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LUMINESCENCES BY ELECTRON IMPACT AND FRAGMENTATIONS OF PYRIDAZINE, PYRAZOLE, 2-PYRAZOLINE, HYDRAZINE, AND 1,1-DIMETHYLHYDRAZINE

Akinori INOUE,* Shuji YOSHIDA, and Nozomu EBARA
Department of Chemistry, College of General Education,
The University of Tokyo, 3-8 Komaba, Meguro-ku, Tokyo 153

Fragmentations of pyridazine, pyrazole, 2-pyrazoline, hydrazine, and 1,1-dimethylhydrazine were studied by means of electron-impact luminescence. Emissions of CN and NH radicals were observed, while emission of molecular nitrogen was absent. It was concluded that the cleavage of N-N bond is important in the fragmentation of these molecules.

Unimolecular fragmentation reaction following electron impact have been studied by use of mass spectrometry. However, the studies made only on the basis of mass numbers of ions have often led to ambiguous fragmentation mechanisms. Auxiliary information concerning formed ions or eliminated neutrals is required in such cases.

Fragment emissions provoked by electron impact may provide such information, especially on neutral species. In the present paper, attempts were made for the use of luminescence data in order to elucidate fragmentation processes. The molecules which contain two adjacent nitrogen atoms were chosen for the investigation. They were pyridazine, pyrazole, 2-pyrazoline, hydrazine, and 1,1-dimethylhydrazine. Most of these compounds have already been investigated by means of mass spectrometry and it has been the central interest for these molecules whether dissociation takes place at the bond adjacent to N-N bond, yielding a nitrogen molecule, or at N-N bond, ultimately giving CN or NH radicals.[1)]

The experimental apparatus consists of a stainless-steel collision chamber, an electron source and a detector. Base pressure of the vacuum system was about 2.7×10^{-4} Pa. Sample gas pressures were 6.5×10^{-3}- 2.7×10^{-2} Pa as monitored by an ionization gauge, and the actual local pressures in the collision region may be higher. Luminescences were measured by a photon counting technique. The resolution of the spectra was about 6 A. In mass spectrometry, the energy of incident electron beam is usually set to about 70 eV, so the energy of electron beam was adjusted to 70 eV in the present experiment, which facilitates direct comparison between the present data and those of mass spectrometry. Electron beam current was about 50 μA. Commercial pyrazole was purified by sublimation in vacuo and the other chemicals by distillation under reduced pressure. The luminescence intensity of each band was proved to be proportional to electron beam current in the range of 100 μA and sample gas pressures in the range of 4×10^{-2} Pa, which indicates that the fragment emissions were induced by one-electron, unimolecular processes.

Pyridazine: According to mass spectrometric investigations on this molecule,2-4) such processes that form nitrogen molecules were most probable fragmentation pathways. Cleavage of N-N bond, which leads to HCN elimination has been supposed to be of much less importance. If this is the case, emission of molecular nitrogen is expected to be observed. The luminescence spectrum (Fig.1), however, shows an intense CN violet emission as well as Balmer lines and CH ($A^2\Delta - X^2\Pi$) bands, but no nitrogen emission was observed in the wavelengths between 300 and 550 nm.

It is unlikely that N_2 emissions were not observed because nitrogen molecules were all produced in their ground electronic state. Ions with high internal energies are produced by electron impact with electron energy of 70 eV, and these excess energies are distributed among fragments.5) Liu et al.6) observed N_2 and N_2^+ emissions by electron impact of 3-chloro-3-methyldiazirine and 1-pyrazoline. Their finding shows that nitrogen molecules ejected in the fragmentations are indeed in their electronic excited states.

The emission of CN violet band has been observed for pyridine,7) pyrazine,8) and naphthylamine.9) Mass spectrometric investigations indicate that eliminations of HCN molecules are essential fragmentation processes in many nitrogen heterocyclic compounds and arylamines.5) These facts imply that HCN is a precursor of CN emission in these molecules.10) The observation of this emission and the absence of N_2 luminescence are strong indication of N-N cleavage. This contradicts

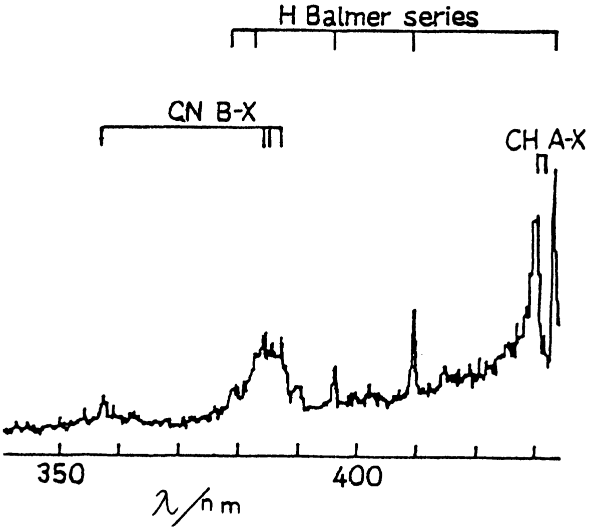

Fig.1 The emission spectrum of pyridazine.

the conclusion reached by the above-mentioned mass spectrometric studies.

At present we can not explain the discrepancy between the present results and those of mass spectrometry.

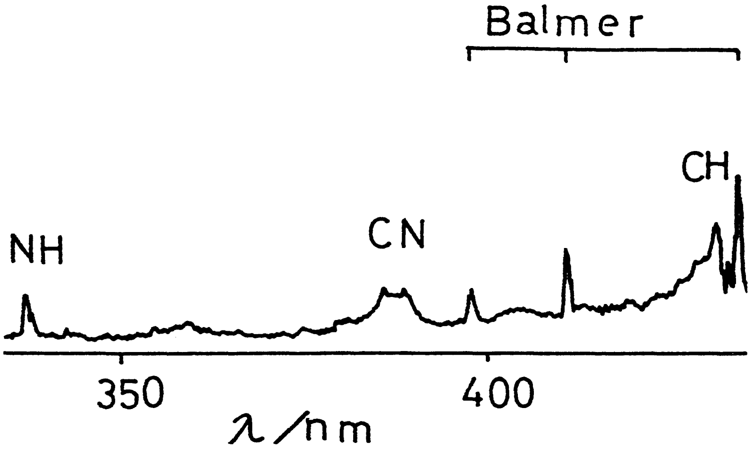

Fig.2 The emission spectrum of pyrazole.

Pyrazole: Jennings and Boggs[11] reported the formation of N_2^+, while Khmel'nitskii et al.[12] and van Thuijl et al.[13] proposed fragmentation paths which accompany the formation of nitrogen molecule. On the other hand, no formation of nitrogen molecule was expected according to the mechanism proposed by Nishiwaki.[1] Figure 2 depicts the luminescence spectrum of pyrazole measured by electron impact. The spectrum consists of a CN violet band, a CH ($A^2\Delta - X^2\Pi$) band, an NH ($A^3\Pi - X^3\Sigma^-$), and Balmer lines, but does not show any indication of N_2 or N_2^+ formation. The present results are indicative of the predominance of N-N cleavage and support the mechanism proposed by Nishiwaki.

2-Pyrazoline: The fragmentation of this molecule has not been studied yet. The study on the 3-methyl derivative shows that dissociation takes place at N-N bond and no nitrogen formation was supposed.[14] If the substitution effect at the 3 position is assumed to be unimportant, this result is consistent with the present emission spectrum, which comprized of NH, CN, CH emissions together with Balmer lines.

Hydrazine and 1,1-dimethylhydrazine: Mass spectrometric investigations on these molecules have been performed by Dibeler et al..[15] In hydrazine, abundant ions have been assigned as $N_2H_4^+$, $N_2H_3^+$, $N_2H_2^+$, and N_2H^+, and small peak observed at m/e 28 has been assigned as N_2^+. The luminescence spectrum of hydrazine (Fig.3) shows neither the emission of N_2^+ nor N_2. Instead, an intense NH ($A^3\Pi - X^3\Sigma^-$) band and Balmer lines were observed. Although detailed mechanism of the NH formation is not known,

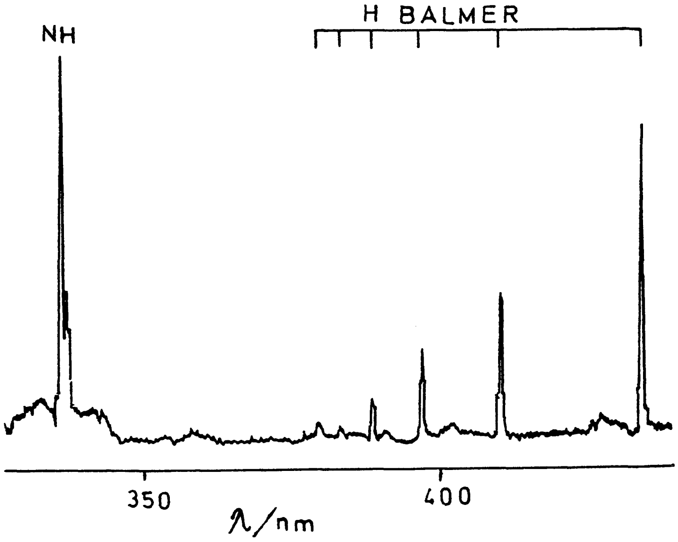

Fig.3 The emission spectrum of hydrazine.

the present results imply that this molecule undergoes rupture of N-N bond. This is in agreement with Dibeler et al.,[15] who have stated that the formation of N_2 or N_2^+ was not important.

The luminescence spectrum of 1,1-dimethylhydrazine was similar to that of hydrazine except for the presence of CH emission. This result is in contradiction to that based on mass spectrum in which abundance of N_2^+ was reported to be large.

Trace of molecular nitrogen was not observed for the molecules studied. The formation of nitrogen molecule was reported for 3-chloro-3-methyldiazirine and 1-pyrazoline,[6] in which N-N bonds have double-bond character. It may be stated that in the fragmentation of molecules containing two adjacent nitrogen atoms, formation of molecular nitrogen is possible only when the N-N bond has a double-bond character.

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