Oxidation products of iminophosphorane and bis-iminophosphorane: An EPR study

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Abstract

Electrochemical oxidation of (C_6H_5)_3P=N(C_6H_5) and (C_6H_5)_3P=N(C_6H_5) leads to EPR spectra which reveal the dimeric structure of the resulting radical cation. In contrast to this behaviour, oxidation of bis-iminophosphorane leads to [(C_6H_5)_3P=N(C_6H_4)N=P(C_6H_5)_3]/C_5^+: In these species the unpaired electron is delocalized on the N(C_6H_4)N moiety and the persistency of the radical depends upon the relative position of the two P=N bonds.

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1. Introduction

With recent developments in molecular electronics, extensive efforts are directed to finding new chemical moieties able to accept or to give an electron and to transmit the resulting signal (charge or spin) to another component of the molecular assembly. Systems containing low-coordinated phosphorus atoms are potentially well suited to this purpose: depending upon the nature of the substituent R, phosphaalkenes R’P=CR_2 are easily reduced (R = alkyl, aryl) [1] or oxidized (R = dimethylamino) [2]. However, double bonds with a trivalent phosphorus atom are generally very reactive. They need to be kinetically protected by a cumbersome group R’ (e.g., Mes*), whose presence often makes difficult the incorporation of the P=O bond in a more elaborate architecture. In this context, iminophosphoranes have been the object of much interest. The pentavalent phosphorus P=N bonds are robust; they can be incorporated in conjugated polymers and are potentially able to give rise to organic conducting materials [3,4]. As shown by Escobar et al. [3], the electron-donating capacity of the iminophosphorane bond is fundamental to explain the properties of these systems; in particular they showed that para bis-iminophosphorane B_{para} possesses two reversible one-electron oxidations. The first chemical oxidation results in a shift of the optical absorption band consistent with the formation of the monocation. This formation of a radical cation from a P=N containing molecule is somewhat in contrast with early EPR results on triphenyl(phenylimino)phosphorane A [5]. Anodic oxidation of this compound leads to a spectrum whose hyperfine structure was not consistent with that of A^+ and which was attributed to an unidentified secondary oxidation compound due to the rapid cleavage of the radical cation and reaction of the fragments with solvent [5]. This prompted us to start EPR investigations on the formation of radical cations from the following systems containing one or two iminophosphorane bonds.
2. Experimental

Syntheses of $A$ [6,7], $B_{ortho}$ [4] and $B_{para}$ [8] have already been reported. $B_{meta}$ was obtained by using Ph$_3$PBr$_2$ and meta-diaminobenzene as reactants. $A_D$ and $B_{para,D}$ were synthesized by using C$_6$D$_4$-NH$_2$ (Fluka) and H$_2$N-C$_6$D$_4$-NH$_2$ (Aldrich) as precursor, respectively.

EPR spectra were recorded with a Bruker 300 spectrometer. Electrochemical oxidation was performed, in situ, in the EPR cavity. Cyclic voltammograms were obtained with a BAS station. DFT calculations were performed at the B3LYP/6-31G* level of theory [9].

3. Results and discussion

3.1. Oxidation of the mono iminophosphorane $A$

3.1.1. EPR spectra

As already reported, cyclic voltammetry of $A$ shows that the primary electrode process is a one-electron oxidation which occurs at $E_0 = 0.8$ V vs. SCE and which is totally irreversible [5]. Whereas no EPR response could be obtained by chemical oxidation of $A$ with [Cp$_2$Fe] PF$_6$, electrochemical oxidation of a solution of $A$ in CH$_2$Cl$_2$ led to the spectrum ($g = 2.0038$) shown in Fig. 1a. These signals are moderately persistent and were still detected, at room temperature, 20 min after voltage was turned off.

This spectrum is rather complex and its analysis could be performed only after deuteration of the phenyl ring bound to the nitrogen atom (compound $A_{D_D}$).

The corresponding spectrum, shown in Fig. 1b, is composed of nine equally spaced lines ($g = 2.0040$). The hyperfine structure clearly results from couplings with two equivalent $^{31}$P nuclei (5.4 G) and two equivalent $^{14}$N nuclei (2.6 G). Then, this type of spectrum can only be accounted for by assuming a dimeric structure. In order to simulate the spectrum of the non-deuterated compound $A$, we assumed that deuteration did not affect $^{31}$P and $^{14}$N coupling constants. Because of the selective deuteration of the aniline residue, the additional hyperfine structure is obviously due to protons of the benzene ring bound to the nitrogen atom. A very good simulation of the spectrum recorded with compound $A$ was obtained by adding a coupling constant of 1.6 G with two equivalent protons and a coupling of 0.8 G with four other protons. The two former couplings (1.6 G) correspond to the $para$ hydrogen atoms on the aniline residues while the four latter couplings (0.8 G) correspond to the $ortho$ protons.

Fig. 1. EPR spectrum obtained with (a) $A$ ($\nu = 9432$ MHz) and (b) $A_{D_D}$ ($\nu = 9425$ MHz).
Therefore, oxidation of Ph₃P=NPh is not followed by cleavage of the resulting cation Ph₃P⁺=NPh, A⁺⁺, but by the addition of this cation to a neutral iminophosphorane molecule to form the dimeric radical cation (A₂)⁺⁺ (Scheme 1). The dimeric structure provokes delocalization of the unpaired electron over both NPh moieties and thus stabilizes the system.

It is worthwhile mentioning that dimerization of some neutral iminophosphoranes and the structure of the resulting diamagnetic diphosphetidines has been reported [10,11].

3.1.2. DFT calculations

DFT calculations were carried out in order to check for consistency between EPR spectra and the proposed structure (A₂)⁺⁺. Optimizations of the geometries of A⁺⁺ and A₀⁺⁺ (A represents H₃P=NPh) lead to real minima (frequency analysis). As shown by Table 1 and Fig. 2, replacement of the phenyl rings by hydrogen atoms has only little influence on the calculated hyperfine couplings and on the SOMOs.

These SOMOs clearly illustrate the aminyl (R(R′)N⁻) character of these species in which a radical nitrogen atom is linked to a phosphonium group and to a phenyl ring. Coplanarity of the PNC fragment and of the phenyl ring allows an appreciable spin delocalization onto the phenyl ring. As expected, the calculated coupling constants given in Table 1 are not compatible with the values measured on the EPR spectrum recorded after oxidation of A. In the optimized geometry of (A₀)₂⁺⁺, the two phosphorus atoms and the two nitrogen atoms lie in a plane which also contains the two Ph⁻N moieties; the P–N bonds form a parallelogram, whose sides are equal to 1.687 and 2.015 Å, respectively. The corresponding SOMO is shown in Fig. 2 while the coupling constants are given in Table 1. These constants agree with the couplings measured with an oxidized solution of A in THF. However, the frequency analysis shows that this structure does not correspond to a minimum but to a saddle point indicating that the dimeric structure tends to dissociate.

The fact that Ph₃P⁺=NPh is not detected experimentally would suggest that it rapidly reacts with a neutral radical (e.g., H abstracted from solvent molecules) or with another radical cation to give Ph₃P⁺=N(H)Ph or Ph₃P⁺=N(Ph)–(Ph)N⁻⁺PPh₃, respectively. However, reaction can also occur between a radical cation and a neutral iminophosphorane molecule to give rise to (Ph₃P=NPh)₊ which is probably slightly stabilized by the solvent cage. The lifetime of this species in THF solution is sufficiently long to allow its EPR detection

Table 1

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>(A)⁺⁺</th>
<th>(A₀)⁺⁺</th>
<th>(A)⁺⁺</th>
<th>(A₀)⁺⁺</th>
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<td>¹⁴N</td>
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<td>6.3 (1)</td>
<td>3.8 (2)</td>
<td>2.6 (2)</td>
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<tr>
<td>¹H</td>
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<td>-6.2 (1)</td>
<td>-4.7 (2)</td>
<td>(-1.6 (2)</td>
</tr>
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<td>-2.8 (4)</td>
<td>(-0.8 (4)</td>
</tr>
<tr>
<td></td>
<td>2.4 (1)</td>
<td>2.3 (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.0 (1)</td>
<td>1.6 (1)</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>-8.5 (1)</td>
<td>-9.4 (1)</td>
<td></td>
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</tr>
</tbody>
</table>

a In parentheses: number of equivalent nuclei.
b Calculated value (DFT).
c Experimental results (only the absolute value is known).

Fig. 2. SOMO for the radical cations formed by oxidation of iminophosphoranes.
but optimization of its structure in the gas phase leads to a ‘stationary’ geometry which tends to dissociate. The relevance of this structure to the observed species in THF is supported by the very good accordance between calculated and measured hyperfine coupling constants.

3.2. Oxidation of bis-iminophosphorane systems

3.2.1. EPR spectra

The voltammogram of Bpara, already reported by Escobar et al. [3] exhibits two reversible oxidation waves at \( E_0 = 0.04 \) and 0.53 V vs. SCE. The EPR spectrum (\( g = 2.0039 \)) obtained by electrochemical oxidation at a potential slightly superior to the first wave is shown in Fig. 3a. The radical is rather persistent at room temperature and is detected 4 h after voltage has been switched off; its formation is accompanied by a change in the color of the solution, which turns from yellow to red. The same spectrum was obtained by chemical oxidation with [Cp2Fe]PF6.

As for compound A, selective deuteration was performed and yielded Bpara,D. As shown by Fig. 3b, the spectrum is considerably simplified when the protons of the phenylene ring of Bpara have been replaced by deuterium nuclei. The hyperfine structure is due to a coupling with two equivalent \( ^{31} \text{P} \) nuclei (\( A_{\text{iso}} = 7.8 \) G) and two equivalent \( ^{14} \text{N} \) nuclei (\( A_{\text{iso}} = 3.5 \) G). The spectrum of the non-deuterated compound was successfully simulated by adding two pairs of equivalent protons (\( A_{\text{iso}} = 1.9 \) and 1.8 G).

The voltammogram of Bortho is composed of three oxidation waves at \( E_0^a = 0.400 \) V (quasi-reversible), \( E_0^b = 0.84 \) V (quasi-reversible) and \( E_0^c = 1.2 \) V (irreversible). An EPR spectrum (\( g = 2.0042 \)) is obtained by applying, at room temperature, a voltage slightly higher than \( E_0^a \). Its hyperfine structure is due to coupling with two equivalent \( ^{31} \text{P} \) nuclei (\( A_{\text{iso}} = 11.9 \) G), two equivalent \( ^{14} \text{N} \) nuclei (\( A_{\text{iso}} = 3.1 \) G), and two pairs of equivalent protons (\( A_{\text{iso}} = 0.2 \) and 0.6 G). These signals immediately disappear when voltage is turned off. The same spectrum was obtained by chemical oxidation with [Cp2Fe]PF6.

The voltammogram of Bmeta shows two irreversible oxidation waves at \( E_0 = 0.79 \) and 1.20 V vs. SCE. These oxidation processes do not cause any change in the color of the solution. No EPR signal could be detected, neither by electrochemical oxidation nor by reaction with [Cp2Fe]PF6.

3.2.2. DFT calculations

In order to rationalize the EPR results and to gain further insight into the shapes of the SOMOs, DFT calculations were performed on the following model bis-iminophosphoranes.

![Bortho, Bmeta, Bpara](image)

As shown in Table 2, the calculated coupling constants agree with the experimental values measured for both the ortho and para derivatives. This confirms

![EPR spectra](image)

Table 2

<table>
<thead>
<tr>
<th>Nucleus</th>
<th>( B_{\text{para}} )</th>
<th>( B_{\text{para}}' )</th>
<th>( B_{\text{ortho}} )</th>
<th>( B_{\text{ortho}}' )</th>
<th>( B_{\text{meta}} )</th>
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<td>( ^{31} \text{P} )</td>
<td>7.8 (2)</td>
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<td>11.9 (2)</td>
<td>-9.2 (2)</td>
<td>-6.9 (2)</td>
</tr>
<tr>
<td>( ^{14} \text{N} )</td>
<td>3.5 (2)</td>
<td>3.5 (2)</td>
<td>3.1 (2)</td>
<td>3.3 (2)</td>
<td>2.7 (2)</td>
</tr>
<tr>
<td>( ^{1} \text{H} )</td>
<td>1.9 (2)</td>
<td>-2.4 (2)</td>
<td>0.6 (2)</td>
<td>-3.4 (2)</td>
<td>-11.1 (2)</td>
</tr>
<tr>
<td></td>
<td>1.8 (2)</td>
<td>-1.4 (2)</td>
<td>0.2 (2)</td>
<td>-0.3 (2)</td>
<td>3.3 (1)</td>
</tr>
</tbody>
</table>

* In parentheses: number of equivalent nuclei.

* Experimental results: absolute value of the coupling.

* Calculated value (DFT).

Fig. 3. EPR spectrum obtained (a) with Bpara (\( \nu = 9434 \) MHz) and (b) with Bpara,D (\( \nu = 9422 \) MHz).
the identification of the detected radicals. The SOMOs calculated for the three model cations are shown in Fig. 4.

A large delocalization is observed on the SOMOs of the three bis-iminophosphoranes $B^\prime$ with an appreciable spin density on the nitrogen atom of each P–N bond ($\rho_N = 0.18$ for ortho and para, $\rho_N = 0.14$ for meta), the remaining part being delocalized on the central phenylene ring with a distribution that depends upon the isomer. For each isomer, the $p_p$ orbital of each nitrogen atom is antibonding with respect to a bonding combination of three adjacent carbon $p_p$ orbitals. The strong contribution of a phosphonium mesomeric form (Ph$_3$P$^+$–N) explains the increase ($\Delta$) in the P–N bond length which accompanies the oxidation of $B^\prime$ ($\Delta = 0.039$ Å for $B^\prime_{\text{para}}$, 0.041 Å for $B^\prime_{\text{ortho}}$, and 0.029 Å for $B^\prime_{\text{meta}}$). A good correlation is observed between the redox properties, stabilities and ionization potentials of the three isomers: by passing from para, to ortho and to meta the calculated ionizing potential increases from 5.6 eV to 5.8 eV and 6.2 eV, while the first oxidation potential increases from 0.04 to 0.4 V and 0.52 V. Moreover, the oxidation is reversible for para, pseudo-reversible for ortho and irreversible for meta while the cation is persistent for para, but not for ortho and could not be detected by EPR for meta.

4. Conclusion

In conclusion, the electron-donating properties of the R$_3$P(=NR) group present considerable interest for the development of new organic materials. In phenyliminophosphoranes, the P=\(N\) bond is not as fragile towards oxidation as could had been expected from early investigations. Stabilization of the radical cations is insured by delocalization on the phenylamino moieties and explains, in part, the detection of the dimeric species ($A_2$)$_2^+$ in solution. For the bis-iminophosphoranes this stabilization is very dependant upon the number and the relative positions of the P=\(N\) bonds in the molecule.

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References