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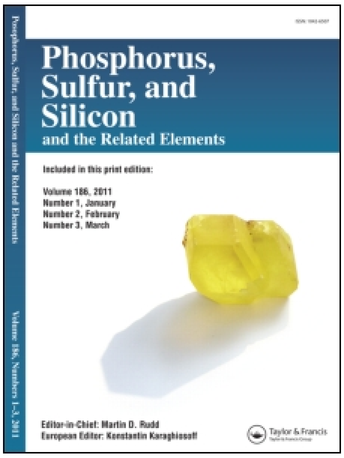

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

TRIS 2,4,6-TRIMETHYLPHENYL-PHOSPHINE AND ARSINE RADICAL CATIONS

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To cite this Article Il'yasov, A. V. , Kargin, Yu. M. , Nikitin, E. V. , Vafina, A. A. , Romanov, G. V. , Parakin, O. V. , Kazakova, A. A. and Pudovik, A. N.(1980) 'TRIS 2,4,6-TRIMETHYLPHENYL-PHOSPHINE AND ARSINE RADICAL CATIONS', Phosphorus, Sulfur, and Silicon and the Related Elements, 8: 3, 259 — 262

To link to this Article: DOI: 10.1080/03086648008078199

URL: http://dx.doi.org/10.1080/03086648008078199

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Phosphorous and Sulfur, 1980, Vol. 8, pp. 259–262
0308-664X/80/0803–0259$04.50/0

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(*Received July 23, 1979*)

The character of electrochemical oxidation of trimesitylphosphine and trimesitylarsine in acetonitrile has been studied on the rotating platinum electrode. Their oxidation has been shown to involve two stages, the first one being the one-electron reversible wave.

Characteristics of common anodic and cathodic waves of degassed solution of substances on stationary electrodes and symmetry of their cyclic voltammetry polarograms indicate the stability of radical cations formed. Electrochemically generated radical cations of tris 2,4,6-trimethylphenyl-phosphine (Mes_3P^+) and -arsine (Mes_3As^+) were studied by ESR spectroscopy.

Hyperfine splitting was found to be $a^P = 250$ gauss, $a^{As} = 279$ gauss and hybridisation ratios $C_p^2/C_s^2 = 13.8$ and 12.3 were established from analyses of anisotropic spectra.

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INTRODUCTION

Radical cations of phosphorous compounds generated either by chemical or electrochemical oxidation and during irradiation of liquids or glassy matrices have been extensively studied.[1–9] There exist both primary radical cations PR_3^+ and secondary dimer ions $PR_3—PR_3^+$ of trialkylphosphines in glassy matrices whereas in liquids oxidation of PR_3 alone gives rise to the spectrum of phosphine dimer radical cation. The principal characteristic of both types of radicals is the large value of hyperfine splitting constant due to the localization of unpaired electron on phosphorous or σ-orbital of P—P-bond, the hybridization ratio (C_{3p}/C_{3s}) being reduced from 9.5 in monomer to ~ 2 in dimer cations. Thus the latter ions may have less distorted tetrahedral bonds as compared with parent PR_3 molecules.

Some authors[10–12] have suggested that π-type phosphine radical cations were formed at complete charge transfer in some donor-acceptor complexes (Ar_3P + TCNE or chloranyl) or by oxidation of phosphines with other agents (as $AgClO_4$). Nevertheless the existence of such positively charged radicals is open to discussion for there is no evidence whatsoever of any formation of such radicals. The phosphorous hyperfine splitting for these systems is approximately of the same value as in appropriate radical anions ($\sim 4 \div 12$ oe).

Calculations of spin density distribution for alkyl cation radicals $PX_3^{+\cdot}$[13] as well as experimental results[5,6] have proved the polarization of P—C-bond to be weak. If this holds true for aryl radical cations as well, large phosphorous splitting in $Ar_3P^{+\cdot}$ is to be expected.

RESULTS AND DISCUSSION

The nature of electrochemical oxidation of Mes_3P and Mes_3As in acetonitrile presented here enables one to carry out spectroscopical studies of intermediates of one-electron process.

Two oxidation waves can be observed on the Mes_3P and Mes_3As polarization curves (Figure 1). The number of electrons transferred was evaluated by comparing the wave heights of oxidation of substances with those of reference substances (*p*-anisyldiphenylamine and phenothiazine). The wave heights in the above substances were established to be due to one-electron transfer. The limiting current of the first wave is due to diffusion because there exists proportional connection of the value of limiting current and the square root of rotational velocity of electrode.

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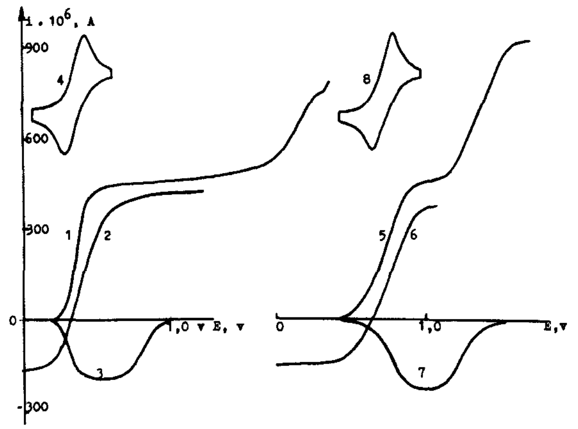

FIGURE 1 The polarization curves trimesitylphosphine (1–4) and trimesitylarsine (5–8) in acetonitrile on the platinum electrode: 1–on the rotating disk electrode (360 rpm); 2–on the rotating ring electrode (360 rpm), $E_D = 0.75v$; 3— on the rotating ring electrode (360 rpm), $E_R = 0v$, $E_D = 0 \div 2.0v$; 4–on the stationary electrode, ($C = 5 \cdot 10^{-3}$, M, $V = 1.2v/min$); 5–on the rotating disk electrode (360 rpm); 6–on the rotating ring electrode (360 rpm), $E_D = 1.0\,v$; 7–on the rotating ring electrode (420 rpm), $E_R = 0v$, $E_D = 0 \div 1.6v$; 8–on the stationary electrode, ($c = 5 \cdot 10^{-3}$ M, $V = 4.8\,v/min$).

Absence of the reduction peak at potentials of the first wave on the cyclic voltammetric curve of Mes_3P and appreciable decrease of the wave height of one-electron level[14] seemed to be concerned with insufficient purity of the experiment. The anodic and cathodic pair of the peaks were distinctly observed on the stationary electrode when purification of the solvent, the supporting electrolyte and the substances were carefully performed with preliminary blowing of dry argon through the electrolyte.

The symmetry of cyclic waves in potentials and heights of peaks recorded at the low rate of potential change and the existence of the united anodic and cathodic waves on the rotating ring electrode bear evidence to the fact that radical cations of trimesitylphosphine Mes_3P^{+} and trimesitylarsene Mes_3As^{+} formed are stable enough. The radical cations of Mes_3P are of pink colour and Mes_3As are blue.

Thus oxidation of Mes_3P and Mes_3As at the first reversible one-electron wave potential results in the formation of primary radical cations

$$Mes_3P - e \rightleftarrows Mes_3P^{+}$$

$$Mes_3As - e \rightleftarrows Mes_3As^{+}$$

The ESR spectra of radical cations during electrochemical oxidation of trimesitylphosphine and trimesitylarsine at the first wave potentials are given in Figure 2–3, their parameters presented in the Table I.

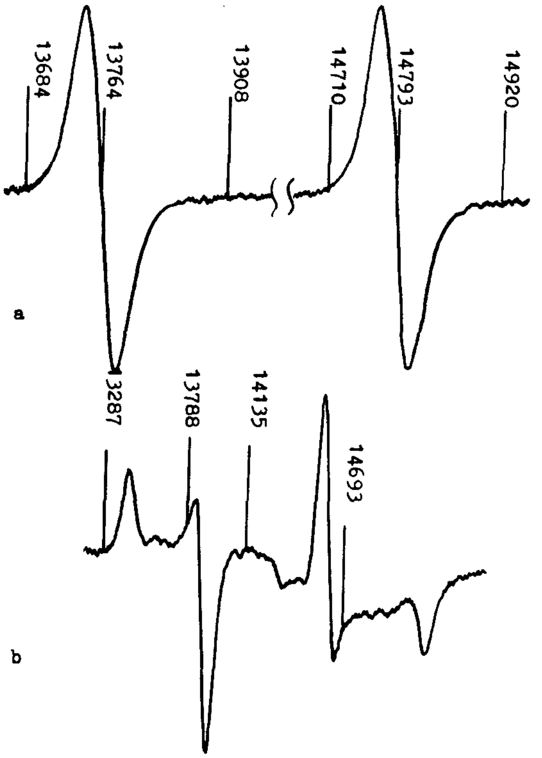

FIGURE 2 ESR spectra of radical cation Mes_3P^{+} at room temperature (a) and at 77°K (b).

TABLE I

Line widths, g values and hyperfine splittings of radical cations Mes_3P^{+} and Mes_3As^{+}

Radical cations	δH, $\pm 0.1G$	g factor ± 0.001			a_{iso}, $\pm 0.1G$	$A_{\parallel}$, $\pm 0.5G$	$A_{\perp}$, $\pm 0.5G$	C_p^2/C_s^2
		g_{iso}	$g_{\parallel}$	$g_{\perp}$				
Mes_3P^{+}	9.0	2.005	2.008	2.016	250.0	152	410	13.8
Mes_3As^{+}	12.0	2.016	1.960	2.044	279.0	462	193	12.3

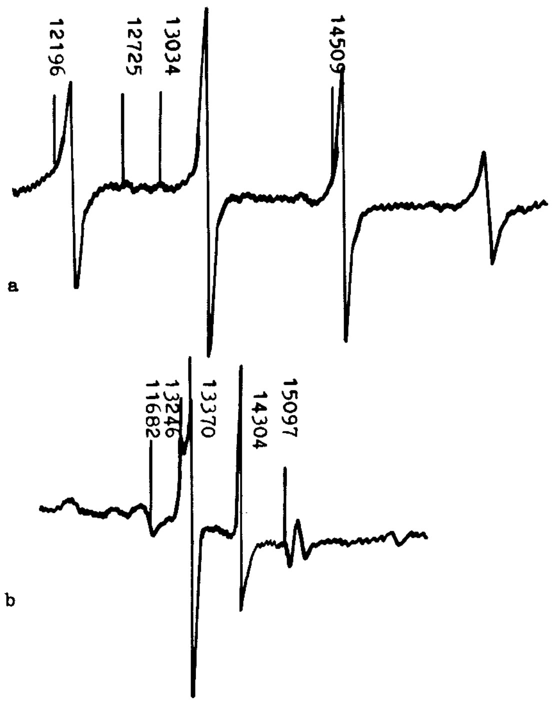

FIGURE 3 ESR spectra of radical cation Mes_3As^{+} at room temperature (a) and at 77°K (b).

It should be noted that generation at the more positive potentials results in the destruction of radical cations.

ESR spectrum of the radical cations Mes_3P^{+} consists of two and that of Mes_3As^{+} of four hyperfine lines due to interaction of unpaired electron with phosphorous ($I = \frac{1}{2}$) or arsenic ($I = \frac{3}{2}$) nuclei (Figure 2a and 3a). Anisotropic interaction is observed in ESR spectra of fluid solution even at temperatures higher than room temperature. The ESR spectra of frozen radical solutions (Figures 2b and 3b) correspond with the ordinary anisotropic spectra of axial symmetry, the hyperfine structure being due to the interaction of unpaired electron with P and As nuclei. Evaluation of hyperfine splitting constants and g-tensor was performed according to the Breit-Raby approximation.[3] Deviation of average values of anisotropic parameters of ESR spectra from values in liquids and frozen solutions may be due to the change of electric field symmetry in the vicinity of the localization of unpaired electrons and to approximation involved in determining anisotropic parameters.

The significant value of hyperfine interaction of atoms of elements may be due to the localization of the unpaired electrons on the atoms of the elements, the great p-orbital spin density values being consistent with formation of monomer radical cations.

ESR spectra of paramagnetic phosphine products formed with a strong electron acceptor seem to be due to the radical anion rather than to that of a cation and this may be connected with the transfer of electrons to phosphorous compounds, radical anions of the acceptor (TCNE, quinones) being formed in solution.

Thus the ESR spectra of positive and negative ions P and As differ in contrast to the ESR of radical anions and cations of alternant hydrocarbons.[15]

EXPERIMENTAL

Electrochemical oxidation of trimesityl-phosphine and -arsine was studied with the help of voltammetric methods using platinum stationary electrode and rotating disk electrode (Pt) with a ring (Pt in acetonitrile with supporting electrolyte 0.1 M $NaClO_4$). The concentration of phosphine and arsine was 5.10^{-3} M. The reference electrode was the amalgamated tip of a silver wire in 0.01 M solution of $AgNO_3$, in acetonitrile. The experimental procedure was described earlier in.[14]

Electrochemical generation of radical cations Mes_3P^{+} and Mes_3As^{+} for the ESR study was performed on the platinum electrode with a silver reference electrode in a special vacuum cell, described in.[16] The cell was pumped up to 10^{-5} tor or blown off with argon. The potential of the working electrode was controlled within the accuracy of ± 0.05 v with the help of a special home-made potentiostat. The ESR spectra were recorded on the ESR spectrometer ER 9 (Carl Zeiss, Jena, DDR) at temperature interval $-70° \div +70°C$. The solutions were the same as those used for polarographic study.

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