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Effective Atomic Charges and Bonding Character of Y=P-Orbitals in Four-Coordinated Phosphorus Compounds Studied by Photoelectron Spectroscopy Data

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EFFECTIVE ATOMIC CHARGES AND BONDING CHARACTER OF Y=P-ORBITALS IN FOUR-COORDINATED PHOSPHORUS COMPOUNDS STUDIED BY PHOTOELECTRON SPECTROSCOPY DATA

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Effective atomic charges in $Y=PX_3$ -molecules ($Y=O$ or S for $X=F, Cl, Me, OMe$; $Y=BH_3, CH_2, NH$ for $X=Me$) were calculated from gas-phase core-electron chemical shifts ΔE utilizing the equations set

$$\Delta E_A = k_A q_A + \sum_{B \neq A} \frac{q_B}{R_{AB}} + 1 \quad (I)$$

The applied calculations which take into account the surrounding atoms potentials (molecular potential) does not confirm the high electronegativity of atom S in $S=PX_3$. This contradicts with the widely accepted method of linear correlations of ΔE_A with atomic charge q_A . The slight alteration of ΔE_P while substituting O by S in $Y=PMe_3$, is due to compensation of charges in the first and second member in the equation for ΔE . It has been shown that the universal proportional coefficient between ΔE_P and q_P cannot be found in case of phosphorus compounds. Values of charges q_P obtained by this method and by the method of MNDO are in linear correlation. The significance of accounting of $P3d$ -orbitals occupancy in k_P -selection is discussed. Comparison of $\Delta E(OIs)$ with ionization potential of $O2p_{\pi}$ -electrons in ONX_3 ($X=F, Me$) reveals the antibonding character of $O2p_{\pi}$ -orbitals in nitrogen compounds. In phosphorus compounds, due to $p_{\pi}-d_{\pi}$ -interaction, these orbitals are bonding.

(I) Siegbahn K., Nordling C., Fahlman A., e.a. Electron Spectroscopy. - Moscow: Mir, 494 p.p., (1971).