

QUANTITATIVE EXPLANATION OF THE BOND SCISSION  
OF CYCLOALKANES IN MASS SPECTRA  
WITH THE "MOLECULAR ORBITAL THEORY"

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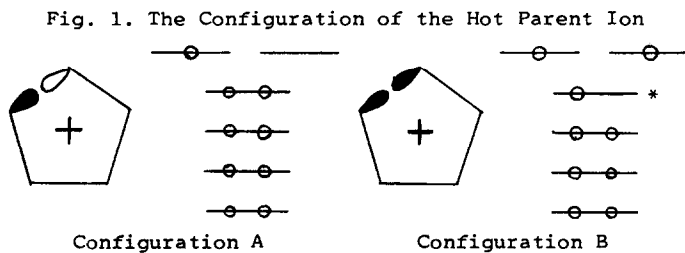
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Scission probabilities of the skeletal C-C bond in the mass spectra could be explained quantitatively on normal alkanes (1), branched alkanes (2), alkyl ketones (3), alkyl amines (4) etc. by applying the LCBO-MO theory.

In order to apply the LCBO-MO theory to mass spectra other than chain compounds, scission probability of the C-C bonds of four cycloalkanes has been calculated by introducing a new assumption on the second bond-scission, which is required necessarily to produce fragment ions.

The method will be explained briefly on cyclopentane. At the moment of electron impact, the hot parent ion produced would take an electronic configuration similar to A shown in Fig. 1, where a bond is opened and the electron loss, i.e., positive charge, is localized on an outermost  $sp^3$   $\sigma$  hybrid orbital. Some of such ions will appear in the

spectra, but the electronic state at the terminal carbon atom will turn into a  $sp^2 \pi$  hybrid orbital. Besides, the hot parent ion will take mainly another configuration B, where the electron loss is distributed over all the bonds, and the two highest levels correspond to the two non-bonding electrons. Therefore, the probability of the second bond-scission will be given in proportion to the positive charge density at the level shown by asterisk in Fig. 1 ("new assumption").



The positive charge density at the energy level in problem can be determined by the expanding coefficients of the molecular orbital at the highest orbital of the secular equation (1) as a result of simple reasoning.

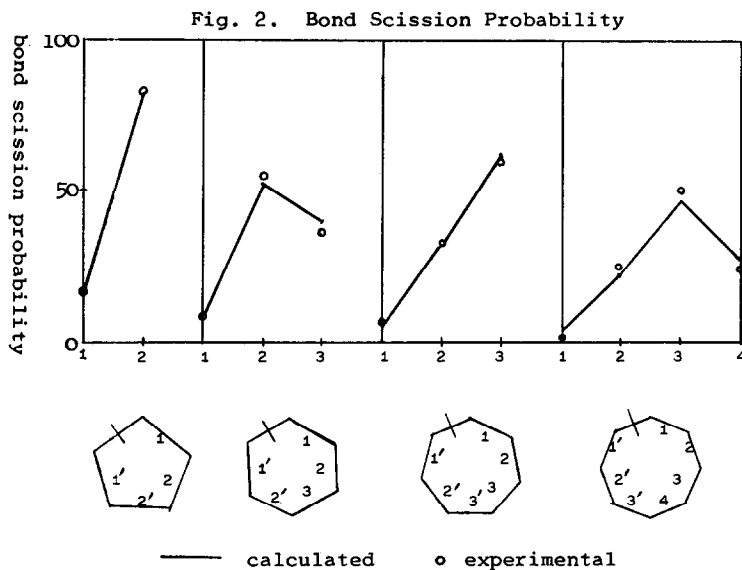
$$\begin{vmatrix} \lambda+m_1 & 1 & 0 & 0 \\ 1 & \lambda & 1 & 0 \\ 0 & 1 & \lambda & 1 \\ 0 & 0 & 1 & \lambda+m_1 \end{vmatrix} = 0 \quad (1)$$

In Eq. (1),  $\lambda$  equals to  $(\alpha - E)/\beta$ , where  $\alpha$  and  $\beta$  being coulombic and exchange integrals concerning the C-C bond orbitals except the terminal ones. And the united atom approximation is adopted for the  $\text{CH}_2$  group.

Besides, the exchange integral between the outermost  $\text{sp}^3$  hybrid orbital and the bond orbital with respect to the terminal C-C bond is neglected for the simplicity of calculation, while the coulombic integral of the terminal bond is expressed by  $\alpha + m_1\beta$ , where  $m_1$  is a constant.

By putting  $m_1$  to be 0.8, the scission probabilities of each C-C bond are determined on cyclopentane, cyclohexane, cycloheptane and cyclooctane. The observed values can be determined by analyzing the amount of fragment ions of the mass spectra of these compounds. The procedure is easy, because there are few peaks which must be ascribed to rearrangement peaks and those produced by multiple scission.

The calculated values of the second scission probabilities are compared with the observed ones, and their agreement is satisfactorily good as shown in Fig. 2, where the calculated values are plotted against the bond number, which is explained by the corresponding figure shown below. The degree of agreement does not change so much, even if the  $m_1$  is changed to some extent.



It will be noteworthy that the present result is obtained without any knowledge of  $\alpha$  and  $\beta$  values, and since the same was true for chain alkanes (1), it can be said that the scission probability of the skeletal bond is determined mainly by the structure of the compounds.

In view of the above result, the MO theory is found to be more promising to explain the mass spectra quantitatively.

#### References

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