Proton Hyperfine Splittings in the ESR of Some Alkylphosphine Dimeric Radicals

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The triplet splittings due to protons were observed for the ESR of the dimeric cation radicals of $P(CH_3)_3$, $P(CH_2CH_3)_3$, and $PH(CH_3)_2$; they were formed by the γ irradiation of the rigid CH_2Cl_2 solutions of these alkylphosphines at 77 K. The observed proton hyperfine splittings for the dimer-cation radicals, $[(CH_3)_3P–P(CH_3)_3]^+$ and $[(CH_3CH_2)_3P–P(CH_2CH_3)_3]^+$, were assigned to the hyperfine interaction with two of the methyl and with two of the methylene protons respectively, while those for the $[(CH_3)_2HP–PH(CH_3)_2]^+$ radical were assigned to the hyperfine interaction with the two P–H protons. In the former two radicals, the rotations of the methyl and the ethyl groups are restricted. The conformations of the methyl and the ethyl groups have been estimated on the basis of the observed proton hyperfine splittings. The P–H protons of the $[(CH_3)_2HP–PH(CH_3)_2]^+$ radical have an extremely large isotropic coupling constant of 58 G; it may be attributed to the direct interaction with the unpaired electron in the anti-bonding σ^* orbital of the P–P bond.

When γ-irradiated trialkylphosphines are examined by ESR at 77K, clear parallel and perpendicular features, separated by over 1000 G, are often observed. These hyperfine patterns have been assigned by Lyons *et al.*1) to alkylphosphine dimer-cation radicals of the $(R_3P–PR_3)^+$ type. From the observed phosphorus hyperfine interaction, they concluded that these radicals are σ^* radicals which have their unpaired electrons in anti-bonding σ^* orbitals. In these investigations, the ESR of the dimer cation radicals showed only phosphorus splittings; no proton hyperfine splittings have not been resolved. During the course of our investigations of γ-irradiated phosphorus compounds, we found the ESR of dimer-cation radicals to show further splittings due to protons for the dichloromethane solutions of trimethylphosphine, triethylphosphine, and dimethylphosphine. In this paper we will report some information of the radical structure mainly obtained through these proton hyperfine splittings.

Experimental

The dimethylphosphine $[PH(CH_3)_2]$, trimethylphosphine $[P(CH_3)_3]$, and triethylphosphine$[P(CH_2CH_3)_3]$ were obtained as has been described elsewhere.2) The deuterated compound of dimethylphosphine $[PD(CH_3)_2]$ was prepared by the reaction of $PH(CH_3)_2$ with D_2O in the presence of DBr, while $PH(CD_3)_2$ was prepared by using CD_3I instead of CH_3I in the course of the preparation of $PH(CH_3)_2$. $P(CD_3)_3$ was prepared by dissolving $(CD_3)_3PH^+I^-$, formed from $PH(CD_3)_2$ and CD_3I, into a KOH-dimethyl sulfoxide suspension; thereafter the product was separated from the solution by vacuum distillation. The CH_2Cl_2 solutions of these compounds were irradiated by ^{60}Co γ-rays in ESR sample tubes at 77 K after they has been degassed. The ESR spectra were measured with a Hitachi 771 ESR spectrometer with 100 kHz field modulation.

Results and Discussion

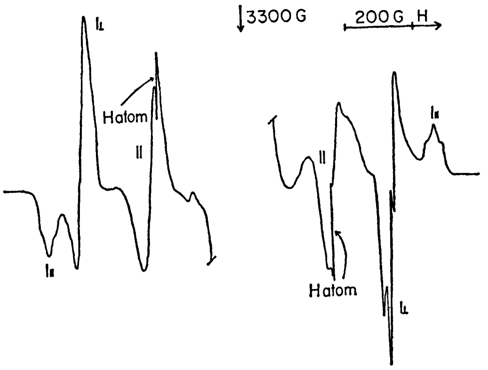


Fig. 1. ESR Spectrum of γ-irradiated $P(CH_3)_3$ at 77 K in CH_2Cl_2. ESR absorption I is assigned to $[(CH_3)_3P–P(CH_3)_3]^+$ and II to $P(CH_3)_3CH_2Cl$.2)

Figure 1 shows the ESR spectrum obtained from the γ-irradiated CH_2Cl_2 solution of $P(CH_3)_3$ at 77K. An ESR absorption similar to the outermost features in the figure (labelled I) is observed for all the compounds treated here; it is assigned to the dimer-cation radicals of the alkylphosphines by reference to Lyons and Symons' assignment for the triethyl- and tributylphosphine dimer-cation radicals.1) The expected central component ($M_I^{^{31}P}=0$) is considered to be hidden under the intense absorptions due to other radical species. Though Lyons *et al.*'s assignments of the dimer-cation radicals were made by the analogy between the reaction and that of trialkylarsines to form their dimer cations, conclusive evidence for the assignment of the spectra is given by the observation of the triplet splittings due to the two P–H protons in the radical $[(CH_3)_2HP–PH(CH_3)_2]^+$ (*vide infra*). It was also observed that the relative intensity of the dimer cation to the monomer-cation radical clearly changes in proportion to the concentration of the parent phosphine in the case of the $P(CH_2CH_3)_3$ solution.

The high-field-side signals for the dimer-cation radicals are shown in Figs. 2—4. The parallel and perpendicular features for the undeuterated compounds show triplet splittings. It is apparent that the triplet splittings for the $[(CH_3)_3P–P(CH_3)_3]^+$ radical arise from the hyperfine interaction with the methyl protons, since the dimer-cation radical of $P(CD_3)_3$ does not show such triplet splittings (Fig. 2). For the case

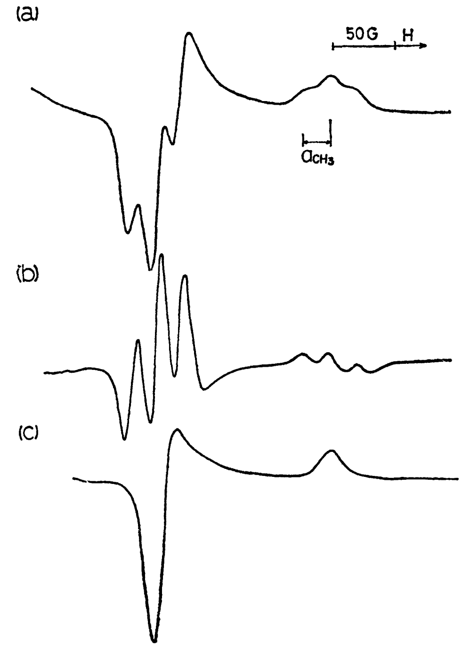


Fig. 2. High field components of ESR spectra for the radicals a) $[(CH_3)_3P\text{-}P(CH_3)_3]^+$ and c) $[(CD_3)_3P\text{-}P(CD_3)_3]^+$ at 77 K, and b) the derivative curve of (a) (2nd derivative ESR spectrum).

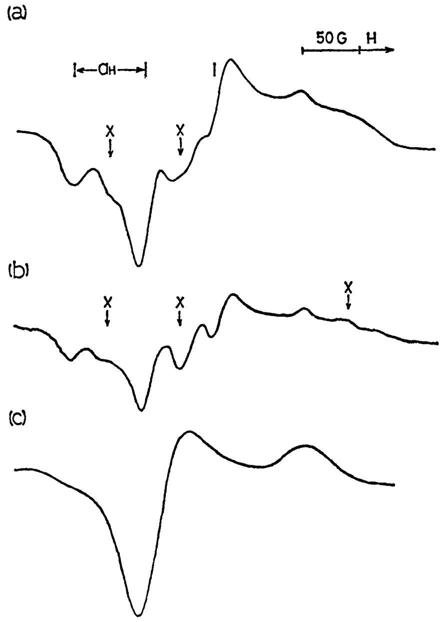


Fig. 3. High field components of ESR spectra for the radicals a) $[(CH_3)_2HP\text{-}PH(CH_3)_2]^+$, b) $[(CD_3)_2HP\text{-}PH(CD_3)_2]^+$ and c) $[(CH_3)_2DP\text{-}PD(CH_3)_2]^+$. See text for X in a) and b).

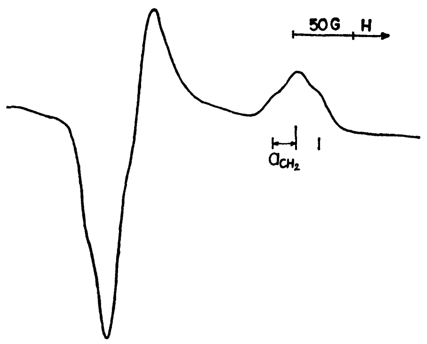


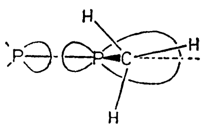
Fig. 4. High field component of the ESR spectrum for the $[(CH_3CH_2)_3P\text{-}P(CH_2CH_3)_3]^+$ radical.

of the $[(CH_3)_2HP\text{-}PH(CH_3)_2]^+$ radical, the triplet splittings were not observed when the P–H protons were deuterated, though the $[(CD_3)_2HP\text{-}PH(CD_3)_2]^+$ radical shows the same triplet splittings as the undeuterated dimer-cation radical. This apparently indicates that the triplet splittings in the $[(CH_3)_2HP\text{-}PH(CH_3)_2]^+$ radical arise from the hyperfine interaction with the P–H protons. The signals labelled "X" in Fig. 3 are probably due to the dimer-cation radical in which one of the P–H protons is replaced with the chlorine of the solvent. When diethylether was used as the solvent, the X signals were not observed. The ESR parameters obtained are summarized in Table 1, together with the orbital populations of the unpaired electron, which were determined by the use of the atomic parameters in the literature.[4)]

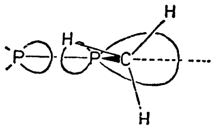
As may be seen from the p/s ratios in Table 1, the phosphorus orbitals occupied by the unpaired electrons take the sp^3 hybridization. This indicates that Lyons *et al.*'s model[1)] is reasonable for the present system also. An interesting result in the present system is the appearance of the proton hyperfine splittings. The triplet splittings due to the methyl protons in the $[(CH_3)_3P\text{-}P(CH_3)_3]^+$ radical indicate that only two among 18 methyl protons have an observable hyperfine interaction. This suggests that the rotation of the methyl groups is strongly restricted and that the radical takes a conformation where only two protons are at the positions of the maximum overlap with the anti-bonding σ^* orbital of the P–P bond containing the unpaired electron. That is, one of the three methyl groups on each phosphorus takes the Ia conformation, where one of the C–H bonds eclipses the lobe of the anti-bonding σ^* orbital, while the other two methyl groups take the Ib conformation, where the methyl group rotates about 60° from the conformation of Ia. In the latter conformation, though one of the C–H bonds is located at a position

TABLE 1. ESR PARAMETERS AND ORBITAL POPULATIONS FOR SOME DIMER-CATION RADICALS

Radical	$g_{\parallel}$	$g_{\perp}$	Hyperfine coupling/G				a_s^2(%)	a_p^2(%)	p/s
			$^{31}P_{\parallel}$	$^{31}P_{\perp}$	$^{31}P_{iso}$	^1H			
$[PH(CH_3)_2]_2^+$	2.003	2.014	581	442	488	58	13.4	45.1	3.3
$[P(CH_3)_3]_2^+$	1.992	2.012	569	439	482	20	13.3	42.2	3.2
$[P(CH_2CH_3)_3]_2^+$	1.990	2.009	549	415	460	18	12.6	43.2	3.4



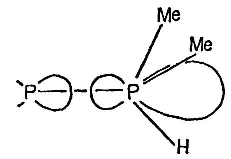
Ia



Ib

parallel to the σ^* orbital, it has no significant hyperfine interaction. It was observed that the triplet splittings smear as the temperature increases from 77 K, though the radical promptly decays above 150 K. The smearing of the proton hyperfine splittings may indicate the onset of the rotation of the methyl groups.

It may be noteworthy that the hyperfine interaction of the P–H protons in the $[(CH_3)_2HP\text{–}PH(CH_3)_2]^+$ radical has the large isotropic coupling constant of 58 G. In the case of the methyl radical, it has been shown by theoretical calculations[5)] that the contribution of the direct interaction with the unpaired electron does not exceed the spin polarization effect on the isotropic hyperfine interaction, even when the radical deforms to a pyramidal structure, and that the hyperfine coupling constant of 23.04 G for the planar structure is the largest value which can be expected for the radical. In view of this fact, the hyperfine coupling constant observed in the present system is surprisingly large; it is probably due to the direct overlap of the unpaired electron orbital with the P–H protons, which are located on the same side as the big lobe of the unpaired electron orbital in the tetrahedral conformation of phosphorus (II).



II

The triplet splittings observed for the $[(CH_3CH_2)_3P\text{–}P(CH_2CH_3)_3]^+$ radical may be attributed to the two methylene protons of the radical by analogy with the case of the $[(CH_3)_3P\text{–}P(CH_3)_3]^+$ radical. The observation of the splittings also suggests that the rotation of the ethyl groups about the P–Et bond is restricted and that the ethyl groups take a conformation where two of the methylene protons are placed near the positions of the maximum overlap with the unpaired electron orbital, as in the case of the $[(CH_3)_3P\text{–}P(CH_3)_3]^+$ radical.

References

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3) To be discussed elsewhere.

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