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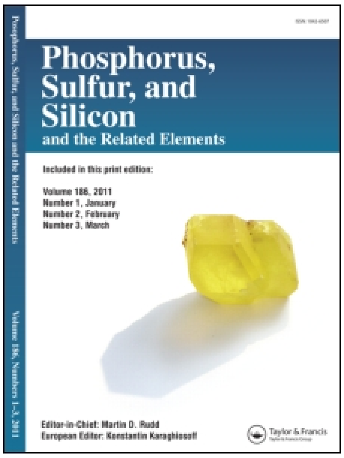

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THE REDUCTION OF CYCLIC DISULPHIDES WITH TRIARYLPHOSPHINES IN AQUEOUS ORGANIC SOLVENTS

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THE REDUCTION OF CYCLIC DISULPHIDES WITH TRIARYLPHOSPHINES IN AQUEOUS ORGANIC SOLVENTS

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The kinetics of the reduction of cyclic disulphides with triphenylphosphine have been studied in aqueous ethanol at various temperatures. Solvent effects on the reaction of 4-phenyl-1,2-dithiolane with tris-(4-chlorophenyl) phosphine in a number of aqueous organic solvents have been analysed in terms of the Kirkwood, Y and E_T^N functions.

Key words: Cyclic disulphides, triarylphosphines, solvent effects.

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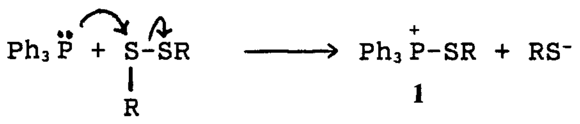
INTRODUCTION

It has been known for some time that aryl disulphides are reduced to thiols in high yield by reaction with triphenylphosphine in aqueous methanol[1,2] (Equation {1}).

$$\mathrm{ArSSAr + Ph_3P + H_2O \longrightarrow Ph_3PO + 2ArSH} \qquad \{1\}$$

Overman and his co-workers carried out a detailed kinetic study of the corresponding reaction with dialkyl, diaryl and ethyl aryl disulphides in 50% (v/v) aqueous dioxane.[3–5] Their data at both low and high pH were consistent with a two-step mechanism involving formation of a phosphonium ion intermediate **1** (Equations {2} and {3}).



$$\mathrm{Ph_3\ddot{P}} + \underset{\substack{|\\ \mathrm{R}}}{\mathrm{S}}\mathrm{{-}SR} \longrightarrow \underset{\mathbf{1}}{\mathrm{Ph_3\overset{+}{P}{-}SR}} + \mathrm{RS^-} \qquad \{2\}$$

$$\mathbf{1} + \mathrm{H_2O} \longrightarrow \mathrm{Ph_3P{=}O + RS^-} \qquad \{3\}$$

They ruled out an alternative mechanism based on biphilic attack by Ph_3P on the S—S bond to form a phosphorane intermediate (Equation {4}) because of the sensitivity of the reaction rate to change in the solvent polarity as indicated by correlation with Grunwald Y values ($m = 0.89$).[3]

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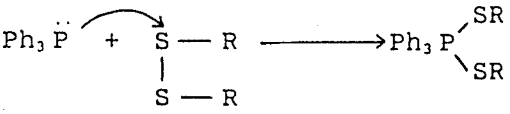
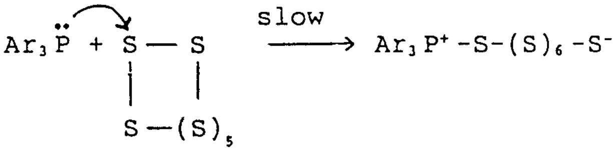


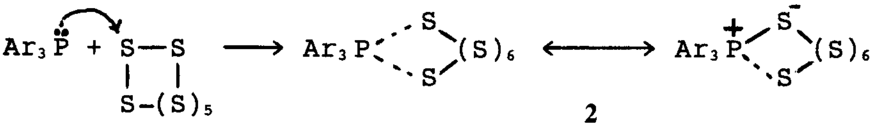
{4}

A similar sensitivity to solvent effects for the reaction of elemental sulphur with triphenylphosphine in benzene as solvent led Bartlett & Meguerian to propose an analogous rate determining ionization of the S—S bond (Equation {5}).[6]



{5}

Hall and his co-workers have extended Bartlett's earlier study to include the reaction in toluene of a series of tri-coordinate phosphorous compounds with elemental sulphur.[7] The rate sequence observed for reaction with S_8 [Ph_2POR · > $PhP(OR)_2$ > $P(OR)_3$ > PPh_3] was very similar to that observed for reaction with diethyl peroxide as substrate and for which a biphilic non-polar transition state has been proposed.[8] Hall has suggested therefore that reaction of tri-coordinate phosphorus compounds with elemental sulphur could occur via a biphilic mechanism in which the P—S bonds of the transition state possess a high degree of ionic character as in **2** (Equation {6}) arising from backdonation from S^- to P^+.[8]



{6}

2

In this paper we report a kinetic study on the reaction of a series of cyclic disulphides [4-phenyl-1,2-dithiolane(**3**); 1,2-dithiane(**4**) and 1,2-dithiepane(**5**)] with tris-(4-chlorophenyl)phosphine and triphenylphosphine respectively in aqueous organic solvents.

RESULTS AND DISCUSSION

Kinetics—The rate of reaction of both 1,2-dithiane and 1,2-dithiepane with triphenylphosphine in aqueous organic solvents could be conveniently studied by U.V. spectrophotometry. Reaction of the unsubstituted 1,2-dithiolane was too rapid to follow by this method and the reaction of tris-(2-chlorophenyl)phosphine with 4-phenyl-1,2-dithiolane was used as a model for reaction with a five-membered cyclic disulphide.

All reactions were followed in aqueous organic solvents which contained 0.05 *M* hydrochloric acid as a buffer to reduce the possibility of reverse or side reactions of any thiolate ion intermediates. Ultraviolet analysis of the reaction products in all reactions studied showed only triphenylphosphine oxide and no evidence of phosphine sulphides which could arise from such processes.

Under the conditions used, clean pseudo-first-order kinetics were observed and the values of k_1 obtained were directly proportional to the concentration of disul-

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phide as shown typically for the reaction of 1,2-dithiane with triphenylphosphine in Table I. The resulting second-order rate constants ($k_2 = k_1/[S—S]$) determined at two or more phosphine concentrations at different temperatures are summarized in Table II and the Arrhenius parameters shown in Table III. The relatively large negative values of S‡ are consistent with those observed in bimolecular reactions such as that formulated for the open-chain disulphides in Equations {2} and {3}. Whilst 1,2-dithiane reacts with triphenylphosphine slightly faster than 1,2-dithiepane as might be anticipated from the relative ring strains in the two systems,[9,10] it is difficult to relate these reactivities to that of 4-phenyl-1,2-dithiolane because of the effect of a phenyl substituent and the substituted phosphine used. In benzene as solvent, the relative nucleophilicities of triphenylphosphine and tris-(4-chlorophenyl)phosphine towards elemental sulphur were observed to be approximately one hundred to one.[6]

Solvent Effects—Values of the second-order rate-coefficient, k_2, for the reaction of **3** with tris-(4-chlorophenyl)phosphine as a function of solvent composition are shown in Table IV for a series of mixed aqueous organic solvents. The reaction rate is sharply dependent on solvent polarity as illustrated in Figure 1 and is characteristic of reactions proceding via a highly ionic transition state. Analysis of

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TABLE I

Values of k_1 and k_2 for the reaction of 1,2-dithiane with Ph_3P in 90% EtOH-H_2O (v/v) at 26.0°C

10^3 [Dithiane]	10^4 [Ph_3P]	k_1/m^{-1}	$k_2/l\ mol^{-1}\ m^{-1}$
1.50	1.50	0.218	145
2.00	1.50	0.279	140
1.60	0.959	0.237	148
2.50	0.950	0.356	142

TABLE II

Values of k_2 ($l \cdot mol^{-1}\ m^{-1}$) for the reaction of cyclic disulphides with arylphosphines in 90% EtOH-H_2O (v/v) at different temperatures

Disulphide	Phosphine	26.0°	30.0°	35.0°	40.0°	43.0°
3	$(ClC_6H_4)_3P$	1.65[a]	2.50	3.58	4.86	6.20
4	Ph_3P	144	172	216	259	270
5	Ph_3P	130	160	200	243	260

[a] At 25.0°C.

TABLE III

Arrhenius parameters for the reduction of cyclic disulphides with arylphosphines in 90% EtOH (v/v)

Disulphide	Ar_3P	ΔH‡[a]	ΔS‡[b]
3	$(ClC_6H_4)_3P$	12.30	−16.3
4	Ph_3P	6.70	−26.7
5	Ph_3P	7.30	−24.7

TABLE IV

Values of k_2 ($l \cdot mol^{-1} m^{-1}$) for the reduction of **3** with tris-(4-chlorophenyl)phosphine in aqueous organic solvents at 26.0°C

% (v/v) Org. Solvt.	EtOH	MeOH	Bu^{t}OH	DMF	MeCN
90	1.65	—	—	—	1.23
85	2.55	5.08	1.10	0.61	1.71
80	3.30	6.73	1.23	0.98	2.33
75	4.35	9.56	1.44	1.55	3.00
70	5.84	15.1	1.67	2.62	3.50
65	8.81	23.7	1.90	4.77	4.55
60	13.0	38.0	2.08	11.2	5.83
55	17.3	60.0	2.39	17.7	7.59
50	27.5	93.1	2.87	31.8	10.6

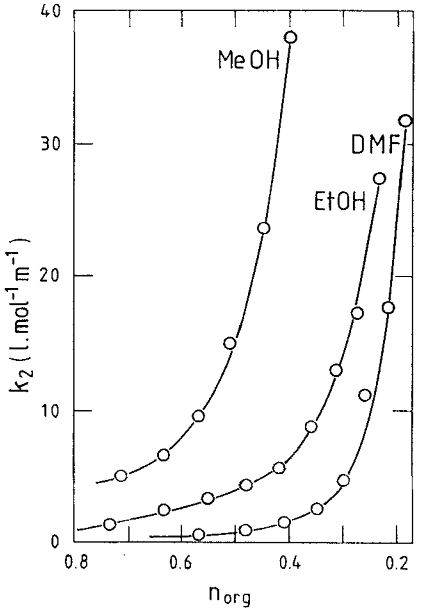

FIGURE 1 Plots of second-order rate-coefficients for the reaction of **3** with tris-(4-chlorophenyl)phosphine as a function of mole fraction of organic solvent at 26°C.

the data in terms of the Kirkwood function $(\varepsilon - 1)/(2\varepsilon + 1)$ does not lead to a linear correlation (Figure 2).[11] This treatment attempts to correlate solvent effects which arise purely from electrostatic interactions and the lack of correlation suggests that other factors which contribute to the overall polarity of the solvent are important.

Dimroth & Reichardt used their empirical solvatochromic E_T (30) scale to study the polarity of a variety of binary aqueous organic solvents.[13] Analysis of our data for aqueous ethanol, dimethylformamide and acetonitrile as a function of the normalised E_T^N function shows a much improved correlation over the use of the Kirkwood function although some curvature is still observed (Figure 3). It is generally

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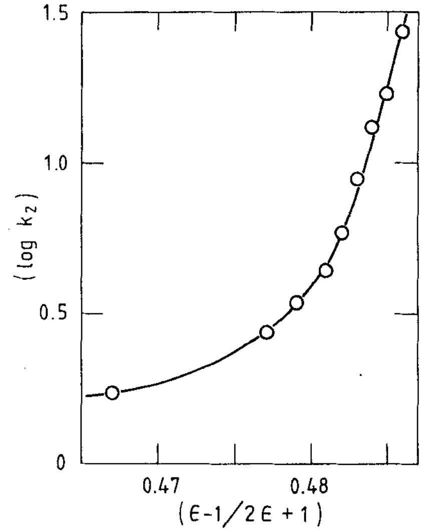

FIGURE 2 Plot of log k_2 for the reaction of **3** with tris-(4-chlorophenyl)phosphine in ethanol-H_2O verses the Kirkwood function (values of ε from Reference 11) at 26°C.

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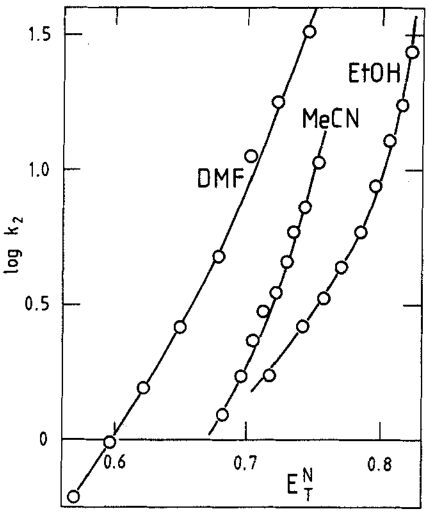

FIGURE 3 Plots of log k_2 verses E_T^N for the reaction of **3** with tris-(4-chlorophenyl)phosphine in aqueous organic solvents at 26°C.

assumed that E_T^N values reflect a combination of both non-specific and specific contributions to "polarity".[15] In order to better compare non-electrostatic forces on the reaction of a phosphine with cyclic disulphides, isodielectric rate constants (k_2^{iso}) were calculated, for four pairs of binary solvents for which literature data were available, from plots of log k_2 verses mole fraction of organic solvent (n_{org}) using values directly read from plots of ε verses n_{org}. The plot of k_2^{iso} versus E_T^N (Figure 4) shows quite a good correlation of slope 6.7 (r = 0.966) in spite of the

TABLE V

Isodielectric second-order rate coefficients for the reaction of **3** with tris-(4-chlorophenyl)phosphine at 26.0°C

Solvent	$n_{org}(\varepsilon = 52)$	$k_2(\mathrm{l \cdot mol^{-1}\, m^{-1}})$	E_T^N (Reference 12)
MeOH-H_2O	0.417	28.2	0.815
EtOH-H_2O	0.245	24.2	0.820
MeCN-H_2O	0.372	5.00	0.640
DMF-H_2O	0.736	0.150	0.505

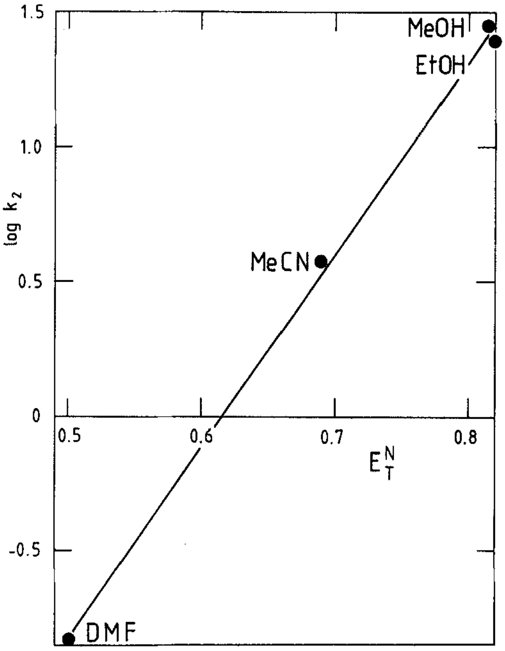

FIGURE 4 The variation of log k_2^{iso} with E_T^N at constant dielectric constant (ε = 52) for the reduction of **3** with tris-(4-chlorophenyl)phosphine in aqueous organic solvents at 26°C.

limited data available. The slope of the plot of log k_2 verses Grunwald-Winstein *Y* values for the reaction of **3** with tris-(4-chlorophenyl)phosphine in aqueous methanol is 0.72 ($r = 0.998$) and is of a similar magnitude to that observed by Overman and his group for the reaction of diaryl disulphides with triphenylphosphine (0.89).[3]

The marked dependence of the rate of reaction of **3** with tris-(4-chlorophenyl)phosphine on solvent polarity and the similarity of this behaviour to that shown by acyclic disulphides with triphenylphosphine[3] and aminophosphines[16] and of elemental sulphur with aryl phosphines[6] leads us to prefer the fully ionic mechanism shown in the scheme.

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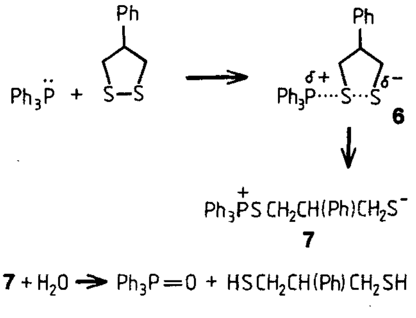

SCHEME

TABLE VI

Arrhenius parameters for the reduction of **3** with tris-(4-chlorophenyl)phosphine in aqueous organic solvents

Solvent (v/v)	ε^{12}	$k_2(\mathrm{l \cdot mol^{-1}\ m^{-1}})^{a}$	$\Delta H\ddagger^{b}$	$\Delta S\ddagger^{c}$
40% Bu^{t}OH	53.0	3.01	11.6	−17.8
40% DMF	73.2	28.8	11.8	−12.3
40% MeCN	53.6	34.9	12.2	−10.9

[a] At 26.0°C.

[b] $\mathrm{kcal \cdot mol^{-1}}$.

[c] $\mathrm{cal \cdot deg^{-1} \cdot mol^{-1}}$.

The rate of reduction of **3** with tris-(4-chlorophenyl)phosphine is similar in both 40% aqueous DMF and MeCN but significantly depressed in 40% aqueous Bu^{t}OH (Table VI). The values of $\Delta H\ddagger$ for reaction in all three mineral solvents are very similar. The origin of the rate difference lies in the much more negative value of $\Delta S\ddagger$ for aqueous Bu^{t}OH. The observed values are consistent with the formation of a highly charged transition state (**6**) from neutral molecules for which translational and rotational degrees of freedom on the polar solvent molecules are much more reduced in the case of Bu^{t}OH-H_2O than in the other two solvents.

EXPERIMENTAL

Materials. Both 1,2-dithiane and 1,2-dithiepane were prepared via the lead salt of the corresponding dithiol using Field & Barbee's method—1,2-dithiane as colourless needles (after sublimation) m.p. 29–31°C (lit.,[17] 29–30°C) and 1,2-dithiepane as a colourless liquid b.p. 61°C/2 mm (lit.,[15] 55–60°C/1.7 mm). 4-Phenyl-1,2-dithiol prepared from the corresponding ditosylate[18] was oxidised with iodine to give 4-phenyl-1,2-dithiolane (37%) as a pale yellow oil b.p. 99–102°C/0.3 mm (lit.,[19] 76–78°C/0.005 mm).

Kinetic Procedure. The rates of reaction were determined spectrophotometrically by following the disappearance of phosphine at 260 nm using a Perkin-Elmer Model 554 U.V. spectrometer with a thermostatted cell compartment (±0.1°C). The phosphine (20 μl in ethanol) was added to 3.0 ml of the disulphide ($1.5–2.5 \times 10^{-3}$ M) in the aqueous organic solvent in a 1 cm pathlength cell at the required temperature. Values of k_1 were calculated from the standard equation using a least squares procedure.

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