THE KINETICS AND MECHANISM OF THE REACTION OF TRICO-ORDINATE PHOSPHORUS COMPOUNDS WITH TETRACYANOQUINODIMETHANE AND TETRACYANOETHYLENE

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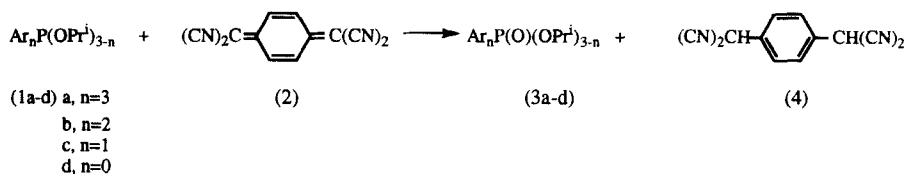Strand, London WC2R 2LS, United Kingdom*

Trico-ordinate phosphorus compounds, $Ar_nP(OPr^i)_{3-n}$ where $n = 0$–3, react with tetracyanoquino-dimethane (TCNQ) in acetonitrile in the presence of water to give the corresponding phosphoryl compounds, $Ar_nP(O)(OPr^i)_{3-n}$ and 1,4-bis-dicyanomethylbenzene (TCNQH$_2$) in quantitative yield. The kinetics of these reactions are reported together with the Hammett ρ-parameters from variation of substituents in the aryl group for $n = 1, 2$ and 3. On the basis of the available evidence, a mechanism is proposed involving one electron transfer from phosphorus (the donor) to TCNQ. A kinetic study of the reaction of triarylphosphines with TCNE in aqueous acetonitrile, however, suggests rate-limiting nucleophilic attack on nitrogen rather than the radical cation mechanism.

INTRODUCTION

The reactions of trico-ordinate phosphorus compounds with a variety of electron acceptor species including quinones and activated alkenes have been studied extensively over the past twenty-five years.[1,2] Some of these reactions involving powerful electron acceptors appear to proceed via single electron transfer mechanisms involving the phosphinium radical cation[3,4] which may be generated through electrochemical oxidation[5,6] or by γ-irradiation of phosphines[7] and observed by e.s.r. On the basis of stereochemical and kinetic studies, the phosphinium radical cation was also postulated as an intermediate in the acid-catalysed reaction of triaryl phosphines (**1**, $n = 3$) with TCNQ (**2**) which gave the triarylphosphine oxides (**3a**) and reduced TCNQ (**4**) as the exclusive products in quantitative yield.[8a,b] Consequently, it was decided that further kinetic studies of the reaction of phosphinites (**1**, $n = 2$), phosphonites (**1**, $n = 1$) and phosphites (**1**, $n = 0$) with TCNQ might provide new experimental evidence to verify the mechanistic proposals and this paper reports the results of the work.

$$Ar_nP(OPr^i)_{3-n} \ + \ (CN)_2C{=}\hspace{-1em}\bigcirc\hspace{-1em}{=}C(CN)_2 \ \longrightarrow \ Ar_nP(O)(OPr^i)_{3-n} \ + \ (CN)_2CH{-}\hspace{-1em}\bigcirc\hspace{-1em}{-}CH(CN)_2$$

(1a-d) a, n=3   (2)   (3a-d)   (4)
       b, n=2
       c, n=1
       d, n=0

RESULTS AND DISCUSSION

1. Tetracyanoquinodimethane

a. *Product analysis.* The reaction of **(1b–d)** with **(2)** in aqueous acetonitrile gave quantitative yields of the corresponding phosphoryl compounds **(3b–d)** and **(4)** which, in representative cases, were isolated and identified by m.p., i.r., and ^{1}H/^{31}P n.m.r. spectroscopy (see experimental). The ^{31}P n.m.r. chemical shifts of **(1b–d)** and **(3b–d)** are shown in Table I.

b. *Kinetics.* The reaction of triarylphosphines **(1a)** with **(2)** in aqueous acetonitrile were catalysed by hydrochloric acid and the rates were followed by u.v. spectroscopy.[8b] The reactions of isopropyl diphenylphosphinite **(1b**, Ar = Ph) and di-isopropyl phenylphosphonite **(1c**, Ar = Ph) with **(2)** under the same conditions were also catalysed by acid but were too fast to be studied by conventional spectroscopic methods. Observable rates were achieved, however, in the absence of the acid catalyst and the results of a series of kinetic experiments are summarised below.

With **(1a–d**, Ar = Ph) the reactions were monitored by disappearance of TCNQ at λ = 394 nm and were found to be first order in tricoordinate phosphorus, first order in TCNQ but zero-order in water over the range of 0.55–5.54 mol^{-1} (1–10% w/v) as shown in Table II which includes the second order rate constants for all four types of tricoordinate phosphorus under identical conditions. Using a variety of substituted arylphosphinites the reactions were accelerated by electron-donating substituents (Table III) to give a Hammett correlation with σ (Figure 1) and a ρ-

TABLE I

^{31}P nmr data of reactants, Ar$_n$P(OPr$'$)$_{3-n}$ and products Ar$_n$P(O)(OPr$'$)$_{3-n}$ with n = 0–3 for the reaction with TCNQ

a) Phosphinites, (X C$_6$H$_4$)$_2$POPr^i and b) phosphinates (X C$_6$H$_4$)$_2$P(O)OPr^i X:

X :	p-MeO	pPr^{i}O,H	p-MeO,H	m-Me	H	p-F	p-Cl	p-CF$_3$	3,5-di-Cl
a) δ^{31}P (C$_6$D$_6$) :	106.2	105.2	105.2	105.5	105.8	103.3	101.9	100.4	105.9
b) δ^{31}P (C$_6$D$_6$) :			all *ca.* 28 ppm.						

c) Phosphonites, X C$_6$H$_4$P(OPr^i)$_2$ and d) phosphonates, X C$_6$H$_4$P(O)(OPr^i)$_2$

X :	p-Me$_2$N	p-Pr^{i}O	p-MeO	p-Me	H	p-Cl	p-CF$_3$
a) δ^{31}P (C$_6$D$_6$) :		153.6	152.0	151.7	151.5	151.2	149.4	149.0
b) δ^{31}P (C$_6$D$_6$)		all *ca.* 17 ppm.					

(Pr^{i}O)$_3$P, δ^{31}P = 137 ; (Pr^{i}O)$_3$P(O), δ^{31}P (C$_7$D$_8$) = -4.6

Ph$_3$P(CD$_3$CN) δ^{31}P = -5.9 ;   Ph$_3$P(O) , δ^{31}P (CD$_3$CN) = 34.7 or 30.1 (C$_6$D$_6$)

TABLE II

Second order rate coefficients (k_2) for the reaction of $Ph_nP(OPr^i)_{3-n}$ ($n = 0$–3) with TCNQ in aqueous acetonitrile at 25°C

$[Ph_nP(OPr^i)_{3-n}] = 10^{-5}$ M	$[TCNQ] = 10^{-5}$ M			
$[H_2O]$ / M	k_2 (l mol^{-1} s^{-1})			
	$n = 2$	$n = 1$	$n = 0$	$n = 3$
0.555	5.29×10^2	$4.59 \times 10_2$	13.3	3.0*
1.110	$5.10 \times 10_2$	4.72×10	-	-
2.77	5.43×10^2	4.38×10^2	12.6	-

* In good agreement with the value of 2.5×10^4 for the spontaneous rate derived from earlier work - ref. 8b.

TABLE III

Second order rate coefficients (k_2) for the reaction of phosphinites (**1b**) and phosphonites (**1c**) with TCNQ (**2**) in CH_3CN (99%)—H_2O (1%) at 25°C

a) <u>Phosphinites</u> $(X\ C_6H_4)_2POPr^i$

X :	p-MeO	p-Pr^{i}O,H	p-MeO,H	m-Me	H	p-F	p-Cl	p-CF$_3$	3,5-di-Cl
$10^{-2}k_2$ (l mol^{-1}s^{-1}) :	185	68.7	40	15.6	5.29	1.29	0.191	3.1×10^{-4}	1.59×10^{-4}
$\Sigma\sigma^a$	-0.54	-0.45	-0.27	-0.14	0	0.12	0.46	1.1	1.49

b) <u>Phosphonites</u> $X\ C_6H_4P(OPr^i)_2$

X :	p-Me$_2$N	p-Pr^{i}O	p-MeO	p-Me	H	p-Cl	pCF$_3$
$10^{-2}k_2$ (l mol^{-1}s^{-1}) :	242	40.0	22.3	12.4	4.59	1.5	0.49
σ^a	-0.83	-0.45	-0.27	-0.17	0	0.23	0.55

a σ-values from 1) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958, **23**, 420 and ii) C. D. Ritchie and W. F. Sayer, *Prog. Phys. Org. Chem.*, 1964, **2**, 334.
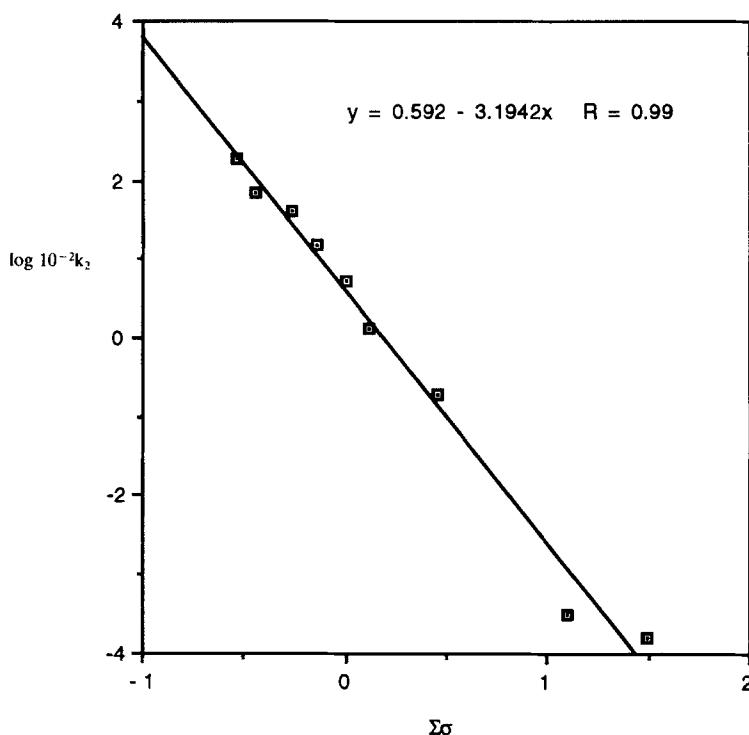
FIGURE 1   Hammett plot of log k_2 values vs. $\Sigma\sigma$ for the reaction of (**1b**) with (**2**) in $CH_3CN(99\%)/$ $H_2O(1\%)$ at 25°C.

value of -3.19. A series of aryl phosphonites under identical conditions gave a similar correlation (Table III) and a p-value of -1.99 (Figure 2) to compare with the p-value of -3.19 for the triarylphosphine/TCNQ reaction.[8b]

It is quite clear that all four types of tricoordinate phosphorus (triarylphosphine-triisopropyl phosphite) react with TCNQ in the presence of water to give the respective oxide (**3**) and $TCNQH_2$ (**4**) in virtually quantitative yield. Although mechanisms involving conventional nucleophilic attack of the P(III) compounds on TCNQ were considered, stereochemical studies using an optically active phosphine and a series of kinetic experiments showed[8b] that the mechanism for the triarylphosphine reaction involved rate-limiting, acid-catalysed dissociation of the molecular complex (**5a**) or ion-pair (**5b**) to form the phosphinium radical cation which then reacted rapidly with water to form the products (Scheme I).

In view of the similar product pattern and kinetic behaviour, it seems reasonable to assume that the phosphinites, phosphonites and phosphite react by a similar mechanism. The rate sequence for the series of phosphorus compounds is **1b** > **1c** > **1d** > **1a** in the ratio of 176:153:4.4:1. This is not in line with the rate sequence found for the attack of tricoordinate phosphorus on sp^3 carbon (**1a** > **1b** > **1c** > **1d**)[9] but is in accord with the sequence found for the reactions of tricoordinate phosphorus compounds with peroxides,[10] S_8,[11] trisulphides[12] and the azo link[13] where the results were explained by back-donation of charge from the substrate

$$y = 0.7291 - 1.9937x \quad R = 1.00$$

log $10^{-3}k_2$

$\Sigma\sigma$
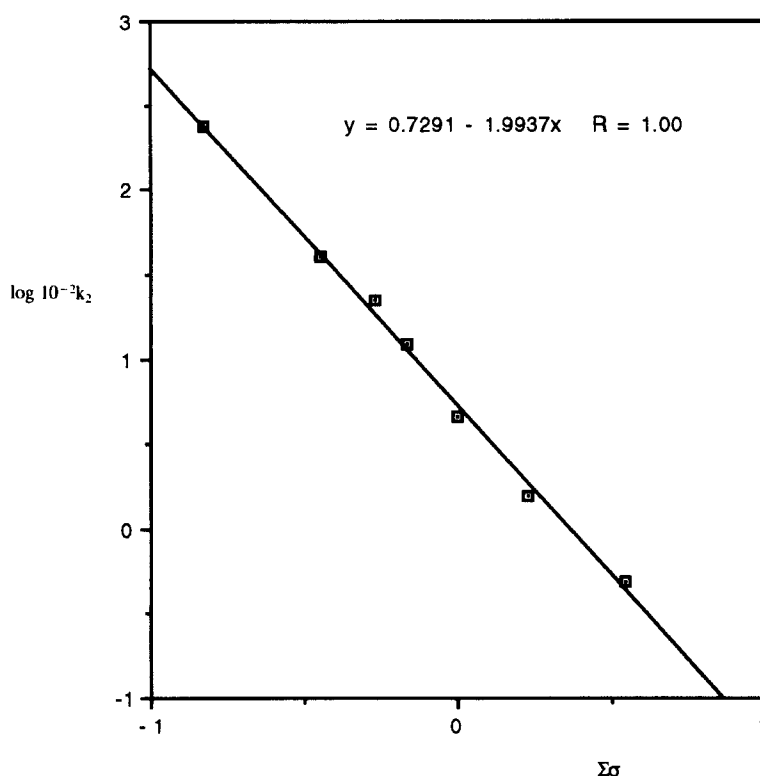
FIGURE 2   Hammett plot of log k_2 values vs. $\Sigma\sigma$ for the reaction of (**1c**) with (**2**) in $CH_3CN(99\%)/$ $H_2O(1\%)$ at 25°C.

$$Ar_3P \quad + \quad TCNQ \quad \rightleftharpoons \quad Ar_3P\text{····}TCNQ \quad \rightleftharpoons \quad \overset{+\cdot}{Ar_3P}\text{····}TCNQ^{-\cdot}$$

$$(1a) \qquad\qquad (2) \qquad\qquad\qquad (5a) \qquad\qquad\qquad (5b)$$

$$(5a/b) \quad \xrightarrow[\text{rls}]{HX\,/\,H_2O} \quad [\,\overset{+\cdot}{Ar_3P}\,] \quad + \quad [TCNQH^{\cdot}] \quad + \quad X^-$$

$$(6)$$

$$[(6)] \quad + \quad H_2O \quad + \quad TCNQ \quad \xrightarrow{\text{fast}} \quad Ar_3PO \quad + \quad TCNQH_2 \quad + \quad H^+$$
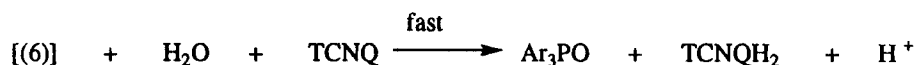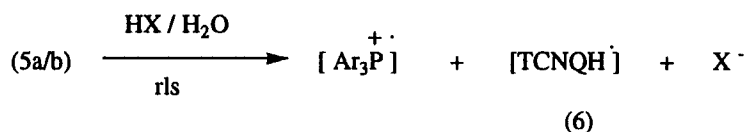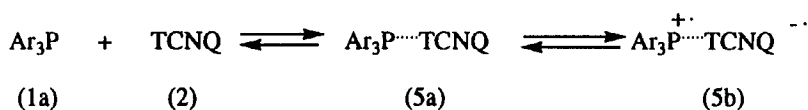
SCHEME I

to the positive charge developing on the attacking nucleophile giving rise to a transition state with pentacoordinate character. The kinetic data for phosphinite and phosphonites shows first order behaviour in (**1b, c**) and (**2**) but zero order kinetics in [H_2O] which suggests that the rate-limiting step is dissociation of the

molecular complex (or ion-pair) followed by rapid attack of the water on the resultant radical cation (Scheme II). If this is true, then the phosphinium radical cation formed in the rate-limiting step must follow the stability sequence $(1b)^{+\cdot} > (1c)^{+\cdot} > (1d)^{+\cdot} > (1a)^{+\cdot}$. This may be justified if the radical cations are viewed as *tbp* structures with the radical lobes of the molecular orbital situated apical-equatorial or di-equatorial (Scheme III) and interconverted by the conventional pseudorotation mechanism. It should be noted that under this scheme, the two most stable radical cations would be those from the phosphinite (two equatorial aryl groups and one apical isopropoxy group) and the phosphonite radical cation with one equatorial aryl group and two apical isopropoxy groups which would explain their fast rates of reaction. The triarylphosphine radical cation must have at least one energetically unfavourable apical aryl group and the phosphite radical cation at least one energetically unfavourable equatorial isopropoxy group thus accounting for their relatively slow rates. The sensitivity of the phosphonite reaction to substituent effects ($\rho \sim -2.0$) is lower than that for either the phosphinite ($\rho \sim -3.2$) or phosphine ($\rho \sim -3.2$) cases. The ρ-values indicate development of substantial positive charge on phosphorus but clearly, the values are not controlled by the "reactivity-selectivity" principle[14] since the phosphinite reacts 60 times *faster* than the phosphine but at almost the same rate as the phosphonite. The most stable conformations of the intermediate radical cations may, however, explain the results since the phosphine and phosphinite both have apical-equatorial distribution of the

$$(1b,c) \; + \; \text{TCNQ} \; \rightleftharpoons \; [\,(1b,c).....\text{TCNQ}\,] \; \rightleftharpoons \; [\,(1b,c)......\overset{+\cdot}{\text{TCNQ}}^{-\cdot}\,]$$

molecular complex   ion-pair

rls

$$(3b,c) \; + \; (4) \; \xleftarrow{\text{H}_2\text{O, fast}} \; [\,(1b,c)^{+\cdot}\,] \; + \; [\,\overset{-\cdot}{\text{TCNQ}}\,]$$

SCHEME II

| phosphine radical cation | phosphinite radical cation | phosphonite radical cation | phosphite radical cation |
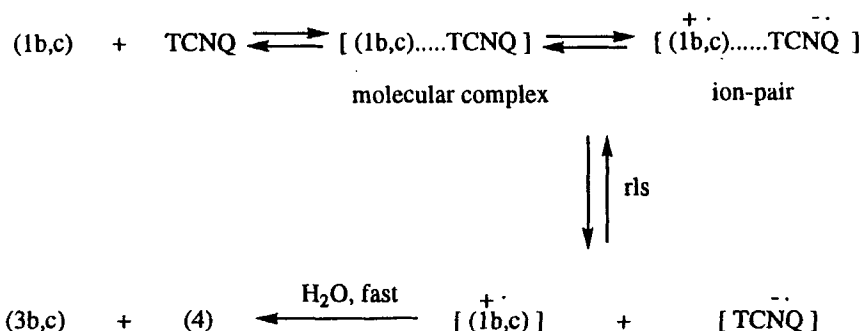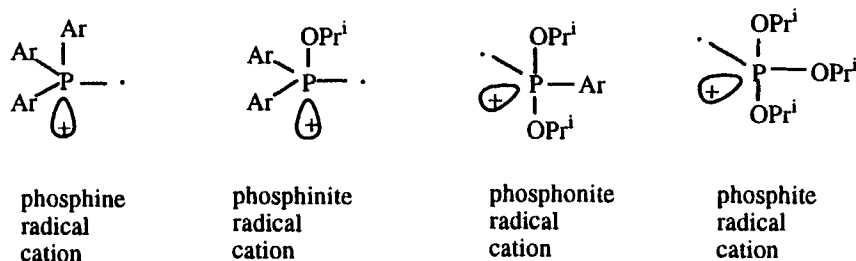
SCHEME III

radical cation whereas the phosphonite would favour the diequatorial mode. In summary, the reactions of TCNQ with tricoordinate phosphorus in the presence of water are best explained by a mechanism involving formation of the phosphinium radical cation in the rate-limiting step of the reaction.

2. Tetracyanoethylene

Earlier work by Powell and Naan[8] established that triarylphosphines (1a) react with tetracyanoethylene (7) in acetonitrile in the presence of aqueous acid to give triarylphosphine oxide (3a) and 1,1,2,2-tetracyanoethane (8).

$$Ar_3P \quad + \quad (CN)_2C=C(CN)_2 \quad \xrightarrow{H_2O/H^+} \quad Ar_3PO \quad + \quad (CN)_2CHCH(CN)_2$$

(1a)   (7)   (3a)   (8)
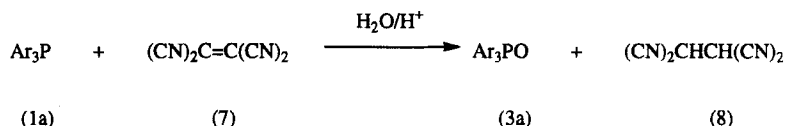
Use of an optically active phosphine gave racemic oxide and the phosphinium radical cation was proposed as an intermediate in the reaction. In order to substantiate this proposal a kinetic study of the reaction of (7) with a range of triarylphosphines was undertaken. The reactions of (1a) with (7) in 10% aqueous acetonitrile and in the presence of hydrochloric acid were followed by observing the disappearance of (7) at 282 nm and were found to be first order in phosphine and TCNE (overall second order) but zero order in water over the range from 0.55–2.77 mol^{-1} and acid over the range 10^{-2}–5 $\times$ 10^{-3} mol^{-1} (Table IV). The second order rate constants for a range of arylphosphines are shown in Table V which gives rise to a Hammett plot (Figure 3) with a ρ-value of -0.85. Thus the kinetic data differ markedly from the TCNQ system in that there is *no* acid catalysis and the sensitivity of the reaction to substituents as measured by ρ, is much lower than that observed with TCNQ ($\rho = -3.2$) even though the reaction rates for TCNE and TCNQ are very similar. A change of mechanism is evident and the data with the TCNE are not compatible with rate-limiting formation of the phos-

TABLE IV

Second order rate coefficients (k_2) for the reaction of
triphenylphosphine with TCNE (7) in aqueous
acetonitrile at 25°C

[Ph$_3$P] = 1.25 x 10^{-3} M	[TCNE] = 1.25 x 10^{-3} M	
[H$_2$O] / M	[H$^+$] / M	k_2 (l mol^{-1}s^{-1})
0.56	10^{-2}	0.92
2.78	10^{-2}	0.93
5.55	10^{-2}	0.90
5.55	8 x 10^{-3}	0.94
5.55	5 x 10^{-3}	0.91

TABLE V

Second order rate coefficients for the reaction of triarylphosphines (X $C_6H_4)_3$P with TCNE in CH_3CN (90%) — H_2O (10%) in the presence of hydrochloric acid [1 × 10^{-2} M] at 25°C

X :	2xp-MeO,H	p-MeO, 2xH	3xm-Me	p-Me, 2xH	H	p-F	m-Cl
k_2(1 mol^{-1}s^{-1})	2.68	1.97	1.90	1.30	0.90	0.51	0.12
$\Sigma\sigma$	-0.54	-0.27	-0.21	-0.17	0	0.186	1.12
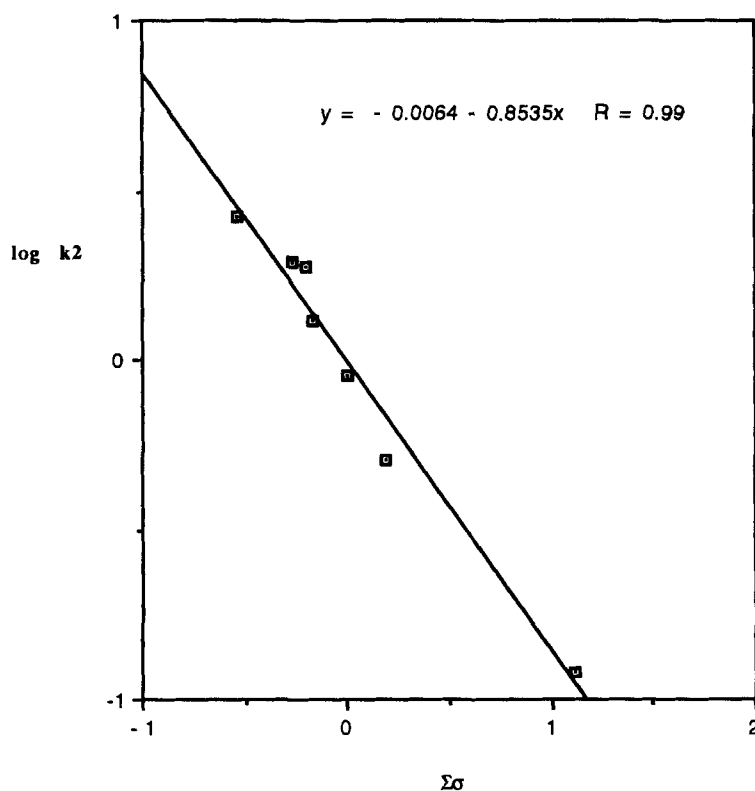
FIGURE 3   Hammett plot of log k_2 values vs. $\Sigma\sigma$ for the reaction of (**1a**) with (**7**) in CH_3CN(90%)/ H_2O(10%) in the presence of HCl (10^{-2} M) at 25°C.

phinium radical cation as the essential intermediate. One alternative mechanism involves attack on olefinic carbon to form a betaine (**9**) followed by hydrolysis (Scheme IV) but this seems unlikely since phosphorus-carbon bonds in phosphonium salts are relatively stable to hydrolysis (especially under acidic conditions) and betaines of type (**9**) have been shown to hydrolyse to phosphonium amides of type (**10**).[15] The remaining mechanism involves rate-limiting attack on nitrogen. The resultant betaine (**11**) may add water to form the pentacoordinate structure (**12**)

$$Ar_3P \quad + \quad TCNE \qquad\qquad\qquad Ar_3\overset{+}{P}\!-\!C(CN)_2^-\!C(CN)CONH_2 \quad \overset{Cl^-}{}$$

$$(10)$$

rls   HCl / H₂O

$$\overset{+}{Ar_3P}\!-\!C(CN)_2^-\!\overset{-}{C}(CN)_2 \qquad\qquad Ar_3P(O) \quad + \quad (CN)_2CHCH(CN)_2$$

$$(9)$$

HCl / H₂O

$$H_2O$$ OH

$$\overset{+}{Ar_3P}\!-\!C(CN)_2^-\!CH(CN)_2 \quad Cl^- \;\rightleftharpoons\; Ar_3P\!-\!C(CN)_2^-\!CH(CN)_2$$

SCHEME IV

$$Ar_3P \quad + \quad TCNE \qquad\qquad\qquad (3a) \quad + \quad (8)$$

rls

$$H_2O$$ OH

$$\overset{+}{Ar_3P}\!-\!N\!=\!\overset{-}{C}\!-\!\underset{CN}{C}\!=\!C(CN)_2 \quad\xrightarrow{\;H_2O\;}\quad Ar_3P\!-\!N\!=\!C\!=\!\underset{CN}{C}\!-\!CH(CN)_2$$

$$(11) \qquad\qquad\qquad\qquad\qquad (12)$$
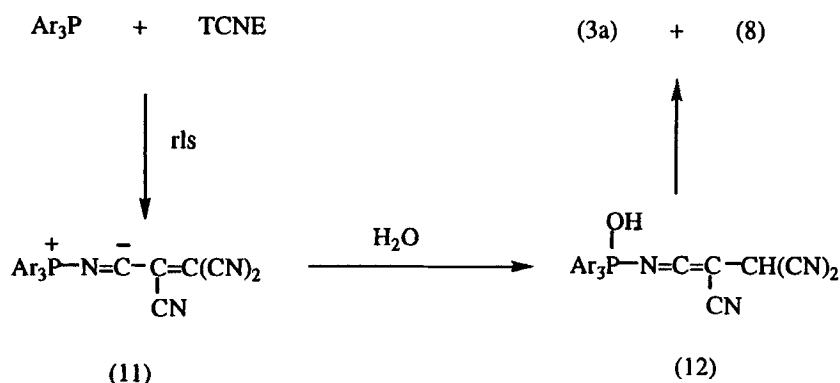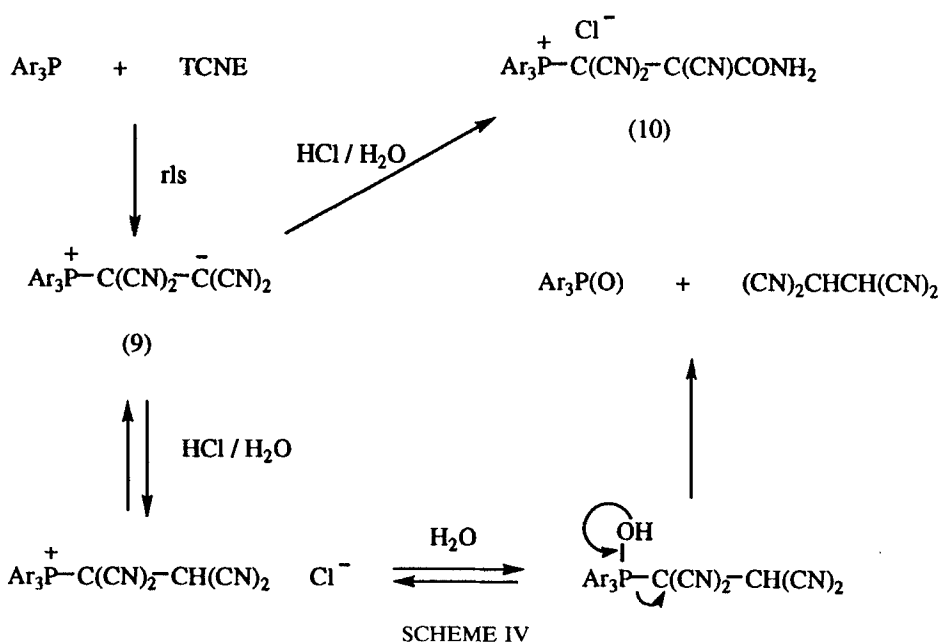
SCHEME V

which may pseudorotate to racemise the chiral intermediate before eliminating (8) and forming the oxide (3a), Scheme V.

The ρ-value of -0.85 is very similar to that found for the attack of tricoordinate phosphorus on azo-N ($\rho \sim -0.5$)[13] and there is precedent for attack of tricoordinate phosphorus on the nitrogen of TCNE in *aprotic medium* which forms (14) via the 1:1 intermediate (11) and the betaine (13).[16]

Thus it seems likely that in this case, the preferred route for the hydrolysis involves attack on nitrogen and a pentacoordinate intermediate rather than the phosphinium radical cation which serves to illustrate the fine energetic balance

$$Ar_3\overset{+}{P}-N=C=C(CN)\,\overset{-}{}C(CN)_2 \quad + \quad TCNE \quad \longrightarrow \quad Ar_3\overset{+}{P}-\overset{}{N}=C=C(CN)\,\overset{-}{}C(CN)_2$$

$$\begin{array}{c} C(CN)_2 \\ | \\ \overset{-}{C}(CN)_2 \end{array}$$

(11)

(13)

(14)

between mechanisms involving "conventional" nucleophilic attack or single electron transfer.

EXPERIMENTAL

[31]P nmr data were recorded in $CDCl_3$, C_6D_6 or C_7D_8 on Brüker HFX 90 or Brüker WM 250 spectrometers operating at 36.43 MHz or 100.8 MHz respectively, and all chemical shifts are reported in p.p.m. (downfield, positive) relative to 85% H_3PO_4. All the solvents were rigorously dried and deoxygenated before use and the tricoordinate phosphorus compounds were obtained either commercially (Alfa, Lancaster, Maybridge or Strem) or synthesized and purified as described previously.[10] Routine kinetics were monitored on a Pye Unicam SP1700 spectrometer fitted with a thermostatted cell holder maintained to $\pm0.1°C$ by circulating water and with an external recorder to monitor absorbance changes with time at any required wavelength in the range 210–800 nm. Tetracyanoquinodimethane and tetracyanoethylene were obtained and purified as described previously.[8b]

Reaction of Tricoordinate Phosphorus Compounds with TCNQ

The procedure for the reaction of phosphines (1a) with TCNQ has been described earlier.[8b]

a) *Phosphinites.* A typical procedure was as follows:

A solution of TCNQ (0.1 g, 5×10^{-4} g mol) in acetonitrile (10 ml) was added to a solution of isopropyl diphenylphosphinite (0.122 g, 5×10^{-4} g mol) in a mixture of acetonitrile (5 ml) and water (0.5 ml). After 10 min the solvent was removed under vacuum and the residue was triturated with chloroform (10 ml). The resulting crystals were filtered and washed with chloroform (2×10 ml) to give 1,4-bis-dicyanomethylbenzene (4, 0.18 g, 88%) m.p. 243–45°C, lit[17] m.p. 246–248°C. The i.r. spectrum was consistent with an authentic sample of (4).[8b] The filtrate was evaporated to give (0.13 g, 100%) of isopropyl diphenylphosphinate, m.p. 97–97.5°C, lit[18] m.p. 97–99°C, δ [31]P (C_6D_6) = 28.0, δ [1]H ($CDCl_3$), 1.35 (6 H, d, ^3J_H = 6 Hz), 4.4–4.9 (1 H, m) and 7.15–8.04 (10 H, m).

b) *Phosphonites.* A typical procedure was as follows:

A solution of (2, 0.05 g, 2.5×10^{-4} g mol) in acetonitrile-water (5 ml, 99%/1%) was added to a solution of di-isopropyl phenylphosphonite (0.056 g, 2.5×10^{-4} g mol) in acetonitrile (1 ml). After 10 min the solvents were removed under vacuum and the residue was triturated with deuteriobenzene (1 ml) to give (4) and a solution with a single ^{31}P nmr signal at 16.6 ppm corresponding to di-isopropyl phenylphosphonate (3c). A similar procedure was used for the reaction of (1d) with (2) to give (3d) and (4).

The Reaction of Triarylphosphines (**1a**) *with TCNE* (**7**) *in the Presence of Water and Acid*

A solution of (**7**, 0.037 g, 2.87 × 10^{-4} g mol) in acetonitrile (0.5 ml) was added to a solution of (**1a**, X = H, 0.075 g, 2.87 × 10^{-4} g mol) in acetonitrile-water (25 ml, 90%/10%) containing hydrochloric acid (10^{-2} M). After 1h the solvents were removed under vacuum and the residue was triturated with CD$_3$CN (1 ml) to give (**8**, 0.035 g, 2.8 × 10^{-4} g mol, 90%) m.p. > 150°C(d) and with an i.r. spectrum identical to an authentic sample.[8b] The CD$_3$CN solution gave a ^{31}P nmr signal at δ = 34.7 enhanced by addition of an authentic sample of triphenylphosphine oxide.

Kinetic Procedures

1. *TCNQ.* Acetonitrile containing water (1% v/v, 3 ml) was thermostatted at 25°C in a uv cuvette for 30 min. A stock solution of TCNQ in acetonitrile (0.01 M) was prepared and a 3 μl sample was injected into the cuvette to give a 10^{-5} M solution with an absorbance of *ca.* 0.2 at λ = 394 nm. Solutions of each tricoordinate phosphorus compound in acetonitrile were also prepared at a concentration of 0.01 M and for each run, a 3 μl sample was injected into the cuvette. The decay of the absorbance at 394 nm was monitored against time and the second order rate coefficients (k$_2$) were derived from plots of 1/[TCNQ] vs time which were linear to at least 80% reaction. Runs were carried out in duplicate or triplicate to give a precision of ±5% in the k$_2$ values.

2. *TCNE.* A solution of hydrochloric acid (10^{-2} M) in acetonitrile-water (90%/10%) was thermostatted at 25°C for 30 min. A stock solution of TCNE in acetonitrile (0.01 M) was prepared and a 25 μl sample was injected into the CH$_3$CN/H$_2$O/H$^+$ solution to give a TCNE solution at 1.25 × 10^{-3} M. Typically, a 50 μl sample of a 0.05 M solution of each phosphorus nucleophile was then injected into the TCNE solution to give a final concentration of phosphorus nucleophile at 1.25 × 10^{-3} M. A 250 μl sample of this solution was then transferred to a 0.1 mm uv cell thermostatted at 25°C and the decay of the TCNE chromophore was monitored at λ = 282 nm. The absorbance values were converted to concentrations and the second order rate constants (k$_2$) were derived from plots of 1/[TCNE] vs time which were linear up to at least 80% reaction. Runs were carried out in duplicate or triplicate to give a precision of ±5% in the k$_2$ values.

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