2278 BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 2278—2280 (1972) [Vol. 45, No. 8

On the Emission Spectra of the Unimolecular Reaction of Methylamine by Electron Impact

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(Received January 20, 1972)

The emission spectra of the following excited species produced from methylamine by electron impact (the energy of 150 eV) at a low pressure were observed: NH($A^3\Pi-X^3\Sigma$), CN($B^2\Sigma-X^2\Sigma$), CH($A^2\Delta-X^2\Pi$), and H(Balmer series). It was confirmed that the excited species are produced by a unimolecular reaction of methylamine. The replacement by deuterium decreases the production of the excited hydrogen atom from methylamine by about 40%, this supports the idea that the excited hydrogen atom is produced through a superexcited state of methylamine. It was also determined that the production of the excited hydrogen atom of the methyl group was less than that of the amino group by about 20%. This is in contrast to the findings on the mass spectrum of CD_3NH_2, where the peak of $CD_2NH_2^+$ was much higher than that of CD_3NH^+. The NH radical in the $A^3\Pi$ state was produced from methylamine and dimethylamine, while the NH radicals in the $A^3\Pi$ and the $c^1\Pi$ states were produced from ammonia.

The probability of the bond-scission of amines in a mass spectrometer has been studied by Hirota *et al.* In their study, it was pointed out that the skeletal bond-scission of the molecules proceeds through a superexcited state. On the other hand, the contribution of the superexcited state has been verified by a study of the isotope effect on the ionization yield.[2] In the present study, the possibility of superexcited state for the primary process of the bond-scission in a simple amine is examined.

The authors presumed that the contribution of the superexcited state can be verified by observing the Balmer-β line (the transition from $n=4$ to 2 of hydrogen) under electron impact. The excited hydrogen atom should be produced through a state with a higher energy than the ionization potential of methylamine (8.97 eV),[3] *i.e.*, a superexcited state, because the atom is in a higher energy state than 8.97 eV. In addition, the isotope effect on the dissociation of the C–H or the N–H bond in the molecule through such a superexcited state is studied.

Futhermore, the primary process of the ionization and dissociation of methylamine by electron impact will be discussed on the basis of the results on both the emission spectra and the mass spectra. The relative scission probavility of the C–H and N–H bond of methylamine as well as the isotope effect will be examined. It should be noticed that the electronic states of the NH radical produced from ammonia differ from those of hydrazine,[4] methylamine, and dimethylamine This problem will be discussed briefly in the present paper.

Experimental

Methylamine hydrochloride ($CH_3NH_2 \cdot HCl$, $CD_3NH_2 \cdot HCl$, or $CH_3ND_2 \cdot DCl$) was mixed with an excess of CaO which had been dried at 400°C in a vacuum to liberate the methylamine in the gas phase. Furthermore, the purification of methylamine by vacuum distillation was repeated at −90°C until it was about 99.9%, as determined by gas chromatography. In the present experiments, all the reagents used were of a guaranteed grade.

The $CH_3ND_2 \cdot DCl$ was prepared by the exchange of the amino hydrogen with heavy water. For the isotopic analysis of the deuterated methylamines, mass spectrometry was done by means of a Hitachi RMU-5 mass spectrometer. The CH_3ND_2 contained CH_3NDH of 34%, and the CD_3NH_2 contained CD_3NHD of 2% and CD_2HNH_2 of 2%. The mass spectrometry of CD_3NH_2 was done by means of the mass spectrometer in order to estimate the scission probabilities of the C–H bond and the N–H bond in $CD_3NH_2^+$ with the electron impact energy of 80 eV.

The principle of our apparatus for observing the emission spectra in the gas phase was the same as that used by Ogawa *et al.*[5] To observe the emission spectra, a Narumi RM-23 grating monochromator with an EMI-6256B photomultiplier was used. In the present study, the emission spectra from the fragments of methylamine were observed in the region from 300 nm to 500 nm. The dependence of the intensity of the Balmer-β line and the (0, 0) band of NH-($A^3\Pi-X^3\Sigma$) on both the electron-beam current (target current) and the pressure in the collision chamber was examined. The pressure was measured by means of an ionization gauge connected to the chamber. The ratio of the intensity of the D_β line (the transition from $n=4$ to 2 of deuterium) to that of the H_β line (the transition from $n=4$ to 2 of hydrogen) was observed (the difference in the wave lengths was about 0.13 nm) by means of a Shimadzu GE-100 grating monochromator of a higher resolution equipped with a photomultiplier.

Results and Discussion

The emission spectrum of the fragments of methylamine in electron impact (energy of electron: 150 eV) is shown in Fig. 1, where the 336 nm and 337 nm bands were assigned to the (0,0) and (1,1) bands of NH-($A^3\Pi-X^3\Sigma$) respectively. The sequence of (0,0), (1, 1), (2, 2), (3, 3), and (4, 4) bands of CN($B^2\Sigma-$

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[1] For example, K. Hirota, I. Fujita, M. Yamamoto, and Y. Niwa, *J. Phys. Chem.*, **74**, 410 (1970).

[2] R. L. Platzman, *Vortex*, **23**, 372 (1962); W. P. Jesse and R. L. Platzman, *Nature*, **195**, 790 (1962); W. P. Jesse, *J. Chem. Phys.*, **38**, 2774 (1963); R. L. Platzman, *ibid.*, **38**, 2775 (1963); J. C. Person, *ibid.*, **43**, 2553 (1965); J. C. Person and P. P. Nicole, *ibid.*, **53**, 1767 (1970).

[3] K. Watanabe, *ibid.*, **24**, 623 (1956).

[4] H. Bubert and F. W. Froben, *J. Phys. Chem.*, **75**, 769 (1971).

[5] T. Ogawa, I. Fujita, M. Hatada, and K. Hirota, This Bulletin, **44**, 659 (1971).

$X^2\Sigma$) was found in the region from 388 nm to 385 nm, and the emissions at 431 nm and 432 nm were assigned to the (0, 0) and (2, 2) bands of CH($A^2\Delta-X^2\Pi$) respectively. Moreover the emissions at 397, 410, 434, and 486 nm were assigned to the ε, δ, γ, and β lines of the Balmer series respectively.

The intensity of emission from the excited hydrogen atom and the (0, 0) band of the triplet NH radical depends linearly on the target current, as is shown in Fig. 2, when the pressure in the collision chamber is 5×10^{-4} Torr. This result shows that the excited species are produced by a single collision of the parent molecule with an electron. As is shown in Fig. 3, the intensity of the emission seems to depend linearly on the pressure of the collision chamber when the energy of the electron impact is 150 eV. This result could indicate that the excited species are produced directly through the unimolecular dissociation of the original molecule.

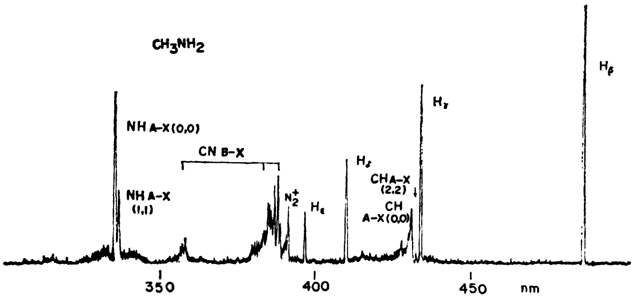


Fig. 1. Emission spectrum observed in electron impact of CH_3NH_2. The energy of electron impact is 150 eV. The pressure of the collision chamber is 3×10^{-4} Torr.

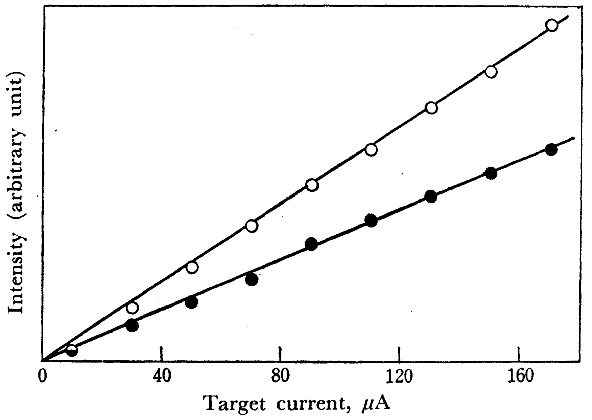


Fig. 2. Dependency of emission intensities on the target current. ○: Balmer-β line. ●: (0, 0) band of NH($A^3\Pi$-$X^3\Sigma$). The energy of electron impact is 150 eV. The pressure of the collision chamber is 5×10^{-4} Torr.

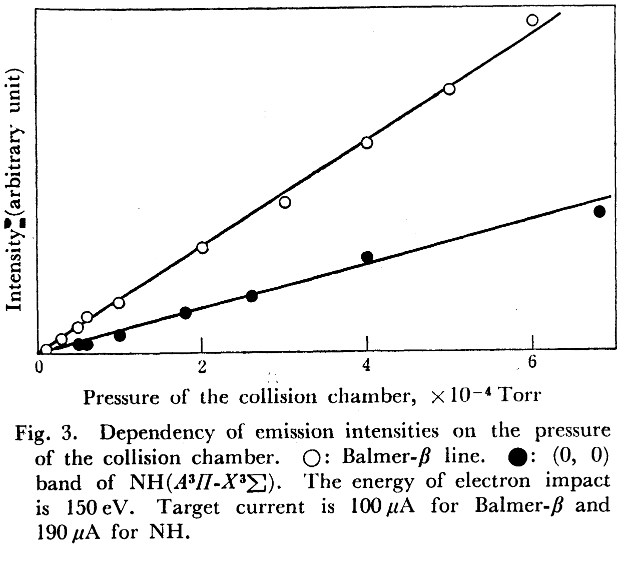
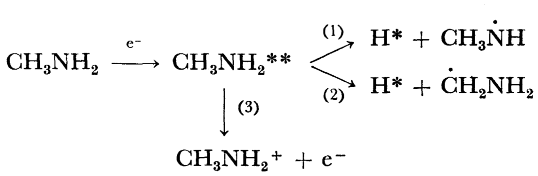


Fig. 3. Dependency of emission intensities on the pressure of the collision chamber. ○: Balmer-β line. ●: (0, 0) band of NH($A^3\Pi$-$X^3\Sigma$). The energy of electron impact is 150 eV. Target current is 100 μA for Balmer-β and 190 μA for NH.

Both results show that the excited species are produced in the primary processes of the decomposition of methylamine. It is also established in the case of NH_3 that the excited hydrogen atom and the triplet NH radical are produced through a unimolecular reaction. It is also presumed that other species, *e.g.*, CH($A^2\Delta$) and CN($B^2\Sigma$), are produced in a similar process.

Putting the pressure, the temperature in the collision chamber, and the radius of methylamine at 10^{-4} Torr, 300°K, and 5×10^{-8} cm⁶⁾ respectively, the collision time of an ideal gas for methylamine in the system is about 6×10^{-4} sec. Hence, the excited species emit the photon within a shorter peroid than the collision time under the given conditions.

As for the production of excited hydrogen atoms from methylamine, it may be presumed as a necessary condition that they are produced through a superexcited state of methylamine, because they have a higher energy than the ionization potential of methylamine (8.97 eV). Therefore, the following mechanism of bond-scission for methylamine under electron impact seems reasonable:



$$\begin{tikzcd} CH_3NH_2 \arrow[r, "e^-"] & CH_3NH_2^{**} \arrow[r, "(1)"] \arrow[dr, "(2)"'] \arrow[d, "(3)"] & H^* + CH_3\dot{N}H \\ & CH_3NH_2^+ + e^- & H^* + \dot{C}H_2NH_2 \end{tikzcd}$$

In this mechanism, H* shows an excited hydrogen atom, and $CH_3NH_2^{**}$ shows a superexcited state of methylamine whose lifetime is known to be shorter than or in the same order as the period of one vibration. A dissociation process, (1) and/or (2), competes with the ionization process (3) from the superexcited state. If the mechanism is valid, substitution by the heavier isotope may decrease the probability of the (1) and (2) dissociations and may increase the probability of ionization (3). By the use of CD_3NH_2 and CH_3ND_2 the isotope effect on the dissociation, and also the ratio of the probability of dissociation (1) to that of (2) can be found.

Letting the observed intensity ratios of D_β to H_β be I_D/I_H for CD_3NH_2 and I_D'/I_H' for CH_3ND_2, the relations:

$$\frac{I_D}{I_H}=\frac{3\lambda\varepsilon_C}{2\varepsilon_N} \quad \text{and} \quad \frac{I'_D}{I'_H}=\frac{2\lambda\varepsilon_N}{3\varepsilon_C}$$

are obtained, where ε_N and ε_C represent the effects of the difference in the kind of bonding on the scission probability— *i.e.*, the N–H and C–H bonds of methylamine, respectively, and λ repersents the isotope

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6) This value is a rough one.

effect on the bond-scission. As CH_3NH_2 contained CH_3NDH, and as CD_3NH_2 contained small amounts of CD_3NDH and CD_2HNH_2, in the above calculation corrections of I_D/I_H and I_D'/I_H' were made on the basis of the results of mass spectrometery. Putting the corrected values of 0.7 and 0.5 into I_D/I_H and I_D'/I_H' respectively, $\varepsilon_C/\varepsilon_N$ and λ were determined to be 0.8 and 0.6 respectively. From these results, the contribution of the (2) pathway to the production of the excited hydrogen atom is less than that of the (1) pathway by about 20% for each bond, and the isotope effect of deuteration on the dissociation process is shown to be a decrease of about 40%.

This isotope effect is consistent with the decrease in the (1) and (2) dissociations by the replacement by a heavier isotope, as is to be expected from the above mechanism including the superexcited state.

Contrary to the dissociation process of the neutral methylamine, the $CH_3NH^+/CH_3NH_2^+$ ratio of 0.2 was smaller than the ratio $CH_2NH_2^+/CH_3NH_2^+$ of 2.4 in the mass spectrum.

$$CH_3NH_2^+ \begin{array}{l} \nearrow CH_3NH^+ + H \\ \searrow CH_2NH_2^+ + H \end{array}$$

However, we can not say which of bonds, the C–H bond or the N–H bond, in $CH_3NH_2^+$ dissociates more easily, because there are two possibilities: the scission of the C–H bond may occur more easily than the N–H bond, and the CH_3NH^+ may decompose further and so be little detected. It should be noticed that, in the decomposition of the positive ion, the hydrogen atom in the ground state is, in view of the energy, more favorable than that in the excited state. Thus, the hydrogen atom produced from $CH_3NH_2^+$ may contribute little to the emission.

The similar facts that the CH_3O^+/CH_3OH^+ and CH_2OH^+/CH_3OH^+ ratios were 0.2 and 1.6[7] respectively in mass spectrum (electron imapct energy: 80eV) should also be noticed. $\varepsilon_C/\varepsilon_O$ and λ had the same values of 0.8 in the case of CH_3OH[8].

Last, the production of the NH radical from methylamine may be discussed in relation to that from ammonia and dimethylamine. The emission spectra of the NH radical produced from methylamine and ammonia by electron impact are shown in Fig.4. Both the $c^1\Pi$ and $A^3\Pi$ state of the NH radical appeared in the emission spectrum of ammonia, while only the $A^3\Pi$ state of the NH radical appeared in those of methylamine and dimethylamine in the present study.

In a former study,[9] the NH radical in the $A^3\Pi$ state is not produced from ammonia by photon impact with energies up to about 11.87 eV (λ=105 nm), a value which is higher than the ionization potential of ammonia (10.15 eV).[10] Hence, if the $A^3\Pi$ state of the NH radical is supposed to be produced from ammonia in a triplet excited state, the ratio of the emission intensity of the $A^3\Pi$ state to that of the $c^1\Pi$ state should depend on the energy of the impact electron, because the spin-forbidden transition is possible in the case of excitation by an electron impact with a lower energy. However, in the present study it did not depend on the impact energy in the region from 40 eV to 150 eV. Therefore, it can be supposed that the $A^3\Pi$ state of the NH radical is produced only through a superexcited state of ammonia with a higher energy than 11.87 eV.

Fig. 4. The spectra of NH (the energy of electron impact: 150 eV). a) CH_3NH_2. b) NH_3. An arrow (↓) at 323 nm indicates R-head of (0, 0) band of NH($c^1\Pi$-$a^1\Delta$). Sharp bands at 336 and 337 nm are (0, 0) and (1, 1) bands of NH($A^3\Pi$-$X^3\Sigma$).

The fact that the electronic state of the NH radical produced from methylamine and dimethylamine as well as hydrazine[4] differs from that produced from ammonia by electron impact can be explained by the spin conservation rule and redistribution of the excitation energy in the parent molecule. In addition, the type of the decomposition of the substituent group to ammonia probably determines the electronic state of the NH radical produced from the molecules.

In the present study, it can not be mentioned whether or not the NH($A^3\Pi$), CH($A^2\Delta$), and CN($B^2\Sigma$) radicals are produced through a superexcited state of methylamine, because the energy of these species does not exceed the ionization potential of methylamine and because the threshold energy which is needed to form the excited species is not known.

The authors would like to express their gratitude to Professors Shigero Ikeda and Yu Yokoyama for use of their Shimadzu GE-100 monochromator. The authors also wish to thank Dr Motoyoshi Hatada for his technical advice as constructing the collision chamber and Professor Kozo Hirota for his encouragement throughout this work.

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7) Unpublished result by I. Fujita.

8) I. Fujita, M. Hatada, T. Ogawa, and K. Hirota, This Bulletin, **44**, 1751 (1971).

9) H. Okabe and M. Lenzi, *J. Chem. Phys.*, **47**, 5241 (1967).

10) K. Watanabe, *ibid.*, **26**, 542 (1957).