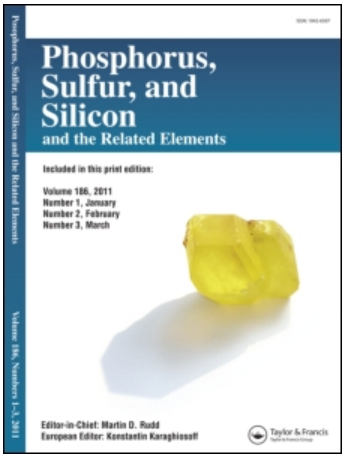

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Bonding in Phosphorus Compounds[1]: Reduction Potentials of $R_2(Y)P$-substituted Aromatic π Systems[2] and Gasphase Syntheses of 18 Valence Electron Molecules X-P=Y[3,4]

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To cite this Article Bock, H. , Bankmann, M. , Hänel, P. and Lechner-knoblauch, U.(1987) 'Bonding in Phosphorus Compounds[1]: Reduction Potentials of $R_2(Y)P$-substituted Aromatic π Systems[2] and Gasphase Syntheses of 18 Valence Electron Molecules X-P=Y[3,4]', Phosphorus, Sulfur, and Silicon and the Related Elements, 30: 1, 109 — 112
To link to this Article: DOI: 10.1080/03086648708080534
URL: http://dx.doi.org/10.1080/03086648708080534

Phosphorus and Sulfur, 1987, Vol. 30, pp. 109–112
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BONDING IN PHOSPHORUS COMPOUNDS[1]: REDUCTION POTENTIALS OF $R_2(Y)P$-SUBSTITUTED AROMATIC π SYSTEMS[2] AND GASPHASE SYNTHESES OF 18 VALENCE ELECTRON MOLECULES X-P=Y[3,4]

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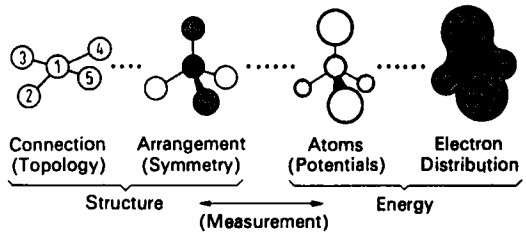
Abstract. An up to date concept of bonding in phosphorus compounds, which has to consider the individual molecular states, their dynamics and reaction channels, is illustrated by representative examples. The reduction potentials of $R_2(Y)P$-substituted π systems to their radical anions, measured under aprotic conditions and discussed by first order perturbation, yields a sequence of increasing acceptor effects ranging from R_2P to $R_3P^{\oplus}$. The gasphase syntheses of novel molecules like H_3C-P=CH_2, Cl-P=O or Cl-P=S, partly by surface reactions, has been optimized by photoelectron spectroscopic real-time analysis. Their radical cation state ionization patterns are assigned by quantum chemical calculations, which allow to rationalize the bonding to the only doubly coordinated P center.

Molecules changes their structure and hence their properties on acquisition or loss of energy. Therefore, an up to date concept of bonding in phoshorus compounds has to consider the respective states of the individual molecules[5], which in a simplified way



may be approached by subdividing into aspects of connectivity (topology), three-dimensional arrangement (symmetry), core potentials (effective nuclear charges) and electron distribution[6].

Measurements allow to characterize the state of a molecule by the energy difference to the preceding or subsequent state and by the respective charge distribution. Suitable models of bonding advantageously are based on the comparison of equivalent states of chemically related molecules[1,6], using quantum chemical calculations as appropriate guidelines. In addition, molecular dynamics should be taken into account, because three-dimensional molecules store their energy in the 3n-6 degrees of freedom of motion. This is also one essential facet of the microscopic reaction pathways of molecules, which for medium-sized ensembles at best can be approximated rather crudely by semiempirical hypersurface calculations.

For phosphorus compounds, the concept of bonding outlined above, is illustrated by the following examples:

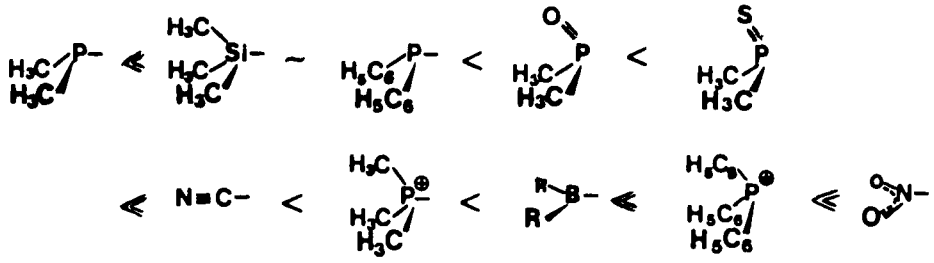
- topological aspects by v. Schnering's rationalization of P_nH_m cage structures applying Euler's formula for convex polyhedra[6],
- symmetry classification by the radical cation states of PH_3[1],
- core potentials by the ESCA and PES ionization energies for inner and valence shell electrons of phosphorus[1],
- electron distribution by comparing the structures of F_3P and F_3PO[1],
- molecular dynamics by the pseudorotation of P_5H_5 and energy barriers as approximated by hypersurface calculations[7], and
- reaction channels by the thermal dissoziation $P_4 \rightleftarrows 2P_2$ and its pathway as suggested by a semiempirical hypersurface calculation[8].

In summary, the molecular state approach to bonding in phosphorus compounds provides new insight into their fascinating chemistry.

From ongoing research of the Frankfurt group, two projects are presented in detail: the electrochemical series of phosphorus compounds measured under aprotic conditions and the gasphase syntheses of reactive small phosphorus molecules.

ACCEPTOR EFFECTS OF SUBSTITUENTS $-P(Y)R_2$ ON THE ONE-ELECTRON REDUCTION POTENTIALS OF AROMATIC π SYSTEMS

The half-wave reduction potentials of 23 phosphororganic compounds $R^{\pi}(PR_2)_n$, and $R^{\pi}(P^{\oplus}R_3)_n$ and $R^{\pi}(PYR_2)_n$ with R^{π} e. g. benzene, biphenyl, naphthalene or thiophene, and phosphorus substituents R = CH_3, C_6H_5 as well as Y = O, S, Se, NR and n = 1,2 have been determined by cylic voltammetry in DMF under aprotic measurement conditions. Statistical analysis within a perturbation model and comparison with the CV data of other 1,4-disubstituted benzene derivates establishes the following sequence of increasing acceptor effect of the substituents:

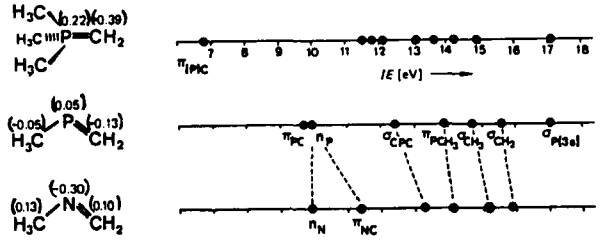


The potential difference between $(H_3C)_2P-$ and $(H_5C_6)_3P^{\oplus}$-1,4-substitution in benzene amounts to over 1,5 V (!) surpassing the effect of the electron-deficient R_2B group. Starting from the CV data, novel radical anions of phosphorus compounds have been generated[9], the spin distribution of which as determined by ESR provides detailed information on the π perturbation by phosphorus substituents[9].

RADICAL CATION STATES OF MOLECULES X-P=Y

Chlorodimethylphosphane, when heated to 770 K in a pyrolysis flow system, splits off HCl to yield $H_3C-P=CH_2$[4], another 18 valence electron molecule[3,4] predicted to be bent by the Walsh rules[4]. The thermolysis conditions are advatageously optimized by real-time PE spectroscopic gas analysis[10], based on the characteristic ionization pattern of the compound containing phosphorus of coordination number 2. Therefore, the question whether the charge distribution (in brackets: calculated by MNDO) corresponds to that of an

ylide can be answered by radical cation state comparison with those of related compounds:



Accordingly, the new molecule $H_3C-P=CH_2$ is best characterized as being a 2-phosphapropene and not an ylide.

Other 18 valence electron molecules containing two-coordinated phosphorus like Cl-P=O or Cl-P=S[3] can be synthesized by reacting the corresponding trichlorides $Cl_3P=Y$ with a silver surface: for Y = O only AgCl can be formed for thermodynamic reason, while for Y = S a mixture of AgCl and Ag_2S results. The structures of the molecules Cl-P=Y as calculated using wave functions of double zeta quality show little deviation from bond lengths d_{PY} and angles ∢ ClPY in the precursors $Cl_3P=Y$.

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