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Formation of H(n=4) and CH($A^2\Delta$) by the Electron Impact Dissociation of Benzene, Pyridine, and Pyrazine

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Benzene, pyridine, and pyrazine were excited by electron impact (0—70 eV) under low pressure conditions. In the wavelength region of 250—510 nm, emissions from H, CH, C_2, and CN (except for benzene) fragments were observed. Formations of H(n=4) and CH($A^2\Delta$) from benzene, pyridine, and pyrazine were investigated. The appearance potentials for the hydrogen Balmer β emission were determined to be 19.5±1.0 eV in benzene, 19.7±1.0 eV in pyridine, and 19.6±1.0 eV in pyrazine. The appearance potentials for the CH(A-X) emission were also determined to be 12.7±1.0 and 21.4±1.0 eV in benzene, 20.1±1.0 eV in pyridine, and 18.5±1.0 eV in pyrazine. No emissions from the excited parent species of pyridine and pyrazine were observed.

When a relatively large molecule is excited by electron impact, photoemission from small fragments is observed more easily than that from the parent molecule. This is probably because the parent molecule has many degrees of freedom of motion and non-radiative processes become important. However, aromatic molecules are one of the exceptions, where excited parent species give intense fluorescence upon electron impact. The fluorescence ($S_1 \rightarrow S_0$) from benzene by electron impact has been studied extensively.[1-4] On the other hand, nitrogen-heterocycles in the vapor phase hardly emit radiation,[5,6] because radiationless processes among excited states are particularly efficient.

As stressed by Platzman[7] for benzene, neutral excited states having excitation energy in excess of its ionization play an important role in the formation of neutral fragments. Recently, emissions for these neutral fragments from benzene have been studied.[8-10] However, as for large nitrogen-heterocycles such as pyridine and pyrazine, very little is known at this time about the fragments and the mechanism of fragmentation from the excited parent species by electron impact.[11]

The fragmentation of molecules by electron impact has been studied by mass spectrometry, but the information thus obtained has been restricted to relatively large ionic fragments; furthermore, only little has been known about the excited states leading to the ionization.

In the present paper the emission spectra of the fragments produced by electron impact dissociation of benzene, pyridine, and pyrazine are assigned and the appearance potentials for the fragments are determined.

Experimental

Figure 1 shows a schematic drawing of the apparatus, which consists of an electron source, a collision chamber and an optical detection system. The electron source and the collision chamber are evacuated by an oil diffusion pump to about 0.27 mPa, as measured by an ionization gauge. The negative potential from 0 to 70 eV was applied to a tungsten filament (0.1 mm diameter) heated by 3 V d.c. Electrons accelerated and focused by three electrodes were introduced into the collision chamber through an aperture (3 mm diameter). The maximum beam current measured at a Faraday cage (g) was about 0.8 mA at 70 eV. For measurement of the excitation functions electron-beam currents ranging from 10 μA at the threshold to 60 μA at higher energies were used.

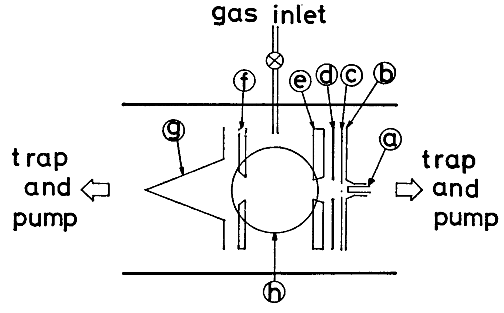


Fig. 1. Schematic diagram of the collision chamber and the electron gun.
a: Tungsten filament, b: repeller electrode, c, d, e, and f: electrodes, g: Faraday cage, h: quartz window.

The sample gases were fed into the collision chamber through a nozzle (1 mm diameter) at a constant pressure controlled by the temperature of the sample holder and a variable leak valve. The sample pressures during the emission measurements, as measured by an ionization gauge, were 5—40 mPa.

A 30 cm Czerny-Turner scanning monochromator equipped with a 1200 Gr/mm grating blazed at 300 nm, an HTV R585 photomultiplier, and an HTV C1230 photon-counter were used. With a slit-width of 200 μm spectral resolution of 0.6 nm (FWHM) was obtained and was used for measurement of the excitation function.

The energy scale for the incident electrons was calibrated using the excitation functions for the (0, 0) band of the N_2-($C^3\Pi$-$B^3\Pi$) emission by Finn *et al.*[12] and the (0, 0) band of the N_2^+($B^2\Sigma$-$X^2\Sigma$) emission by Borst and Zipf.[13] About 5% of nitrogen gas was mixed with the sample gas and their excitation functions were measured simultaneously. A slight discrepancy was observed in the steepness of the excitation function for the N_2(C-B) emission in the threshold region (Fig. 2); it is probably because of the energy spread of about 2 eV in the present experiment.

The samples of benzene, pyridine, and pyrazine were of guaranteed grade from Nakarai Chemicals. Pyridine was fractionally distilled over sodium hydroxide under a stream of nitrogen.[6] Pyrazine was recrystallized from its diethyl ether solution.[14] The samples were degassed by several freeze-pump-thaw cycles just before use.

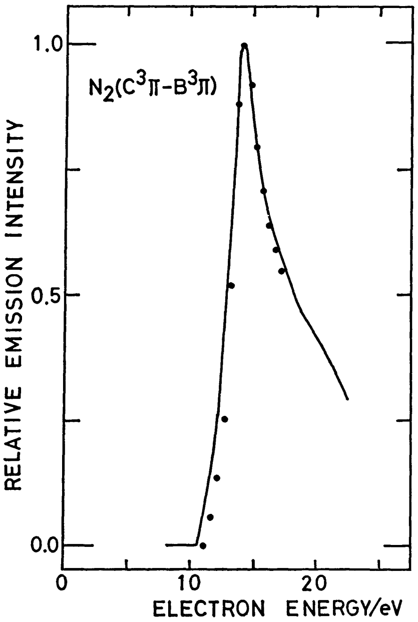


Fig. 2. Excitation functions for the (0,0) band of the N_2(C-B) emission normalized at the peak value. ——: This work, ●●●: Finn *et al.*[12]

Results and Discussion

Emission Spectra. The observed emission spectra by electron impact on benzene are similar to those reported by Smith[1] and Ogawa *et al.*[9] Figure 3 shows the emission spectra obtained from pyridine and pyrazine in the region of 250—510 nm at electron energy of 70 eV. Many sharp bands in these spectra were assigned to the following fragment species; the hydrogen Balmer series (n=4—10→2), the CH($A^2\Delta$-$X^2\Pi$), the C_2($A^3\Pi$-$X^3\Pi$), and the CN($B^2\Sigma$-$X^2\Sigma$) bands.

The photoemission intensities of the hydrogen Balmer β (H_β) and the CH($A^2\Delta$-$X^2\Pi$) band from benzene, pyridine, and pyrazine, and the CN($B^2\Sigma$-$X^2\Sigma$) band from pyridine and pyrazine were found to be proportional to the electron-beam current up to 0.5 mA. In the measurement of the excitation functions, the gas density of the parent molecule in the column of electron-beam (0.4 cm^3) is estimated to be less than 3×10^{12} molecule/cm^3 and is two orders of magnitude lower than the electron density in the collision region, 6×10^{14} electron/s, for a beam current of about 0.1 mA. Such a low gas density was necessary because low-energy electrons formed by ionization can reach the electron collector and affect the Faraday cage current.

Therefore, the H and CH species from benzene, pyridine and pyrazine seem to be formed by fragmentation *via* a single collision, and two-step collisions of the electron with the sample molecule and intermolecular quenching processes seem to be negligible.

As for pyrazine, fluorescence and phosphorescence[15] were expected especially near the excitation threshold. Neverthless, no emission from the parent species was observed even at the sample pressure as high as 47 mPa.

Excitation Functions and Appearance Potentials. Figures 4 and 5 show the excitation functions for the H_β and CH(A-X) emissions from benzene, pyridine, and pyrazine near their thresholds. The electron energy scale for each experiment was calibrated using the well-known thresholds for the N_2(C-B) and N_2^+-(B-X) emissions which lie close in energy to the thresholds for the H_β and the CH(A-X) emissions. Although each excitation function near the threshold is broadened by the electron energy distribution of about 2 eV (FWHM), the appearance potential in each excitation function is determined using a linear extrapolation (see Figs. 4 and 5). We estimate that

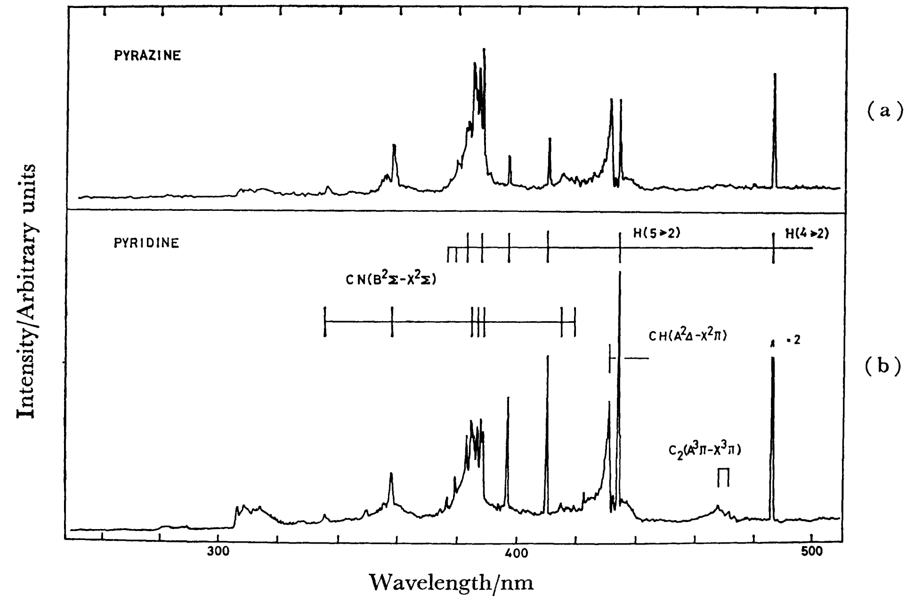


Fig. 3. Emission spectra by electron impact at 70 eV and 0.5 mA. The fragment emission peaks observed are assigned except for the broad peaks near 310 nm. (a): Pyrazine at 16 mPa. (b): Pyridine at 19 mPa.

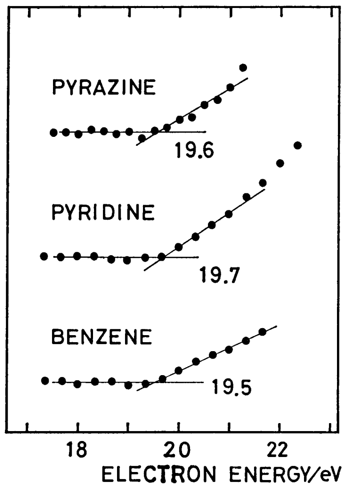


Fig. 4. The excitation functions for H_β from benzene, pyridine, and pyrazine near the thresholds. Typical data are presented. The standard deviation is about twice as large as the diameter of the circles.

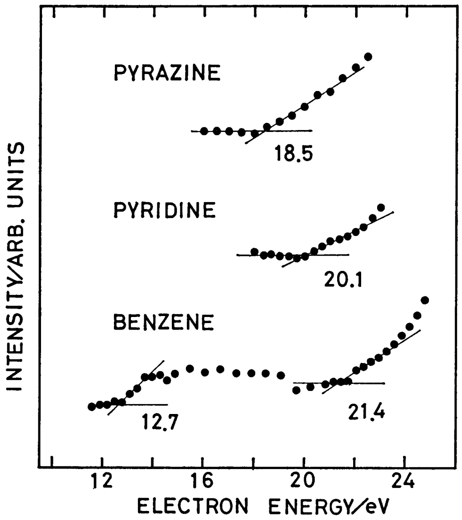


Fig. 5. Same as Fig. 4 for the CH(A-X) emission. The standard deviation is nearly as large as the diameter of the circles.

this calibration is accurate to 1 eV[16] and the random error of each calibrated appearance potential is about 0.4 eV. The appearance potentials thus determined for the H_β and the CH(A-X) emissions are summarized in Table 1 in comparison with previous work.[10]

Formation of H(n=4). The onset for H_β from benzene is found at 19.5±1.0 eV: this value agrees well with 19.3±1.0 eV reported by Beenakker and de Heer.[10] The absence of structure near the threshold indicates that only one state or at most a few states of benzene are involved in the formation of excited hydrogen atoms. By comparison of the observed threshold energy with the dissociation energy of the C–H bond, 4.87 eV,[17] and the excitation energy of H(n=4), 12.7 eV, the following dissociation process, which is reported by Beenakker and de Heer,[10] seems to play an important role in the formation of excited hydrogen atoms.

Table 1. Appearance potentials for the H_β and the CH($A^2\Delta$-$X^2\Pi$) emissions determined from their excitation functions (in eV)

	H_β		CH($A^2\Delta$-$X^2\Pi$)	
	This work	Beenakker *et al.*[a]	This work	Beenakker *et al.*[a]
Benzene	19.5±1.0	19.3±1.0	12.7±1.0	15.0±1.0
			21.4±1.0	
				29 ±1
Pyridine	19.7±1.0		20.1±1.0	
Pyrazine	19.6±1.0		18.5±1.0	

a) Ref. 10.

$$C_6H_6(19.5\,\mathrm{eV}) \longrightarrow C_6H_5(X^2\tilde{A}_1) + H(n{=}4) + 1.9 \pm 1.0\,\mathrm{eV}$$

The onsets for H_β from pyridine and pyrazine are observed at 19.7±1.0 and 19.6±1.0 eV, respectively. A similar consideration on the energy balance with the dissociation energy of the C–H bond, 4.87 eV,[17] because the dissociation energy of the C–H bond of pyridine and pyrazine are not known, leads to the following processes

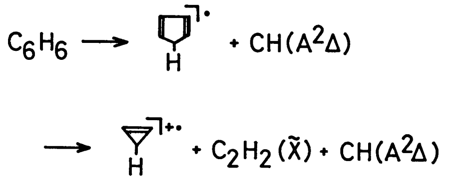
$$C_5H_5N(19.7\,\mathrm{eV}) \longrightarrow C_5H_4N(X) + H(n{=}4) + 2.1 \pm 1.0\,\mathrm{eV}$$

and

$$C_4H_4N_2(19.6\,\mathrm{eV}) \longrightarrow C_4H_3N_2(X) + H(n{=}4) + 2.0 \pm 1.0\,\mathrm{eV}.$$

Formation of CH(A). The excitation function for the CH(A-X) emission from benzene indicates some structure and a shallow dip near 20 eV. Hence, several states of benzene seem to be involved in the formation of CH(A), and further, the formation of CH(A) seems to compete with other processes: probably ion formations. The onsets for the CH(A-X) emission from benzene are observed at 12.7±1.0 and 21.4±1.0 eV; the first value is lower than 15.0±1.0 eV obtained by Beenakker and de Heer.[10] The second value, 21.4 eV, is even lower than 29±1 eV reported by Beenakker and de Heer.[10] Comparing the observed excitation function for the CH(A-X) emission with theirs, we conclude that the structure leading to this second appearance potential is different from that reported by Beenakker and de Heer.

Dissociation processes leading to the formation of CH(A) from benzene are still uncertain. Neverthless, if one assumes that the threshold energy consists of the difference between heats of formation of benzene and products[18–20] and the electronic energy of CH(A),[21] the following dissociation processes are considered to occur. Heats of formation and bond dis-



14.3 eV (1)

22.9 eV (2)

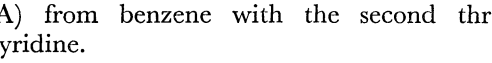
Table 2. Heats of formation and bond dissociation energies used for the calculation of threshold energies

Species	ΔH_f° / kJ mol^{-1}	Ref.	D(R-H) / eV	Ref.
Benzene	82.89±0.54	18	4.87	17
Pyridine	144.56±0.5	18	4.87[a]	
Cyclopentadiene	130.25	18	4.87[a]	
C_2H_2	227.29	19		
HCN	135.5	19		
CH	592.5	19		
$C_3H_3^+$ (Cyclopropenyl ion)	1196.6 ±8[b]	20		

a) The value in benzene is used. b) This is the value of $C_4H_4^+$ (cyclobutadienyl) ion because the formation processes of $C_3H_3^+$ and $C_4H_4^+$ have identical thermochemical thresholds.[20)]

sociation energies used for the calculation of the thresholds are summarized in Table 2. Process (1) seems to play an important role in the formation of CH(A) near the first threshold. Dissociation into more than two neutral fragments may happen at an intermediate energy region, 14—22 eV, because $C_4H_4^+$, $C_4H_3^+$, $C_4H_2^+$, and $C_3H_3^+$ ions from benzene are relatively abundant;[22,23)] furthermore, dissociations producing only neutral fragments such as CH(A) proceed via so-called super-excited states competing with these ion formations. Process (2) including an ionic byproduct seems to play an important role in the formation of CH(A) near the second threshold. Some processes including $C_5H_5^+$ ion seems to be unimportant because $C_5H_5^+$ ion appears only very weakly or is not observed.[20,22)]

The appearance potentials for CH(A) from pyridine and pyrazine are determined to be 20.1±1.0 and 18.5±1.0 eV, respectively. The absence of structures near the thresholds indicates that only one state or at most a few states of pyridine and pyrazine are involved in the formation of CH(A). On the basis of a similar consideration (see Table 2), the following dissociation process from pyridine is considered to occur because $C_3H_3^+$ (cyclopropenyl) ion is relatively abundant in photo-ionization mass spectrometry of pyridine.[20,24)] It is impossible to derive dissocia-



21.3 eV

tion processes from pyrazine because the relevant dissociation energies are not known. Neverthless, processes forming CH(A) from pyrazine presumably include the formation of an ionic fragment and may correspond to the dissociation processes forming CH(A) from benzene with the second threshold and pyridine.

In summary, the appearance potentials for H_β from benzene, pyridine, and pyrazine are nearly equal and H(n=4) may dissociate by a similar mechanism. The two appearance potentials for CH(A) from benzene are found from the structures in the excitation function for the CH(A-X) emission, while no corresponding structures exist near the thresholds of the excitation functions for the CH(A-X) emission from pyridine and pyrazine.

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