速 報

SHORT NOTES**Pressure Effect on The Peaks due to (P-HCN)⁺ Ion
in Mass Spectra of Pyridines**

MITSUO UCHIDA*

(Received 19 June 1975)

It has been well known by mass spectral investigations of substituted pyridines that the elimination of HCN from the molecular ion is a characteristic fragmentation process for compounds with small substituent group¹⁻⁴⁾. In this fragmentation, the molecular ion undergoes the skeletal rearrangement to form the ion having the five membered ring.

On mass spectral investigations of aromatic amine N-oxides, such as picoline N-oxides⁵⁾ or quinazoline N-oxides⁶⁾, the relative intensities of the fragment ions concerned with the fragmentations including the skeletal rearrangement and with the hydrogen rearrangement greatly depend upon the sample pressure even at pressures in the normal working range of 10^{-6} to 10^{-5} Torr.

In this paper, the pressure effect on the peaks due to (P-HCN)⁺ ion in mass spectra of methylpyridines, aminopyridines and hydroxypyridines is discussed from the result recorded at various sample pressures. The logarithm of the observed ion intensities was plotted as a function of the logarithm of the

sample pressure. The ion intensity-pressure curves of (P-HCN)⁺ ions in methylpyridines, aminopyridines and hydroxypyridines thus obtained are shown in Figs. 1, 2 and 3, respectively. Other principal fragment ions are shown in Table 1 as the relative abundance of the molecular ion at pressures in the range of 10^{-6} to $5 \cdot 10^{-5}$ Torr. They show the pronounced pressure dependency owing to some interaction of the primary ion. In order to elucidate the pressure effect of (P-HCN)⁺ ions, the secondary ions were also detected and are shown in Table 1 as the relative abundance of the molecular ion at pressure of $5 \cdot 10^{-5}$ Torr.

The mass spectra of methylpyridines^{1,2)}, aminopyridines³⁾ and hydroxypyridines⁴⁾ show that the peaks due to (P-HCN)⁺ ions at mass 66, 67 and 68 formulated as the cyclopentadiene ion $C_5H_6^+$, the pyrrole ion $C_4H_5N^+$ and the furan ion $C_4H_4O^+$, respectively, are the abundant ions created in the first cleavage of the molecular ion. And then, by the elimination of C_2H_3 group from the cyclopentadiene ion⁷⁾, C_2H_2 or CH_2N group from the pyrrole ion⁸⁾ and CHO group from the

* Shizuoka College of Pharmacy (2-2-1, Oshika, Shizuoka, 422 Japan)

Fig. 1. Logarithmic ion intensity-pressure curves of methylpyridines.
 ○ parent ion of 2-isomer, ● (P-HCN)⁺ ion of 2-isomer,
 △ parent ion of 3-isomer, ▲ (P-HCN)⁺ ion of 3-isomer,
 ◇ parent ion of 4-isomer, ◆ (P-HCN)⁺ ion of 4-isomer.

Fig. 2. Logarithmic ion intensity-pressure curves of aminopyridines.
 ○ parent ion of 2-isomer, ● (P-HCN)⁺ ion of 2-isomer,
 △ parent ion of 3-isomer, ▲ (P-HCN)⁺ ion of 3-isomer,
 ◇ parent ion of 4-isomer, ◆ (P-HCN)⁺ ion of 4-isomer.

Fig. 3. Logarithmic ion intensity-pressure curves of hydroxypyridines.
 ○ parent ion of 2-isomer, ● (P-HCN)⁺ ion of 2-isomer,
 △ parent ion of 3-isomer, ▲ (P-HCN)⁺ ion of 3-isomer,
 ◇ parent ion of 4-isomer, ◆ (P-HCN)⁺ ion of 4-isomer.

Pressure Effect on The Peaks due to (P-HCN)⁺ Ion in Mass Spectra of Pyridines

Table 1. The relative intensities of the primary and secondary ions of methylpyridines, aminopyridines and hydroxypyridines.

	Methylpyridine			Aminopyridine			Hydroxypyridine		
	2-	3-	4-	2-	3-	4-	2-	3-	4-
Primary ion ^{a)}									
P ⁺ ^{b)}	100	100	100	100	100	100	100	100	100
(P-H) ⁺ ^{c)}	26-21	38-32	29-25	8- 7	16-15	16-12	8- 4	10- 7	26-20
C ₂ H ₃ N ⁺ ^{d)}	7- 4	11- 5	13- 7	70-32	87-40	91-35	50-35	29-15	45-38
C ₂ H ₃ ⁺ ^{e)}	72-37	112-56	89-44	79-31	80-31	79-23	71-55	61-32	67-32
(P-CO) ⁺ ^{f)}							153-61	43-17	58-24
Secondary ion ^{g)}									
P ₂ ⁺	0.01	0.03	0.04	0.14	0.17	0.26	0.08	0.01	0.04
(P ₂ -H) ⁺				0.03	0.08	0.11	0.07	0.01	0.14
(P-H) ₂ ⁺				0.01	0.10	0.04	0.01	0.06	0.03
(P ₂ -HCN) ⁺	0.02	0.06	0.06	0.04	0.03	0.04	0.05	0.05	0.02
(P ₂ -H ₂ CN) ⁺	0.05	0.18	0.15	0.03	0.11	0.20			
(P-HCN) ₂ ⁺	0.07	0.19	0.17	0.04	0.07	0.10			
(P ₂ -HCN-H ₂ CN) ⁺	0.05	0.12	0.10	0.07	0.09	0.13	0.01	0.02	0.03
(P-H ₂ CN) ₂ ⁺	0.11	0.25	0.24	0.04	0.17	0.14			
(P+HCN) ⁺	0.03	0.13	0.11	0.25	0.03	0.01	0.14	0.10	0.19
(P ₂ -CH ₂ O) ⁺							0.04	0.03	0.02
(P ₂ -CO-CHO) ⁺							0.03	0.03	0.02
(P-CHO) ₂ ⁺							0.10	0.07	0.14
(P+CO) ⁺							0.09	0.05	0.08

a) the range of pressure is 10⁻⁶ to 5 · 10⁻⁵ Torr. b) the molecular ion, c) the ion having seven membered ring, d) the azirine ion, e) the cyclopropenyl ion, f) the pyrrole ion, g) at pressure of 5 · 10⁻⁵ Torr.

furan ion⁹⁾, the fragment ions C₃H₃⁺ and C₂H₃N⁺ at mass 39 and 41 formulated as the cyclopropenyl ion and azirine ion are formed.

As seen in Figs. 1, 2 and 3, the inclinations of the ion intensity-pressure curve of (P-HCN)⁺ ions are smaller than those of the molecular ions. So it seems that (P-HCN)⁺ ions are formed not only by the unimolecular decomposition of the molecular ion but also by some interaction of the primary ion. As seen in Table 1, the secondary ions of these compound are also detected and are formed particularly in the fragmentation process concerned with the skeletal rearrangement of the primary ion,

namely, the ring expansion to form the ions having the seven membered ring and the successive ring contraction to form the ions having the five or three membered ring from the molecular ion. So it may be considered that (P-HCN)⁺ ions are formed by the two dissociation pathways. One is the skeletal rearrangement^{10, 11)} of the molecular ion and another is the dissociation of the secondary ion formed by the ion-molecular reaction of the primary ion to be similar to that of the ion detected on the chemical ionization mass spectrometry^{12, 13)} These dissociation pathways are shown as follows.

It has been well known that the intensities of the secondary ion formed with the ion-molecular reaction vary with pressure more rapidly than those of the primary ion. Therefore, the equilibrium of the formation of the secondary ions shown above also depend upon the sample pressure, and then the intensity of $(P-HCN)^+$ ions vary with the sample pressure.

As seen in Table 1, the relative intensities of other primary ion also depend upon the sample pressure. In mass spectra of hydroxypyridines, the peaks due to $(P-CO)^+$ ion at mass 67 formulated as the pyrrole ion $C_4H_5N^+$ show a similar behavior to the peaks due to $(P-HCN)^+$ ion.

Pyridine derivatives were commercial samples of reagent grade purchased from Wako Pure Chem. Ind. Ltd. The purity of these compounds were tested by a combined gas chromatograph-mass spectrometer. Ion abundances were measured on a Hitachi RMS-4 mass spectrometer employing 75 eV electrons. Exact mass measurements were made on a JEOL JMS-01SG-2 mass spectrometer combined with a JEC-6 spectrum computer or employing the photoplate recording.

References

- 1) Catalog of Mass Spectral Data, American Petroleum Institute Research Project 44, Carnegie Institute of Technology, Pittsburgh, Pa., spectrum No. 1535.
- 2) Catalog of Mass Spectral Data, Manufacturing Chemists Association Research Project, Carnegie Institute of Technology, Pittsburgh, Pa., spectra No. 5 and 6.
- 3) J. H. Beynon, R. A. Saunders and A. E. Williams, "The Mass Spectra of Organic Molecules", Elsevier Publishing Co., Amsterdam, 1968, p. 300.
- 4) G. Spiteller and M. Spiteller-Friedmann, *Monatsh.*, **93**, 1395 (1962).
- 5) M. Uchida, *Mass Spectroscopy Japan*, **23**, 93 (1975).
- 6) M. Uchida, T. Higashino and E. Hayashi, *ibid.*, **21**, 245 (1973).
- 7) Ref. 1) spectrum No. 1610.
- 8) H. Budzikiewicz, C. Djerassi, A. H. Jackson, G. W. Kenner, D. J. Newman and J. M. Wilson, *J. Chem. Soc.* 1949 (1964).
- 9) J. Collin, *Bull. Soc. Chim. Belges.*, **69**, 449 (1960).
- 10) F. W. McLafferty, *Anal. Chem.*, **31**, 82 (1959).
- 11) P. Brown and C. Djerassi, *Angew. Chem.*, **79**, 481 (1967).
- 12) M. S. B. Munson and F. H. Field, *J. Am. Chem. Soc.*, **88**, 2621 (1966).
- 13) M. S. B. Munson, *Anal. Chem.* **43** (13), 28A, (1971).