are also listed in the third column of Table 2. Dissociation processes which are expected to play an important role in the formation of H(n=4), CH(A), and NH(A) from pyrrole and pyrrolidine are shown in the first column of each table. The threshold energies

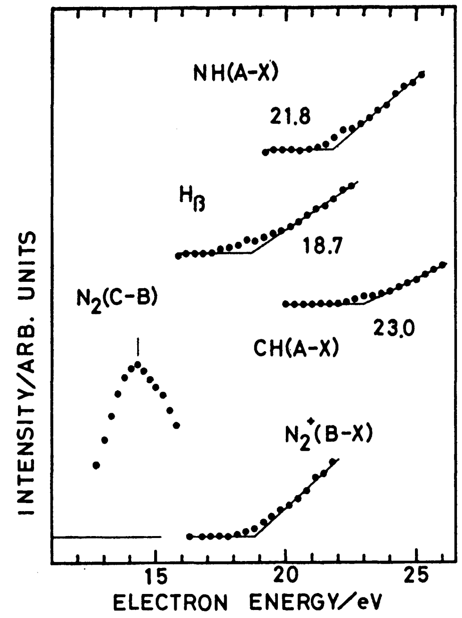

Fig. 3. Same as Fig. 2 from pyrrolidine.

TABLE 1. DISSOCIATION PROCESSES FOR THE FORMATION OF H(n=4), CH($A^2\Delta$), AND NH($A^3\Pi$) FROM PYRROLE

	Dissociation processes	Threshold eV Calcd	Threshold eV Obsd
(1)	$C_4H_5N \longrightarrow C_4H_4N(\tilde{X})+H(n=4)$	17.3±0.3a)	19.4±0.8
(2)	$\longrightarrow C_2H_3(\tilde{X})+HCN(\tilde{X})+CH(A^2\Delta)$	12.2a)	
(3)	$\longrightarrow C_3H_2^+(\tilde{X})+NH_2(\tilde{X})+CH(A^2\Delta)$	18.7±0.5b)	19.7±0.8
(4)	$\longrightarrow 2C_2H_4(\tilde{X})+NH(A^3\Pi)$	10.8a)	
(5)	$\longrightarrow C_3H_2^+(\tilde{X})+CH_2(\tilde{X})+NH(A^3\Pi)$	19.5±0.5b)	20.0±1.0

a) See Text. b) Calculated from the appearance potential for $C_3H_2^+$ ion, 15.8±0.5 eV, and the electronic energy of CH(A) or NH(A).12)

TABLE 2. DISSOCIATION PROCESSES FOR THE FORMATION OF $H(n=4)$, $CH(A^2\Delta)$, AND $NH(A^3\Pi)$ FROM PYRROLIDINE

Dissociation processes	Threshold eV Calcd[a]	 Obsd
(1) $C_4H_9N \longrightarrow C_4H_8N(\tilde{X})+H(n=4)$	17.1 ± 0.2[b]	18.7 ± 0.8
(2) $\longrightarrow CH_3CH_2NH(\tilde{X})+CH_2(\tilde{X})+CH(A^2\Delta)$	14.8	
(3) $\longrightarrow C_3H_5^+(\tilde{X})+NH(\tilde{X})+H_2(X)+CH(A^2\Delta)$	22.5 ± 0.5	23.0 ± 0.8
(4) $\longrightarrow C_3H_3^+(\tilde{X})+NH_3(\tilde{X})+H_2(X)+CH(A^2\Delta)$	23.7 ± 0.5	
(5) $\longrightarrow C_2H_3(\tilde{X})+C_2H_5(\tilde{X})+NH(A^3\Pi)$	11.2	
(6) $\longrightarrow C_2H_3^+(\tilde{X})+C_2H_5(\tilde{X})+NH(A^3\Pi)$	20.0 ± 0.5	21.8 ± 1.0
(7) $\longrightarrow C_2H_2^+(\tilde{X})+C_2H_6(\tilde{X})+NH(A^3\Pi)$	21.6 ± 1.0	

a) See Text. b) Calculated from bond dissociation energy of the C–H or N–H bond estimated according to the method by Allen.[13]

TABLE 3. HEATS OF FORMATION USED FOR THE CALCULATION OF THE THRESHOLDS

Species	ΔH°_{f0} kJ mol^{-1}	Ref.
Pyrrole	108.28	13
Pyrrolidine	-3.6	14 and estimated
H_2	0	15
CH	590.8 ± 0.4	15
CH_2	386 ± 4	15
C_2H_3	278	13 and estimated
C_2H_4	61.0 ± 0.3	15
C_2H_5	107.5	13
C_2H_6	-84.68	13
NH	339 ± 10	15
NH_3	-47.7	13
CH_3CH_2NH	174	13 and estimated
$C_2H_2^+$	1328	2, 16
$C_2H_3^+$	1125	17
$CH_2{=}CHCH_2^+$	964	2, 17
$C_3H_3^+$ (cyclopropenyl)	1075	2, 17
$CH{\equiv}C{-}CH_2^+$	1175	2, 17

of the dissociation processes leading to the formation of the excited fragments, listed in the second column of Tables 1 and 2, are calculated by using the electronic energies of the excited species and the thermochemical data. The heats of formation used for the calculation of the thresholds are summarized in Table 3.

Discussion

*Formation of H(*n*=4).* The onset for the H_β from pyrrole is found at 19.4±0.8 eV. By comparison of the observed threshold energy with the bond dissociation energy of the C–H bond estimated from benzene,[18] 4.86 eV, or the N–H bond,[13] 4.24 eV (estimated), and with the excitation energy of $H(n=4)$, 12.74 eV, the dissociation process for the formation of $H(n=4)$ from pyrrole is considered to be mainly process (1) in Table 1. The onset for the H_β from pyrrolidine is found at 18.7±0.8 eV. A similar consideration on the threshold energy for pyrrolidine leads to process (1) in Table 2. The excess energy of 1.6—2.1 eV for the difference between the observed and calculated threshold in these processes (Tables 1 and 2) is probably dissipated as the kinetic energy of the leaving hydrogen atom. These dissociation processes for the formation of excited H atoms are similar to those with benzene[5,7] and pyridine and pyrazine.[7]

Formation of CH(A) and NH(A). The onsets for the CH(A-X) and NH(A-X) emissions from pyrrole are found at 19.7±0.8 and 20.0±1.0 eV, respectively, and those from pyrrolidine are also found at 23.0±0.8 and 21.8±1.0 eV, respectively. These appearance potentials observed for CH(A) and NH(A) are much higher than the first ionization potentials for pyrrole, 8.97 eV,[19] and for pyrrolidine, 9.0 eV;[2] accordingly, it appears that ionic fragments are possible to be by-products in the formation of CH(A) and NH(A). Dissociation processes leading to the formation of CH(A) and NH(A) from pyrrole and pyrrolidine are still uncertain because available heats of formation of ionic products are insufficient. Nevertheless, if one assumes that the threshold energy consists of the thermochemical values and electron excitation energies of CH(A) and NH(A), main dissociation processes leading to the formation of CH(A) and NH(A) from pyrrolidine seems to include an ionic by-product. Namely, in Table 2, processes (3) and (4) and processes (6) and (7) seem to play an important role in the formation of CH(A) and NH(A) from pyrrolidine, respectively.

Dissociation processes (3) and (5) in Table 1 are expected to play an important role in the formation of CH(A) and NH(A) from pyrrole, respectively. The threshold energies for these processes from pyrrole were calculated from the appearance potential for $C_3H_2^+$ ion from pyrrole reported by Hissel[1] because the heat of formation of $C_3H_2^+$ ion is not known. Furthermore, Gallegos and Kiser[2] have pointed out that the appearance potentials reported by Hissel[1] from tetrahydrofuran and pyrrolidine are in every case lower than the appearance potentials reported by Gallegos and Kiser[2] with the exception of the parent-molecule ions in both molecules. According to these facts, the threshold values for processes (3) and (5) in Table 1 seem to be the lower limits. The threshold energies for dissociation processes from pyrrole including other relatively abundant ions reported by Hissel,[1] $C_3H_3^+$, $C_3H_4^+$, and $C_2H_2N^+$, are higher than the observed values.

Another possibility for the formation of CH(A) and NH(A) from pyrrole and pyrrolidine is that by-products are formed in their electronically excited states, because the thresholds calculated for the dissociation processes including only neutral by-products in their ground state are much lower the observed thresholds. This possibility will be examined by the photon-photon coincidence technique.[20]

In summary, the appearance potential for H_β from pyrrolidine is slight lower than that from pyrrole, but $H(n=4)$ atoms from both molecules are probably formed *via* a similar mechanism following neither cleavage of skeletal bonds nor new bond formation. The dissociation processes for the formation of CH(A) and NH(A) from pyrrole and pyrrolidine seem to include a fragment ion as a by-product.

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