to those who need spectroscopic information of ion radicals. We are most willing to provide the data from our measurements on several hundred substances which will be published in due course.

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Electron Spin Resonance Spectra of γ-Irradiated or Photolyzed Arsines

A. R. Lyons and M. C. R. Symons*

Contribution from the Department of Chemistry, The University, Leicester LE1 7RH, England. *Received November 7, 1972*

Abstract: Exposure of trialkylphosphonium and trialkylarsonium ions in sulfuric acid glasses at 77 K to ^{60}Co γ-rays gave radicals whose esr spectra are shown to be characteristic of the radical cations R_3P^+ and R_3As^+. The results confirm that these radicals are pyramidal with C_{3v} symmetry, the unpaired electron being in an orbital having a p:s ratio of about 8 which is strongly confined to the central atom. No proton hyperfine coupling was detected. These results are discussed in relation to a recent suggestion that R_3As^+ radicals have a very low spin density on As when R is aromatic. Results recently reported for R_2As radicals are largely confirmed, and attention is called to the remarkable similarity between the hyperfine tensor components for Me_2As and Ph_2As radicals. These results show conclusively that π delocalization of the unpaired electron into the aromatic rings in Ph_2As radicals is negligibly small.

In a most interesting paper, Preer, *et al.*, have recently presented esr spectra for various uv irradiated arsines in rigid alcoholic solutions.[1] In view of the importance of these compounds as ligands in transition-metal complexes, it seemed of interest to outline some of our own work in this area and to call attention to a remarkable facet of the results which was not previously mentioned.

Some time ago we reported esr results for the series of isoelectronic radicals R_3Al^-, R_3Si, and R_3P^+,[2] and deduced from the derived orbital populations on the central atoms that, while all three types of radical are pyramidal, there is a pronounced flattening on going from aluminum to phosphorus. This, we suggested, is best understood in terms of Pauling's electronegativity principle.[3]

More recently,[4] we showed that when pure alkyl phosphines or arsines are γ-irradiated, cation dimers, $R_3P-PR_3^+$ and $R_3As-AsR_3^+$, are formed rather than the simple cations. We have not, however, reported results for the R_3As^+ cations themselves. Also, in some of these radiation studies, we have obtained esr spectra very similar to those assigned by Preer, *et al.*,[1] to R_2As radicals; we agree entirely with their assignment, but differ slightly in the derived magnetic parameters.

Experimental Section

Materials. Trimethyl-, triethyl-, and triphenylphosphines and -arsines were of the highest grade available and were used, in general, as supplied since further purification had no effect on the esr results. Sulfuric acid was *ca.* 98% AnalaR grade. Solutions were prepared at *ca.* 273 K and immediately frozen, as small beads, to 77 K.

Irradiation. These samples were exposed at 77 K to ^{60}Co γ-rays in a Vickrad source at a nominal dose rate of 4 Mrad hr^{-1}. Irradiation times ranged from 0.1 to 2 hr.

Esr Spectroscopy. Spectra were obtained at 77 K using a Varian E3 spectrometer and were calibrated with diphenylpicrylhydrazyl. Samples were annealed *in situ* either using a Varian variable-temperature accessory or by removing the liquid nitrogen from the dewar insert and allowing the sample to warm slowly, liquid nitrogen being added again as soon as appreciable changes in the esr spectra were noticed.

Results

For the trimethyl and triethyl compounds in sulfuric acid, the central region (± 100 G) of the esr spectra was dominated by features from $R_2\dot{C}-PH^+R_2$ or $R_2\dot{C}As^+-HR_2$ radicals, as described previously.[5,6] However, except for the triphenyl compounds, the outer spectral regions for the phosphonium salts comprised a doublet with distinct parallel and perpendicular features as indicated in Figure 1. These features are assigned to Me_3P^+ radical cations for reasons that have been outlined previously.[2] The arsonium ions gave rather similar outermost features (Figure 2) which are assigned to the $M_I = \pm {}^3/_2$ parallel and perpendicular components of spectra for R_3As^+ radical cations. The $M_I = \pm {}^1/_2$ lines are hidden by features previously assigned to β radicals, $R_2\dot{C}CH_2AsH^+R_2$.[7] Some derived parameters are given in Table I. These have been obtained using the Breit–Rabi equation.

Also given in Table I are the corresponding orbital populations for the unpaired electron on phosphorus and arsenic. Although admittedly very approximate,

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(1) J. R. Preer, F.-D. Tsay, and H. B. Gray, *J. Amer. Chem. Soc.*, **94**, 1875 (1972).

(2) A. Begum, A. R. Lyons, and M. C. R. Symons, *J. Chem. Soc. A*, 2290 (1971).

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(6) A. R. Lyons, G. W. Neilson, and M. C. R. Symons, *J. Chem. Soc., Faraday Trans. 2*, 1063 (1972).

(7) A. R. Lyons and M. C. R. Symons, *ibid.*, **68**, 622 (1972).

Table I. Esr Parameters Assigned to Various Arsenic and Phosphorus Radicals

Parent material	Radical	Medium	^{31}P or ^{75}As hyperfine components, G $A_{\parallel}$	$A_{\perp}$	Derived orbital parameters, %[a] $a_s{}^2$	$a_p{}^2$	(p + s)	p/s	g-Tensor components $g_{\parallel}$	$g_{\perp}$
Me_2AsI	Me_2As[b]	EtOH	220	±5.0	2.2	77.6			2.000	2.002
Ph_3As	Ph_2As[b]	EtOH	220	±5.0	2.2	77.6			2.000	2.002
Ph_3As	Ph_2As[c]	Ph_3As	220	±5.0	2.6	100[d]			2.00	2.075
Et_3AsH^+	Et_3As^+[c]	H_2SO_4	550	280	11	97	108	8.8	2.00	2.03
Et_3As	$(Et_3As)_2{}^+$[e]	Et_3As	465	375	11.8	32.8	44.6	2.8	2.002	2.020
Me_3PH^+	Me_3P^+[c]	H_2SO_4	598	301	11.0	96.0	107	8.7	2.002	2.023
Et_3PH^+	Et_3P^+[f]	H_2SO_4	488	283	10.6	98.5	109	9.3	2.002	2.009
Et_3P	$(Et_3P)_2{}^+$[e]	Et_3P	540	412	12.5	41.4	53.9	3.2	2.002	2.012

[a] Derived in the normal manner (see P. W. Atkins and M. C. R. Symons, "The Structure of Inorganic Radicals," Elsevier, Amsterdam, 1967) using $A^0(^{31}P) = 3640$ G, $2B^0(^{31}P) = 206$ G. [b] Reference 1. [c] This work. [d] Using positive sign for $A_{\perp}$. [e] Reference 5. [f] Reference 4.

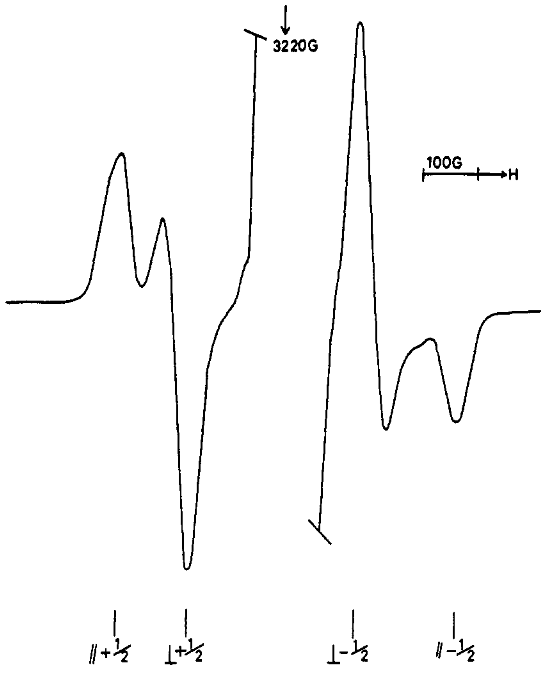

Figure 1. A first derivative esr spectrum for a solution of trimethylphosphine in sulfuric acid at 77 K after exposure to ^{60}Co γ-rays showing features assigned to Me_3P^+ radicals.

these nevertheless allow direct comparison between the two sets of data and certainly give a fair idea of the orbital involved.

Our spectra for R_2As radicals were indistinguishable from those reported already[1] and require no further elaboration. Unfortunately, our attempts to obtain Ph_3As^+ radicals from Ph_3As or Ph_3AsH^+ have so far failed.

Discussion

R_2As Radicals. The most clear-cut result for these radicals is the appearance of four parallel hyperfine components having $A_{\parallel} \approx 220$ G and $g_{\parallel} = 2.000$ (*cf.* Figures 2 and 4 of ref 1). As stressed by Preer, *et al.*, the esr results agree well with expectation for such π radicals (see Table I). Although our interpretation of the parallel data is the same, we differ with respect to the choice of perpendicular features. Thus, in our view, $g_{\perp} \sim 2.075$, while Preer, *et al.*, give $g_{\perp} \sim 2.002$. Theoretically, a positive shift from the free-spin value is to be expected for both in-plane g components (g_{zz} and g_{yy}).[8] The key to the correct assignment, however, comes from the relative intensities of the $M_I = +{}^3/_2$ and $M_I = -{}^1/_2$ parallel features. Our results, and those of ref 1, show conclusively that the $M_I = +{}^3/_2$ parallel component is more intense than the $M_I = -{}^1/_2$ line. This must mean that the $M_I = +{}^3/_2$ perpendicular line is closer to its parallel shoulder than is the $M_I = -{}^1/_2$ perpendicular line to its parallel shoulder. This agrees with our assignment and seems to rule out the alternative.[1] In fact, several spectra show a second $M_I = +{}^3/_2$ component just to low field of the major, nearly isotopic $M_I = +{}^1/_2$ line (*cf.* Figure 4 of ref 1).[8]

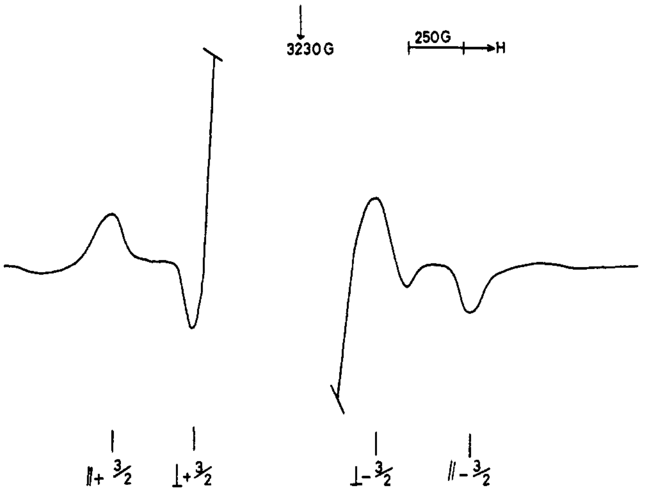

Figure 2. A first derivative esr spectrum for a solution of triethylarsine in sulfuric acid at 77 K after exposure to ^{60}Co γ-rays showing features assigned to Et_3As^+ radicals, which correspond to the outer lines for radicals having $M_I = \pm{}^3/_2$ for the $\Delta M_I = 0$ transitions. The $M_I = \pm{}^1/_2$ lines, together with any "forbidden" transitions, are obscured by the intense central features.

The extra structure clearly visible on some of the $+{}^1/_2$ lines (Figure 3 of ref 1) is the major reason for the alternative assignment previously proposed. It is clear from Figure 3 of ref 1 that the computer reconstruction on the basis of two equivalent arsenic atoms is better than that for six equivalent protons (from the two methyl groups of Me_2As radicals), and this led to the suggestion that the intense line at $g = 2.075$ is due to radical cations such as Ph_3As^+, etc.[1] Unfortunately,

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[8] It is probable that g_{xx} and g_{yy}, comprising the "perpendicular" components, are not exactly equal. Unfortunately, the complexity of powder spectra renders any differentiation almost impossible.

this is an oversimplification of the problem, since the proton reconstruction only pertains to the $+{}^1/_2$ component, which is assumed to be completely isotopic. In fact, it is unlikely that $H(+{}^1/_{2\parallel}) = H(+{}^1/_{2\perp})$. Furthermore, one expects that the $+{}^3/_2$, $-{}^1/_2$, and $-{}^3/_{2\perp}$ features will make some contribution in this region, although that from the $-{}^3/_2$ line will certainly be small. Yet another factor to contend with is the probability that neither the g nor the A tensors are likely to be strictly axial. We are inclined to the view that proton hyperfine coupling is, in fact, responsible for the central three or even five features, since in our spectra and that previously given (Figure 4 of ref 1) for the Ph_2As radical this structure is absent. This leads to narrower components in the $M_I = +{}^1/_2$ region, and hence one can detect several of the predicted "perpendicular" features for these radicals (Table I). Yet another factor to consider is that with $A_\perp$ so small, there should be a strong quadrupole effect that will give rise to extra lines and modify the intensities of the normally allowed transitions. Unfortunately, resolution is too poor to test this suggestion.

Two other factors point in favor of the present assignment. One is that, at S band (*ca.* 3000 MHz) the spectrum is much more symmetrical, and, in particular, the $M_I = \pm{}^3/_2$ lines are nearly equal in intensity. This should not have occurred if $g_\parallel \approx g_\perp$. Also, we have recently obtained several similar phosphorus radicals, $R_2\dot{P}$, which all have $g_\parallel \approx 2.002$ and $g_\perp$ in the 2.010 region. We can confidently predict that the g shift should be considerably greater than this for the arsenic analogs.

Thus, there seems to be no compelling reason for postulating the coincidental appearance of features from another radical in the $g = 2.075$ region.[1] Indeed, our results show that, on annealing, all these features are lost simultaneously.

R_3As^+ Radicals. It is, however, worth considering the suggestion that corresponding positive ions are responsible for these features, in the light of our results for similar species. These results (Table I) show that, as expected, these ions are pyramidal, having nearly unit spin density on arsenic, and a 4p:4s ratio of *ca.* 8. When pure R_3As compounds are irradiated, the corresponding dimers, $R_3As{-}AsR_3^+$, are formed.[4] The esr results show that these dimers have the unpaired electron in a σ^* orbital largely located on the two arsenic atoms (Table I).

Preer, *et al.*,[1] clearly recognized that the results they attributed to R_3As cations and to diars$^+$ could not possibly apply to radicals having the structure we have found for the alkyl derivatives. This rules out the Me_2AsI^+ ion completely, but it remains possible that the aromatic cations have their unpaired electrons preferably in the π framework.[1] In other words, there are two extreme structures for these cations: (i) that in which the bonding to arsenic is pyramidal as in the trialkyl cations, and (ii) that in which the arsenic bonding is planar, the unpaired electron being largely delocalized onto the aromatic ring(s).[1] Structure i does not fit the reported results[1] but is the structure we would favor. Structure ii could possibly fit the data but seems to us to be ruled out by the very large g shift reported ($g_\perp = 2.075$). If the electron were largely in the aromatic ring, such a large shift would be unprecedented; if not, then the parallel ^{75}As coupling should be much larger.

In fact, the very interesting results for $Me_2\dot{A}s$ and $Ph_2\dot{A}s$ radicals seem also to rule out structure ii, and hence the presence of the radical cations. All the results (Table I) for these radicals show that delocalization onto the aromatic rings in $Ph_2\dot{A}s$ radicals is negligible. This is, at first sight, most surprising when compared, for example, with the large delocalization found for such radicals as $Ph_3\dot{C}$ or $Ph_2\dot{N}$ and is, in our view, the most interesting aspect of the results of Preer, *et al.*[1] We have previously shown that when the radicals $H_2\dot{C}NR_2$ and $H_2\dot{C}PR_2$ are compared, delocalization onto nitrogen is extensive, whereas that onto phosphorus is negligible.[6] It was suggested that this might occur because of the greater tendency for the phosphorus atom to remain pyramidal, thus disfavoring overlap and charge transfer. The present results for $Ph_2\dot{A}s$ are almost the reverse, the results showing conclusively that the electron is essentially in a pure 4p orbital on arsenic. We conclude either that overlap between the $2p(\pi)$ carbon orbital and the 4p arsenic orbital is so inefficient that delocalization is minimal, or that, for some reason, the aromatic rings are strongly twisted out of the radical plane.

Finally, it seems that the photolyses can best be explained as

$$R_3As \longrightarrow R_2\dot{A}s + R$$

$$R + SH \longrightarrow RH + S$$

when SH is a solvent molecule. Indeed, esr spectra of both uv[1] and γ-irradiated pure diarsine indicated the presence of trapped methyl radicals in addition to the R_2As radicals.