NOTE

BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 1873—1874 (1973)

A Theoretical Treatment of the Fragmentation Rules in the Mass Spectrometry of Organic Compounds[1]

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(Received September 27, 1972)

The statistical theory of mass spectra[2-4] (QET) has clearly accounted for the fragmentation of saturated hydrocarbons. This approach, however, seems not to be readily adaptable to a general appreciation of the fragmentation of complex organic molecules, such as those of particular interest to organic chemists. Meanwhile, independently of the theoretical works,[5] organic chemical approaches[6] have provided some simple rules for break-down processes. These rules have been successful in predicting the major fragmentation paths of various compounds.[7] We will here propose a theoretical treatment of the fragmentation rules in terms of the QET and, at the same time, an interpretation of the relationship between the fragmentation rules and the QET.

Theory

According to the Bell[8] and Evans and Polanyi[9] (BEP) principle, the activation energy, ΔE, for a given reaction can be written in a linear form:

$$\Delta E = X + Y\Delta H, \tag{1}$$

where X and Y are constants in the same system and where ΔH is the heat of the reaction.

The QET provides several correlation formulae between the rate constant (k) and the activation energy (ΔE). Among them, for the model composed wholly of harmonic oscillators the general expression[3] in the rate constant is simply:

$$k = \nu\left(\frac{E-\Delta E}{E}\right)^{s-1}, \tag{2}$$

where E is the internal energy, ν is a constant with the dimension of cm^{-1}, and s is the effective number of degree of freedom.

If Eq. (1) holds in the mass-spectral reactions, then the ratio of the rate constants, k_1/k_2, for any two of the fragmentation paths:

$$\begin{tikzcd}
(\mathrm{P{-}Q{-}R})^{\cdot+} \arrow[r, "k_1", "\text{Path A}"'] \arrow[d, "k_2", "\text{Path B}"'] & (\mathrm{P{-}Q} + \mathrm{R})^{\cdot+} \\
(\mathrm{P} + \mathrm{Q{-}R})^{\cdot+} &
\end{tikzcd}$$

will be given by:

$$\frac{k_1}{k_2} = \left(\frac{E'-\Delta H_1}{E'-\Delta H_2}\right)^{s-1}, \tag{3}$$

where $E'=(E-X)/Y$.

Equation (3) indicates that the fracture occurs more predominantly at the position which gives the smallest ΔH; one can predict the most probable position of bond-scission by simply comparing the sum of the total energies of the fragments. That is, if the total energy of the $(\mathrm{P{-}Q} + \mathrm{R})^{\cdot+}$ state is lower than that of the $(\mathrm{P} + \mathrm{Q{-}R})^{\cdot+}$ state, the fragmentation path A will be more important.

Table 1. Total energies of fragments (a.u.)

Fragment	Symmetry[a]	Radical[b]	Ion[c]
CH_3	D_{3h}	−9.1167	−8.6687
C_2H_5	C_s	−17.8337	−17.4580
$CH_3CH_2CH_2$	C_s	−26.5264	−26.1680
$CH_3(CH_2)_2CH_2$	C_s	−35.1888	−34.8077
$(CH_3)_2CH$	C_s	−26.5325	−26.2113
$(CH_3)_3C$	C_{3h}	−35.2423	−34.9561
NH_2	C_{2v}	−12.9377	−12.4110
CH_2NH_2	C_{2v}	−21.5352	−21.2964
CH_3CHNH_2	C_s	−30.2366	−30.0213
$H_2NCH_2CH_2$	C_s	−30.2471	−29.8451
$H_2N(CH_2)_2CH_2$	C_s	−38.9409	−38.5563
$CH_2CH_2CHNH_2$	C_s	−38.9268	−38.7154
$CH_2{=}CH(sp)$	C_{2v}	−16.0884	−15.7406
$CH_2{=}CHCH_2$	C_{2v}	−24.8304	−24.4726
CH_2OH	C_s	−27.5460	−27.2385
CH_3CHOH	C_s	−36.2494	−35.9788
OH	C_∞	−18.9900	−18.3504
CH_3CO	C_{3v}	−34.5607	−34.2921

a) The conformations were all set to be staggered.
b) By the open-shell CNDO/2 method.
c) By the closed-shell CNDO/2 method.

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[1] An MO Approach to the Interpretation of Organic Mass Spectra. II. Part I.; M. Ogata and H. Ichikawa, This Bulletin, **45**, 3231 (1972).

[2] H. M. Rosenstock, M. B. Wallstein, A. L. Wahrhaftig, and H. Eyring, *Proc. Nat. Acad. Sci.*, **38**, 667 (1952).

[3] H. M. Rosenstock and M. Krauss, *Adv. Mass Spectr.*, **2**, 251 (1963).

[4] H. M. Rosenstock, *Adv. Mass Spectr.*, **4**, 523 (1968).

[5] Among theoretical works, the quantum chemical method, based on the relationship between the scission probability and the net-charge density at the highest occupied orbital of the molecule ion, has been most successful in predicting the position of bond-scission (*e.g.*, a) J. Lennard-Jones and G. G. Hall, *Trans. Faraday Soc.*, **48**, 581 (1952); b) K. Hirota and M. Itoh, This Bulletin, **39**, 1406 (1966)). However, the inconsistence of the theory with the experimental results has also been pointed out by some authors (*e.g.*, a) N. D. Coggeshall, *J. Chem. Phys.*, **30**, 593 (1959); b) J. C. Lorquet, *Mol. Phys.*, **9**, 101 (1965)).

[6] F. W. McLafferty, ed., "Mass Spectrometry of Organic Ions," Academic Press, New York, 1963, Chapter 7.

[7] H. Budzikiewicz, C. Djerassi, and D. H. Willians, "Mass Spectrometry of Organic Compounds," Holden-Day, San Francisco, 1967.

[8] R. P. Bell, *Proc. Roy. Soc., Ser. A*, **154**, 414 (1936).

[9] M. G. Evans and M. Polanyi, *Trans. Faraday Soc.*, **32**, 1340 (1936).

TABLE 2. TOTAL ENERGIES OF MOLECULE IONS AND PRODUCED FRAGMENTS (a.u.)

Molecule ion	Total energy[a]	Fragmentation	Total energy	ΔH[b]
$CH_3CH_2NH_2$	−30.8091	1*[c] $CH_3\cdot + CH_2{=}NH_2^+$	−30.4130	0.3961
		2 $CH_3CH_2^+ + \cdot NH_2$	−30.3957	0.4134
$CH_3CH_2CH_2NH_2$	−39.4964	1 $CH_3\cdot + {}^+CH_2CH_2NH_2$	−38.9619	0.5347
		2* $CH_3CH_2\cdot + CH_2{=}NH_2^+$	−39.1301	0.3663
		3 $CH_3CH_2CH_2^+ + \cdot NH_2$	−39.1056	0.3908
$CH_3CH_2CH_2CH_2NH_2$	−48.1846	1 $CH_3\cdot + {}^+CH_2(CH_2)_2NH_2$	−47.6730	0.5116
		2 $CH_3CH_2^+ + \cdot CH_2CH_2NH_2$	−47.7051	0.4795
		3* $CH_3CH_2CH_2\cdot + CH_2{=}NH_2^+$	−47.8227	0.3619
		4 $CH_3(CH_2)_2CH_2^+ + \cdot NH_2$	−47.7454	0.4392
$CH_3CH_2CH{=}CH_2$	−33.9639	1* $CH_3\cdot + {}^+CH_2CH{=}CH_2$	−33.5893	0.3746
		2 $CH_3CH_2\cdot + {}^+CH{=}CH_2$	−33.5706	0.3933

a) Calculated by the open-shell CNDO/2 method.
b) The difference of the energies, $E(\text{radical}) + E(\text{cation}) - E(\text{molecule ion})$.
c) Asterisk indicates the most abundant fragmentation. See Ref. 7.

The adaptability of Eq. (3) may be responsible for the BEP principle. This principle has proved extremely valuable in a variety of chemical reactions.[10] With regard to mass-spectral reactions, some authors[11] have pointed out that the stability of the produced fragments plays an important role in the cleavage reaction. Actually, it should be pointed out that in the establishment of the fragmentation rules,[6,7] the stability of the produced fragments, based on the consideration of the ground-state chemical structure, has always been taken into account. These facts indicate that the fragmentation rules represent the approximate reactions of the electronically ground-state ion,[12] that the BEP principle mostly holds in the mass-spectral reactions, and that, therefore, the fragmentation rules suggest the path with the lower activation energy.

Results

The total energies of several cations and radicals obtained by means of the CNDO/2 method are listed in Table 1. The combination of these fragments would give a variety of fragmentation modes. Shown as examples in Table 2 are ΔH values calculated for the fragments given by the skeletal-bond cleavages of some simple amines and 1-butene, which are selected as model compounds showing the β-bond cleavage.[13] The positive charge should be put on the fragment with the lower I_p value so that the total energy of the system is made as low as possible.

The sum of the total energies of the fragments which are formed by the β-bond cleavage is generally the least, indicating that such a β-bond is most inclined to cleave. Though being qualitative, these results, of course, agree with the experimental results. We believe that the application of this method to various compounds will prove its validity and that it is possible to some extent to predict the quantitative abundance of the bond-scission for the ground-state molecule ion. Finally, though the CNDO/2 method is not well adaptable to the estimation of the total energy, as the results indicate, the method is sufficiently useful for such a qualitative problem as bond-scission.

The calculations were carried out on a HITAC 5020E computer at the Computation Center of the University of Tokyo.

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[10] M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill, New York, 1969, Chapter 8.

[11] a) H. Budzikiewicz, J. I. Brauman, and C. Djerassi, *Tetrahedron*, **21**, 1855 (1965); b) H. Budzikiewicz, C. Fenselau, and C. Djerassi, *ibid.*, **22**, 1391 (1966).

[12] The main reactions of the fragmentation rules mostly give rise to metastable peaks.[7] Such reactions belong to Class I reactions, according to the classification of R. C. Dougherty (*J. Amer. Chem. Soc.*, **90**, 5780 (1968)), which occur with vibrational excitations.

[13] This paper follows the definition by McLafferty.[6]