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Citation for published version (APA):

Janssen, R. A. J., Aagaard, O. M., Woerd, van der, M. J., & Buck, H. M. (1990). The nature of three-electron phosphorus-sulfur bonds studied by ESR. *Chemical Physics Letters*, 171(1-2), 127-130.
[https://doi.org/10.1016/0009-2614\(90\)80062-I](https://doi.org/10.1016/0009-2614(90)80062-I)

DOI:

[10.1016/0009-2614\(90\)80062-I](https://doi.org/10.1016/0009-2614(90)80062-I)

Document status and date:

Published: 01/01/1990

Document Version:

Publisher's PDF, also known as Version of Record (includes final page, issue and volume numbers)

Please check the document version of this publication:

- A submitted manuscript is the version of the article upon submission and before peer-review. There can be important differences between the submitted version and the official published version of record. People interested in the research are advised to contact the author for the final version of the publication, or visit the DOI to the publisher's website.
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The nature of three-electron P–S bonds studied by ESR

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Received 21 March 1990

An ESR study on three-electron P–S bonds in progressively substituted trialkylphosphine sulfide phosphoranyl radicals $R_3\dot{P}SR_n^{n-1}$ ($n=0, 1, 2$) is presented. The experiments show, in contrast with quantum chemical calculations, that the structure is not seriously affected by the electronegativity of the sulfur fragment. It is concluded that three-electron bonds can be formed in condensed phases, despite an unfavourable balance of the ionization potentials of the fragments involved.

1. Introduction

During the past few years the structure and stability of $2\sigma-1\sigma^*$ three-electron bond radicals have received increasing theoretical and experimental attention [1–8]. The large number of studies dealing with homonuclear three-electron A–A bonds reflects the intrinsic stability of a symmetrical $2\sigma-1\sigma^*$ configuration. Recently, however, several heteronuclear three-electron bonds have been reported between different types of atoms [9–11]. Asymmetric three-electron A–B bonds are of special interest since they generally possess a lower stability than their homonuclear analogues. The reduced stability towards bond fission is a consequence of the electronegativity difference between the two atoms. This results in an energy difference between the two resonance structures $A\cdot B$ and $A\cdot\cdot B$, which causes an asymmetric distribution of the unpaired electron. Accordingly, Clark obtained a general equation, based on *ab initio* quantum chemical calculations, which describes the dissociation energy of odd-electron σ bonds in terms of the energy, Δ_{IP} , required to transfer an electron from one partner in the complex to the other [1]. Since these calculations apply strictly to isolated radicals it is of interest to determine the effect of Δ_{IP} on the structure and stability of these systems in solution or in the solid phase.

Using single-crystal ESR we recently established the structure and spin density distribution of three-electron bond $R_3\dot{P}S^-$ radical anions, generated via

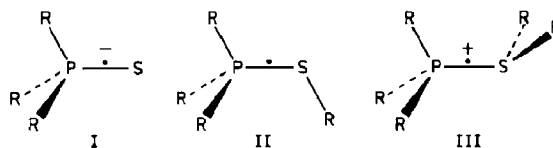


Fig. 1. Structure of $R_3\dot{P}SR_n^{n-1}$ ($n=0, 1, 2$) three-electron bond phosphoranyl radicals.

an X-ray induced electron capture reaction of the corresponding neutral trialkylphosphine sulfides (R_3PS) [12,13]. These radicals are formed in spite of the large difference between the ionization potentials of the two fragments involved. In the present paper we extend these studies and report the formation of P–S $2\sigma-1\sigma^*$ configurations in radicals containing a trialkylphosphine moiety and a progressively substituted sulfur atom. It will be shown that the spin density distribution of structures I, II, and III (fig. 1) is rather similar and not seriously affected by increasing substitution and electronegativity of the sulfur fragment.

2. Experimental

Trimethylphosphine (Me_3P) was prepared from the corresponding silver iodide complex (Janssen Chimica) by heating in *vacuo*. Dimethylsulfide (Me_2S , Janssen Chimica) and $CFCl_3$ (Aldrich) were used as received. Methylthiotriethylphosphine io-

dide ($\text{Et}_3\text{PSMe}^+\text{I}^-$) was prepared by reacting triethylphosphine sulfide [12] (0.8 g) and methyl iodide (8.52 g) in 25 ml of nitromethane at 45°C for 3 h. Single crystals were obtained by slow evaporation of a solution of $\text{Et}_3\text{PSMe}^+\text{I}^-$ in pentane/methyl iodide in a stream of dry nitrogen (^{31}P NMR, $\delta=71.6$ ppm). Solutions of Me_3P and Me_2S in CFCl_3 were degassed and frozen at 77 K. ESR quartz tubes containing CFCl_3 solutions or oriented single crystals were exposed to X-rays from a Cu source operating at 40 kV and 20 mA for 4 h. ESR spectra were recorded on a Bruker ER 200D X-band spectrometer. Single crystals were rotated perpendicular to the magnetic field direction, in 10° steps, by using a single-axis goniometer. Temperature was controlled with the aid of a Bruker ER 4111 variable temperature unit.

3. Results and assignment

The ESR spectrum of an X-irradiated single crystal of methylthiotriethylphosphonium iodide ($\text{Et}_3\text{PSMe}^+\text{I}^-$) recorded at 105 K (fig. 2) reveals the features of a phosphorus-centred radical with a large ^{31}P hyperfine coupling. The radical is present in two magnetically distinct orientations. The angular variation of the ESR transitions was obtained by rotating the crystal in three mutual orthogonal planes, and used in an iterative procedure to obtain the ^{31}P and \mathbf{g} tensors via an exact diagonalization of the appropriate spin Hamiltonian (table 1) [13]. It appears that the parallel hyperfine interactions of the

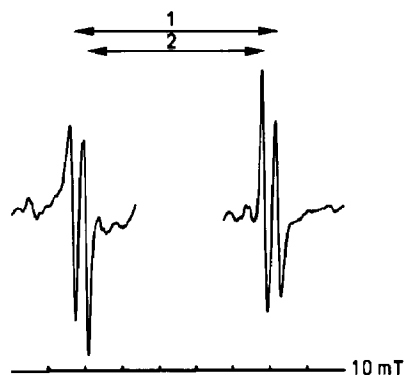


Fig. 2. Single-crystal ESR spectrum of the Et_3PSMe radical at 105 K showing two distinct magnetic orientations.

two orientations of the radical in the crystal are inclined by an angle of 103°. Using the principal values of the ^{31}P hyperfine coupling tensor it is possible to calculate the isotropic (A_{iso}) and dipolar (A_{dip}) contributions and to estimate the phosphorus 3s and 3p contributions to the singly occupied molecular orbital (SOMO) [14]. This analysis results in $\rho_{3s}=10.7\%$ and $\rho_{3p}=29.6\%$, which is comparable to the spin density distribution of the previously detected Et_3PS^- radical anion ($\rho_{3s}=12.5\%$ and $\rho_{3p}=38.7\%$) [12]. Based on this similarity there is no doubt that the present species is the Et_3PSMe phosphoranyl radical (structure II, fig. 1), formed via an electron capture reaction of the cationic precursor. Compared to Et_3PS^- , the p/s ratio of Et_3PSMe is slightly reduced: 2.77 versus 3.10 (table 2). Additional support to our assignment comes from the fact that Me_3PSMe radicals have been detected by Giles

Table 1
Hyperfine ^{a)} and \mathbf{g} tensors ^{b)} of the Et_3PSMe radical

	Total tensor	Isotropic part	Dipolar part	Direction cosines		
				x	y	z
g	2.000	2.009		-0.585	0.464	-0.665
	2.008			0.016	0.826	0.563
	2.019			0.811	0.319	-0.490
A	1305	1428	-123	-0.707	0.080	-0.703
	1333		-95	-0.706	-0.148	0.693
	1645		217	0.049	-0.986	-0.161

^{a)} **A** in MHz.

^{b)} The z axis of the ESR reference frame was chosen perpendicular to the face of the plate-shaped crystals, the x and y axes were defined by the extinction directions of the crystal perpendicular to z.

Table 2
Spin-Hamiltonian parameters ^{a)} and valence orbital spin densities

Radical	A_{\perp}	A_{\parallel}	A_{iso}	$2A_{dip}$	g_{\perp}	g_{\parallel}	g_{iso}	ρ_s (%)	ρ_p (%)	p/s	ref.
Et ₃ PSMe	1333 1308	1645	1428	217	2.008 2.019	2.000	2.009	10.7	29.6	2.77	
Me ₃ PSMe ₂ ⁺	1385	1840	1537	303	2.006	2.003	2.005	11.5	41.3	3.59	
Me ₃ P ⁺ b)	813	1636	1087	549	2.007	2.002	2.005	8.1	74.8	9.19	
Me ₃ P-PMe ₃ ⁺	1333	1605	1424	181	2.006	1.998	2.003	10.7	24.7	2.32	
Me ₃ PS ⁻	1660 1647	2021	1776	245	2.003 2.010	2.004	2.006	13.3	33.3	2.50	[12]
Et ₃ PS ⁻	1517 1517	1943	1659	284	2.006 2.006	2.002	2.005	12.5	38.7	3.10	[12]
Me ₃ PSMe			1539				2.009	11.5			[15]

^{a)} A in MHz. ^{b)} $A_{\parallel}(H) = 33.2$ MHz, $A_{\perp}(H) = 34.2$ MHz, with coupling to nine equivalent protons.

and Roberts after reaction of thyl radicals with trimethylphosphine in liquid propane [15]. They report an isotropic ³¹P hyperfine coupling of 1539 MHz (54.73 T, $g = 2.0091$) which is similar to $A_{iso} = 1428$ MHz for Et₃PSMe in the solid state. The signals assigned to Et₃PSMe are irreversibly lost from the ESR spectrum at 140 K. No secondary phosphorus centred radicals are observed.

Radiogenic formation of R₃PSR₂⁺ radical cations in a single crystal via an electron-capture reaction requires a dicationic R₃PSR₂²⁺ precursor, which is unknown to us ^{#1}. An alternative route to R₃PSR₂⁺ radical cations proceeds via X-irradiation of a 1:1 mixture of a trialkylphosphine and a dialkylsulfide in a freon matrix. It is well known that various cationic radicals can be generated via ionization of their precursors in a halocarbon matrix [17,18]. Moreover, it has been demonstrated that in sufficiently concentrated solutions of phosphines or sulfides it is possible to generate both the parent cationic R₃P⁺ and R₂S⁺ radicals as well as the homodimeric species R₂P-PR₃⁺ and R₂S-SR₂⁺ resulting from a reaction of the parent radical cation with a second precursor molecule [19-25]. After X irradiation of a 1:1 mixture of trimethylphosphine (Me₃P) and dimethylsulfide (Me₂S) in CFCl₃ the ESR spectrum shown in fig. 3a is obtained. Compared to the spectrum of pure Me₃P in CFCl₃ (fig. 3b), giving signals due to the Me₃P⁺ and Me₃P-PMe₃⁺ radical cations [19,20], the spectrum in fig. 3a shows an additional set of lines which we attribute to the asymmetric Me₃PSMe₂⁺ dimer radical cation (structure III, fig.

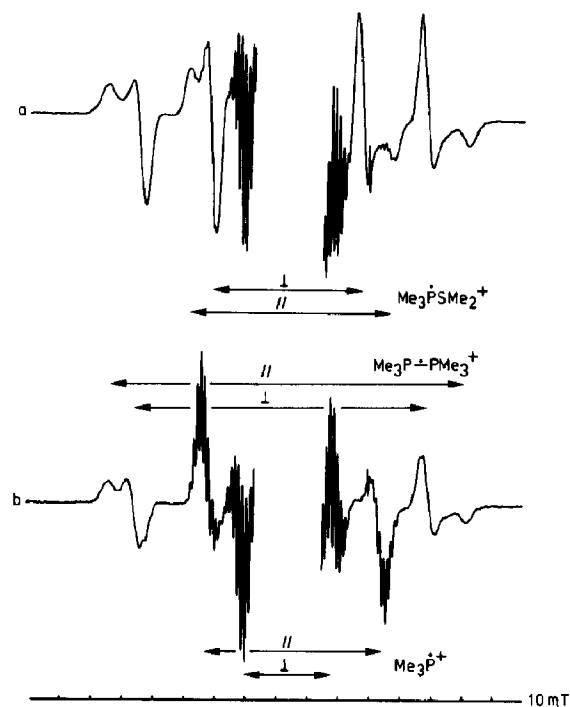


Fig. 3. ESR spectrum of CFCl₃ solutions after exposure to X-rays at 77 K. (a) 1:1 mixture of Me₃P and Me₂S in CFCl₃, showing the extra features assigned to Me₃PSMe₂⁺. (b) pure Me₃P in CFCl₃ with signals of Me₃P⁺ and Me₃P-PMe₃⁺ radical cations.

1). The perpendicular and parallel hyperfine couplings of Me₃PSMe₂⁺ lead to $A_{iso} = 1537$ and $2A_{dip} = 303$ MHz, again very similar to those of related species like Me₃PS⁻, Et₃PS⁻, Et₃PSMe, and Me₃PSMe (table 2). The signals of Me₃PSMe₂⁺ are stable until the sample melts at 145 K. Quantum-

^{#1} For structure and preparation of related dications, see ref. [16].

chemical calculations on the prototype three-electron bond radical $\text{H}_3\dot{\text{P}}\text{SH}_2^+$ have been performed with a variety of methods and reveal a stable structure with a dissociation energy of 13–22 kcal/mol [1,12,26]. The isotropic and dipolar hyperfine interactions, calculated for $\text{H}_3\dot{\text{P}}\text{SH}_2^+$ from the spin-annihilated UHF wave function by computing the expectation values of their corresponding operators, show a close agreement with the present experimental values: $A_{\text{iso}}^{\text{calcd}} = 1438$ and $2A_{\text{dip}}^{\text{calcd}} = 327$ MHz [12].

4. Conclusion

The experiments demonstrate that the spin density distribution of a three-electron P–S bond in $\text{R}_3\dot{\text{P}}\text{SR}_n^{n-1}$ ($n=0, 1, 2$) phosphoranyl radical is fairly insensitive to n , the number of alkyl substituents on the sulfur atom. Table 2 shows that approximately 40–50% of the unpaired electron density in these species is localized on the phosphorus atom with a p/s ratio ranging from 2.5 to 3.6. In contrast to this experimental result, previous quantum-chemical calculations on $\text{H}_3\dot{\text{P}}\text{SH}_n^{n-1}$ prototype systems reveal a stable structure only for $n=2$ and predict a barrierless dissociation for $n=0$ and $n=1$ [12]. This behaviour is in agreement with the respective Δ_{IP} values. Further rationalization of the theoretical results comes from the fact that a contribution of a $\text{R}_3\text{P}^+ \cdots \text{SH}_n^{n-2}$ resonance structure (with the unpaired electron density on phosphorus) to the three-electron bond implies an unfavourable separation of charge for $n=0$ or $n=1$, but not for $n=2$ [1]. The apparent contradiction between experiment and theoretical results can be solved by assuming an effective shielding of the developing charge separation in condensed phases by neighboring molecules. On the basis of the present results it can be expected that a large number of heteronuclear three-electron bonds between a variety of elements is experimentally accessible in solution and in the solid phase, despite an unfavourable balance of the ionization potentials of the fragments involved.

Acknowledgement

This investigation has been supported by the

Netherlands Foundation for Chemical Research (SON) with financial aid from the Netherlands Organization for Scientific Research (NWO).

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