Monomer and Dimer Cations of Trimethylphosphine: A Radiation Chemical and E.S.R. Study

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The ¹H hyperfine coupling for Me₃P⁺⁺ ions generated radiolytically in Freon at 77 K (*ca.* 11.5 G) is much greater than that for the dimer cations (Me₃P)₂⁺ (*ca.* 3.3 G): this is explained in terms of a decreasing tendency for σ - π delocalisation as the pyramidal character of the Me₃P unit increases, coupled with a tendency towards σ -orbital localisation in σ^* -radicals.

Ionizing radiation is a useful tool for generating electron-gain and electron-loss species and the use of solid matrices is an excellent method for prolonging their existence so that their identities and structures can be probed by spectroscopic methods, especially e.s.r. spectroscopy.¹ When pure materials are irradiated it is often possible to detect both primary species, provided electrons cannot transfer between the parent molecules to give electron return. However, we have shown that the resulting electron-loss centres frequently give dimers having σ^* structures.¹ In order to avoid this, we have used sulphuric acid as a diluent, and have tentatively identified a variety of cations formed by attack of SO_4^- or HSO_4 radicals on solute molecules.^{2–4} We, and others, have recently exploited the excellent properties of tetrachloromethane, and especially of fluorotrichloromethane (Freon) as media which uniquely generate radical cations from dilute solutes on





Figure 1. First derivative X-band e.s.r. spectrum for a dilute solution of Me₃P in Freon after exposure to 60 Co γ -rays at 77 K, showing features assigned to Me₃P⁺⁺ cations.

irradiation, 5-7 and we decided to check some of our sulphuric acid results using this medium.

One interesting example is Me_3P^{++} , thought to have been formed in sulphuric acid,⁸ the identification being uncertain because the expected proton hyperfine coupling was not resolved. We now find that the same species is formed in tetrachloromethane or Freon, but the proton coupling is now clearly defined (Figure 1). When concentrated solutions were used the dimer cation was also formed, the total envelope of proton features giving a proton coupling of *ca.* 3.3 G, this being comparable with the upper limits derivable from other spectra for the dimers. This can be compared with the value of 3.6 G obtained from $(Et_3P)_2^+$ in the liquid phase.⁹ Thus there is a dramatic fall in the ¹H coupling on going from Me_3P^{++} to $(Me_3P)_2^+$.

We have observed similar tendencies of unpaired electrons to become localised in σ^* orbitals relative to the parent radicals and have envisaged this as a general property associated with σ -bond formation.¹⁰⁻¹² Very recently an alternative explanation has been put forward.¹³

In this work, attention was called to the marked fall in $A({}^{1}\text{H})$ on going from Me₂S⁺ to $(Me_{2}S)_{2}^{+}$ (Table 1) which was contrasted with the situation for the σ -radical cation formed by Me₃Si⁺, the proton coupling for $(Me_{3}\text{Si}\cdot\text{SiMe}_{3})^{+}$ dimer being almost equal to that for Me₃Si^{-,13} Since the spin-density is formally only 50% on each Me₃Si-unit, this represents an effective increase in $A({}^{1}\text{H})$.

We suggest that two competing mechanisms are involved, one being the 'confinement' previously envisaged, 10-12 the other being the change in σ - π overlap as the pyramidal character of the $-AB_3$ units changes. The latter mechanism (dismissed by Wang and Williams¹³) only applies to AB₃ systems. It hinges on the fact that for 'AMe₃ radicals σ - π overlap (hyperconjugation), which is the major route for the acquisition of positive spin-density by the protons,14 is maximised for the planar species, decreasing rapidly as bending increases. This effect is exemplified by the fall from ca. 11.5G to ca. 6G on going from 'PMe₃⁺ to 'SiMe₃, the latter deviating most from planarity, as shown by the fall in the 3p: 3s ratio for the central atom hybridisation.² Similarly, the ³¹P hyperfine data show that on going from Me_3P^+ to $(Me_3P^-PMe_3)^+$ the p:s ratio falls, as expected since PMe₃ is far more 'bent' than •PMe₃⁺. Hence σ - π overlap is reduced as $A(^{1}H)$ falls. The reverse is true for the silicon derivative which can be visualised as comprising Me₃Si and planar (Me₃Si)⁺. Indeed, our result for the isostructural σ -radical (Me₃Sn·SnMe₃)⁺ suggests that





Figure 2. Qualitative orbital energy level diagram indicating σ - π delocalisation in $(Me_3M^+)^+$ (thick lines) and $(Me_3M^+MMe_3)^+$ radicals (dashed lines).



the two Me₃Sn-units are nearly planar.¹⁵ Hence σ - π overlap is enhanced in the dimer cation, which should increase $A(^{1}H)$.

This simple explanation does not apply to Me₂S⁺ and $(Me_2S^-SMe_2)^+$ since the degree of hybridisation at sulphur is trivial, the σ^* bond being effectively 3p-3p.¹⁶ In this case, we invoke the 'confinement' concept, which is explained qualitatively in Figure 2. This diagram is a simplification since it ignores the possible role of the C-H σ^* -orbitals amongst other things. Nevertheless, it properly accommodates the concept of $\sigma-\pi$ delocalisation and shows why the electron has a smaller tendency to delocalise into the C-H σ -orbital on σ -bond formation in the dimer. Clearly, electron-loss from the σ -orbital results in an effective deepening of the SOMO and hence an increase in the compatibility of this orbital with the C-H σ -orbital with a consequent increase in delocalisation. This explanation is complementary to that given above involving shape changes.

We consider that the alternative explanation given for these changes¹³ is incorrect. It seems to depend on the contributions to $A(^{1}H)$ from the two components of the σ -, or σ^{*} -orbitals in the dimers (Figure 3). It is suggested that in σ -radicals the contributions of *a* and *b* to $A(^{1}H)$ of a given methyl group are reinforcing, whereas in σ^{*} -orbitals they are opposed. We consider that the degree of σ - π overlap between the C-H orbitals of a methyl group on M(*a*) and orbital *b* must be very

Radical	¹ H Hyperfine coupling/G	³¹ P Hyperfine coupling/G				g-Factor		
		A_{\parallel}	A_{\perp}	A_{180}	2 <i>B</i> `	g_{\parallel}	g_{\perp}	gav,
Me ₃ P ⁺ [Me ₃ P] ₉ +	11.5 (9H) ^a ca. 3.3 ^a	584 592	285 458	385 503	199 89	2.0018	2.008	2.0059
$[Et_3P]_2^+$ Me ₂ S ⁺	$3.6 (12H)^{b}$ 20.4 (6H) ^c			468			(2.0019))
	20.4 (011)					2.0233	2.0088	2.0113
$[Me_2S]_2^+$	6.8 (12H) ^d 6.3 (12H) ^e							2.0103
Me ₃ Si	$6.28 (9H)^{t}$							2.0102
IM. 011+	$6.42 (9H)^{g}$						2 0077	2.0031
$[101e_3S1]_2^+$	$A_{\perp} = 5.55 (18H)^{\mu}$ $A = 5.65 (18H)^{i}$						2.0077	

^a This work. ^b Ref. 9. ^c Ref. 13. ^d B. C. Gilbert, D. K. C. Hodgeman, and R. O. C. Norman, *J. Chem. Soc., Perkin Trans.* 2, 1973, 1748. ^eW. B. S. Gara, J. R. M. Giles, and B. P. Roberts, *J. Chem. Soc., Perkin Trans.* 2, 1979, 1444. [†] P. J. Krusic and J. K. Kochi, *J. Am. Chem. Soc.*, 1969, **91**, 3938. ^e S. W. Bennett, C. Eaborn, A. Hudson, H. A. Hussain, and R. A. Jackson, *J. Organomet. Chem.*, 1969, **16**, 36. ^hJ. T. Wang and F. Williams, *J. Chem. Soc., Chem. Commun.*, 1981, 666. ⁱ T. Shida, H. Kubodera, and Y. Egawa, *Chem. Phys. Lett.*, 1981, **79**, 179. small and hence that this contribution is unlikely to play a major role.

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