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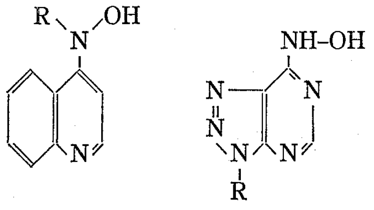
The Characteristic Dependency on the Pressure of the Heteroaromatic Hydroxylamines under the Electron Impact

The mass spectra of heteroaromatic hydroxylamines were studied at the various sample pressures. The relative abundance of the fragment ions depends upon the sample pressure. Especially, $(M-O)^{+\cdot}$ species show the typical pressure dependency.

Keywords——hydroxylaminoquinolines; hydroxylaminotriazolopyrimidines; pressure dependency; relative abundance; $(M-O)^{+\cdot}$ species; mass spectra

In our previous studies of the mass spectra (MS) of heteroaromatic N-oxides, such as quinazoline N-oxides, picoline N-oxides and pyrazolo[3,4-*d*]pyrimidine N-oxides, the relative abundance of $(M-O)^{+\cdot}$ species greatly depended upon the sample pressure, and it was much at the low sample pressure, while it was small at the high sample pressure.[1]

As this was also found in heteroaromatic hydroxylamines, such as 4-hydroxylaminoquinoline (Ia),[2] 4-(N-methylhydroxylamino)quinoline (Ib),[3] 7-hydroxylamino-3-methyl-(IIa)[4] and 7-hydroxylamino-3-phenyl-3*H*-1,2,3-triazolo[4,5-*d*]-pyrimidine (IIb),[4] we report MS of these compounds studied at the various sample pressures.



Ia: R=-H IIa: R=-CH$_3$
Ib: R=-CH$_3$ IIb: R=-C$_6$H$_5$

Fig. 1. Hydroxylamines used in This Study

The partial MS of I and II were shown in Table I. Each shows that the relative abundance of $(M-O)^{+\cdot}$ species, which were known the characteristic fragment ion in the aromatic hydroxylamines,[5] greatly depended upon the sample pressure.

The behavior of the pressure dependency is parallel to those of heteroaromatic N-oxides, that is, the relative abundance of $(M-O)^{+\cdot}$ species is much at the low sample

Table I. Partial Mass Spectra of I and II

Compound	Sample pressure[a] (10^{-6} Torr)	Relative abundance (%)[b]		Base peak[c] (*m/e*)
		M^+	$(M-O)^{+\cdot}$	
Ia	1.0(1.0)	100(100)	58(50)	160(160)
	40 (35)	100(100)	15(14)	160(160)
Ib	0.8(0.8)	100(100)	38(55)	174(174)
	32 (27)	100(100)	13(12)	174(174)
IIa	1.2(1.2)	100(100)	19(30)	166(166)
	40 (20)	100(100)	5(7)	166(166)
IIb	1.0(1.1)	27(41)	33(39)	77(103)
	27 (27)	27(37)	5(7)	103(103)

a) Values in parentheses show the sample pressure under the low ionization energy (15 eV).
b) Values in parentheses are the relative abundance obtained from the ionization energy of 15 eV.
c) Values in parentheses are *m/e* of the base peak under the low ionization energy (15 eV).

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4) Unpublished data.
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pressure, while it is small at the high sample pressure, as shown in Table I. For example, the relative abundance of $(M-O)^{+\cdot}$ species in Ia is 58% at the sample pressure of 1.0×10^{-6} Torr, while it is 15% at the sample pressure of 4.0×10^{-5} Torr in contrast with that of the molecular ion, the base peak in whole range of the sample pressure. However, we can not clear as yet, what kinds of the interaction act on the dissociation with the ionized molecules in gaseous phase. Anyway, these pressure dependency are characteristic and useful for the mass spectral studies of the hydroxylamino derivatives. The further discussions and the detail will be published in the near future.

MS were recorded on a Hitachi RMS-4 mass spectrometer at the ionization energy of 75 eV and 15 eV. Exact mass measurements were made on a JEOL JMS-01SG-2 mass spectrometer. Samples were vaporized in a direct inlet system.

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