Kinetics and Mechanism of the Reaction of Trico-ordinate Phosphorus Compounds with Octasulphur

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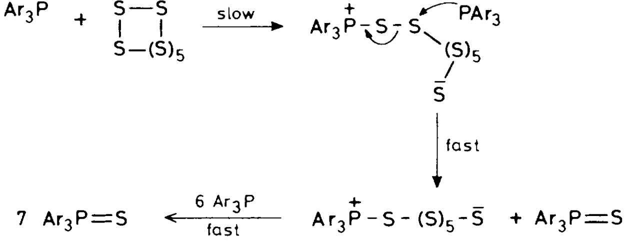
Kinetic data and activation parameters are reported for the reactions of a series of phosphites, arylphosphonites, diarylphosphinites, and triarylphosphines with octasulphur (S_8) in toluene as solvent. For the phosphites the data are explained in terms of changes in *p*-character of the lone-pair orbital on phosphorus and inductive electron donation by the alkyl groups. The rates of reaction of series of arylphosphonites, diarylphosphinites, and triarylphosphines correlate with the Hammett σ constants to give ρ values of −3.0, −3.0, and −2.5, respectively, and the results are discussed in terms of the Reactivity–Selectivity Principle and the biphilic mechanism for insertion of trico-ordinate phosphorus into σ-bonds.

Commercial sulphur consists almost entirely of an octa-atomic cyclic structure, S_8, and this crown-shaped molecule is the thermodynamically stable form of sulphur up to 95 °C.[1] The reaction of tertiary phosphines with S_8 gives a quantitative yield of the corresponding tertiary phosphine sulphides[2] with retention of configuration at phosphorus,[3] and a thorough investigation revealed a second-order reaction which was highly sensitive to solvent polarity.[4] The rate was not directly proportional to the dielectric constant of the medium but was related to the hydrogen-bonding capacity of the solvent, suggesting that the rate increase was associated with the dispersal of negative charge. In addition, using a series of *para*-substituted arylphosphines, Bartlett obtained a ρ value of −2.5 and proposed a mechanism involving rate-limiting attack of the phosphorus on sulphur, thus opening the sulphur ring to a linear octasulphide. The resultant dipolar ion then suffered a series of *rapid* nucleophilic displacements to yield eight moles of sulphide per mole of S_8 (Scheme 1). The availability of a wide range of trico-ordinate phosphorus compounds, $Ar_nP(OR)_{3-n}$ (**1**) with n = 0—3, prompted us to investigate this reaction [equation (1)] more thoroughly, with the objective of assessing

$$8\ Ar_nP(OR)_{3-n} + S_8 \longrightarrow 8\ Ar_n\overset{\overset{\displaystyle S}{\|}}{P}(OR)_{3-n} \qquad (1)$$

(**1**) (**2**) (**3**)

the effect of structural variations within the nucleophile on (i) the reaction rate for n = 0—3 *and* (ii) the Hammett ρ values for reactions involving n = 1—3.



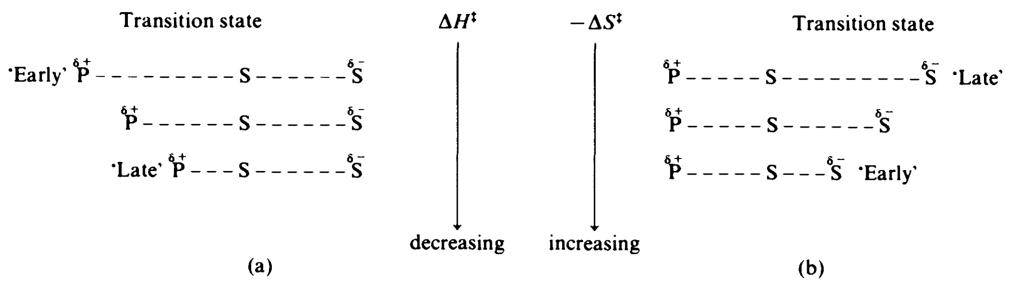
Scheme 1.

Results and Discussion

Reactions of Acyclic Phosphites with S_8.—The reactions of trialkyl phosphites (**1**; n = 0, R = Me, Et, Pr^n, Pr^i, or Bu^n) with S_8 in toluene all gave the expected thiophosphates,[5] as evidenced by the ^{31}P n.m.r. data (Table 1). The rate of each reaction was followed by u.v. spectroscopy (disappearance of S_8); the results were consistent with second-order behaviour for all the phosphites (Table 2).[4] The second-order rate coefficients over a temperature range from 30 to 45 °C are shown in Table 3 together with the resultant activation parameters. Triphenyl phosphite showed no detectable reaction with S_8 after 24 h at 31.0 °C.

The slowest reaction is with trimethyl phosphite; all the subsequent straight-chain alkyl phosphites (R = Et, Pr^n, or Bu^n) show similar rates about fifty times higher than trimethyl phosphite. This is reflected in the free energies of activation and, for R = Me, Et, Pr^n, or Bu^n, decreasing enthalpies of activation are compensated by increasing negative entropies of activation, indicating either a gradual increase in the degree of bond formation between phosphorus and sulphur relative to S–S bond cleavage in the transition states for these four nucleophiles [Scheme 2(a)], or a decrease of S–S bond cleavage (relative to P–S bond formation) through the same series of transition states [Scheme 2(b)]. The latter explanation seems the more likely since the late transition state (low P ··· S to S ··· S ratio) would then correspond to the reaction with the highest $\Delta H^{\ddagger}$ value, which in turn would correspond to the slowest reaction (with trimethyl phosphite). Tri-isopropyl phosphite is twenty times more reactive than tri-n-propyl phosphite, with the significant energy difference probably originating in the enthalpy of activation. It seems reasonable to suggest that the rate increase across the series is explained in part by an increase in the O–P–O bond angle from R = Me through R = n-alkyl to R = Pr^i, with a concomitant increase in the *p*-character of the lone pair on phosphorus giving rise to a greater degree of orbital overlap in the transition states across the series. Stabilisation of the charge developing on phosphorus by the increasing inductive effects from R = Me to R = Pr^i may also play a part in increasing the reaction rate. It is interesting that with the n-alkyl phosphites (R = Et, Pr^n, or Bu^n), where inductive and steric effects would not change substantially throughout the series, the rates are all very similar, and that any decrease in $\Delta H^{\ddagger}$ is compensated by an increase in $-\Delta S^{\ddagger}$.

Reaction of Acyclic Phosphonites, Phosphinites, and Phosphines with S_8.—The reactions of arylphosphonites and diarylphosphinites (**1**; n = 1 or 2, R = Et or Pr^i) with S_8 in toluene all gave the expected phosphonothioates (**3**; n = 1) and phosphinothioates (**3**; n = 2), as evidenced by the ^{31}P n.m.r. data (Table 1). The disappearance of S_8 was again monitored by u.v. spectroscopy and the behaviour was consistent with



Scheme 2. Representations of possible transition states: (a) increasing degree of P–S bond formation; (b) decreasing degree of S–S bond cleavage.

Table 1. Reactions of $Ar_nP(OR)_{3-n}$ with S_8; ^{31}P n.m.r. data relative to 85% H_3PO_4

$Ar_nP(OR)_{3-n}$	δ_p (C_7D_8) (p.p.m.)	Product	δ_p (C_7D_8) (p.p.m.)
Phosphites			
$(MeO)_3P$	140	$(MeO)_3P{=}S$	73.0
$(EtO)_3P$	138	$(EtO)_3P{=}S$	67.6
$(Pr^nO)_3P$	138	$(PrO)_3P{=}S$	68.2
$(Bu^nO)_3P$	140	$(Bu^nO)_3P{=}S$	69.0
$(Pr^iO)_3P$	137	$(Pr^iO)_3P{=}S$	64.3
Phosphonites			
$PhP(OEt)_2$	155	$PhP(S)(OEt)_2$	86.5
$PhP(OPr^i)_2$	151	$PhP(S)(OPr^i)_2$	82.6
Phosphinites			
$Ph_2P(OEt)$	110	$Ph_2P(S)(OEt)$	79.1
$Ph_2P(OPr^i)$	105	$Ph_2P(S)(OPr^i)$	72.1
Phosphines			
Ph_3P	−6.0	$Ph_3P{=}S$	41.6

Table 2. Rate coefficients (k_2) for the reaction of trialkyl phosphites with S_8 in toluene

Trimethyl phosphite	39.9 °C		
$10^2[(MeO)_3P]$/mol l^{-1}	9.83	13.1	15.50
$10^2[S_8]$/mol l^{-1}	1.21	0.823	1.41
10^3 k_2/l mol^{-1} s^{-1}	0.36	0.33	0.39
Triethyl phosphite	40.2 °C		
$10^2[(EtO)_3P]$/mol l^{-1}	6.69	8.11	14.08
$10^2[S_8]$/mol l^{-1}	0.789	0.695	1.23
10^3 k_2/l mol^{-1} s^{-1}	17.0	17.0	16.0
Tri-n-propyl phosphite	30.9 °C		
$10^2[(Pr^nO)_3P]$/mol l^{-1}	7.46	7.46	7.17
$10^2[S_8]$/mol l^{-1}	0.710	0.711	0.711
10^3 k_2/l mol^{-1} s^{-1}	8.9	8.4	8.0
Tri-n-butyl phosphite	31.0 °C		
$10^2[(Bu^nO)_3P]$/mol l^{-1}	6.47	8.62	10.58
$10^2[S_8]$/mol l^{-1}	0.695	0.695	0.695
10^3 k_2/l mol^{-1} s^{-1}	9.0	9.2	9.4
Tri-isopropyl phosphite	31.0 °C		
$10^2[(Pr^iO)_3P]$/mol l^{-1}	2.76	2.76	
$10^2[S_8]$/mol l^{-1}	0.345	0.345	
10^3 k_2/l mol^{-1} s^{-1}	151	139	

second-order reactions in every case. The second-order rate coefficients at various temperatures are shown in Table 4 together with the resulting activation parameters.

It is immediately obvious that the phosphonites and phosphinites are considerably more reactive towards S_8 than are the corresponding phosphites. For example, comparison of Tables 3 and 4 reveals factors of 230 for phosphonites *vs.* phosphites with R = Et, and 580 for phosphinites *vs.* phosphites with R = Et. For R = Pr^i, the rate ratios are 45 for phosphonites *vs.* phosphites and 44 for phosphinites *vs.* phosphites. These rate differences are again accounted for by differences in the enthalpies of activation rather than changes in activation entropies, which suggests a higher degree of bond formation (*i.e.* orbital overlap) relative to S–S bond cleavage in the transition states for phosphonites and phosphinites as compared with those for the corresponding phosphites. In addition there may be a greater degree of stabilisation of the charge on phosphorus in the transition state for phosphinites and phosphonites relative to phosphites, due to phenyl groups replacing alkoxy groups.*

The effect of substituents in the aryl groups attached to phosphorus is shown in Table 5; the rates correlate with the Hammett σ constants in each case to give ρ values of −3.00 [for (1; n = 1), Figure 1] and −2.98 [for (1; n = 2), Figure 2], with correlation coefficients >0.99. Clearly the reaction is sensitive to substituent effects, with phosphorus developing a high degree of positive charge in the transition state consistent with the interaction of a soft, highly polarizable, nucleophile (P^{III}) with a 'soft' electrophile (S in S_8).[6] This conclusion is supported by a study of the effect of solvent polarity on the rate of reaction between (1; n = 1, R = Pr^i) and S_8 (Table 6). As Bartlett observed with triphenylphosphine,[4] there is a marked increase of rate with solvent polarity, but no linear correlation between the dielectric constant of the medium and reaction rate (Figure 3).

Finally, in order to make a realistic comparison with Bartlett's data,[4] the rates of reaction of a series of triarylphosphines with S_8 in toluene were determined at 25 °C; the results are shown in Table 7. The value of k_2 for triphenylphosphine (0.42 × 10^{-3}) compares favourably with that reported by Bartlett for the same reaction in benzene at 25 °C (1.27 × 10^{-3}) and the ρ value derived from the data in Table 7 is −2.5 ± 0.3 (Figure 4), identical, within experimental error, with Bartlett's value.

The conclusions drawn from these data are as follows. First, the reactions proceed *via* a polar transition state with phosphorus acquiring positive charge, as evidenced by the negative ρ values and a substantial solvent effect.

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* This latter explanation will not stand alone however, because triphenylphosphine reacts more *slowly* than phosphinites or phosphonites[4] (*see later*) and has E_a = 14.5 kcal mol^{-1} with $\Delta S^‡$ = −19 cal mol^{-1} K^{-1} based on rates of reaction at two temperatures in benzene given in ref. 4.

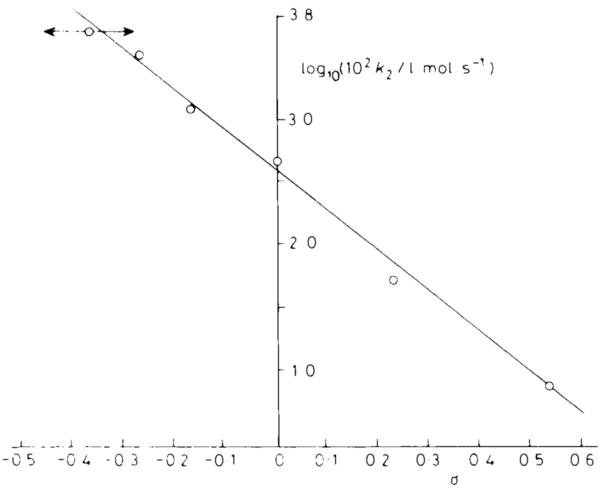


Figure 1. Hammett plot of log k_2 *versus* σ for the reaction of $ArP(OPr^i)_2$ with S_8 in toluene at 25 °C

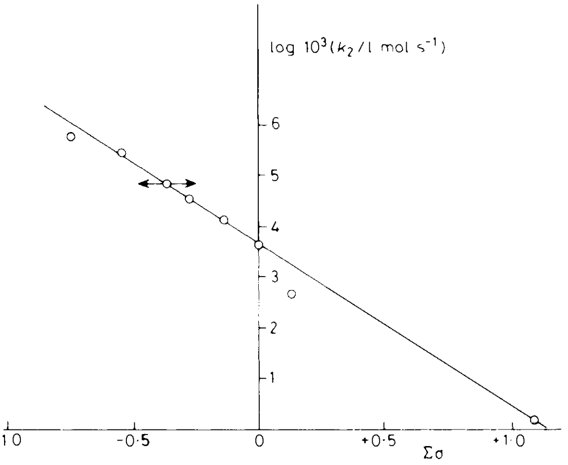


Figure 2. Hammett plot of log k_2 *versus* Σσ for the reaction of Ar_2POPr^i with S_8 in toluene at 25 °C

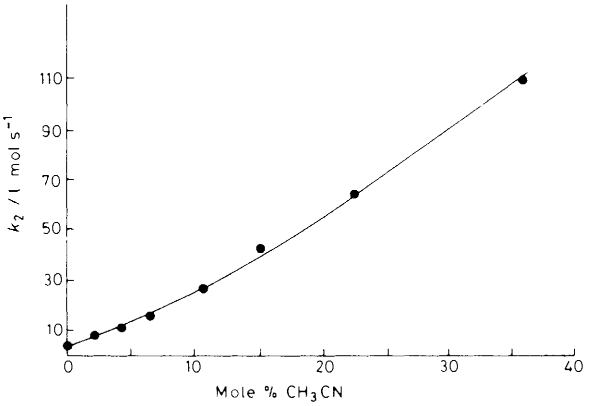


Figure 3. Plot of rate coefficients (k_2) for the reaction of $PhP(OPr^i)_2$ with S_8 at 25 °C *versus* mole % of CH_3CN in toluene

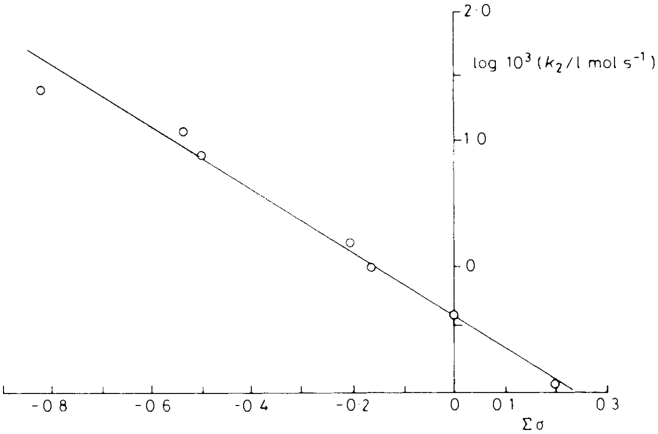


Figure 4. Hammett plot of log k_2 *versus* Σσ for the reaction of Ar_3P with S_8 in toluene at 25 °C

Secondly, despite the fact that the nucleophile is trico-ordinate phosphorus in each case, the magnitudes of the ρ values are not inversely related to the rates of reaction. In fact, quite the reverse is observed; the lowest ρ value (for Ar_3P) involves rate coefficients which are 10^4 times smaller than for Ar_2POPr^i and $ArP(OPr^i)_2$, which apparently contradicts the Reactivity–Selectivity Principle.[7] These observations might be attributed, however, to a higher transmission coefficient[8] for Ar_2POPr^i relative to Ar_3P, perhaps brought about by inductive electron withdrawal by the oxygen of the isopropoxy group in the polar transition state. In this case, however, one would have expected an even higher degree of electron withdrawal in the phosphonites, $ArP(OPr^i)_2$, and hence an even higher transmission efficiency and a correspondingly higher ρ value. The constancy of ρ values for the reactions of (**1**; n = 1—3) with diethyl peroxide, despite a ten-fold rate difference across the series, has already been reported,[9] and a similar phenomenon has been observed with Ar_2S_3,[10] Ar_2S_2,[11] PhN=NPh,[11] and activated alkenes[11,12] as substrates. The implication is that the transmission coefficients for each type of trico-ordinate phosphorus are very similar. But, if this is so *and* one assumes the Reactivity–Selectivity Principle holds, then the value of ρ cannot be a direct measure of selectivity in these systems. Instead, ρ should be regarded as an indication of the degree of charge transfer in the transition state which, in turn, is dependent to a very large extent on the nature of the substrate. This is reminiscent of the semi-empirical relation derived by Hudson[13] [equation (2)], where Z gives a direct measure of

$$\log k = Z\,\mathrm{p}K_a + \mathrm{B} \qquad (2)$$

bonding and charge-transfer in the transition state and in this context Z becomes synonymous with ρ.

A corollary of the Reactivity–Selectivity Principle is that low reactivity corresponds to a 'late' transition state. As McLennan[6] and others[14] have pointed out however, when one considers both parallel and perpendicular modes in the transition state for multicentre reactions, a 'late' transition state corresponds to a low bond length *ratio* for bond formation *vs.* bond cleavage in the transition state. If one then assumes an approximately constant degree of bond formation throughout the series of transition states [as depicted in Scheme 2(b)] the late transition state would correspond to relatively high $\Delta H^\ddagger$ and a relatively low $-\Delta S^\ddagger$ value. It follows that an earlier transition state would correspond to a *higher ratio* of bond formation to bond cleavage, which would produce a lower $\Delta H^\ddagger$ value but a relatively high value of $-\Delta S^\ddagger$. This is precisely what is found in comparing phosphinites (or phosphonites) with phosphines in reactions with S_8 as substrate, where the faster reactions (phosphinites or phosphonites) have higher $-\Delta S^\ddagger$ values

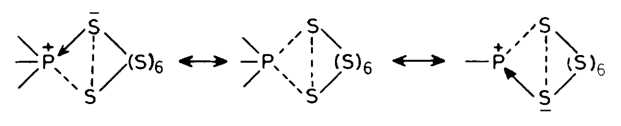
Table 3. Second-order rate coefficients for the reaction of trialkyl phosphites, $(RO)_3P$, with S_8 in toluene over a range of temperatures, together with the resultant activation parameters

R	Temp. (°C)	$10^4\,k_2$/ l mol^{-1} s^{-1}	E_a/ kcal mol^{-1}	10^4k_2 (298 K)/ l mol^{-1} s^{-1}	$\Delta G^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal K^{-1} mol^{-1}
Me	45.3	5.9 ± 0.3				
	39.9	3.7 ± 0.3	14.5 ± 1.0	1.2 ± 0.1	22.8 ± 0.1	−30 ± 4
	30.7	1.9 ± 0.3				
Et	40.2	167 ± 8				
	35.9	120 ± 2	10.8 ± 1.4	62 ± 5	20.5 ± 0.1	−35 ± 4
	31.0	96 ± 3				
Pr^n	45.7	185 ± 6				
	40.5	144 ± 8	10.3 ± 0.4	60 ± 4	20.5 ± 0.1	−36 ± 2
	35.9	108 ± 3				
	30.9	85 ± 5				
Bu^n	40.2	133 ± 6				
	35.9	115 ± 7	7.7 ± 0.5	71 ± 3	20.4 ± 0.1	−45 ± 2
	31.0	92 ± 2				
Pr^i	41.5	2 520 ± 60				
	35.5	1 950 ± 50	10.3 ± 1.6	960 ± 80	18.9 ± 0.1	−31 ± 5
	34.5	1 630 ± 50				
	31.0	1 450 ± 80				

Table 4. Second-order rate coefficients for the reaction of phenylphosphonites (**1**; n = 1, R = Et or Pr^i, Ar = Ph) and diphenylphosphinites (**1**; n = 2, R = Et or Pr^i, Ar = Ph) with S_8 in toluene, together with the corresponding activation parameters

n	R	Temp. (°C)	k_2/ l mol^{-1} s^{-1}	E_a/ kcal mol^{-1}	k_2 (298 K)/ l mol^{-1} s^{-1}	$\Delta G^{\ddagger}$/ kcal mol^{-1}	$\Delta S^{\ddagger}$/ cal mol^{-1} K^{-1}
1	Et	31.7	1.9 ± 0.1				
		36.7	2.4 ± 0.2	7.1 ± 0.9	1.5 ± 0.1	17.2 ± 0.1	−36 ± 3
		42.2	2.8 ± 0.3				
1	Pr^i	7.5	2.3 ± 0.1				
		21.0	4.2 ± 0.2	5.8 ± 0.6	4.2 ± 0.2	16.6 ± 0.1	−38 ± 2
		38.5	7.5 ± 0.4				
		52.5	9.7 ± 0.5				
2	Et	31.0	4.9 ± 0.2				
		36.0	6.2 ± 0.3	7.8 ± 0.8	3.9 ± 0.2	16.7 ± 0.1	−33 ± 3
		42.0	7.5 ± 0.4				
2	Pr^i	6.5	2.4 ± 0.2				
		16.5	3.3 ± 0.2	5.8 ± 0.3	4.4 ± 0.2	16.6 ± 0.1	−38 ± 1
		30.5	4.9 ± 0.3				
		44.5	8.4 ± 0.4				

(Table 4 *vs.* data of refs. 4 and 6).* Thus the earlier transition state *is* associated with the faster reaction and the fallacy occurs in automatically equating higher ρ values with the later transition state (or lower rate coefficient). Perhaps the same degree of bond formation in the transition state results in the same degree of charge development on phosphorus and hence the same ρ value in spite of varying degrees of S–S bond cleavage. Nevertheless it is intuitively reasonable to expect a higher degree of negative charge developing on sulphur as bond cleavage increases, which should in its turn give rise to a higher degree of positive charge on phosphorus. A solution to this paradox may be found in the rate sequence for the reaction of trico-ordinated phosphorus with S_8 [$Ph_2POR > PhP(OR)_2 > P(OR)_3 > PPh_3$]. This is similar to that observed with diethyl peroxide as substrate[9] [$Ph_2POR > PhP(OR)_2 > P(OR)_3$] but quite different from that associated with an S_N2 reaction at tetrahedral carbon, for which the expected rate sequence $Ph_3P > Ph_2POR > PhP(OR)_2 > P(OR)_3$ was observed.[12,15,16] The anomalous rate sequence has been offered as part of the evidence in favour of a biphilic mechanism for insertion of trico-ordinate phosphorus into weak σ-bonds,[9,17–19] in which the transition state is alleged to have some pentaco-ordinate character. Application of the same argument suggests that a degree of back-donation from S^- to P^+ exists in the transition state of the S_8 reaction. This would be equivalent to a biphilic mechanism with a high degree of polar character to the P–S bonds of the transition state as represented by the resonance hybrid (**4**) with (**b**) as a minor contributor. This hypothesis might explain why, irrespective of the degree of bond formation or cleavage in the transition state, the charge on phosphorus remains fairly constant and hence the ρ values for all three types of trico-ordinate phosphorus are very similar and apparently dependent only on the nature of the substrate.



(**4a**) (**4b**) (**4c**)

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* In transition states dominated by bond formation (*i.e.* a constant degree of bond cleavage as in Scheme 2(a)], it is the earlier transition state which would display relatively high $\Delta H^{\ddagger}$ and low $-\Delta S^{\ddagger}$.

Table 5. Rates of reaction of S_8 with $XC_6H_4P(OPr^i)_2$ and $(XC_6H_4)_2POPr^i$ in toluene at 25 °C

$XC_6H_4P(OPr^i)_2$		
X	k_2/ l mol^{-1} s^{-1}	σ^a
p-CF_3	0.078	+0.54
p-Cl	0.525	+0.23
H	4.68	0
p-Me	12.3	−0.17
p-MeO	33.9	−0.27
p-Pr^iO	47.9	-0.37^b
$(XC_6H_4)_2POPr^i$		
X	k_2	$\Sigma\sigma^a$
2 × p-CF_3	0.00143	1.11
2 × p-F	0.417	0.12
2 × H	4.47	0
2 × m-Me	13.6	−0.14
H, p-MeO	34.7	−0.27
H, p-Pr^iO	53.7	-0.37^b
2 × p-MeO	302	−0.54
2 × p-Pr^iO	427	-0.74^b

[a] Values from (i) D. H. McDaniel and H. C. Brown, *J. Org. Chem.*, 1958 **23**, 420, and (ii) V. A. Pal'm, *Russ. Chem. Rev.*, 1961, **30**, 471. [b] There is considerable discrepancy in values of σ for p-Pr^iO; the value used is an average of those quoted (−0.28 and −0.45).

This problem will be discussed further in a subsequent paper dealing with Ar_2S_3 and Ar_2S_2 as substrates where multiple substitution experiments have been performed (on substrate and nucleophile) in order to eliminate the possibility of the transmission coefficient affecting the magnitude of ρ.

Experimental

Routine ^1H and ^{31}P n.m.r. data were obtained as described previously.[9] All the trico-ordinate phosphorus compounds were obtained and purified as described previously,[9] and all solvents were rigorously dried and deoxygenated before use. Fison's amorphous sulphur was recrystallised (× 3) from toluene and dried to give lustrous yellow crystals, m.p. 113.3—114.5 °C (lit.,[1] 112.8 °C).

Kinetic Procedures.—(a) *Phosphites.* Stock solutions of sulphur (0.2M) and each phosphite (0.2M) were made up in dry toluene and maintained at the required temperature by thermostat. Samples of each solution (*e.g.* 5.00 ml of sulphur solution plus 2.0 ml of the phosphite solution) were pipetted, mixed, placed in a photometer cell and thermostatted in the cell housing of a Unicam SP 500 spectrometer. Absorbance readings at 345 nm were taken at suitable time intervals and second-order plots were derived from the data from which values of k_2 were calculated. Each run was carried out in duplicate (at least); in some cases as many as six runs were used to obtain each k_2 value.

(b) *Phosphonites, phosphinites, and phosphines.* A stock solution of S_8 (0.017M ≡ 0.136M in sulphur) in dry toluene (*ca.* 15 μl) was injected into the thermostatted cuvette containing toluene (3 ml). An exact 7 molar excess of a solution of the nucleophile in toluene was then added and, after thorough mixing, the reaction was monitored in the thermostatted cell-housing of a Unicam SP 6-400 spectrometer at 300 nm. The decrease in absorbance was recorded with an external (Servoscribe) recorder and the readings were converted into concentration data. The second-order plots derived from these data were linear up to >90% reaction and were used to obtain the recorded k_2 values, which are averages of at least two runs.

Table 6. Rate coefficients for the reaction of (**1**; n = 1, R = Pr^i, Ar = Ph) with S_8 in mixtures of toluene and acetonitrile at 25 °C

% Acetonitrile (v/v)	k_2/l mol^{-1} s^{-1}
0	4.4
1	8.0
2	11.2
3	14.8
5	26.0
7	42.2
10	64.0
15	108.9

Table 7. Rates of reaction of triarylphosphines $[(XC_6H_4)_3P]$ with S_8 in toluene at 25 °C

X	10^3 k_2/l mol s^{-1}	Σσ
2 × H, 1 × p-NMe_2	23.8	−0.83
1 × H, 2 × p-MeO	11.7	−0.54
3 × p-Me	7.71	−0.51
3 × m-Me	1.61	−0.21
2 × H, 1 × p-Me	0.948	−0.17
3 × H	0.423	0
3 × p-F	0.109	+0.21

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