Reactions of Radical Anions. Part XVII.[1] The Reactions of Triphenylphosphine Oxide with Alkali Metals in Ethereal Solvents

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The reactions of alkali metals with dilute solutions ($\leqslant 10^{-3}$M) of triphenylphosphine oxide in dimethoxyethane (DME), tetrahydrofuran (THF), and 2-methyltetrahydrofuran (MTHF) have been studied. In DME and THF, reaction with potassium or rubidium, produces paramagnetic products with well-defined e.s.r. spectra. The structure and formation of these radical anions are consistent with the following mechanism:

$$Ph_3PO + 2M \longrightarrow M^+Ph_2\bar{P}O + PhM$$

$$M^+Ph_2\bar{P}O + M \longrightarrow M^+(M^+Ph_2\bar{P}O)^{\cdot-} \quad (M = K \text{ or } Rb)$$

Only one alkali-metal splitting-constant was observed and this is attributed to the alkali metal attached to the phosphorus atom. The alkali-metal splitting-constant is consistent with an ionic $\overset{+}{M}\overset{-}{P}$ bond. When M = Na, the behaviour was found to be anomalous. In MTHF no radical anions could be found for any of the alkali metals.

Variation of the temperature, solvent, or alkali metal results in a change in the phosphorus coupling constants when K^+ and Rb^+ are the gegenions.

THE reactions of triphenylphosphine oxide with potassium in both dimethoxyethane (DME) and tetrahydrofuran (THF) have been partially investigated by various workers with confusing results.[2-4] It appears, however, that two species may be generated depending upon the experimental conditions. Thus Cowley and Hnoosh [2] have observed an e.s.r. spectrum which they attribute to the $K^+Ph_2KPO^{\cdot-}$ species in DME, whilst in THF, $K^+Ph_3PO^{\cdot-}$ appears to be the main radical-anion formed. No explanation has, as yet, appeared concerning this behaviour.

Very many aryl phosphines and phosphine oxides appear to be susceptible to cleavage reactions,[5] depending upon the experimental conditions employed. We have, therefore, reinvestigated the reaction using sodium, potassium, rubidium, and caesium as alkali metals, in DME, THF, and 2-methyltetrahydrofuran (MTHF) as solvent.

The results and discussion presented in this paper are concerned with reaction in dilute solution only ($\leqslant 10^{-3}$M).

EXPERIMENTAL

Triphenyl Phosphine Oxide.—This compound was obtained from Strem Chemicals Ltd. as the hemihydrate. The material was purified by repeated vaporisation under high-vacuum conditions (it boils without decomposition [6]). On cooling, the purified solid was removed and stored in an air-tight vessel; m.p. 156 °C (lit.,[6] 156 °C).

Solvents.—DME, THF, and MTHF were purified by distillation from Na–K alloy under high-vacuum conditions in a manner similar to that described previously.[7]

Alkali Metals.—Sodium, potassium, rubidium, and caesium films were prepared under high vacuum as described previously.[8,9]

Procedure.—Solutions containing 1×10^{-3}M-phosphine oxide were made in each of the three solvents and passed over the appropriate alkali-metal film using the high-vacuum apparatus described previously.[7] Reaction at −80 °C was effected by first cooling the solutions in a solid CO_2–acetone bath.

E.s.r. spectra were obtained using a Varian E-3 paramagnetic resonance spectrometer fitted with a Varian E-4557-9 temperature-controlling unit.

Computer-simulated spectra were obtained from empirically determined hyperfine and line-width parameters on an ICL System 4-70 machine with 236 K store. The spectra were plotted on a Calcomp model 563 drum plotter.

RESULTS

The reactions were performed over the range 20 to −78 °C in an attempt to see whether, or not, the reaction temperature influences the nature of the paramagnetic species produced. However, very little difference in reaction was noticed, except, of course, longer reaction times at the lower temperature. The detailed results for each metal and solvent are given below.

Potassium and Rubidium in THF, DME, and MTHF.—The reaction in DME and THF was rapid for both metals even at −80 °C and initially resulted in the formation of brown-red solutions which did not exhibit e.s.r. signals. Concentration of the solution, addition of unchanged phosphine oxide, or alteration of the temperature could not induce any paramagnetism in the products. However, continued treatment of this solution with metal rapidly resulted in the formation of strongly paramagnetic products which exhibited very well resolved e.s.r. spectra and which were stable at room temperature.

Essentially these e.s.r. spectra consisted of a large doublet of 0.8 to 0.9 mT from the phosphorus, each line of which was further split into a group of seven with hyperfine coupling constant 0.2 to 0.25 mT by the *ortho*- and *para*-protons. The seven lines were clearly visible when rubidium was the gegenion. However, when the alkali metal was potassium, the outermost lines of the group were broadened to such an extent that at the low-field side the

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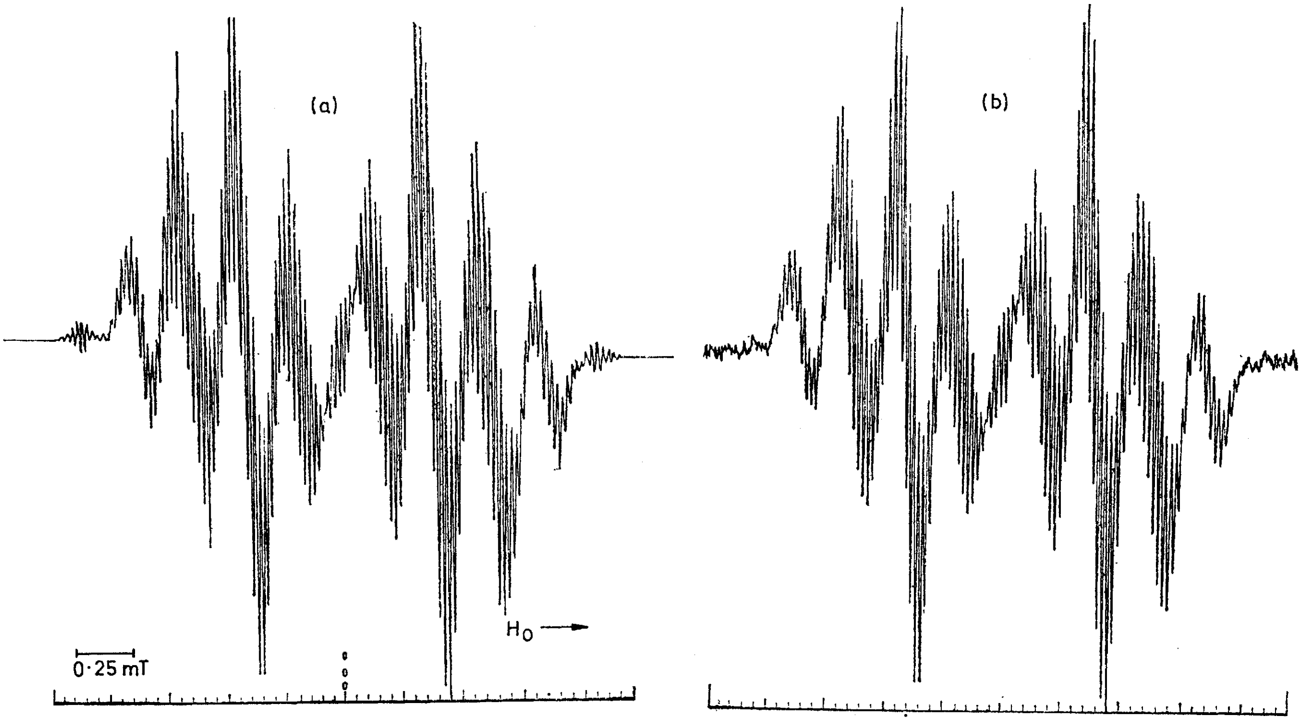
[7] J. E. Bennett, A. G. Evans, J. C. Evans, E. D. Owen, and B. J. Tabner, *J. Chem. Soc.*, 1963, 3954.

[8] A. G. Evans, J. C. Evans, and E. H. Godden, *Trans. Faraday Soc.*, 1967, **63**, 136.

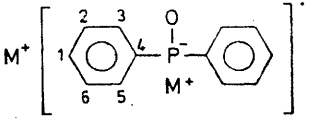
[9] A. G. Evans, J. C. Evans, P. J. Emes, C. L. James, and P. J. Pomery, *J. Chem. Soc.* (*B*), 1971, 1484.

outer line was unobservable, whilst to the high-field side, the outer line could only just be detected above the noise level.

The remaining hyperfine structure is due to a quintet from the *meta*-protons of splitting constant 0.08 mT, and a quartet from the alkali-metal of splitting constant 0.02 mT. The spectrum obtained using K^+ as gegenion is given in the Figure and a computer simulation on the above basis agrees excellently with the observed spectrum. This analysis indicates that the radical anion could have structure (I). The splitting constants are given in Table I.



Calculated (a) and experimental (b) spectra for the potassium-generated radical-anion in DME at room temperature



(I)

TABLE 1

Experimentally obtained splitting constants for the various radical anions at room temperature

Radical anion	Solvent	Metal	Experimentally obtained splitting constants (mT × 10^{-1})				
			1	3,5	2,6	P	M^+
(I)	DME	K	2.40	2.40	0.80	8.00 ±0.10	0.20
	DME	Rb	2.50	2.50	0.80	8.50 ±0.10	0.20
	THF	K	2.30	2.30	0.80	8.32 ±0.10	0.20
	THF	Rb	2.50	2.50	0.80	8.80 ±0.10	0.20

The reaction in MTHF proceeded initially in a manner similar to that described for DME and THF except at a very much slower rate. Again brown-red products were obtained which did not exhibit e.s.r. spectra even when the experimental conditions of concentration, temperature, *etc.* were altered. In this case, however, further treatment of the solution with alkali metal did not induce paramagnetism.

Caesium in THF, DME, and MTHF.—For THF and DME reaction sequences similar to those found for potassium and rubidium were obtained giving red-brown solutions which, on continued contact with metal, gave paramagnetic products with moderately strong e.s.r. spectra, which were stable at room temperature. The spectra, however, were very broad and devoid of any significant hyperfine detail. Consequently, little information could be gained from them. In MTHF as solvent, the reaction was very slow, and the product was not paramagnetic.

Sodium in THF, DME, and MTHF.—In THF and DME red-brown products were initially produced which did not give rise to e.s.r. spectra. Concentration of the solution, addition of unchanged phosphine oxide, or alteration of the temperature did not induce paramagnetism in these products. Continual contact of this solution with sodium, however, resulted in a gradual darkening of the colour and the formation of products which exhibited well resolved e.s.r. spectra. These spectra were the same in DME and THF and were stable at room temperature. Their analysis showed conclusively that the radical-anion was biphenyl sodium.

In MTHF the reaction proceeded initially in a manner similar to that in DME or THF, except at a very much slower rate. Brown-red products were obtained which failed to exhibit e.s.r. signals even after continued contact with sodium.

Effect of Alkali Metal, Solvent, and Temperature on the E.s.r. Spectra.—An inspection of Table 1 shows that at room temperature the phosphorus hyperfine coupling constants are dependent on the solvent and the nature of the gegenion. Significant changes in the phosphorus coupling constant with temperature were also observed when potassium was the gegenion (Table 2). The low-field lines of the ^{31}P doublet were considerably broader than their high-field counterparts at low temperature. In the case of rubidium as gegenion, the line-width effects made measurement of the hyperfine coupling constant very difficult below −40 °C.

DISCUSSION

The reaction proceeded smoothly in all three solvents, even at −80 °C. However, in MTHF the reaction was very slow indeed and did not give rise to paramagnetic products. We believe these observations to be primarily due to the poor solvating power of MTHF in comparison with that of DME or THF. Similar slow reactions have been observed for other phosphorus compounds in MTHF.[10]

TABLE 2

Effect of temperature on the observed splitting constants (mT × 10^{-1}) with potassium as gegenion

	Experimental splitting constants									
	DME					THF				
θ_c/°C	P	1	3,5	2,6	M	P	1	3,5	2,6	M
20	8.00	2.40	2.40	0.80	0.20	8.32	2.30	2.30	0.80	0.20
0	8.10	2.40	2.40	0.80	0.20	8.55	2.30	2.30	0.80	0.20
−20	8.375	2.30	2.30	0.80	0.20	8.75	2.30	2.30	0.80	0.20
−40	8.525	2.30	2.30	0.80	0.20	8.80	2.30	2.30	0.80	0.20
−60	8.775	2.30	2.30	0.80	0.20	8.975	2.30	2.30	0.80	0.20
−80	8.90	2.20	2.20	0.80	0.20				0.80	0.20

Potassium and Rubidium as Gegenions.—(a) *The structure and formation of the radical-ion.* The reaction of potassium and rubidium proceeds smoothly *via* a two-stage process. The products of the first stage are highly coloured and diamagnetic, whilst those of the second are strongly paramagnetic. Such behaviour is typical of radical-anion formation *via* a cleavage reaction and is a common occurrence for aromatic phosphine and phosphine oxides (disproportionation reactions, *etc.*, can be eliminated due to the insensitivity of the first-stage products to changes in experimental conditions).

The appearance of the radical-anions can be rationalised *via* the mechanism suggested by Cowley and Hnoosh.[2]

$$Ph_3PO + 2M \rightarrow M^+Ph_2\bar{P}O + PhM$$

followed by

$$M^+Ph_2\bar{P}O + M \rightarrow (M^+Ph_2\bar{P}O)^{\cdot -} M^+ \quad (M = K \text{ or } Rb)$$

Excellent agreement between the experimental spectra and that calculated for $M^+(M^+Pn_2\bar{P}O)^{\cdot -}$ is obtained when the empirically obtained experimental hyperfine coupling constants and line widths are used as a basis for calculation (Figure). This agreement is found only when *one* alkali-metal interaction is used in the calculation. In the radical-anion structure we propose the two metal ions are in different environments. We attribute the metal splitting to that ion which is intimately associated with the phosphorus atom, *i.e.* that within the bracket.

The value of the metal-ion splitting constant indicates a very small spin density at the K^+ and Rb^+ nuclei. Calculation[11] gives $\rho_{K^+} \simeq 0.003$, $\rho_{Rb^+} \simeq 0.0006$. Such values would be expected in the case of an ionic $\overset{+}{M}\overset{-}{P}$ bond.[10,5c]

Finally, it should be noted that in the dilute solutions studied here, $\leqslant 10^{-3}$M, no evidence was found for the $M^+Ph_3PO^{\cdot -}$ species.

(b) *The effect of solvent, alkali metal, and temperature on the e.s.r. spectrum.* The phosphorus hyperfine-coupling constants show a moderate dependence on the experimental conditions. Alteration of the solvent, alkali metal, or temperature result in small but significant changes in the experimental values. Such changes could occur by a change of the *s*-character of the P–C, P–O, or $\overset{+}{M}\overset{-}{P}$ bonding electrons [since spin polarization of the electrons in these bonds contributes appreciably to the appearance of $A(^{31}P)$], or by a redistribution of π electron-spin density throughout the molecule.

Changes in the unpaired π electron-spin distribution arising due to changes in the structure of the radical–solvent complex(es) have been observed for other phosphorus radical-anions.[1] To determine which of these two effects is operating in the present case, we would require more detailed molecular-orbital calculations simulating the changes in experimental conditions.

The analysis given by Cowley and Hnoosh[2] for the e.s.r. spectrum of the radical-anion obtained in the Ph_3PO–K system differs from our analysis. These workers attribute a splitting of 0.08 mT to K^+ and 0.00 mT to the *meta*-protons, whereas we found values of 0.02 mT for K^+ and 0.08 mT for the *meta*-protons. The spectrum found by Cowley and Hnoosh was incompletely resolved.

Caesium as Gegenion.—No e.s.r. data could be determined for these systems because of the very broad spectra obtained which were devoid of hyperfine detail.

Sodium as Gegenion.—Sodium appears to react anomalously with phosphine oxide. The e.s.r. spectrum obtained shows that the only paramagnetic species formed is that of (biphenyl)$^{\cdot -}$. Similar observations concerning the reaction of this metal with arylphos-

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[11] P. Kusch and H. Taub, *Phys. Rev.*, 1949, **75**, 1477.

phines[10,12] and phosphine oxides[13] have been made previously.

The fact that (biphenyl)$^{\overline{\cdot}}$ is observed in these solutions for sodium, but not for K, Rb, and Cs, suggests that the phenyl radical produced by the initial cleavage of the P–Ph bond by the metal[3] dimerises to biphenyl in the former case, but not in the latter.

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[5/2140 *Received, 3rd November,* 1975]

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