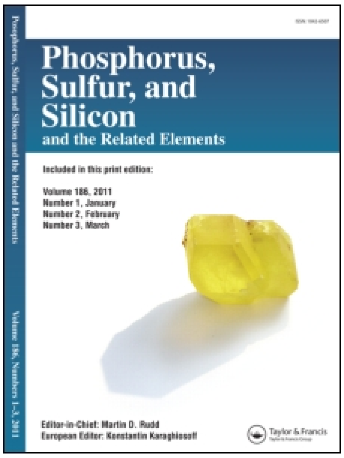

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Novel Properties of Iodophosphonium Ions: Kinetically Labile Behaviour and Secondary Bonding

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NOVEL PROPERTIES OF IODOPHOSPHONIUM IONS: KINETICALLY LABILE BEHAVIOUR AND SECONDARY BONDING

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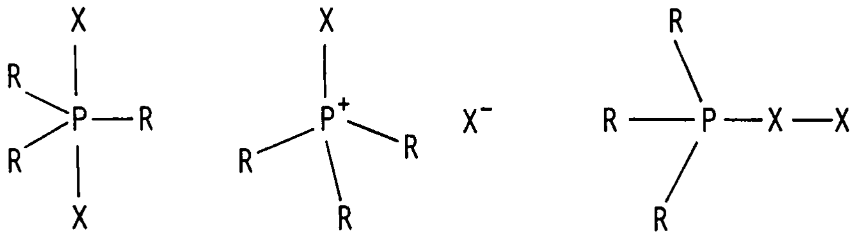
Abstract. Neutral species R_3PX_2 in equilibria with halogenophosphonium halides $R_3PX^+X^-$ do not always contain hypervalent phosphorus (10-P-5)! Iodophosphonium ions R_3PI^+ show $R_3P\text{-}I\cdots X$ interaction in many cases, leading to hypervalent iodine (10-I-2). Evidence for secondary $I\cdots X$ bonds is provided by n.m.r. spectra and X-ray crystal structure determinations.

Rapid Te^o and I^+ transfer reactions between phosphanes have been explained by nucleophilic attack at tellurium in phosphane tellurides R_3PTe and at iodine in iodophosphoniumions R_3PI^+ leading to $10e^-$-species $R_3P\text{-}Te\text{-}PR_3$ or $R_3P\text{-}I\text{-}PR_3{}^+$ as transition states or intermediates [1]. The acceptor properties of iodine atoms adjacent to phosphonium centers lead to anion ⟶ cation donor/acceptor interactions in the ground state of iodophosphonium salts $R_3PI^+X^-$. $I\cdots X^-$ contacts are significantly shorter than the van der Waals distances [2, 3, 4]. ^{31}P-NMR spectroscopy provides a very sensitive method to detect the significant increase in electrophilic character of the halogen atom going from chloro- to bromo- to iodophosphonium salts. Furthermore, the first X-ray crystal structure analysis of a "diiodophosphorane" shows that, in the solid state, a linear arrangement P-I-I with a (10-I-2) situation at the central iodine atom, i.e., a new structural type for dihalogeno-phosphoranes is present [3] (Fig. 1).



(10-P-5) (8-P-4) (8-P-4), (10-X-2)

Fig. 1: Alternative structures of compounds R_3PX_2

$$R_3PI + I_2 \xrightarrow{(i)} R_3P\text{-}I\text{-}I \xrightleftharpoons{(ii)} R_3PI^{\oplus}I^{\ominus}$$

$$R_3PI^{\oplus} + :\overset{*}{P}R_3 \rightleftharpoons R_3P\text{-}I\text{-}\overset{*}{P}R_3{}^{\oplus} \rightleftharpoons R_3P: + I\text{-}\overset{*}{P}R_3{}^{\oplus} \quad (iii)$$

$$R_3PI^{\oplus}I^{\ominus} + I_2 \rightleftharpoons R_3PI^{\oplus}I_3{}^{\ominus} \quad (iv)$$

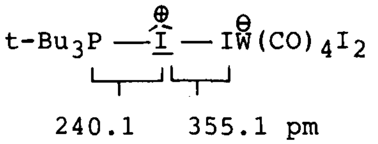
$$R_3PI^{\oplus}I^{\ominus} + ML_n \rightleftharpoons R_3PI^{\oplus}IML_n{}^{\ominus} \quad (v)$$

When the reaction of tri-tert-butylphosphane with various amounts of elemental iodine in CH_2Cl_2 is followed by n.m.r. spectroscopy, one observes continous changes in chemical shifts and coupling constants during the addition of iodine. When the 1:1 ratio of phosphane to iodine is attained, continued addition of iodine leads to further 31-P downfield shift and to further increasing $^3J(^{31}P, ^1H)$. These observations are in accord with a pronounced acceptor character of the iodine atom bonded to the phosphonium center toward nucleophiles like $I^{\ominus}$, PR_3, $I_3{}^{\ominus}$:

1. If t-Bu_3P is present in excess, t-Bu_3PI_2 undergoes rapid $I^{\oplus}$ exchange, and n.m.r. shifts and coupling constants are averaged (step iii).

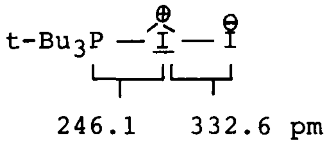
2. $t\text{-}Bu_3PI_2$ shows considerable iodine-iodine interactions in aprotic dipolar solvents and in the solid state (yellow solutions, yellow crystals); in water [colorless solution, large 31-P downfield shift and large $^3J(^{31}P, ^1H)$] the cation $t\text{-}Bu_3PI^{\oplus}$ is well-separated from the anion (step ii).
3. With iodine in excess, iodophosphonium triiodide is formed. The $I_3^{\ominus}$ ion is less nucleophilic than $I^{\ominus}$ and the addition of iodine to $t\text{-}Bu_3PI_2$ in CH_2Cl_2 leads to downfield shifts in 31-P-NMR (step iv).
4. The ability of $I^{\ominus}$ for nucleophilic attack at iodophosphonium ions is also lowered by coordination with main group or transition metal Lewis acids (step v).

Variations in P-I and I-I or I-X bond lengths (Tab. 1) may be explained by competition of R_3E (E = N, P, As) and various donor anions for coordination with $I^{\oplus}$.

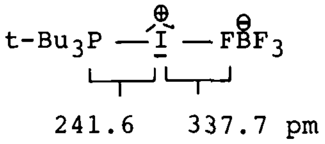


$$\underbrace{t\text{-}Bu_3P-\overset{\oplus}{I}}_{240.1}\underbrace{-\overset{\ominus}{I}W(CO)_4I_2}_{355.1\ pm}$$

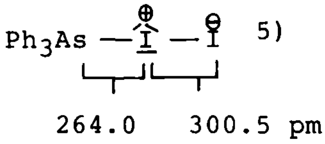
6)



$$\underbrace{t\text{-}Bu_3P-\overset{\oplus}{I}}_{246.1}\underbrace{-\overset{\ominus}{I}}_{332.6\ pm}$$



$$\underbrace{t\text{-}Bu_3P-\overset{\oplus}{I}}_{241.6}\underbrace{-F\overset{\ominus}{B}F_3}_{337.7\ pm}$$



$$\underbrace{Ph_3As-\overset{\oplus}{I}}_{264.0}\underbrace{-\overset{\ominus}{I}}_{300.5\ pm}$$

5)

Increasing donor ability of R_3E (E = N, P, As) leads to weakening of the I-I bond, but linear coordination geometry at the central (10-I-2) iodine atom persists in all known cases, independent from a more charge-transfer-complex-like [Me_3N-I-I, d(I-I) = 283 pm] or a more ion pair with secondary bonding-like [$t\text{-}Bu_3P$-I-I] character of the compounds.

Lowering the donor ability of $I^{\ominus}$ (formation of $I_3^{\ominus}$, $W(CO)_4I_3^{\ominus}$, $AlI_4^{\ominus}$) allows strong $R_3E \rightarrow I^{\oplus}$ coordination (P-I single bonds, like in $PI_4^+AlI_4^-$) and only weak secondary cation-anion interactions remain. But even these weak interactions, like in t-$Bu_3P\overset{\oplus}{I}$-$BF_4^{\ominus}$ obey the rule of linear coordination geometry at hypervalent (10-I-2) iodine.

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