

# Electron ionization and dissociative electron attachment to dicyclohexyl phthalate molecule.

M. Lacko, P. Papp, L. Moravský, Š. Matejčík

*Comenius University in Bratislava, Faculty of Mathematics, Physics and Informatics, Mlynská dolina F2, Bratislava 84248, Slovakia*

Electron ionization and dissociation as well as dissociative electron attachment to dicyclohexyl phthalate (DCP) molecule is discussed in this work. The crossed electron molecular technique coupled with mass spectrometry analyzes is used to identify the positive and negative ionic fragments of DCP which can be used for clear determination of DCP from other phthalates.

## 1. Introduction

The production of polyvinyl chloride uses Phthalic acid ester (“phthalates”) molecules as plasticizer. The arbitrary structural formula of phthalates can be derived from the formula of dicyclohexyl phthalate illustrated in Fig. 1 by replacing the two cyclohexyls with an arbitrary R and R’ hydrocarbons. European Union in Directive 2005/84/EC created limits for concentration of phthalates in children toys, which contains DEHP (diethylhexyl phthalate), DBP (dibutyl phthalate), BBP (benzyl butyl phthalate), DINP (diisonyl phthalate), DIDP (diisodecyl phthalate) and DNOP (di-n-octyl phthalate) [1]. Moreover, the European Chemical Agency tagged phthalates (DHP, DPP, DIPP, DMEP, DIBP, BBP, DEHP, DBP and n-pentyl-isopentyl phthalate) as “toxic for reproduction” [2]. The health risk of phthalates is investigated continuously for decades and the results indicated a potential threat not only for children and humans [3-7], but also for environment [8-11]. Analyses denote a decreasing number of products with concentration of phthalates over recommended or enactment concentrations [12-16]. Those concentration limits are unfortunately not created for many human products (like a food cover) and also many countries don’t limit phthalates concentrations.

## 2. Experimental setup

The investigation of phthalates concentration in plastics is very often made via gas chromatography method, which is frequently accompanied by mass spectrometry. Analysis of phthalates positive mass spectra shows an intensive product at  $m/z$  149, which is dominant almost for all phthalates. However those peaks which could lead to a clear determination of phthalates from each other are much weaker. In this study we present electron induced processes on dicyclohexyl phthalate (DCP,

see Fig. 1) with the crossed electron and molecular beam technique [17] built at the Department of Experimental Physics of Comenius University in Bratislava. The molecular beam is introduced into a high vacuum via a small capillary where it collides perpendicularly with the electron beam formed by a trochoidal electron monochromator (resolution of electron energy  $\sim 200$  meV). A weak electric field extracts the produced ions from the reaction region into the ion optics of the quadrupole mass analyzer. For the positive ions of DCP standard mass spectrum was recorded at electron energy  $\sim 70$  eV (Fig. 1). In the case of negative ions the mass spectra depend more strongly on the energy of the electrons due to a resonant character of the reactions in the energy scale (0–13 eV), therefore the knowledge of the positions of the resonances for electron attachment and dissociative electron attachment reaction for particular molecule is important. Varying the incident electron energy, ion efficiency curves for particular ions (for given  $m/z$ ) as function of the electron energy were measured, both for positive and negative ions.

## 3. Results and discussion

### 3.1. Electron ionization of DCP

The mass spectrum of DCP in Fig. 1 has a typical feature with the dominant peak at  $m/z$  149, observed at almost all phthalates mass spectra [18,19] which represents the dissociation of both (R and R’) hydrocarbons and one oxygen atom replaced by a hydrogen atom from R or R’. In case of DCP molecule studied in this work it means the dissociation of two identical  $R = R' =$  cyclohexyl ring. The residual positive ion with  $m/z$  149 however does not carry information about phthalate type. As well, the second most intensive ion with  $m/z$  167 is observed in more phthalates, in the recent study it represents the dissociation of DCP into a  $C_6H_4(COOH)C(OH)_2^+$  ion. The positive ion with

$m/z$  249 is a result of loss of one cyclohexyl group wherein its two hydrogen atoms remain on the ion; however this peak also cannot be used for distinguishing DCP from other phthalates with one R = cyclohexyl.

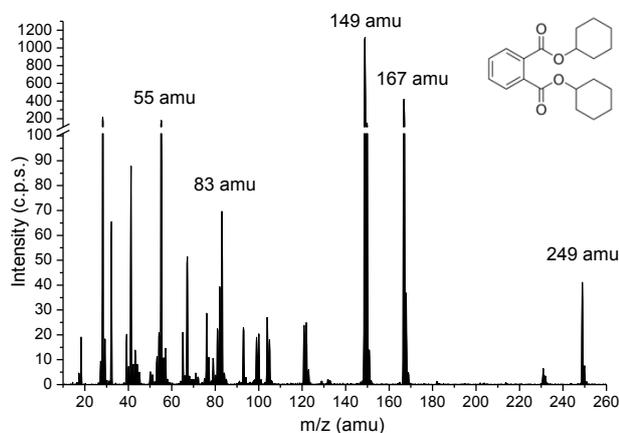


Figure 1: Mass spectrum of dicyclohexyl phthalate at incident electron energy 70 eV.

The presence of cyclohexyl on the measured phthalate is proved at  $m/z$  83; there the positive charge remains on the cyclohexyl. The intensive peaks below  $m/z$  83 (67, 55 and 41) are preferably created by dissociation of cyclohexyl, because the position of these peaks is similar with the peaks  $m/z$  69, 56 and 41 of cyclohexane mass spectrum [20]. The positive ion of parent DCP was not detected.

### 3.2. Dissociative electron attachment to DCP

The relative cross sections of dissociative electron attachment (DEA) to DCP are presented in Fig. 2. Here, contrary to positive ions, production of  $\text{DCP}^-$  ( $m/z$  330) is the most intensive process, where the energy of incident electron is close to 0 eV. At the same energy we observed other single particle resonance products with  $m/z$  148 and 45. The ion at  $m/z$  148 has a similar character as its positive counterpart at  $m/z$  149 discussed already in the previous chapter. In the DEA process an electron with  $\sim 0$  eV is entrapped to the oxygen atom as proposed in Fig. 3. Mazurkiewicz and Deinzer [21] observed this ion as well, for different phthalates. Finally, the negative ion with  $m/z$  45 can be described as dissociation of  $\text{COOH}^-$ , where a hydrogen atom is added probably from cyclohexyl. In all DEA processes discussed above capture of the electron to the COO can be expected.

Negative ions via DEA to DCP can be produced at higher energies as well; these are associated with core excited resonances (bottom of Fig. 2) and are presented in Fig. 3. Except the ion with  $m/z$  247 (loss of one R from DCP) which has one more

resonance  $\sim 2$  eV all other core excited have the threshold situated at  $\sim 4.5$  eV. Core excited channel is open for one of the single particle products as well; the  $m/z$  148 ion  $\text{C}_6\text{H}_4(\text{CO})\text{COO}^-$ .

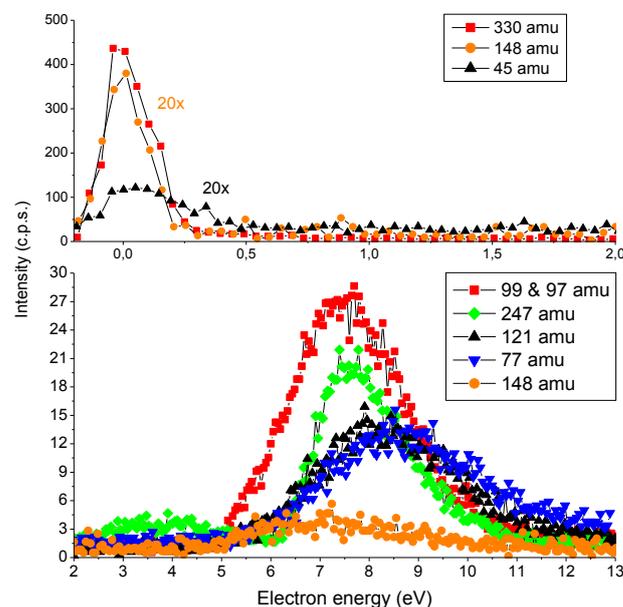


Figure 2: Relative cross sections of particular ions from dissociative electron attachment to DCP.

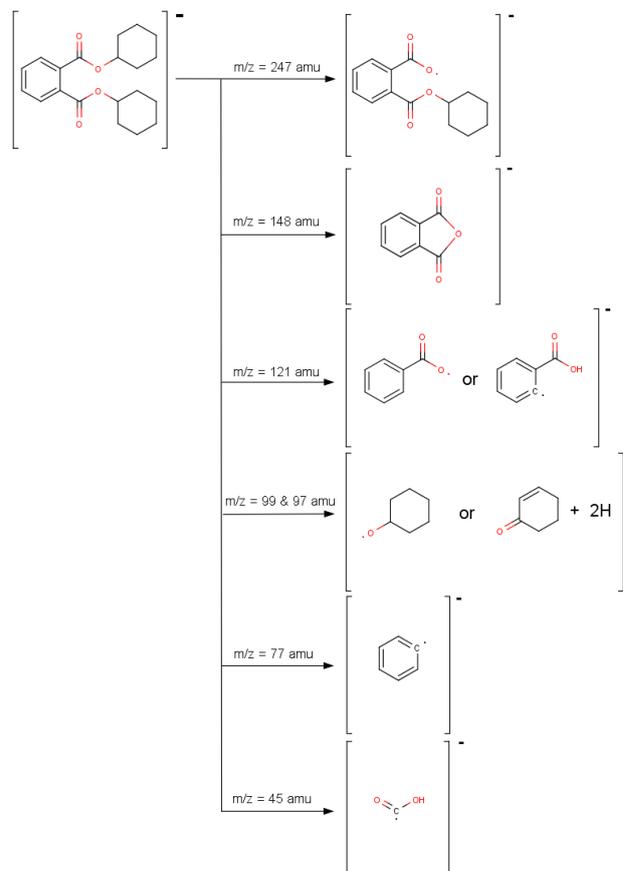


Figure 3: Schema of the core excited resonance ions produced via DEA to DCP.

Other new ions with  $m/z$  121 and 77 were detected; both represented by loss of the benzyl group and particular hydrogen shifts; the  $C_6H_5COO^-$  or  $C_6H_4COOH^-$  ion as well the  $C_6H_5^-$  ion respectively.

The resonance combined from  $m/z$  99 and 97 was conducted as a result of using a worse mass resolution during the experiment. The cross section of separated ions is not presented, but measurements indicate a similar position of resonances for both products. For  $m/z$  99 the cyclohexyl with one oxygen atom is produced, where a negative charge is probably located on oxygen. The negative charge can be spontaneously transferred into a cyclohexyl ring where is delocalized, that can lead to creation of double bond between oxygen and cyclohexyl carbon, whereby the two hydrogen atoms are dissociated. This process leads to negative ion at  $m/z$  97.

Mazurkiewicz and Deinzer [21] presented negative ion resonances for 7 o-phthalates. Resonance maxima of production of negative parents are localized mostly around 0.5 eV followed by second resonances around 1 eV. A relative cross section for o-methyl phthalate and o-butyl cyclohexyl phthalate indicated that resonances are mostly localized into region from 0 to 2 eV. This contrast can be associated with difference bond strength between oxygen atom and cyclohexyl and with different electron affinity of products. The expected negative ion at  $m/z$  164 via dissociation of both R groups was not observed in our experiment.

#### 4. Conclusions

Electron ionization and dissociation of DCP molecule leads to several intensive products in the mass spectrum of this molecule; however most of them cannot be used to distinguish the DCP molecule from other phthalates containing a cyclohexyl group with a potential high health risk to human body. Identification of toxic phthalates from nontoxic phthalates used in ordinary products is important due to exclusion of toxic products from our everyday life. We have identified a strong ion yield of  $DCP^-$  at  $\sim 0$  eV electron energy; which is the most dominant feature of the DEA to DCP. In a combination with other analytical techniques the DEA to phthalates can be used not only for identification of their origin but also their concentration limit in the sample.

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