

IONIC FRAGMENTATION OF ORGANOCHLORINE COMPOUNDS BY ELECTRON IMPACT ION SOURCE OF MASS SPECTROMETER

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ABSTRACT

Molecules, when ionized, can be controlled by electric fields and / or magnetic, and both can be kept constant or varied rapidly. This undoubtedly is one of the most relevant with respect to a mass spectrometer. Among the various existing methods of ionization, the ionization mode electron impact stands out in the application for determination of volatile organic compounds. This mode of ionization is the collision of electrons generated from a heated filament, which are issued at a voltage of constant intensity of 70 eV and clash against the molecules of the analyte gas, causing a destabilization in the electronic layer of the same, possibly causing the ejection of a secondary electron from the electronic layer of the compound, which in turn, tends to clash with a second molecule, resulting in a second positive ion and so on. This mechanism apparently chaotic, however, does not occur randomly, but governed by a series of molecular fragmentation rules that explain the greatest abundance of ion fragments in the mass spectrum generated from a given analyte. The fragmentation of molecules in a mass spectrometer can be provided according to some rules of molecular fragmentation. Therefore this paper presents some suggestions for mechanisms of fragmentation for the compound heptachlor, chlordane and pentachlorophenol when subjected to the source of electron impact ionization, the ionic fragments different reasons and their mass / charge. The work also aims to contribute with regard to the elucidation of their isotopic abundances.

1. INTRODUCTION

The interest in elucidating the structure of matter has always been inherent in man. The story presents its first reports in about 500 b.C. by Greek philosophies, his thoughts about the Aristotelian theory of four elements, opposed to the atomistic theory of Leucippus and Democritus. These ideas are beginning to be put to the test already in the eighteenth and nineteenth centuries, through the evolution of atomic models and in parallel, technological advances notorious for its time. F.W. Aston, through the creation of the mass spectrograph found the cause of differences in mass number of non-radioactive isotopes. Introducing the neon gas on his instrument, he observed four lines corresponding to reasons mass/charge ratio of 10, 11, 20 and 22. The first pair corresponds to doubly charged ions and the second pair, the ions monoionized. Also A. J. Dempster, working in the U.S., has developed its mass

spectrometer and was able to accurately measure isotopic abundances of several elements. The first experimental analysis of organic compounds was conducted in 1940 by Hoover and Washburn who analyzed a mixture of hydrocarbons [1]. From these pioneering experiences, the science of mass spectrometry began, emerging with instruments sector and later with the development of quadrupole instruments, time of flight, cyclotronic resonance, among others [2-4].

One thing to stand out in relation to mass spectrometers is the way in which the analyte molecules are ionized, since they must be ionized by electromagnetic fields, whether static or dynamic. The various existing ionization methods have been developed with the aim of expanding the range of compounds that could be taken and ionized gas phase, regardless of physical form or characteristic molecular weight volatiles, etc. [5-13]. Among the main existent methods, we highlight the impact ionization of electrons is an important method of ionization used in the analysis of organic molecules. Figure 1 schematically represents a source of ions by impact of electrons coupled to a two-dimensional quadrupole mass analyzer.

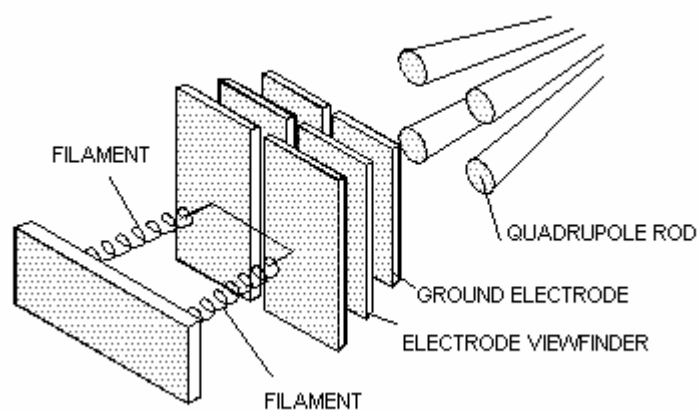


Figure 1. Schematic representation of ion source by impact of electrons coupled to a two-dimensional quadrupole mass analyzer.

Sources of electron impact ionization have a filament, usually tungsten or rhenium, which warmed vacuum of 10^{-5} to 10^{-6} mbar emits electrons that are accelerated to the ionization chamber by a potential difference of 70 eV, although different ionization energies can be used (Figure 1) [14-17]. The electron beam produced is then collimated through a slit of the ionization chamber and collides with the molecules vaporized from the sample [18]. When the neutral gas molecules interact with the beam, an electron is removed from the molecule with the concomitant deposition of more than 100 kcal of internal energy within the new radical cation produced. When the excess internal energy is redistributed through the molecular ion, enough excitement will be deposited in the various vibrational degrees of freedom, resulting in cleavage of a connection [19]. In the process of ionization for electrons

impact, positive and negative ions are formed, and both has similar settings since they have unpaired electrons. However the yield in the formation of positive ions is about 10⁴ times greater than for negative ions, and for this reason, studies are generally focused on positive ions in electron impact mode [20].

2. FRAGMENTATION

The conventional organic chemical reactions is initiated by chemical reagents, heat or radiant energy. Mass spectrometry in turn, deals with the effects of the bombardment of organic molecules with a beam of electrons ionized at a vapor pressure of about 5.10 mmHg, hence it is of unimolecular processes. In this process, only a small part of the energy required for fragmentation is transferred as a result of the impact [21].

3. THE FORMATION OF THE MASS SPECTRUM

A mass spectrum can provide various types of information as to the nature of a chemical compound. This stems from the fact that a graph of mass spectrum in which the abscissa indicates the ratio mass/charge and ordered indicates the relative abundance of isotopes. The spectrum provides isotopic information of the elements, structural information arising from the study of fragments of the molecule, and in some cases, molecular weight if the molecular ion is present. However, some of this information is not used by analysts who, in many cases, seek only the molecular ion. However, depending on the stability of the molecule under the bombardment of energetic electrons, it is not possible to observe it [22].

It is noteworthy that the simple verification of data on the agreement of the spectra in the standard existing databases in spectrometric libraries and spectrum of target molecule, can be misleading, because the mass spectrum of the target molecule may not be present in the database or misidentifications may occur due to the presence of interfering molecules. Preliminary data such as the origin of the sample, sampling, extraction, among others, are often critical in identifying the compound of interest.

The spectral lines in a mass spectrum correspond to fragmentation reactions of molecules subjected to electron bombardment. Figure 2 illustrates any fragmentation reactions that often occur in the electron impact source.

Formation of molecular ion



Fragmentation

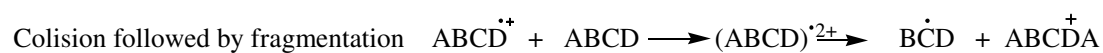
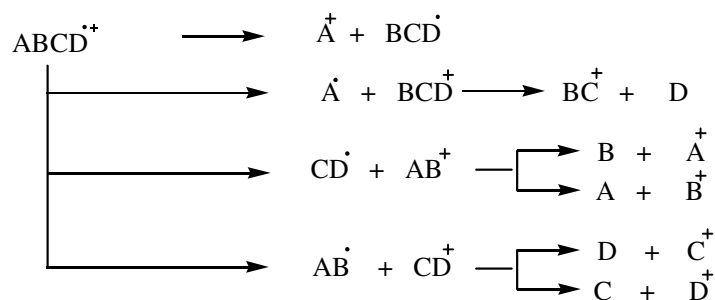


Figure 2. Some reactions of fragmentation on the source of electron impact [23].

The mass spectrum presents a bar graph or in tabular form. Consider, for example, the mass spectrum of organochlorine chlordane, $C_{10}H_6Cl_8$ (Figure 03).

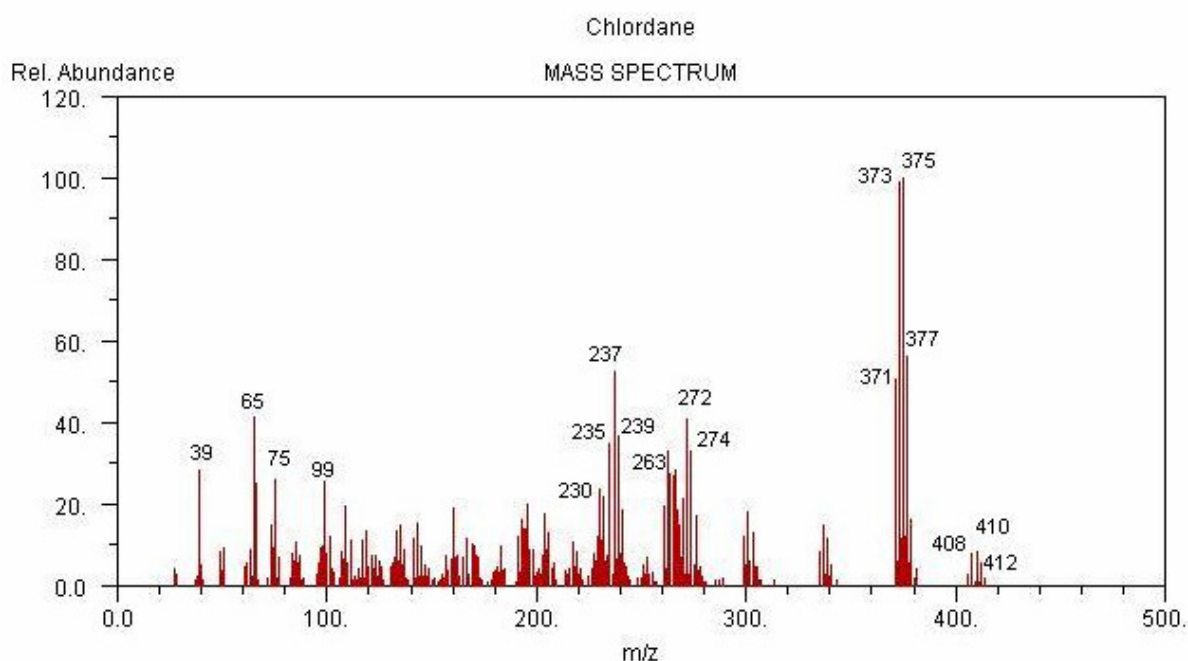


Figure 3. Mass spectrum of heptachlor in the way of impact ionization of electrons with energies of 70 eV [24].

The peak base, defined as the most intense peak of the mass spectrum, is assigned 100%

intensity, with the aim of normalizing the spectrum. The intensity of all other ions is a function of spectral line. Table 1 provides data relative intensity of ions from the mass spectrum of chlordane.

Each process of fragmentation, at least theoretically, may have the positive charge remaining in the same part of the molecule in which it originally resided (charge retention) or there may be movement of charge to a new site in the molecule with loss of the original site of ionization (migration of charge). Depending on the product ion, ions with an odd number of electrons and ions with an even number of electrons perform it in different ways, some involving the movement of a single electron and others with movement of a pair of electrons. Thus we use the notation:

 For the movement of a pair of electrons

 For the movement of a single electron

Table 1. Relations dados on the chlordane mass spectrum obtained in the ionization for electrons impact mode.

Peak(m/z)	Relative Intensity
39	28.4
65	41.4
75	26.0
99	25.6
230	23.7
235	35.3
237	52.6
239	36.7
263	33.0
272	40.9
274	33.0
371	50.7
373	99.1
375	100

4. ISOTOPIC ABUNDANCE OF SOME ORGANOCHLORINES OBSERVED IN THE MASS SPECTRUM

Generally, even in mass spectrometers with low resolution, it is possible to infer from the mass spectrum on the number of atoms of a given element in a compound, considering its isotopic distribution. However the diagnostic value of the transaction is not great, either because the intensity of the molecular peak or fragment is reduced leading to inaccuracy in reading, whether in light of certain masses resulting from ion-molecule reactions, such as the addition of a hydrogen atom ion quasi-molecular or pseudo-molecular ion. In practice, the isotope analysis for the derivation of the molecular formula becomes important only in the case of elements that have relatively abundant isotopes, such as Si, S, Cl and Br. Their isotopic abundances can be checked in Table 2.

Table 2. On natural isotopic abundance of common elements.

Isotopes	Mass, M	%	Mass, M+1	%	Mass, M+2	%
H	1,007825	100	2,014102	0,016	-----	-----
C	12	100	13,003354	1,08	14,00324	0,05
N	14,003074	100	15,000108	0,38	-----	-----
O	15,994915	100	16,999133	0,04	17,99916	0,2
F	18,998405	100	-----	-----	-----	-----
Si	27,976927	100	28,976491	5	29,973761	3,31
P	30,973763	100	-----	-----	-----	-----
S	31,972074	100	32,971461	0,78	33,965896	4,39
Cl	34,968855	100	-----	-----	36,965896	32,7
Br	78,918348	100	-----	-----	80,916344	97,5
I	126,90435	100	-----	-----	-----	-----

Compounds that have the element chlorine in their structure, present in their mass spectrum, M +2 peaks with significant intensities, due to its natural isotopic abundance of ³⁷Cl isotope [21].

The chlordane, for example, is an organochlorine molecular weight 405.79 g / mol. In its mass spectrum with electron impact ionization (Fig. 3), one can observe that the molecular ion m / z 408 has low intensity, as well as isotopes of m / z 410 in / z 412. This can be explained by the high intensity of a fragmentation voltage of 70eV, the existing mode of electron impact ionization. The difference observed between the two units mentioned peaks can be explained by the presence of M +2 peaks, with ³⁷Cl, significant isotopic abundance. The structures related to these peaks, where they demonstrated their atomic masses, are suggested in Figure 4.

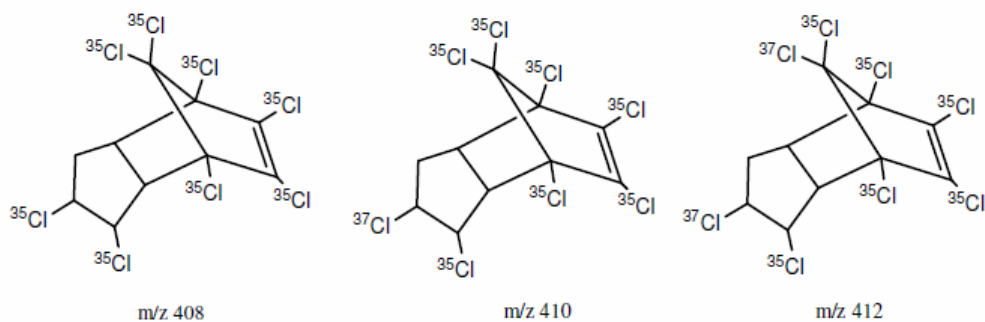


Figure 4. Structures suggested for the isotopes of the ion-molecule chlordane.

The cis/trans chlordane isomers show identical mass spectrums, obviously, they are even compost, however, structural differences confer in mass spectrum, different relative intensities in fragments-ions, that can be conferred in figure 5 and 6.

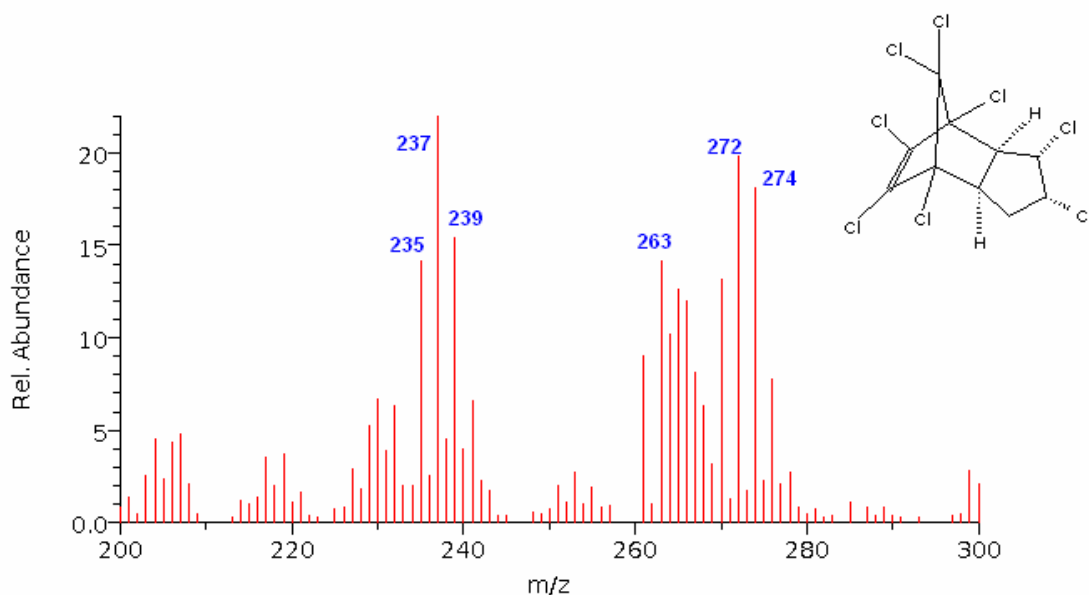


Figure 5. Mass spectrum increased, with interval of m/z 200 to 300 of cis-chlordane and

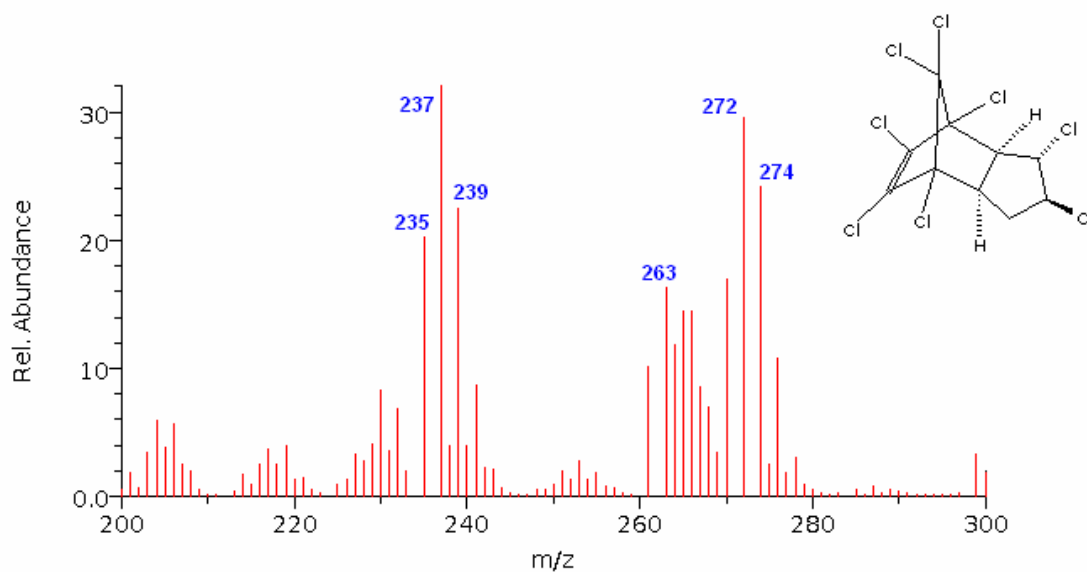


Figure 6. Mass spectrum increased, with interval of m/z 200 to 300 of trans-chlordane

The different intensities mentioned above can be more clearly understood by analyzing the tables 3.a and 3. b.

Table 3. Relative intensity of some ions of the mass spectrum of the (a) cis-chlordane and (b) trans-chlordane.

a		b	
Ion	Relative intensity	Ion	Relative intensity
235	14	235	20
237	22	237	31
239	15,5	239	21
263	14	263	16
272	20	272	25
274	18	274	24

It's worth noting that the ^{37}Cl isotope present in the structures, can take any of the positions for the chlorine atom. The same pattern can be observed isotopic abundance of heptachloro in the molecule (Figure 7).

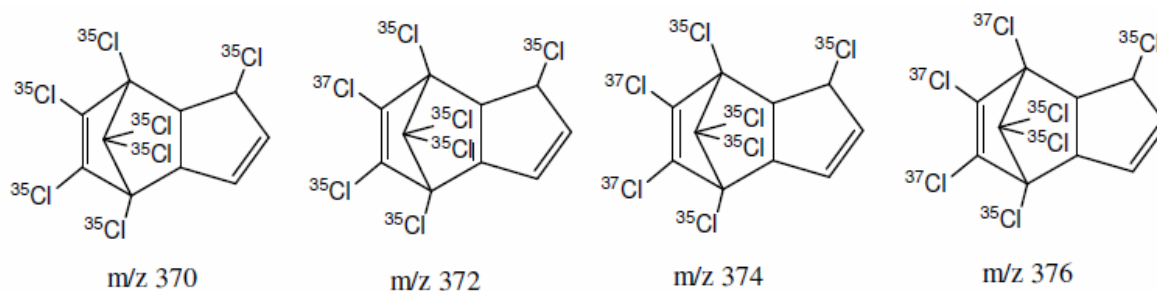


Figure 7. Suggested structures for the isotopes of the ion-molecule heptachlor

This compound has molecular weight 369.82 g / mol. In its mass spectrum with electron impact ionization (Fig. 8), we see that the molecular ion m/z 370 also shows low intensity, as well as isotopes of m/z 372, m/z 374 and m/z 376.

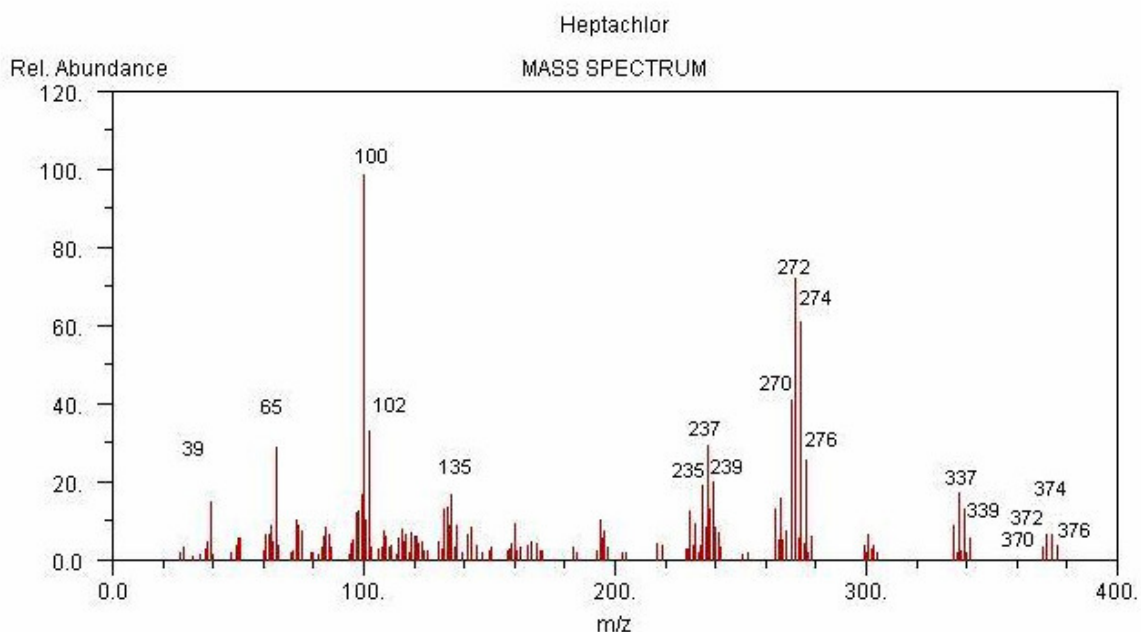


Figure 8. Mass spectrum of heptachlor for ionization by electrons impact with energies of 70 eV [24].

In the case of pentachlorophenol, molecular weight 263.85 g / mol, the difference of two units between the peaks $M+2$ m/z 264, m/z 266, m/z 268 in m/z 270 can also be observed (Figure 9), but the difference is visible in the patterns of intensity of molecular ions of this molecule, compared to the previous ones. This can be explained by the presence of aromatic ring in its structure, since this gives great stability to the molecule.

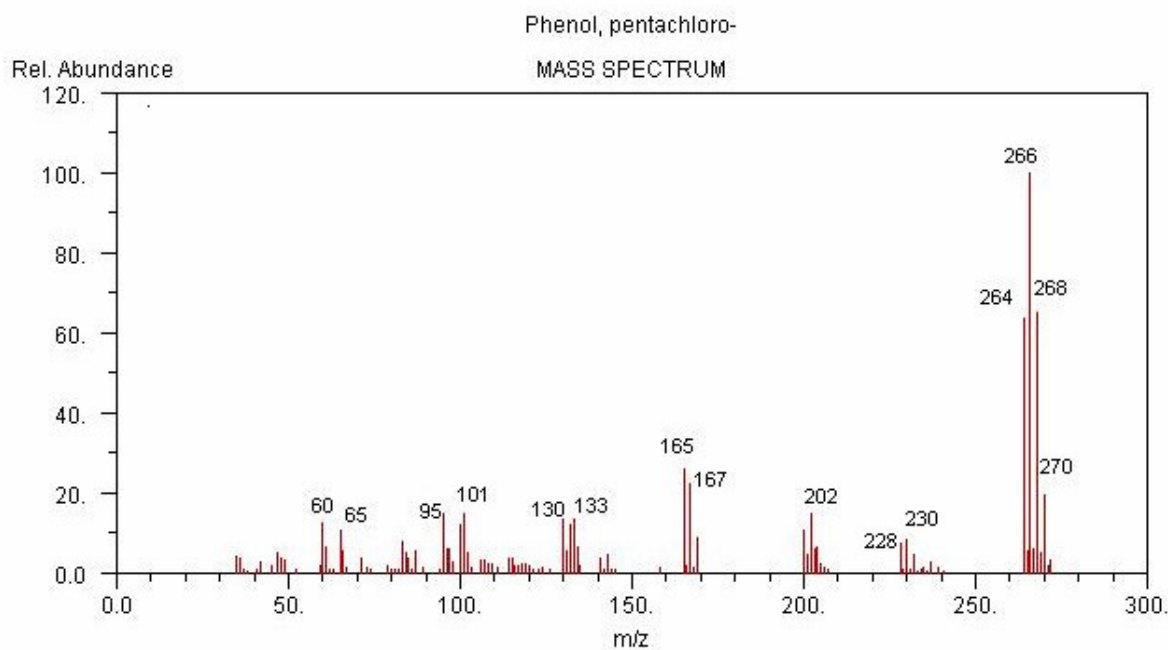


Figure 9. Mass spectrum of pentachlorophenol for ionization by electrons impact with energies of 70 eV [24].

Figure 10 shows the molecular structures related to the isotopes of pentachlorophenol.

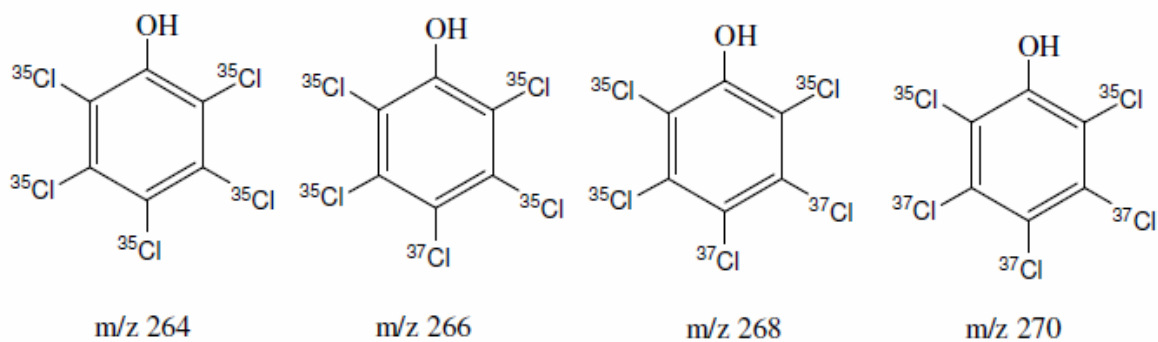


Figure 10. Suggested structures for the isotopes of the ion-molecule pentachlorophenol

5. SITE OF INITIAL IONIZATION

The most vulnerable electron to ejection in molecular orbitals are those of higher energy. In fact, the ionization potential of the molecule is defined as the energy required to completely remove these electrons from a molecule [25]. These orbitals also give rise to the weaker links in the molecules. The energies are similar to those relating to the electronic transitions that affect the ultraviolet spectrum. The molecular orbitals associated with single bonds are designated as sigma orbital (σ) and their corresponding electrons are called electrons σ .

Already, the double bond in an organic molecule contains two types of molecular orbitals: an orbital α , corresponding to a pair of bound electrons and a molecular orbital associated with the other pair. In addition to the orbital σ or π , various organic compounds have unbound electron. These unshared electrons are designated by the letter n. The ionization is usually favored on the order of electrons σ , and n^{23} .

6. SOME SUGGESTIONS FOR FRAGMENTATION MECHANISMS OF ORGANOCHLORINES IN THE SOURCE OF IONIZATION BY ELECTRON IMPACT

6.1. Inductive cleavage (i)

In a single bond, the electron pair shared by different atoms are more strongly attracted by the more electronegative atom pair [26]. The induction charging can occur in molecules with odd number of electrons, as with an even number of electrons. The reactions virtually indistinguishable by mass spectrometry because they lead to the formation of neutral and radical fragments, respectively, both without load and therefore not subject to the action of the electromagnetic field.

The sigma bond cleavage of C - Cl is governed by the inductive effect caused by the electron cloud of the chlorine atom.

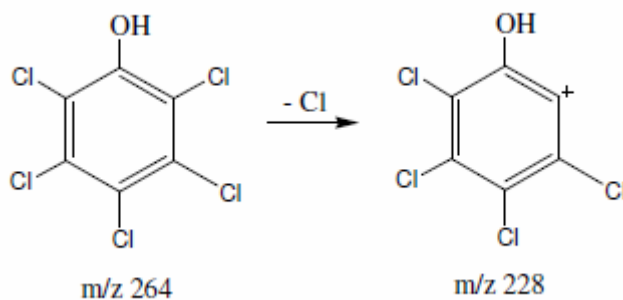


Figure 11. Fragmentation mechanism of Pentachlorophenol by inductive cleavage.

6.2. Decomposition retro Diels-Alder

The reaction is the Diels-Alder reaction between a conjugated diene and a compound containing a double bond, called dienophile. In this reaction, two new connections are formed at the expense of two σ bonds of the diene and the dienophile [27]. In the mass spectrometer observed the reverse reaction [28]. In general the spectra by electron impact of insecticides have polycyclo-dienochlorinated main fragments ions corresponding to the retro Diels-Alder process, with preliminary or subsequent loss of Cl and HCl [29]. This mechanism can be observed in the fragmentation of the molecule that form of heptachlor-ion fragments of m/z 100 and m/z 270 (Figure 12). The related peaks can be observed in Figure 8.

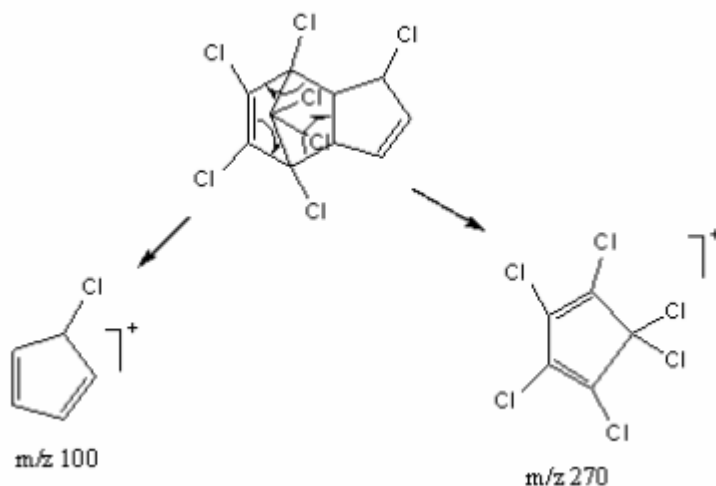


Figure 12. Mechanisms of fragmentation of the ion-molecule heptachlor, a retro Diels-Alder.

The same is true for chlordane molecule with the formation of fragments of m/z 270 and 135 (Figure 13). Their respective peaks can be observed in Figure 3.

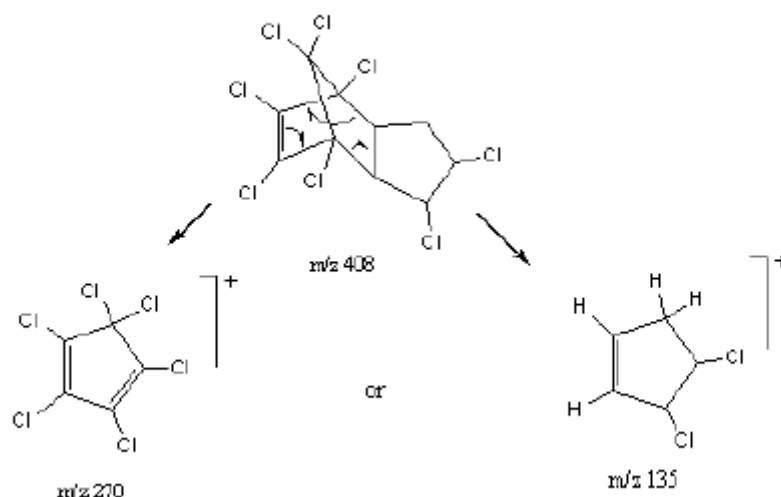


Figure 13. Mechanisms of fragmentation of the ion-molecule heptachlor, a retro Diels-Alder.

6.3. Rearrangement

Pentachlorophenol is a molecule of great stability guaranteed by its aromaticity. Thus, as the peaks relating to ion-fragments in the spectrum is low intensity. The figure shows the fragmentation mechanism for the fragment ions of m/z 170 and 94 (Figure 9). This mechanism starts with a gap α , as a consequence of a strong trend of matching electronic, the electron is donated to form a new connection with an adjacent atom.

The cleavage of α begins in the radical site [30]. This process is accompanied by the breaking of another link to the atom α as in the pentachlorophenol molecule, in which the oxygen atom forms a second bond with the carbon atom at the expense of the breakdown of carbon-carbon sigma bond exists, defined as alpha cleavage (Figure 14.a).

Still in the 14.a figure we can observe the rearrangement of the aromatic system, seeking to stabilize. Tetravalence due to the carbon structure 14.b is not possible electronically, then going instantly to the rearrangement of the π bonds, a carbon migration to electronic device. The structure 14.c illustrates another arrangement of π bond and then the cleavage of which leads σ fragments of m/z 94 and 170 (Figure 14.e).

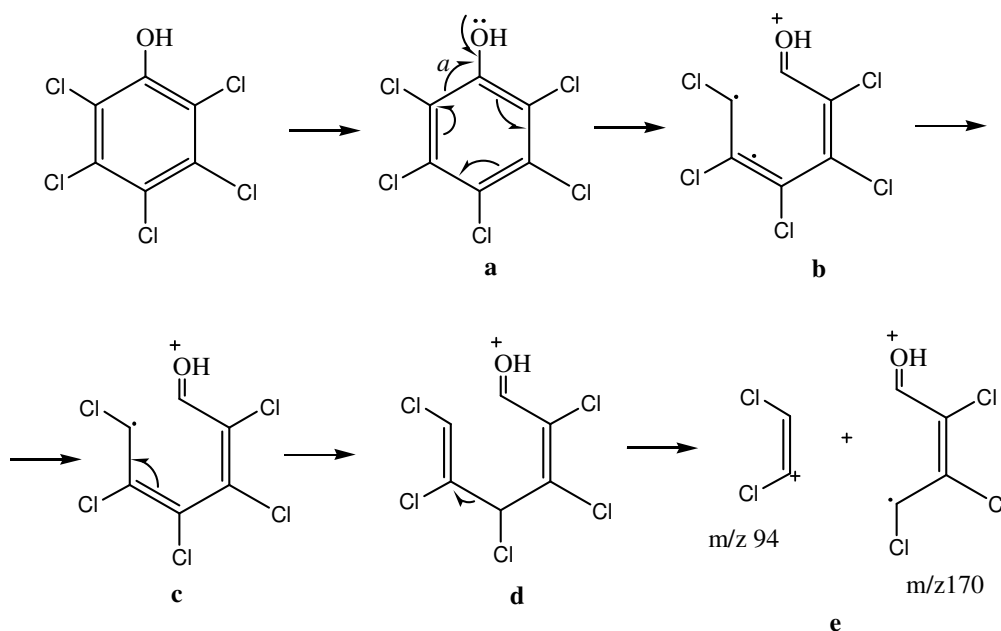


Figure 14. Mechanisms of fragmentation of the ion-molecule pentachlorophenol by rearrangement.

7. CONCLUSIONS

The studies focused on the mechanisms of fragmentation into a source of electron impact ionization is important to understand what happen with the compounds of interest since they are ionized. And therefore, to understand the formation of product ions, and also the reaction path they traveled. In this way this work presents some suggestions for mechanisms of fragmentation for the compound heptachlor, chlordane and pentachlorophenol when subjected to the source of electron impact ionization.

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