SCIENTIFIC REPORT

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Title: LOW ENERGY ELECTRON INTERACTION WITH BIOMOLECULES IN THE GAS PHASE

Purpose of the visit

The purpose of the visit was to investigate interactions of the low energy electrons with biomolecules in the gas phase. The study is a part of the effort to understand radiation damage of DNA basic subunits. As a subject for the experiment the dibutyl phosphate and triethyl phosphate were chosen to simulate the behaviour of the phosphate group in DNA.

Description of the work carried out

The experiments were performed with a crossed electron-molecular beam apparatus. The apparatus consists of an electron source, an oven, a quadrupole mass analyzer and a detection system. An electron beam of the defined energy generated from a trochoidal electron monochromator (resolution 90-120 meV FWHM) crossed perpendicularly with a molecular beam consisting of phosphoric acid esters. To obtain a sufficiently high pressure of intact molecules a temperature of about 370 K (measured by a platinum resistance) was used during the experiments. The generated negative ions are extracted by a small electric field and accelerated by a series of parallel electrodes onto the entrance hole of quadrupole mass analyzer and detected by a single pulse counting technique as a function of incident electron energy. The energy scale was calibrated using the well known resonance in SF_6 near 0 eV generating metastable SF_6^-.

Description of the main results obtained

The dibutyl phosphate (DBP) and triethyl phosphate (TEP) were chosen as a subject of the experiment. These molecules were used to simulate the behaviour of the phosphate group in DNA towards the attack of low energy electron.

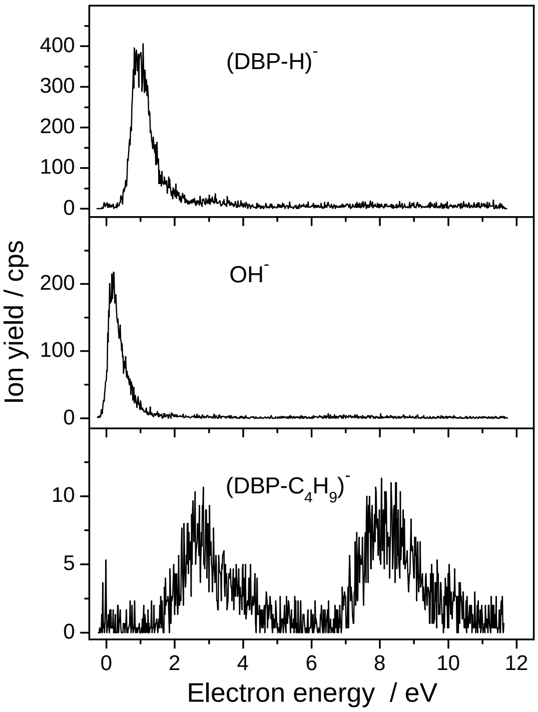

Fig. 1 Ion yield for (DBP-H)$^-$, OH$^-$ and (DBP-C$_4$H$_9$)$^-$ in the dibutyl phosphate as a function of incident electron energy.

Some representative ion efficiency curves from dibutyl phosphate ((C$_4$H$_9$O)$_2$P(O)OH, 210 amu) are shown in Figure 1. It is clearly visible from the spectrum that the most intensive signal appears at mass 209 amu which can be attributed to the molecule after abstraction of the neutral hydrogen atom ((DBP-H)$^-$) with peaks at 1 and 3.2 eV. Electron attachment investigation reveals that dibutyl phosphate is able to form also a stable parent anion but with the much smaller intensity than the ion at 209 amu (not shown in Fig.1). The second dominant feature is a fragment at 17 amu (OH$^-$) with a peak at 0.2 eV. Next fragment, at 153 amu, arises from the dibutyl phosphate due to the loss of an entire neutral butyl group and can be assigned as (DBP-C$_4$H$_9$)$^-$. In this ion spectrum two broad structures are visible - the first, at low energy region, is located at 2.8 eV and the second one at 8 eV.

All above mentioned ions (209 amu, 17 amu, 153 amu) can be created by a single bond cleavage. But the dissociative electron attachment to dibutyl phosphate leads to various P containing fragments which have to be created by a multiple bond cleavage.

The very interesting are two of them PO$_3^-$ and H$_2$PO$_3^-$ at 79 amu and 81 amu, respectively. Both of them are composed of two overlapping resonances appearing at about 0 eV and 0.3 eV (Figure 2). Two of lighter phosphate anions were also observed at neighboring masses at 47 amu and 48 amu assigned as PO$^-$ and HPO$^-$, respectively.

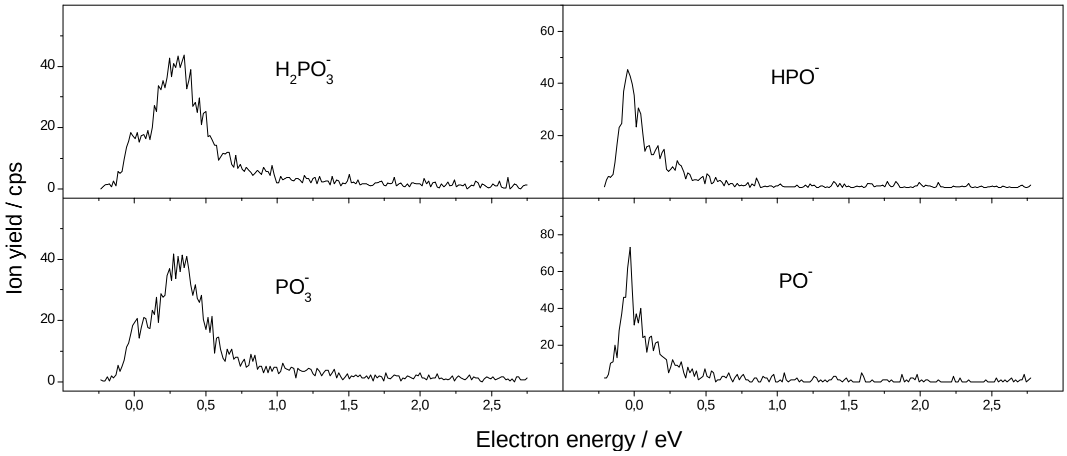

Fig. 2 Ion yield for $H_2PO_3^-$, PO_3^- , HPO^- and PO^- in the dibutyl phosphate as a function of incident electron energy.

Additionally, from the dibutyl phosphate ions at 140 amu ($C_3H_7OP(O)(OH)_2^-$), 114 amu, 109 amu ($C_2H_5OP(O)OH^-$), 92 amu ($C_2H_5OPO^-$) with peaks at about 0 eV and 62 amu (CH_3OP^-) at about 0.7 eV were also observed.

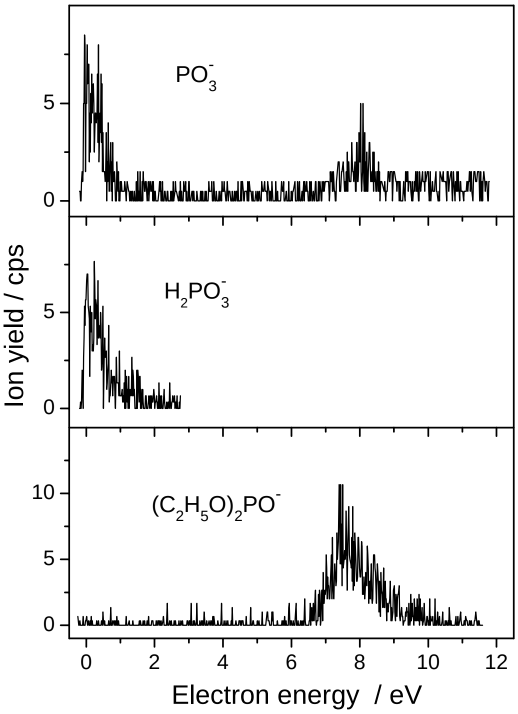

Fig. 3 Ion yield for PO_3^- , $H_2PO_3^-$ and $(C_2H_5O)_2PO^-$ in the triethyl phosphate as a function of incident electron energy.

The experiment performed on triethyl phosphate ($(C_2H_5O)_3PO$, 182 amu) shown that the TEP is not able to form neither stable parent ion nor (TEP-H)⁻.

The dissociative electron attachment to triethyl phosphate leads to much poorer fragmentation than in the case of dibutyl phosphate. Figure 3 presents the ion yields of PO_3^-, $H_2PO_3^-$ and $(C_2H_5O)_2PO^-$ at 79 amu, 81 amu and 137 amu, respectively, from TEP. The $(C_2H_5O)_2PO^-$ is formed by the loss of an entire C_2H_5O group from the temporary negative ion and is characterized by high energy resonance at about 8 eV. For $H_2PO_3^-$ as well as for PO_3^- relatively narrow peaks at about 0.2 eV are observed. For the later one the low energy resonance is followed by a resonance at 8 eV.

Future collaboration with host institution

It is planned to continue the collaboration in the area of electron attachment spectroscopy.

Projected publications resulting from the grant

The publication of presented results was submitted (March 2006), Title: *Dissociative Electron Attachment to Phosphoric Acid Esters: The Direct Mechanism for Single Strand Breaks in DNA.*