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The Application of the Molecular Orbital Theory to the Bond Scission of Aliphatic Amines*

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The relative scission-probabilities of C–C bonds of *n*-propyl, *n*-butyl and isobutyl amines being formed by electron impact (90 V.) were determined by the use of mass spectrometers of the usual type and of the high-resolution type. They were in good accordance with the theoretical values calculated by the LCBO-MO theory which had been proposed and found successful in explaining the mass spectra of *n*-paraffins and methyl alkyl ketones.

It was proposed by Thompson,[1] with regard to the mass spectrum of normal octane, that the relative amount of the abundant ions could be given theoretically if the "scission probability" of each C–C bond in the parent ion were assumed to be proportional to the electron density at the bond on the highest occupied molecular orbital (MO) of a starting molecule, and if the MO were expressed by the linear combination of the bond-orbitals (LCBO). Such a molecular orbital theory could be applied successfully to the relative abundance of the ions produced by several normal paraffins[2] (C_4H_{10}—$C_{10}H_{22}$) and by several methyl alkyl ketones[3]. Nevertheless, the application of this LCBO theory to the other paraffins higher than decane has not proved satisfactorily. This is the reason why there are some objections[4] to this theory, though its application to the evaluation of ionization potentials is generally admitted. The above discordance can, however, be explained by introducing the multiple scission of bonds in the parent ions of large carbon numbers.

The point of criticism on the theory may lie, rather, in a new assumption, one which is quite different from that of the statistical theory of Rosenstock et al.[5] According to this assumption, even the good coincidence may seem to be fortuitous, especially in the cases of ketones which contain lone-pair and π-bonding electrons as well as σ-bonding electrons in the molecules. On the other hand, the scission of the bonds determined by comparing the spectra of ketones labeled with deuterium may arouse some doubt about using them as the experimental data to be compared, because the transposition of deuterium is possible during the process of fragmentation. If it occured markedly, the above comparison would be of little meaning.

It is the object of the present paper to extend the applicability of the theory to the calculation of the relative abundance of ions produced from *n*-propyl (*n*-PA), *n*-butyl (*n*-BA) and isobutyl amines (*i*-BA), using mass spectrometers of the high-resolution type as well as of the usual type, in order to clarify the ambiguity of the assignment of the ion produced.

Experimental

Mass spectra with usual resolutions were obtained with a Hitachi RMU-5B apparatus (magnetic scanning type), with a bombarding electron beam of 90 V. These data, shown in Table I, indicate that the peaks resulting from the scission of the C–N bond are negligible. However, some of the peaks (indicated by asterisks in Table I) (m/e=15, 27, 28, 29, 41, 42, 43) could not be assigned in the cases of *n*-BA and *i*-BA by these spectra alone; e. g., each of the seven peaks corresponding to different fragmentations is described in the third and the fourth columns of Table II. Therefore, for the sake of determining the probability of bond-scission, their ratios (A/B) were determined by their relative peak height in the spectra of the high-resolution type. They were obtained with a Hitachi PMU-7Hr apparatus. Its resolution is at least 5000 at m/e=28. However, it was found unnecessary to make such an allocation in the case of propylamine, so the spectrum of this amine was not measured. The results for the two butylamines are shown in Table II; they were obtained also with a bombarding electron beam of 90 V. The ratio was determined by opening the collector slit so that both tops of the peak to be compared become flat; the mean value for three runs was used.

Assuming the peak-ratio thus obtained to be the same as that in the usual spectra (shown in Table I),

TABLE I. RELATIVE INTENSITY OF MAIN PEAKS IN THE MASS SPECTRA OF THE AMINES[a]

m/e	Assignment	n-$C_3H_7NH_2$	n-$C_4H_9NH_2$	i-$C_4H_9NH_2$
15	*	3.7	2.4	3.1
27	*	8.1	6.0	5.9
28	*	16.5	8.2	11.2
29	*	4.6	3.8	4.9
30	CNH_4	100	100	100
31	CNH_5	11.3	7.4	17.5
41	*	5.9	4.3	7.3
42	*	3.9	2.4	2.7
43	*	2.8	1.8	2.8
44	C_2NH_6	1.7	2.6	3.7
45	C_2NH_7	0.6	0.7	1.1
58	C_3NH_8	2.1	1.9	4.3
59	C_3NH_9	9.5	0.3	0.9
72	C_4NH_{10}	—	0.9	1.5
73	C_4NH_{11}	—	6.8	8.4

a) Measured by H. Otouma, K. Fueki and M. Hatada.

TABLE II. THE RATIO OF THE PEAK HEIGHTS OF THE IONS WHOSE m/e RATIOS ARE THE SAME

C_i	m/e	Possible ions		A/B	
		A	B	n-$C_4H_9NH_2$	i-$C_4H_9NH_2$
C_1	15	CH_3	NH_2	∞	∞
C_2	27	C_2H_3	CNH	17.7	14.0
	28	C_2H_4	CNH_2	0.13	0.56
	29	C_2H_5	CNH_3	1.09	1.63
C_3	41	C_3H_5	C_2NH_3	5.55	31.8
	42	C_3H_6	C_2NH_4	0.042	0.18
	43	C_3H_7	C_2NH_5	0.26	1.11

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* Part V of a series on the molecular orbital theory of mass spectra. Parts II, III and IV are listed in Ref. 3.

[1] R. Thompson, "Applied Mass Spectrometry," Inst. of Petroleum, London (1953), p. 154.

[2] K. Fueki and K. Hirota, *J. Chem. Soc. Japan, Pure Chem. Sect.*, (*Nippon Kagaku Zasshi*), **81**, 212 (1960).

[3] M. Hatada and K. Hirota, This Bulletin, **38**, 599 (1965); *Z. physik. Chem. N. F.*, **44**, 328 (1965); *J. Chem. Soc. Japan, Pure Chem. Sect.*, (*Nippon Kagaku Zasshi*), **86**, 307 (1965).

[4] N. D. Coggeshall, *J. Chem. Phys.*, **33**, 1247 (1960); S. Meyerson, ibid., *J. Chem. Phys.*, **42**, 2181 (1965).

[5] H. M. Rosenstock, M. B. Wallenstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Natl. Acad. Sci.*, **38**, 667 (1952).

the percentages of all the ions concerned are allotted in Table II.

It is noteworthy that the ions produced by the scission of the C–N bond could not be found in both butyl amines; e. g., the ions containing nitrogen (N, NH, NH_2) and those corresponding to C_4H_9, C_4H_8 and C_4H_7 were not observed actually in the case of *n*-butylamine. This is the reason why propyl amine was not subjected to mass spectrometry of the high-resolution type. By combining the other data in Table I with Table II, the relative abundance of all the ions can be obtained to be as shown in Table III.

The relative probabilities of the scission of bonds can be determined from the data in Tables I and III, so a comparison of the theoretical values with the experimental ones becomes possible.

TABLE III. RELATIVE INTENSITIES OF IONS PRODUCED FROM THE AMINES

m/e	Ions	*n*-$C_3H_7NH_2$	*n*-$C_4H_9NH_2$	*i*-$C_4H_9NH_2$
15	CH_3	3.7	2.4	3.1
	NH	0	0	0
27	C_2H_3	8.1[a]	5.7	5.5
	CNH		0.3	0.4
28	C_2H_4	16.5[a]	1.0	0.6
	CNH_2		7.2	10.6
29	C_2H_5	4.6[a]	2.0	1.9
	CNH_3		1.8	3.0
41	C_3H_5	—	3.7	7.1
	C_2NH_3	5.9	0.6	0.2
42	C_3H_6	—	0.1	0.4
	C_2NH_4	3.9	2.3	2.3
43	C_3H_7	—	0.4	1.5
	C_2NH_5	2.8	1.4	1.3

a) The sums of both ions are listed, but they can be estimated to belong mainly to hydrocarbon ions, as is explained in the text.

LCBO-MO Theory

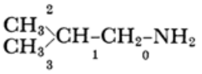
In the case of ethyl alkyl ketone,[3] the bond orbitals of C–C and C=O bonds were calculated under the assumption that CH_2 and CH_3 were united atoms, because the electron density of the C–C bond was practically the same in the case of paraffins whether it was calculated with the united atom approximation[6] or with a more rigorous treatment[7]. Besides, a mutual interaction between only the neighboring bond-orbitals was taken into consideration in both the above papers, as is usually done generally in simple LCAO-MO theory.

These approximations were also adopted in the present paper, regarding NH_2 as a united atom as well as CH, CH_2, and CH_3; e. g.,

n-Propyl amine (*n*-PA) : $CH_3\underset{2}{-}CH_2\underset{1}{-}CH_2\underset{0}{-}NH_2$

n-Butyl amine (*n*-BA) : $CH_3\underset{3}{-}CH_2\underset{2}{-}CH_2\underset{1}{-}CH_2\underset{0}{-}NH_2$

Isobutyl amine (*i*-BA) :



$\begin{matrix} CH_3 \overset{2}{\searrow} \\ CH_3 \underset{3}{\nearrow} \end{matrix} CH\underset{1}{-}CH_2\underset{0}{-}NH_2$

The numbering of each bond-orbital, i, will be indicated by the numerals attached to the bond shown above.

Table IV shows the Coulomb (α) and exchange (β) integrals necessary to solve the secular equation for each molecule: $[e_{ij}-\delta_{ij}E]=0$, where e_{ij} equals α or β, according as $i=j$ or $i\neq j$, the suffix N denotes the integrals concerning the nitrogen atom.

TABLE IV. EXPLANATION OF INTEGRALS.

	$\overset{i}{\text{C—C}}$	$\overset{i+1}{\text{C—C}}$	$\overset{0}{\text{C—N}}$
$\overset{i}{\text{C—C}}$	α	β	β_N
$\overset{i+1}{\text{C—C}}$	β	α	0
C—N	β_N	0	α_N

Among these integrals, α and β were taken to be -13.75 V., and -1.80 V. respectively from Fueki's values,[8] which were determined in the evaluation of the ionization potential of saturated hydrocarbons. The values of α_N and β_N were determined by solving the secular equations for *n*-ethylamine and *n*-butylamine, so that they satisfy their observed ionization potentials, 9.26 and 9.19 V. respectively. The values thus obtained were $\alpha_N=-9.60$ V. and $\beta_N=-1.24$ V.

The necessary electron density can be calculated by the squares of the coefficient, C_i, in the wave function of the highest-occupied orbital, $\Psi=\sum_i c_i\phi_i$.

Results

For the sake of comparison, the calculated ionization potentials for *n*-PA and *i*-BA are shown in Table V, along with the observed values. Though the accuracy of the observed values is not very good, the tendency for the ionization potential to decrease with a decrease in the carbon number is shown by the calculated values in Table V.

TABLE V. CALCULATED AND OBSERVED I.P. VALUES OF THE AMINES

	Observed		Calculated
$C_2H_5NH_2$	9.32[9]	9.19[10]	(9.26)
n-$C_3H_7NH_2$	9.17[9]		9.20
n-C_4H_9NH	9.19[9]		(9.19)
i-$C_4H_9NH_2$	9.00[9]		9.17

N.B. The values in parentheses are used for the calculation.

The squares of the coefficient, C_i, of the *i*th bond orbital in the highest occupied MO concerned are shown in Table VI. In Table VI, case I or II

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[6] G. R. Lester, "Advanc. Mass Spectrometry", Proc. Conf. Univ. London, (1958) **1**, 287 (1959).

[7] G. G. Hall, *Proc. Roy. Soc.*, **A205**, 541 (1951); *Trans. Faraday Soc.*, **49**, 113 (1953).

[8] K. Fueki, *J. Phys. Chem.*, **68**, 2656 (1964).

[9] J. D. Morrison and A. J. Nicholson, *J. Chem. Phys.*, **20**, 1021 (1952).

[10] J. Collin, *Can. J. Chem.*, **37**, 1053 (1059).

represents, respectively when the coefficient of the C–N bond is taken into calculation or when it is not. The values are normalized, in both cases. Since the scission of the C–N bond can be neglected because of the small peaks resulting from its scission, as has been mentioned already, it is unnecessary to consider the electron density at the C–N bond; however, some discussion is desirable and will, therefore, be given. Thus, the case II was used in the comparison of the observed probability with the calculated probability.

Table VI. Square of the C_i's

Bond number		0	1	2	3
n-$C_3H_7NH_2$	obs.	—	88.3	11.7	—
	I	89.26	9.29	1.45	—
	II	—	86.5	13.5	—
n-$C_4H_9NH_2$	obs.	—	85.3	12.5	3.2
	I	87.95	9.62	2.10	0.33
	II	—	79.8	17.4	2.7
i-$C_4H_9NH_2$	obs.[a]	—	87.7	6.15	6.15
	I	87.77	10.55	0.84	0.84
	II	—	86.5	6.75	6.75

a) The contributions of peaks produced by two bond-scissions are not included.

In previous papers[3] the experimental probability of each bond-scission was discussed by comparing the spectrum of ketones with that of the corresponding deuterated species. Similarly, three amines were compared, as is shown in Fig. 1; the degree of coincidence is the same as that in the case of ketones. This result supports the method of research adopted for ketones.

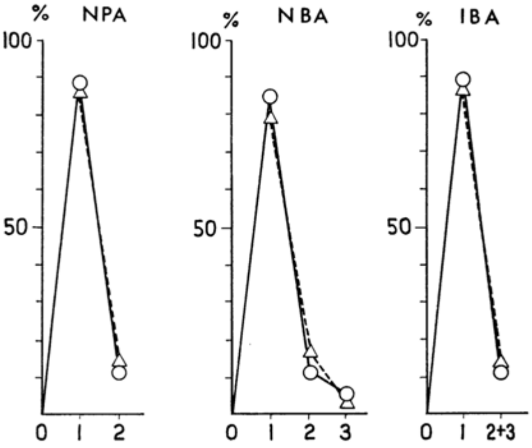

Fig. 1. Bond-scission probability and positive charge distribution.
○——○ : Experimental
△----△ : Theoretical

Discussion

We may now discuss why the adoption of the case II is more justified than that of the case I; i. e., this choice means that only the scission probability of the C–C bond can be considered, with no regard to that of the C–N bond. The same criticism may be given concerning the stability of the C=O bond in the case of alkyl-methyl ketones.

From the standpoint of the rate theory, the scission probability would be proportional to the specific rate, k, which is expressed by the Arrhenius formula:

$$k = X\exp(-E_a/\boldsymbol{R}T) \tag{2}$$

In the cases of comparisons between the same bonds, e. g., C–C, the activation energy, E_a, will be the same. The difference in the scission probability in the case of paraffins is, therefore, determined only by the pre-exponential factor, X. On the other hand, the difference may depend also on E_a in the comparison of scission probabilities between different bonds. This is the reason why fragment ions produced by the scission of C–H and C–N bonds are, respectively smaller and very much smaller, than those produced by the scission of the C–C bond.

Now, as has often been done, the bond energy may be assumed to be proportional to the E_a value, if the potential curves of the bonds have the same shape. This first approximation seems successful as far as C–C (ca. 80 kcal.), C–H (ca. 100 kcal.) and C=O (>127 kcal.) are concerned, because the scission probability decreases in this order: C–C>C–H>C=O.

However, this approximation does not hold well if the C–N bond is considered, because its bond energy is nearly equal to or even smaller than that of the C–C bond. Considering this, the shape of the potential curve of the C–N bond may be quite different from that of the other bonds.

In conclusion, it seems promising to apply the present LCBO-MO theory on mass spectra to substances of kinds other than paraffins, though the theory is completely different in standpoint from the usual statistical theory of Rosenstock et al.[5] However, some assumptions will be necessary in using the theory so as to be able to predict which fragment will be charged after the scission of a bond.

We wish to express our deep thanks to Dr. M. Hatada for his help in this research.

This paper is dedicated to Professor Masao Kotani, the University of Tokyo, in celebration of his 60th birthday.