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APPLICABILITY OF THE MO THEORY PROPOSED BY HIROTA TO FRAGMENT ION DISTRIBUTION AFTER CHARGE EXCHANGE REACTIONS ON ALKANES

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The relation between the distribution of fragment ions and the recombination energy of the incident positive ions after bombardment of a series of n-alkanes with various positive ions has been studied by the use of a double mass spectrometer, TOHOKU CS, and the theory proposed by Hirota was tested.

In 1952, Rosenstock et al.[1] has proposed the quasi equilibrium theory (QET) to account for the mass spectra on dissociation of some alkanes. According to this theory, the molecule-ion produced by electron impact has a lifetime of the order of several vibrations, and the fragmentations arise from competing and successive unimolecular decompositions of the excited molecule-ion. However, the theory was very limited because of too many parameters, as pointed out by several authors.[2)3)4)]

On the other hand, Hirota et al.[5] has developed application of molecular orbital theory to these phenomena. They considered fragment ionization processes on the stabilization of the superexcited molecule, besides the ionization processes proposed by Platzman[6]. According to this assumption, scission probability of the each C-C bond in the parent ion is proportional to the electron density at the bond on the highest occupied molecular orbital of a starting molecule. Hirota has pointed out that the energy range to which the MO theory is applicable is higher than the ionization potential of the molecule (I.P.) plus 10 eV[7].

In this paper we have studied the relation between the distribution of fragment ions and the recombination energy of the incident ions by the use of the charge exchange reactions which did not involve transfer of the momentum. The energy range which was consistent with the MO theory was also determined, firstly for the pure charge exchange reaction in some alkanes.

The charge exchange reactions of various molecules were carried out by the use of a double mass spectrometer, TOHOKU CS[8]. A sketch of the apparatus is shown in Fig.1. The primary ions, produced with a bombarding electron beam (100 V), were accelerated to 800 V, and led into the reaction chamber. Ar^+, Ar^{2+}, Kr^+, Kr^{2+}, Xe^+, Xe^{2+}, CH_2^+, H_2O^+, N_2^+, Cl^+, and He^+ were used as the source of primary ions[9]. The repeller potential in the reaction chamber was about 10 V. The ions produced in the reaction chamber by the charge exchange reactions were drawn into the second analyser system at 3.5 KV, and were detected by the use of an electron multiplier of 16 stages.

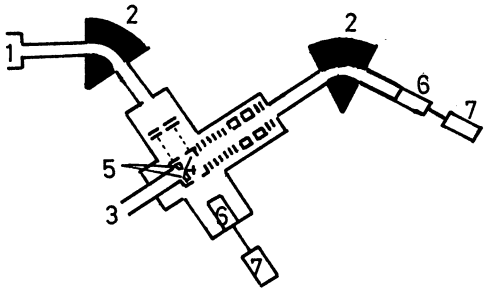


Fig.1. TOHOKU Charge Spectrometer
1: ion source 2: magnet 3: gas inlet
4: reaction chamber 5: repeller
6: electron multiplier 7: counter

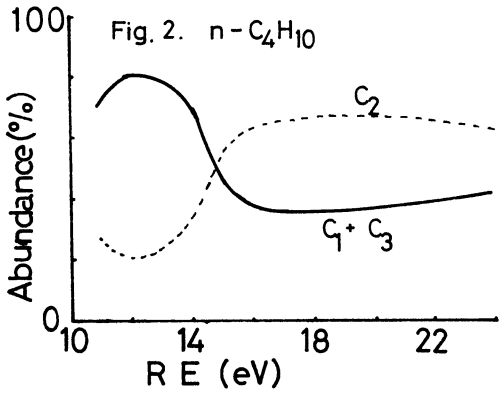
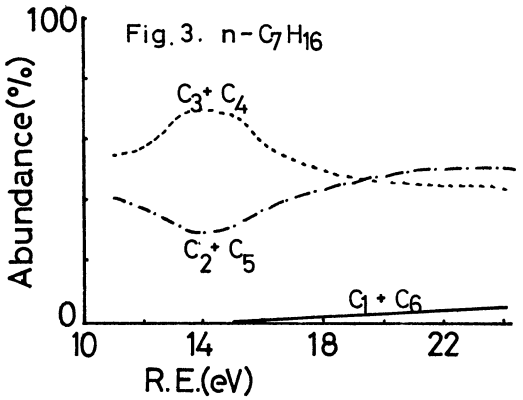


Fig.2. Fragmentation patterns of $n-C_4H_{10}$.



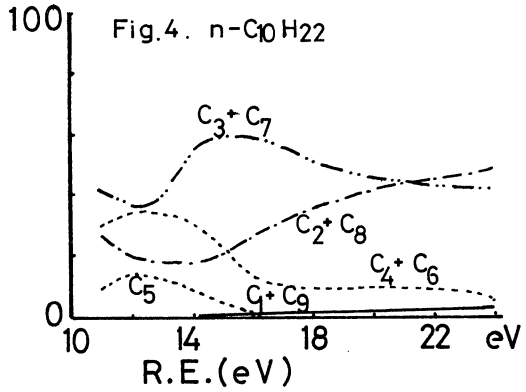


Fig.3-4. Fragmentation patterns of $n-C_7H_{16}$ and $n-C_{10}H_{22}$.

The pressures of the reaction chamber was about 6×10^{-6} mmHg. n-C_4H_{10}, n-C_5H_{12}, n-C_7H_{16}, and n-$C_{10}H_{22}$ were materials of Reagent Grade from Tokyo Kasei Company, and n-C_8H_{18} was spectroscopically pure. n-C_6H_{14} was purified by the use of gas chromatography starting from the material of Reagent Grade.

Fig.2-4 shows the relation between the distribution of the fragment ions and the recombination energy of the incident positive ions after bombardment of n-C_4H_{10}, n-C_7H_{16} and n-$C_{10}H_{22}$ with various positive ions of various recombination energies. All values in these figures are described when total ionization is normalized to be 100 except for the parent ion. In the figures Cn (n=1, 2$\cdots\cdot$) denotes the value $\sum_{m=0}^{2n+1}$ CnHm, summation of abundances of fragment ions having n carbon atoms. Scission probability for each C-C bond is given by Cj + Cn-j where j is the number from the end carbon atom. As studied by Lindholm and his coworker[3], energy imparted to the molecule after pure charge exchange can be described by recombination energy of the incident positive ion (RE) minus ionization potential of the molecule (IP) concerned.

In Fig.5, the predicted values from MO theory by Hirota are compared with the observed values by electron impact[10].

In the figure, scission probability in his theory is replaced by the abundance of ions. (This consideration is necessary to account for our experimental results by his theory).

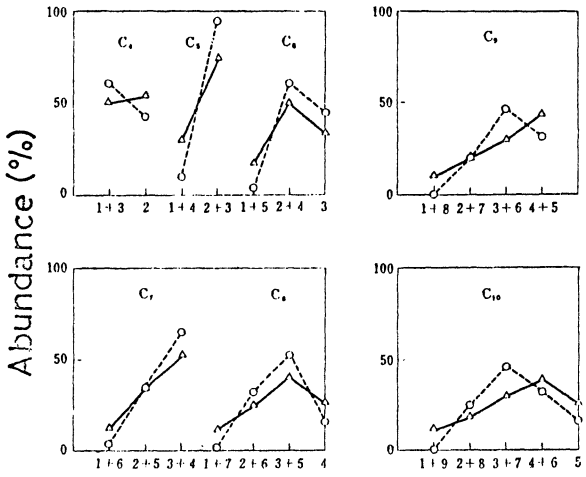


Fig. 5. Comparison of the predicted values by Hirota and the observed values by electron impact[5]

From these results, the energy range to which the MO theory is applicable is shown in Fig.6. The dotted bars for n-C_5H_{12} and n-C_6H_{14} in the figure shown the domain in which the MO theory may be only apparently applicable whereas it is too low in energy to be consistent with Hirota's proposal (I.P + 10 eV).

It is obvious that Hirota's theory has not universal applicability, but is dependent on the alkanes with increasing carbon number.

Inconsistency of the results with MO theory on n-C_4H_{10} and larger n-alkanes than n-C_9H_{20} has been pointed out by several authors[11)12)13)]. This can be explained by the concept of variable energy range according to the carbon number, as described above.

The details of these phenomena and their mechanisms will be reported in the full paper to be published.

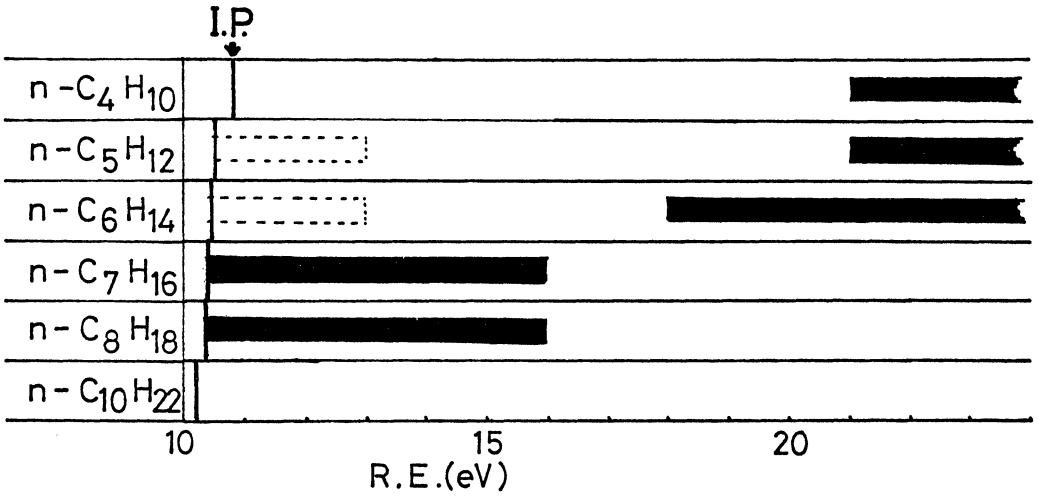


Fig.6. Energy range of fragmentation consistent with MO theory.

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