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A RELATIONSHIP BETWEEN MASS SPECTRA AND ELECTRON DENSITY

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A correlation between the bond scission in mass spectra and the change of electron density on the skeletal bonds from molecules to molecular ions was examined, and it showed that the scission probability of the bond was closely related to the decrease of electron density forming the bonds. This method was applied to several alkylamines.

The molecular orbital theory has been used to explain the fragmentation in mass spectra of various kinds of organic compounds.1) However, it seems that the mechanism of the fragmentation has not been so systematically established.

In this work, the initial fragmentation of mass spectra for several alkylamines was studied by simply comparing the electron density on the bonds between molecules and molecular ions. It is known that the primary process induced by the electron-impact is the removal of one of the electrons. This electron deficiency, or positive charge, is considered to be distributed or localized at some bonds, and subsequently the molecular ion would decompose in a certain pattern. Therefore, it seems to be worthwhile examining the change of electron density to understand the mechanism of fragmentation of mass spectra. Electron densities of the molecules and molecular ions were calculated by the CNDO/2 method, the parameters of which were the same as in the paper of Pople and Seagel.2) In the present calculation, bond lengths (Å) were assumed as follows: C-C, 1.54; C-N, 1.48; C-H, 1.09; N-H, 1.01, and all the bond angles were taken to be $109^{\circ}28'$ (sp^3). It is known that the energy and electron density of a molecule are dependent on its structure, but it is difficult to estimate the structure of the molecular ion. Thus, calculating the total energy of possible structures, the most stable structure in terms of energy was adopted in the calculation of electron densities of molecules and molecular ions. Concerning carbon and nitrogen atoms, the coefficients of 2s, 2px, 2py, and 2pz orbitals were transformed into sp^3 hybrid orbitals, after the CNDO/2 calculation reached the SCF condition. Then electron density in the bond direction was calculated using hybrid orbitals just as in the CNDO/2 method, and the summation of electron density forming the bond was assumed to be the electron density on the bonds.

Methylamine, ethylamine, propylamine, and butylamine were examined by this method. The mass spectra of the alkylamines have been reported and theoretical approaches have been carried out by several investigators.[3)] A comparison of the electron density on the skeletal bonds between molecules and molecular ions are shown in Table 1. The ionization potentials (IP), which were obtained by the difference energies between molecules and molecular ions, are also shown in Table 1.

Table 1. Comparison of the electron densities on the skeletal bonds between molecules and molecular ions

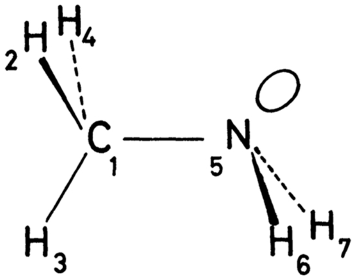
Bond number ethylamine : $\mathrm{NH_2}\underset{1}{-}\mathrm{CH_2}\underset{2}{-}\mathrm{CH_3}$

propylamine : $\mathrm{NH_2}\underset{1}{-}\mathrm{CH_2}\underset{2}{-}\mathrm{CH_2}\underset{3}{-}\mathrm{CH_3}$

butylamine : $\mathrm{NH_2}\underset{1}{-}\mathrm{CH_2}\underset{2}{-}\mathrm{CH_2}\underset{3}{-}\mathrm{CH_2}\underset{4}{-}\mathrm{CH_3}$

compound	IP/eV calc. (exp.)		bond number				
			lone pair	1	2	3	4
ethylamine	12.12 (8.86)	molecule	1.9762	2.0036	2.0052	—	—
		ion	1.2198	1.9882	1.9113	—	—
		difference	0.7564	0.0154	0.0939	—	—
propylamine	11.89 (8.78)	molecule	1.9760	2.0082	1.9992	1.9974	—
		ion	1.2522	1.9862	1.8940	1.9677	—
		difference	0.7238	0.0220	0.1052	0.0297	—
butylamine	11.76 (8.71)	molecule	1.9760	2.0086	2.0030	1.9916	2.0006
		ion	1.2764	1.9833	1.8884	1.9587	1.9806
		difference	0.6996	0.0253	0.1146	0.0329	0.0200

Table 2. Electron densities of C-H and N-H bonds in methylamine molecule and its molecular ion



bond	molecule	ion	difference
C_1- H_2	2.0059	1.9891	0.0168
C_1- H_3	2.0164	1.9173	0.0991
C_1- H_4	2.0059	1.9891	0.0168
C_1- N_5	2.0024	1.9854	0.0170
N_5- H_6	1.9984	1.9615	0.0369
N_5- H_7	1.9984	1.9615	0.0369
lone pair	1.9722	1.1960	0.7762

The calculated IP value was 12.63 eV.

The IP values obtained are greater than those reported in the literatures.4) The CNDO/2 method is not well suited for the estimation of the energy, but this method was sufficiently useful for the elucidation of mass spectra as discussed below.

It is found that a change of electron density from molecules to molecular ions at C-H and N-H bonds is generally small compared with the changes for the skeletal bonds. However, in methylamine, as shown in Table 2, the change of electron density at one of the C-H bond was rather large. Indicating by the numerals attached to the skeletal bonds, as shown in Table 1, electron density decreases in the sequence: 2>1 in ethylamine; 2>3>1 in propylamine; 2>3>1>4 in butylamine. The sequence of the decrease of electron density agrees fairly well with that of the scission probabilities of the skeletal bonds in mass spectra. In ethylamine, propylamine, and butylamine, the C-C bond adjacent to the C-N bond is considered to break most frequently, because the electron density shows a marked decrease at that position upon ionization. In methylamine, the loss of one hydrogen atom seemed to occur predominantly. It is known that the positive charge is localized at the nitrogen lone pair in molecular ions of alkylamines. The present result shows a good agreement in this point as well as in the prediction of scission probability.

These facts indicate that the change of electron density from ground state molecule to energized molecular ion plays an important role in fragmentation. It was found that the more electron density of a bond in a molecule decreases upon ionization, the more easily this bond breaks.

This seems to be reasonable that when electron density decreases on the bond, the bond may be weaker and subsequently a breaking of the bond would occur. At that time a positive charge would remain on the more stable fragment in terms of energy. By this method the initial fragmentation of mass spectra can be explained simply, and the position of bond scission can be predicted.

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