



Photoelectron spectroscopy of some chlorinated phosphate esters

Igor Novak^{a,*}, Branka Kovač^b^a Charles Sturt University, POB 883, Orange, NSW 2800, Australia^b Ruđer Bošković Institute, Bijenička cesta 54, HR-10000 Zagreb, Croatia

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ABSTRACT

The electronic structures of ethylenephosphochloridate, 1,2-phenylenephosphochloridate and 2,2,2-trichloro-1,3,2-benzodioxaphosphole have been studied by HeI/HeII photoelectron spectroscopy (UPS) and Green's function calculations. Our results indicate the importance of hyperconjugative interactions between the 5-membered ring and the fused aromatic ring. Some implications of our results for rates of nucleophilic substitution reactions on phosphorus are discussed.

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1. Introduction

Substituted phosphate esters (containing –POR functional groups) are of fundamental importance in biological chemistry where many biochemical reactions involve nucleophilic substitution reactions on the phosphorus centre: $S_N2(P)$. These esters are not only part of nucleosides (where they bond to nucleotide bases) but are also representatives of transition states involving pentacoordinated phosphorus in enzyme–substrate interactions. Furthermore, phosphate esters can act as biological protective groups which can facilitate diffusion of drugs across cell membrane. The phosphate esters as part of prodrugs can increase drug's bioavailability and facilitate its delivery to body cells [1].

The understanding of electronic structure of phosphate esters and especially the effects of changes in phosphorus coordination from four to five is very important for understanding of the rate enhancements of $S_N2(P)$ type reactions [2]. We have used UV photoelectron spectroscopy (UPS) to investigate the electronic structures of three phosphate esters (I–III) containing tetra and pentacoordinated phosphorus and compared their spectra with the previously reported spectra of tricoordinated phosphorus analogues IV and V (Scheme 1) [3,4].

2. Experimental and theoretical methods

Samples of the compounds I–III were obtained from Fluka (I) and Alfa Aesar (II and III). The selection of studied compounds was governed by their thermal stability and volatility. The

photoelectron spectra (Figs. 1–3) were recorded on the Vacuum Generators UV-G3 spectrometer and calibrated with small amounts of Xe gas which was added to the sample flow. The spectral resolution in HeI and HeII spectra was 30 meV and 70 meV, respectively, when measured as the FWHM of the $3p^{-1}$ ($^2P_{3/2}$) $Ar^+ \leftarrow Ar$ (1S_0) line. The vertical ionization energy values have been determined from intensity maxima. The samples of compounds I–III were recorded at 60, 65 and 50 °C, respectively. The measured spectra were reproducible and showed no signs of decomposition e.g. no sharp peaks corresponding to small molecules as decomposition products were observed. The spectra were reproducible over long time intervals. After the measurements the sample residues were inspected and showed no discoloration or charring.

Quantum chemical calculations were performed with GAUSSIAN 03 software [5] and included full geometry optimization and natural bond orbitals (NBO) at the B3LYP/6-31G(d,p) level for each molecule. The optimized structures corresponded to the minima on the potential energy surface as inferred from the absence of imaginary harmonic vibrational frequencies. The optimized geometries were in agreement with the reported experimentally determined structures of I and II [6a,6c]. The calculated P–O, P=O and P–Cl bond lengths and O–P–Cl bond angles were within ± 0.02 Å and $\pm 1^\circ$ of the experimental values [6]. I and II have different geometries of their phosphochloridate rings. In I the ring is puckered in order to minimize repulsive interactions between oxygen lone pairs [6b] (the puckering angle is 14.5° [6c]). The rigidity of the fused aromatic ring in II prevents the twisting of the phosphochloridate ring. The vertical ionization energies were calculated for the optimized structures using Green's function (GF) method at the 6-311+G(d,p) level which has been used successfully for the assignment of photoelectron spectra previously [7].

* Corresponding author. Tel.: +61 263657815.

E-mail addresses: inovak@csu.edu.au (I. Novak), bkovac@irb.hr (B. Kovač).

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