Fragmentation of *n*-Hexadecane by Electron Impact

Yoshio Niwa and Kozo Hirota

Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka

(Received June 8, 1968)

It has often been concluded¹⁾ that the MO theory for mass spectra is completely inadequate to explain the mass spectra of normal paraffins obtained by electron impact, because it always predicts that bond-scission will occur at, or nearly at, the central bond of the C-C skeleton of higher paraffins; this is contrary to the ordinary mass spectra, where C_3 and C_4 fragments are the most abundant. In order to explain this discrepancy, secondary bond-scissions have been suggested by the present authors.[2,3] The purpose of this communication is to show that this suggestion is plausible.

Generally, fragmentation caused by electron impact is assumed to consist of two kinds of processes:[3] *i. e.*, the primary process, in which the superexcited species takes the main part, and the secondary process, in which the primary product undergoes slow further decomposition due to the localization of excess energy at a particular bond. The primary process is very fast and occurs before the localization of the excess energy, which becomes larger as the ionizing voltage and the temperature of the ionization chamber increase. Therefore, the fragmentation due to the primary process becomes independent of the ionizing conditions.

The MO-theory on mass spectra has to be applied to this primary process, and the statistical theory of Rosenstock *et al.*,[4] to the secondary processes, because the latter theory is applicable to those chemical processes which proceed *via* the activated complex.

Since the secondary processes are suppressed by a decrease in the ionizing voltage and in the temperature of the ionization chamber, one can confirm the above fragmentation scheme experimentally, if both effects on the bond-scission probability are investigated. Of course, the ionizing voltage may affect the secondary process much more than does the temperature. Therefore, the lower the ionizing voltage, the more evident becomes the effect of the temperature.

In order to confirm the above scheme, we investigated the mass spectra of *n*-hexadecane *n*-$C_{16}H_{34}$ in detail. The observed energy-dependence of its fragment distribution indicates that the abundant fragments shift to the C_9 and C_{10} fragments from the C_3 and C_4 fragments with a decrease in the electron energy. The fragment distribution at an ionizing voltage of 10 eV were measured at various temperatures of the ionization chamber. The C_8, C_9 and C_{10} fragments are the most abundant in the range from 100 to 200°C. With a rise in the temperature, the yields of these fragments decrease, while those of the lower fragments increase; C_5 and C_6 fragments come to be the most abundant at 285°C. The mass spectra, however, are practically independent of the temperature when the electron energy is above 15 eV.

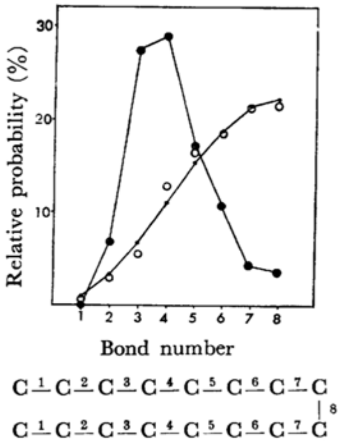

Fig. 1. Relative scission probability *vs.* number of skeletal bond.

—○— 10V, 90°C —•— Calculated
—●— 80V, 200°C

Some of the results are shown in Fig. 1, where the scission probability in % is plotted against the bond number, and where the calculated probability is obtained by the same procedure as was used in a previous study.[2] As expected, the observed values obtained at a low ionizing voltage (*ca.* 10 V) and at a low temperature of the ionization chamber (90°C) coincide well with the calculated values.

---

1) N. D. Coggeshall, *J. Chem. Phys.*, **30**, 595 (1959); Fairbairn, *Nature,* **186**, 152 (1960), *etc.*

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

3) K. Hirota and Y. Niwa, *J. Phys. Chem.,* **72**, 5 (1968).

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