Lecture notes in EI-Mass spectrometry

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1. Basic advise:

1) Identify the mole peak **$M^{+\cdot}$**

2) Nitogen rule: Determine number of N

3) **A+2** elements: **Cl, Br, S, Si**

4) $N_C = 100 \times [M+1]/([M] \times 1.1)$

5) Determine brutto formular

6) Calculate $r + db = N_C – N_H/2 + N_N/2 + 1$
(halogens counts as H)

2. Fragmentation mechanisms in electron impact mass spectrometry (EI-MS).

Introduction: The molecular ion $M^{+\cdot}$ is produced by bombardment of the molecule M in gas phase by 70 eV electrons produced by an electrical wire (filament) (see eq. 1)

$$M + 2e^- \rightarrow M^{+\cdot} + 2e^- \qquad (1)$$

During 1950-80 an important discipline in mass spectrometry research was to investigate the fragmentation mechanisms of $M^{+\cdot}$ ions and establish the rules of EI-MS fragmentation. The leading scientist in this field was Fred McLafferty who together with Frantisek Turecek has written a very famous text book: "Interpretation of Mass spectra "4. Ed. 1993. This textbook is used in many MS courses around the world including the Universities of Copenhagen and Århus. The description of the fragmentation mechanisms taught by Pavia, Lampman and Kriz: "Introduction to Spectroscopy" 3. ed. 2001 is slightly different compared with the world wide accepted McLafferty mechanisms. In the 4. ed. from 2009, however, the authors have adapted the McLafferty mechanisms, which give a better understanding of the fragmentation reactions than the description in 3.ed.

McLafferty formulation: The electrons in an organic molecule are located either in sigma bonds (σ) like C-C, C-C or C-O; π–bonds like C=C, C=O or in benzene rings and lone pairs (n) located on hetero atoms X = N, O, S; and halogens Cl, Br, I. The lone pair electrons (n) have the highest energy whereas the σ electrons have the lowest energies. The ionization energies (IE) of the lone pair electrons are the lower than the π and σ IE values and the lone pair electrons are therefore the easiest electrons to ionize in the molecule. The electrons in a molecule are in general ionized according to the following sequence: $n > \pi > \sigma$.

The 2-butanol molecule i.e. is ionized at the lone pair of the oxygen atom as shown in Figure 1.

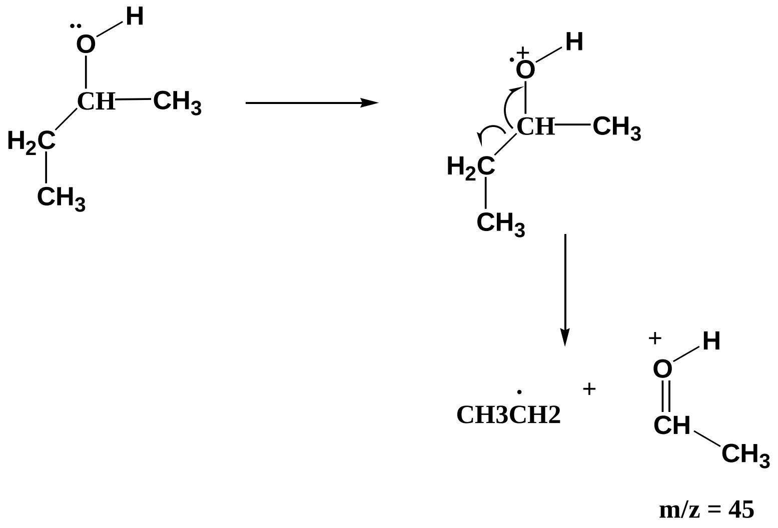

Figure 1 α-Fragmentation of 2-butanol molecule

After the ionization at the oxygen atom a C-C_α bond is cleaved as shown in Figure 1. The C-C_α bond contains two electrons. One of these electrons moves towards the oxygen radical site forming a C=O double bond. The movement of the electrons are shown by a fish hook arrows. The fish hook arrow symbolize the movement of one electron whereas the full arrow indicates the movement of an electron pair. Two products are formed a radical and a cation and only the charged cation is detected in the mass spectrum. The other C_α-C bond may also be cleaved by a α-cleavage forming m/z = 57 ion and a $CH_3^{\cdot}$ radical.

Four mechanisms: McLafferty operates with four fragmentation mechanisms **σ**, **α** , **i** and **rH**
The σ mechanism is responsible for the fragmentation pattern in alkanes as illustrated in Figure 2
The α-clevage is illustrated for alchohols, amines and ketones (Fig. 3-5). The β cleavage is only seen in ethers and for alkyl halides. (Fig. 6) Finally the rearrangement of a H (the McLafferty) mechanism is illustrated in Fig. 7 with a ketone as example.

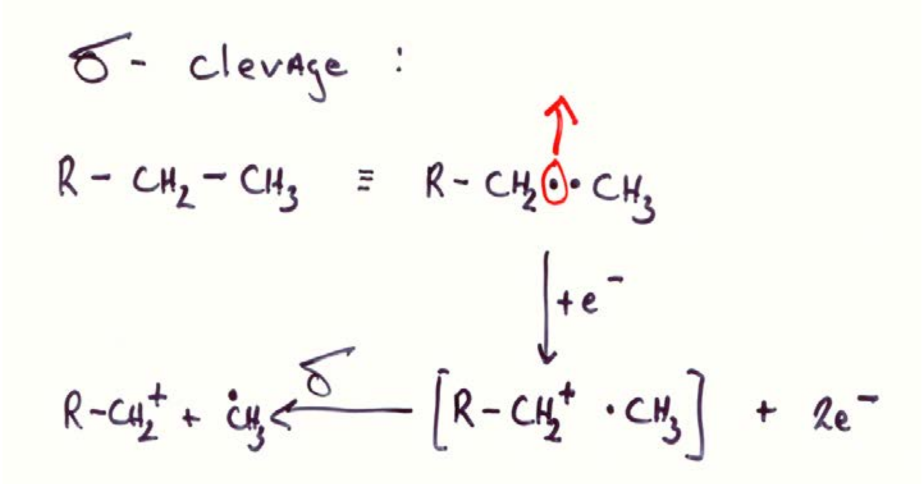

Figure 2 σ-clevage of alkanes.

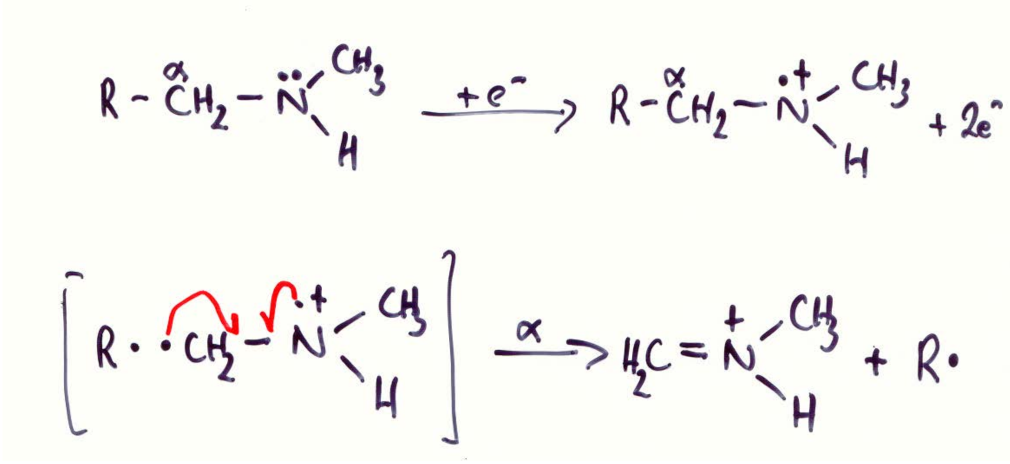

Figure 3 α-cleavage of an amine

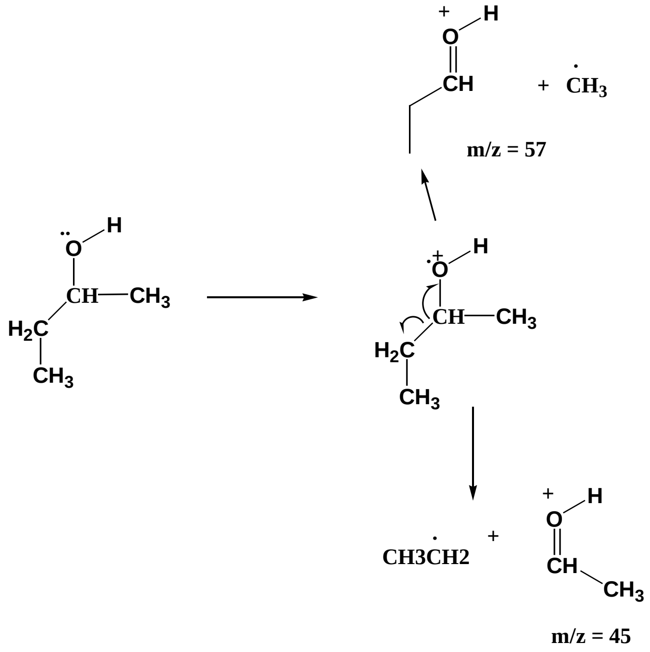

Figure 4 α-cleavage of an alchohol

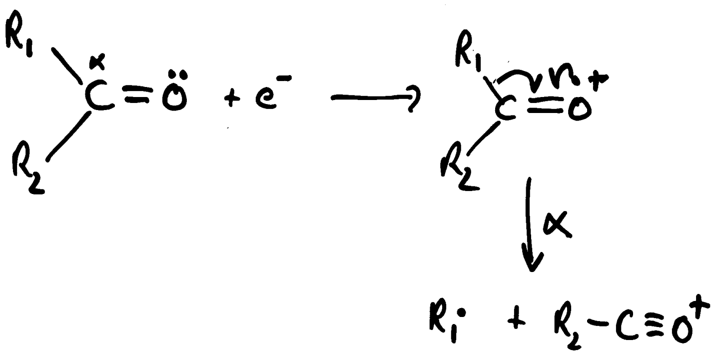

Figure 5 α-clevage of a ketone

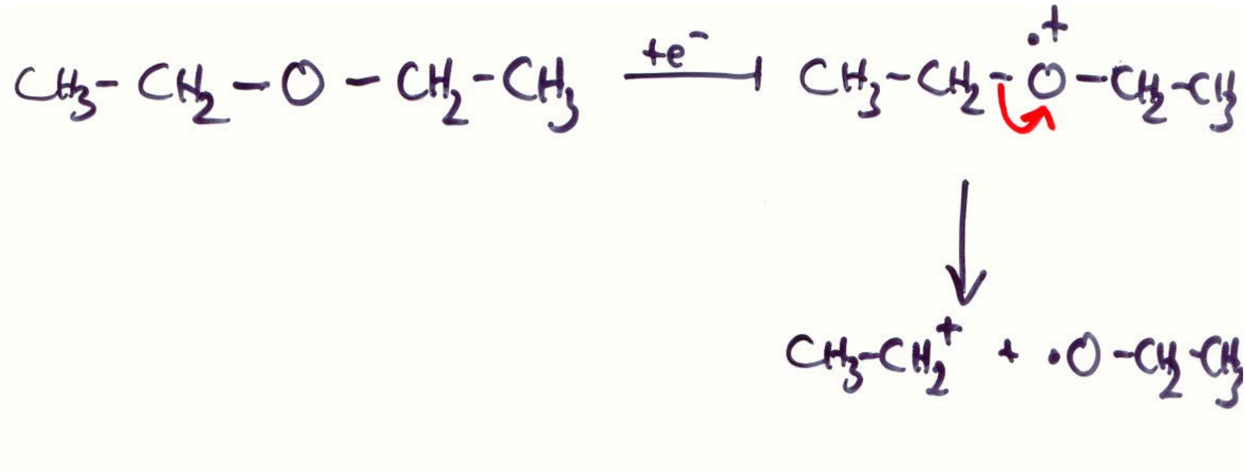

Figure 6 β cleavage of an ether

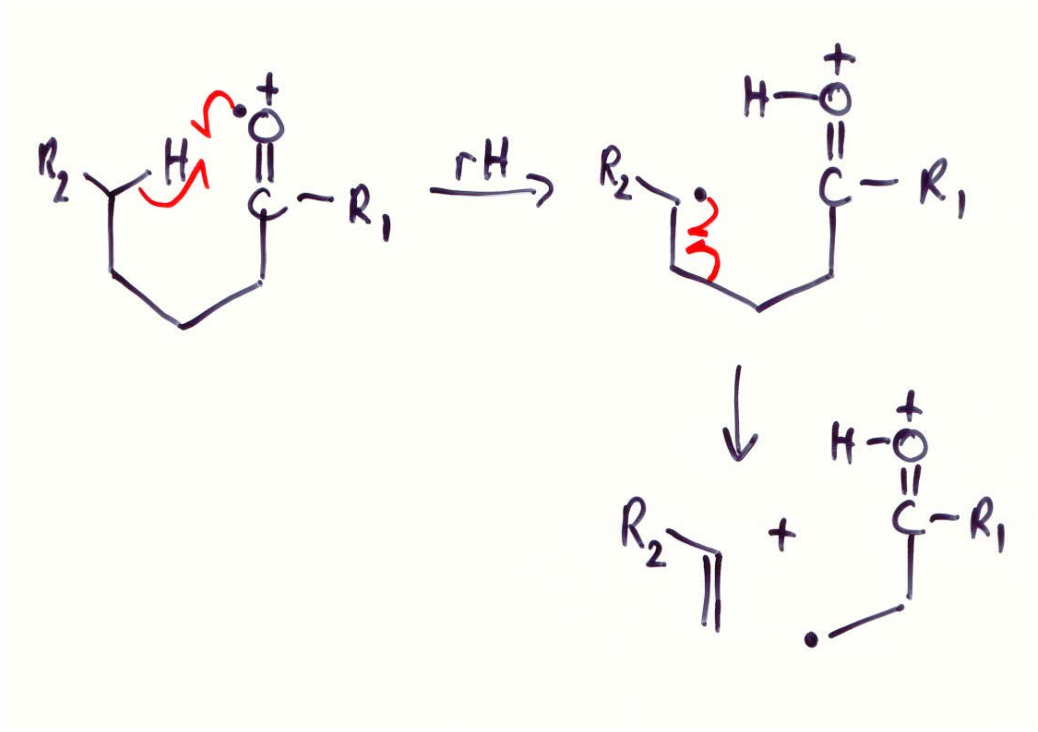

Figure 7 Rearrangement of a H-atom denoted **rH** or McLafferty rearrangement. In H atom is transferred to the carbonyl oxygen through a 6-membred transition state (TS). Observe that the H atom will be quite close to the oxygen atom in TS.

In the following the McLafferty formalism is used to discuss the mass spectra of aliphatic compounds containing a double bond, aldehydes, esters, and carboxylic acids:

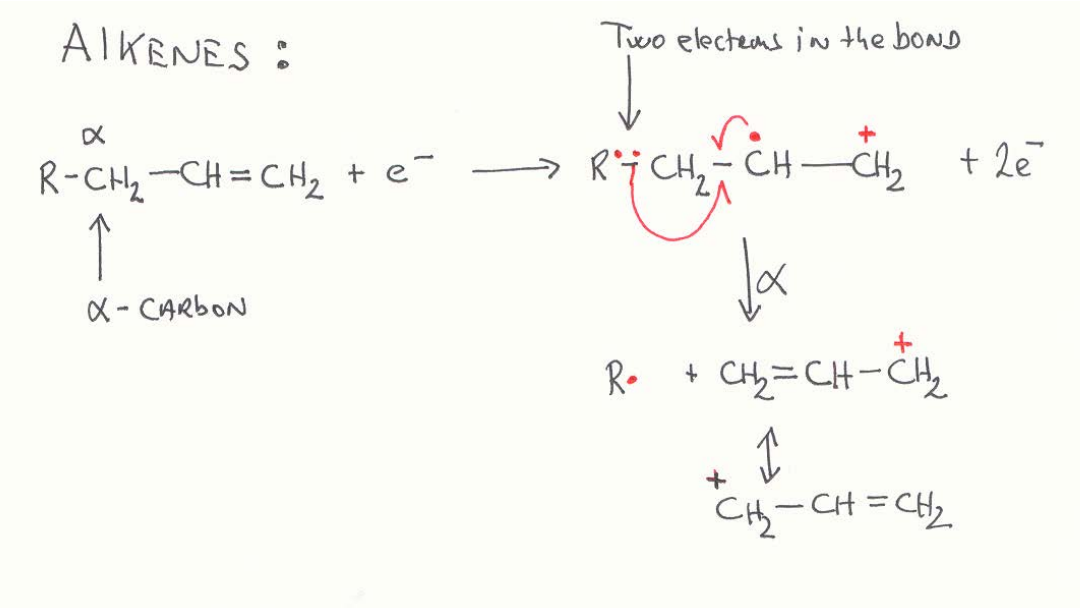

Figure 8 α-clevage of alkenes.

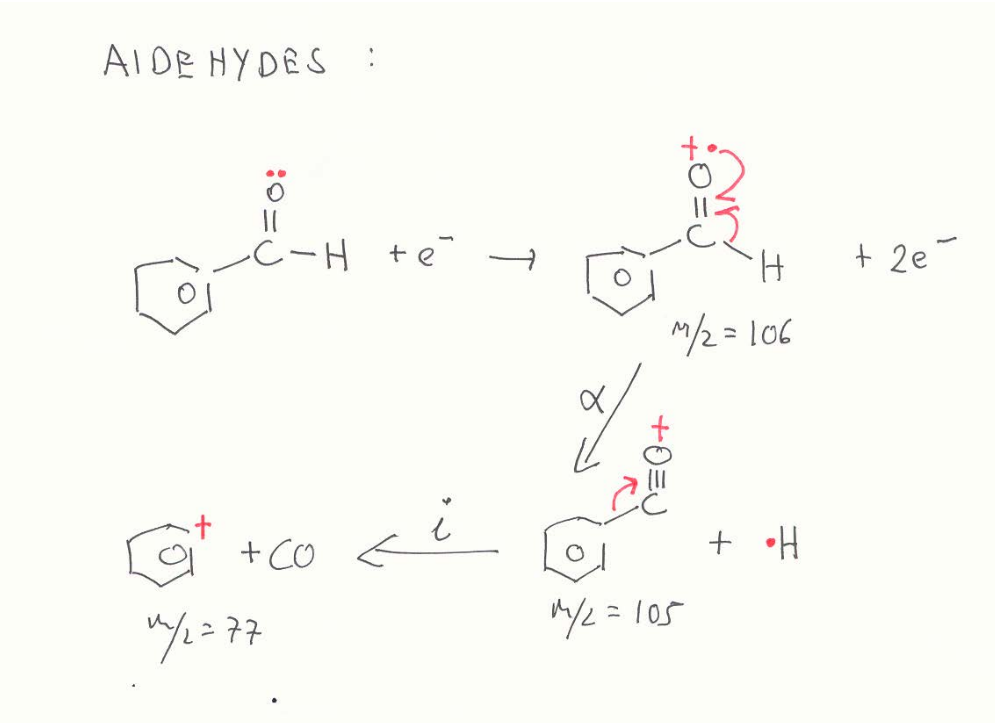

Figure 9 Fragmentation of aldehydes.

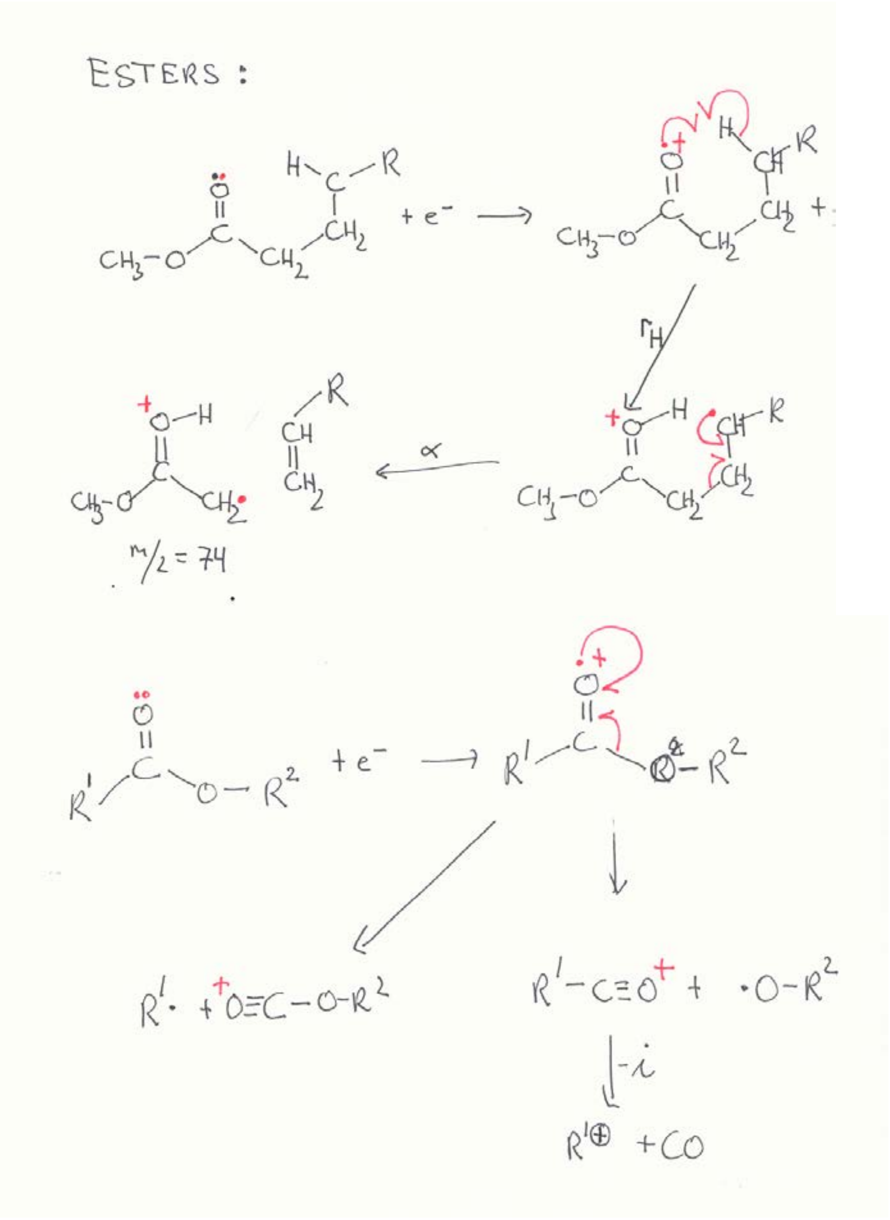

Figure 10 Fragmentation of esters.

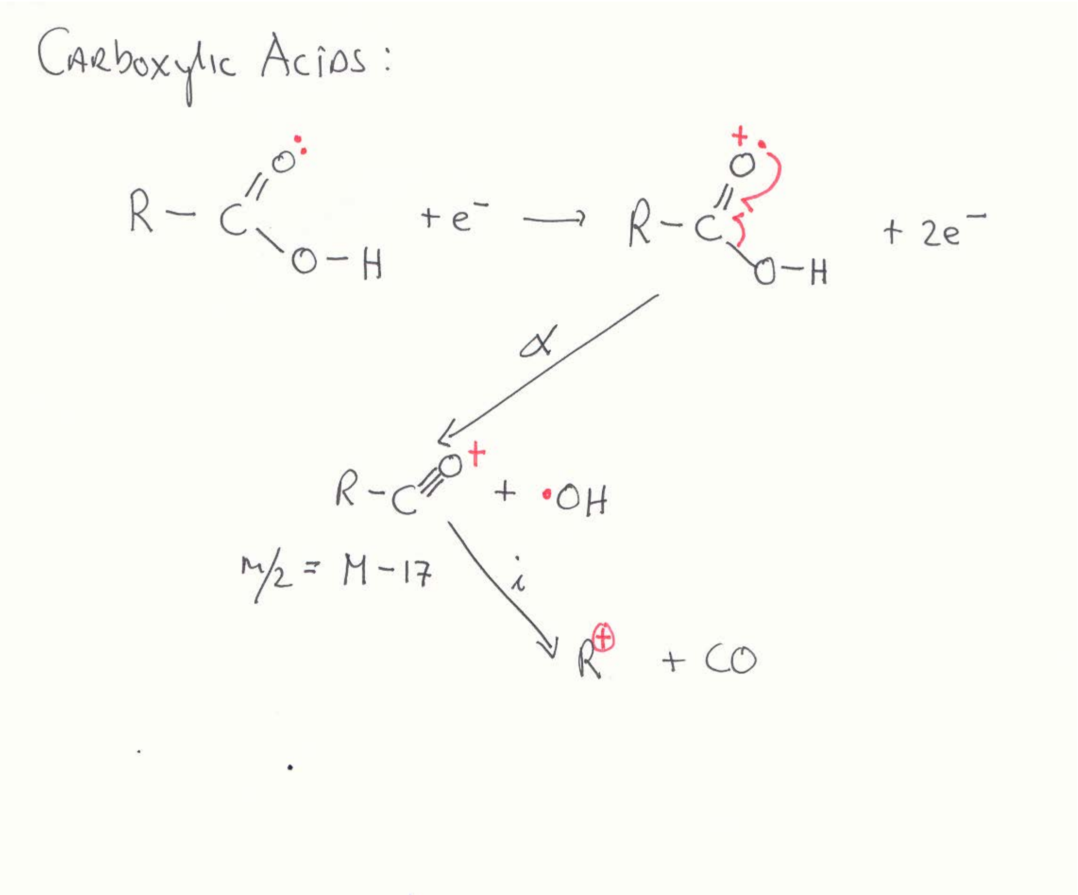

Figure 11 Fragmentation of carboxylic acids.