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Prediction of the Position of Bond-Scission in the Mass Spectrometry of Aliphatic Compounds[1]

Hiroshi Ichikawa and Michihiko Ogata

Hoshi College of Pharmacy[2]

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According to the relationship between the rate constant of bond-scission in the quasi-equilibrium theory of mass spectra and the heat of reaction, the molecular orbital theories for all valence electrons were examined in the mass spectra of aliphatic amines, alcohols, an aldehyde, and a ketone. Among those theories, the MINDO/2 and its unrestricted methods were shown to be best fitted for the purpose. It was shown that the scission-probability can be predicted from the calculated heat of reaction in an almost quantitative exact.

Though the quasi-equilibrium theory (QET) of mass spectra[3] has been successful in explaining the fragmentation of saturated hydrocarbons, it does not appear to explain the fragmentation path of complex compounds which are of special interest to organic chemists. The molecular orbital (MO) theoretical approach, based on the hypothesis that the scission probability is proportional to the net-charge density at the highest occupied orbital of the molecular ion,[4] has been mostly successful in predicting the position of bond-scission. In this approach, however, physical interpretation of the hypothesis has not been given and some problems in the application of the theory have also been pointed out by some authors.[5] Independently of the theoretical work, the organic chemists' approach has provided some simple rules to predict the break-down process.[6] These rules, referred to here as fragmentation rules, have been successful in predicting the major decomposition paths of various compounds. However, this method is devoid of quantitative prediction.

Recently we have proposed a relationship between the rate constant of cleavage in the QET and the heat of reaction, where we have shown that in some aliphatic compounds, a comparison of the heats of reaction can predict the position of the most probable bond-scission,[7] when the total energy of the fragments is calculated by the CNDO/2 method.[8] However, it is known that the CNDO/2 method is not very adaptable to an estimation of the total energy.[9] In this paper, we compare the calculated heats of reaction by the CNDO/2, INDO,[10] and MINDO/2[11] methods with experimental results.

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[2] Location: *2–4 Ebara, Shinagawa-ku, Tokyo.*

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Theory

The Relationship between the Rate Constant of Bond-Scission and the Heat of Reaction——If the Bell, Evans, and Polanyi (BEP) principle[12] holds in mass spectral reactions, the activation energy ($\varDelta E$) for a given fragmentation reaction can be written in a linear form; $E=X+Y\varDelta H$, where X and Y are constants in the same system of the given reaction and $\varDelta H$ is the heat of reaction. For the model composed wholly of harmonic oscillators, the QET provides the rate constant (k) as $k=\nu((E-\varDelta E)/E)^{s-1}$, where E is the internal energy, $\nu(\mathrm{sec}^{-1})$ is a constant, and s is the effective number of degrees of freedom. Combination of these equations provides the ratio of the rate constants, k_1/k_2, for any two of the fragmentation paths;

$$(\mathrm{P\text{-}Q} + \mathrm{R})^{\cdot +} \xleftarrow[\text{path A}]{k_1} (\mathrm{P\text{-}Q\text{-}R})^{\cdot +} \xrightarrow[\text{path B}]{k_2} (\mathrm{P} + \mathrm{Q\text{-}R})^{\cdot +}$$

will be given by;

$$\frac{k_1}{k_2} = c((E'-\varDelta H_1)/(E'-\varDelta H_2))^{s-1}$$

where $E'=(E-X)/Y$, and c is a constant ($c=\nu_1/\nu_2$). Since the competitive reactions occur in a same system, the constant c may be almost unity.

It will be seen that the fracture occurs more often at the position which gives the smallest $\varDelta H$. One can, therefore, predict the most probable position of bond-scission by simply comparing the sum of the total energies of the produced fragments; if the total energy of the $(\mathrm{P{-}Q+R})^{\cdot +}$ state is lower than that of the $(\mathrm{P+Q{-}R})^{\cdot +}$ state, the fragmentation path A will be more important. As long as the BEP principle holds, this concept is applicable. Therefore, adoption of this technique to the fragmentation of compounds, especially those with many functional groups should show its validity under analyses.

MO Calculation——In the method mentioned above, the MO methods for all valence electrons should be used in order to estimate the total energy of a given system. Although some kinds of MO theories such as the extended Hückel,[13] CNDO, INDO, and MINDO theories have been prevalent, unfortunately none of these methods offer an absolutely correct estimate of the total energy. Therefore, they should be re-examined in relation to the well-investigated cases of fragmentations before being adapted to practical use. We have adapted the CNDO/2, INDO, and MINDO/2 methods. The unrestricted MINDO/2 method has not been reported. We extended the original MINDO/2 method[11] for closed-shell systems to the unrestricted method without changing parameters. Despite the problems of simply extending the semi-empirical MO thoery to open-shell systems, the calculated ionization potentials (IP's) for radicals agree well with experimental values, and therefore, we regard this as a valid extension. The details on the unrestricted MINDO/2 method are now in preparation.

The total energy, of course, depends on the geometry; the geometry should be optimized if the present method is applied in a rigorous way. However, from a practical point of view, it is difficult to meet these requirements strictly, and therefore, the appropriate bond-lengths (Å) are assumed as follows: $\mathrm{C}(sp^3)$–$\mathrm{C}(sp^3)$, 1.54; $\mathrm{C}(sp^3)$–$\mathrm{C}(sp, sp^2)$, 1.50; C=C, 1.35; C=O, C=N, 1.25; C=C (conj.), 1.4; C≡O, 1.15; C–H, 1.09; O–H, 1.00; N–H, 1.02.

Results and Discussions

Many papers[14] that deal with the conventional MO treatment[4] have discussed the quantitative ion-abundance by comparison of the height of the peaks. However, two points here arise; (1) the height of the ion-peak is supposed to represent the approximate abundance of each ion, but there is no evidence that the height of the peak is linearly proportional to the number of ions produced; (2) in the fragmentation of the molecular ion, *i.e.*, $(\mathrm{P{-}Q})^{\cdot +}\rightarrow \mathrm{P}\cdot+\mathrm{Q}^+$ or $(\mathrm{P{-}Q})^{\cdot +}\rightarrow\mathrm{P}^{+}+\cdot\mathrm{Q}$, the ratio of the positively charged fragments, $[\mathrm{P}^+]/[\mathrm{Q}^+]$, is impossible to predict.[15] The first point indicates that a rigorous discussion of ion abundance

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[15] From the relationship shown by Stevenson (D.P. Stevenson, *Discuss. Faraday Soc.*, **10**, 35 (1951)), it is possible to know qualitatively which ion is predominant.

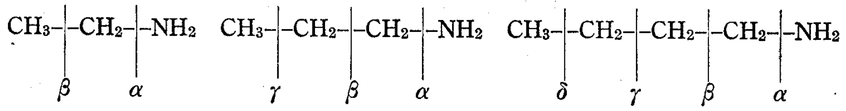
is not pertinent. The second point indicates that the cleavage of the bond between hydrogen and other atoms should not be taken into account since the commercially available mass spectrometer does not generally determine the peak at *m/e* 1. Even if the abundance of hydrogen ions could be observed, the origin of the ion would be almost impossible to determine. Therefore, in this paper the ion-abundance of fragmentation are treated qualitatively and are limited to the skeletal bond-scissions. The total energies of some cations and radicals (in terms of a.u.; 1 a.u.≒27.21 eV) and IP's (in terms of eV) are listed in Table I. Combina-

Table I. Total Energies[a] and Ionization Potentials[b] of Fragments

Fragments[c]	CNDO/2			INDO			MINDO/2		
	Radical[d]	Ion[e]	IP	Radical	Ion	IP	Radical	Ion	IP
CH_3	−9.1167	−8.6688	12.19	−8.8747	−8.4198	12.38	−6.4097	−6.0351	10.19
CH_3CH_2	−17.8456	−17.4746	10.10	−17.3458	−16.9709	10.20	−12.2924	−11.9599	9.05
$CH_3CH_2CH_2$	−26.5350	−26.1686	9.97	−25.7809	−25.4095	10.11	−18.1563	−17.8304	8.87
$CH_3CH_2CH_2CH_2$	−35.2233	−34.8607	9.87	−34.2144	−33.8466	10.01	−24.0189	−23.6971	8.76
$(CH_3)_2CH$	−26.5656	−26.2416	8.82	−25.8094	−25.4816	8.92	−18.1696	−17.8645	8.30
$CH_3CH_2(CH_3)CH$	−35.2538	−34.9303	8.80	−34.2431	−33.9148	8.93	−24.0333	−23.7311	8·22
$(CH_3)_3C$	−35.2782	−34.9862	7.94	−34.2666	−33.9699	8.07	−24.0400	−23.7552	7.75
OH	−18.9900	−18.3504	17.40	−18.1604	−17.4775	18.58	−11.9962	−11.4324	15.34
CH_2OH	−27.5833	−27.2572	8.87	−26.4863	−26.1773	8.41	−17.9233	−17.6129	8.46
CH_2CH_2OH	−36.2631	−35.8745	10.57	−34.9156	−34.5173	10.84	−23.7663	−23.4135	9.60
$CH_2CH_2CH_2OH$	−44.9594	−44.5885	10.09	−43.3563	−42.9800	10.24	−29.6296	−29.2971	9.05
CH_3CHOH	−36.2988	−36.0146	7.73	−34.9462	−34.6753	7.37	−23.8136	−23.5285	7.76
CH_3CH_2CHOH	−44.9892	−44.7089	7.63	−43.3826	−43.1148	7.29	−29.6769	−29.3974	7.60
$CH_3CH(OH)CH_2$	−44.9583	−44.5983	9.79	−43.3557	−42.9900	9.95	−29.6397	−29.3055	9.10
CH_3CO	−34.5750	−34.3083	7.26	−33.2270	−32.9753	6.85	−22.6133	−22.3339	7.60
CH_3CH_2CO	−43.2709	−43.0134	7.01	−41.6684	−41.4246	6.63	−28.4803	−28.2093	7.38
CH_3COCH_2	−43.3176	−42.8869	11.72	−41.7225	−41.2815	12.00	−28.4942	−28.1157	10.30
CHO	−25.8596	−25.4387	11.45	−24.7723	−24.3681	11.00	−16.7151	−16.3548	9.80
CH_2CHO	−34.6160	−34.1727	12.06	−33.2770	−32.8219	12.38	−22.6086	−22.2169	10.66
NH_2	−12.9454	−12.4217	14.25	−12.4520	−11.9069	14.83	−8.6654	−8.2075	12.46
CH_2NH_2	−21.5815	−21.3241	7.00	−20.8379	−20.6000	6.47	−14.5402	−14.2573	7.70
$CH_2CH_2NH_2$	−30.2866	−29.9168	10.06	−29.2768	−28.9026	10.18	−20.4136	−20.0792	9.10
$CH_2CH_2CH_2NH_2$	−38.9701	−38.6047	9.94	−37.7050	−37.3350	10.07	−26.2720	−25.9423	8.97

a) in terms of a.u. (1 a.u.≒27.21 eV)
b) in terms of eV
c) The conformations were all set to be staggered.
d) calculated by the unrestricted method
e) calculated by the restricted method

Table II. Corelation Between Calculated Heat of Reaction[a] and Approximate Abundance of Bond-Scission in Alkylamines



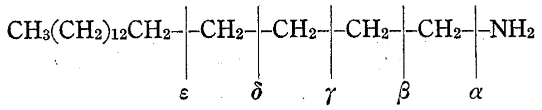
Bond	Ethylamine				*n*-Propylamine				*n*-Butylamine			
	CNDO/2	INDO	MINDO/2	Obs.	CNDO/2	INDO	MINDO/2	Obs.	CNDO/2	INDO	MINDO/2	Obs.
α	0.3776	0.4061	−0.0072	5	0.3935	0.4207	0.0669	5	0.3944	0.4213	0.0674	5
β	0.3567	0.3544	−0.0488	100	0.3378	0.3365	0.0131	100	0.3413	0.3391	0.0164	100
γ					0.4739	0.5050	0.0739	5	0.4381	0.4716	0.0565	40
δ									0.4791	0.5103	0.0780	0

a) In terms of a.u.; following Stenvenson's rule (see ref. 15) the positive charge should be put on the fragment of the lower IP.

tion of these fragments listed in Table I would give a variety of fragmentation modes; the positive charge should be put on the fragment with the lower IP in order to make the total energy of the system lower. Some are discussed separately.

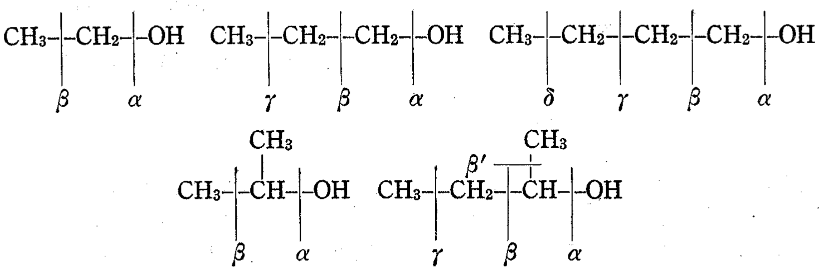
The alkylamines have electron-releasing capabilities through the amino groups, therefore, characteristic cleavages are anticipated. The fragmentation rules show that the expected peak of $R_1R_2C{=}NH_2^+$ is due to the β-bond cleavage. This process provides the most abundant ion in the spectra of primary, secondary, and tertiary alkylamines.[16] Table II shows the heats of reaction for the skeletal bond-scissions of ethylamine, *n*-propylamine, and *n*-butylamine. The results by means of the CNDO/2 method were reported in the previous paper,[7] re-calculations were carried out using the appropriate bond-lengths as assumed in the former section.

The general pattern of mass spectra for *n*-alkylamines may be shown by that of *n*-octadecylamine.[16] The β-bond cleavage is the most important pathway while the probability progressively decreases according to the order, β-> γ-> δ-bond cleavages. This order is considered to correspond to that of ease of bond-scission, since peaks above *m/e* 100 are negligible.


$$\underset{\varepsilon}{CH_3(CH_2)_{12}CH_2\text{-}|}\text{-}\underset{\delta}{CH_2\text{-}|}\text{-}\underset{\gamma}{CH_2\text{-}|}\text{-}\underset{\beta}{CH_2\text{-}|}\text{-}\underset{\alpha}{CH_2\text{-}|}\text{-}NH_2$$

Such is the case for *n*-butylamine; the approximate intensities of ions resulting from α-, β-, γ-, and δ-bond cleavages are listed in the last column of Table II. It will be seen that the MO theories adopted here provide the ΔH's which accord well with experimental results, *i.e.*, the value of ΔH decreases as the abundance of bond-scission increases.

TABLE III. Calculated Heat of Reaction and Approximate Abundance of Bond-Scission in Aliphatic Alcohols



Bond	Ethyl alcohol				iso-Propyl alcohol				*n*-Propyl alcohol			
	CNDO/2	INDO	MINDO/2	Obs.	CNDO/2	INDO	MINDO/2	Obs.	CNDO/2	INDO	MINDO/2	Obs.
α	0.2856	0.2986	0.0699	0	0.0234	0.0077	−0.0261	45	0.2885	0.3023	0.0666	5
β	0.3762	0.3778	0.0034	100	0.1237	0.0997	−0.1036	100	0.3443	0.3491	−0.0121	100
γ									0.4559	0.4802	0.0917	0

Bond	*sec*-Butyl alcohol				*n*-Butyl alcohol			
	CNDO/2	INDO	MINDO/2	Obs.	CNDO/2	INDO	MINDO/2	Obs.
α	0.2411	0.2501	0.0235	0	0.2877	0.3019	0.0694	0
β	0.3012	0.3042	−0.0701	100	0.3461	0.3506	−0.0065	100
β'	0.3358	0.3359	−0.0563	30[a]				
γ	0.4463	0.4606	0.0356	30[a]	0.7893	0.4223	0.0365	5
δ					0.4331	0.4542	0.0560	0

a) The ions for these two paths of cleavage are indistinguishable.

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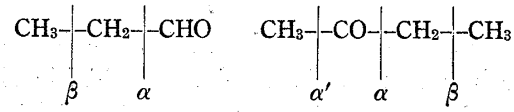
16) R.S. Gohlke and F.W. McLafferty, *Anal. Chem.*, 34, 1281 (1962).

The first process which an alcohol undergoes upon electron-impact is the removal of one of the lone pair electrons of the oxygen atom.[17] This provides a stable oxonium ion through the β-bond cleavage. In the case of primary alcohols in addition to the primary β-bond cleavage, progressively decreasing γ-> δ-> ε-···· bond cleavage is observed. This results in a homologous series of peaks at *m/e* 45, 59, 73, *etc.*[18] Extensive substitution of the α-carbon atom leads to a decomposition pattern in whcih the substituent of largest mass is lost to the greatest extent. This is well illustrated in the mass spectra of isomeric butanols.

As Table III indicates, the agreement of the results obtained by the MINDO/2 method with those obtained experimentally is complete. Neither the CNDO/2 nor INDO method, however, explains the most abundant formation of the $CH_2{=}O^+H$ ion. This may be the result of an incorrect estimate of the total energy for the OH radical and ion, since IP's by these MO theories are far higher than those obtained experimentally (13 eV[19]). Except for this case, both methods are able to predict semiquantitatively the position of bond-scission; *i.e.*, the progressive decrease of γ- and δ-bond cleavage in *n*-butylalcohol and that the substituent of largest mass is lost to the greatest extent.

TABLE IV. Calculated Heat of Reaction and Approximate Abundance of Bond-Scission of Propionaldehyde and Methyl Ethyl Ketone



$$\underset{}{CH_3}\underset{\beta}{\Big|}CH_2\underset{\alpha}{\Big|}CHO \qquad CH_3\underset{\alpha'}{\Big|}CO\underset{\alpha}{\Big|}CH_2\underset{\beta}{\Big|}CH_3$$

Bond	Propionaldehyde				Methyl ethyl ketone			
	CNDO/2	INDO	MINDO/2	Obs.	CNDO/2	INDO	MINDO/2	Obs.
α	0.5206	0.5094	0.0904	100	−1.0920	−1.1025	−0.6322	100
α′					−1.0682	−1.0807	−0.6248	60[a]
β	0.5155	0.5267	0.0939	5	−0.9417	−0.9376	−0.5352	60[a]

[a] The ions for these two processes are indistinguishable.

Finally propionaldehyde and methyl ethyl ketone are examined. The base peak of propionaldehyde is at *m/e* 29, which must be a simple cleavage between the formyl and ethyl groups. In the mass spectrum of methyl ethyl ketone, the base peak is at *m/e* 43, which is due to $CH_3{-}C{\equiv}O^+$, while peaks at *m/e* 57 and 15, which are due to $C_2H_5{-}C{\equiv}O^+$ and CH_3^+, respectively, are also observed. As Table IV shows, independently of the MO theory adopted, the calcaluted ΔH's for above fragmentations decrease as the abundances of ion for corresponding fragmentations increase; this fact accords well with experimental results.

Experimental

All mass spectra were measured with a Hitachi RMS-4 mass spectrometer with ionizing current 62 μA and 20 eV. All samples were obtained from commercial sourcies and were redistilled before measuring their mass spectra.

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[17] C.S. Cummings and W. Bleakney, *Phys. Rev.*, **58**, 787 (1940).

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