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OXIDATIVE DESULPHURISATION AND DESELENATION AT PENTACOVALENT PHOSPHOROUS BY PHOTOGENERATED PEROXIDIC SPECIES

Raj K. Bhardwaj and R. Stephen Davidson

Department of Chemistry, The City University,
Northampton Square, London EC1V 0HB

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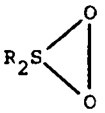
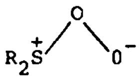
Abstract: The peroxidic species generated by photooxidation of dialkylsulphides and diazocompounds are able to effect oxidative desulphurisation and deselenation at pentacovalent phosphorus.

The photooxidation of sulphides by singlet oxygen shows a remarkable solvent dependence. In non-polar solvents the sulphides act as physical quenchers for singlet oxygen whereas in protic solvents many react to give sulphoxides. The quenching process is thought to involve a charge transfer complex. In protic and polar aprotic solvents, this complex can collapse to give a peroxidic species which is capable of undergoing oxygen transfer reactions [1]. The exact identity of the peroxidic species is not known and structures (A) and (B) have been suggested:

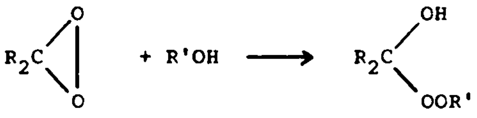


(A)



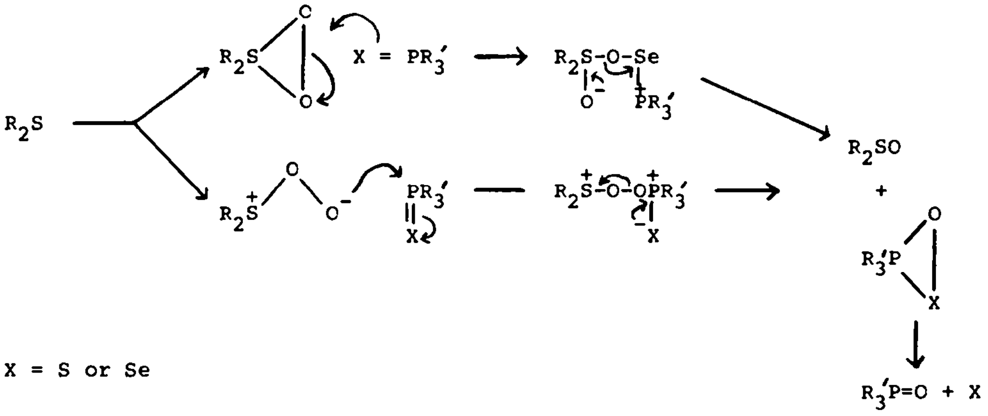
(B)

That the peroxidic species will react with nucleophiles e.g. sulphides to give sulphoxides is in accord with structure (A). The peroxidic species will also react with such compounds as sulphoxides to give sulphones [2] and here it is clearly reacting as a nucleophilic reagent. Careful examination of these reactions has led to the suggestion that the structures (A) and (B) can interconvert, the process being solvent dependent [3]. There is some evidence to support the view that compounds having the structure (A) will have a short lifetime in protic solvents due to their susceptibility to ring opening [4]:



The oxygen transfer reactions of the sulphur peroxidic species are parallelled by those of carbonyl oxides which can be generated by direct or dye-sensitised oxidation of diazoalkanes [5]. The reactivity of the carbonyl oxides, i.e. susceptibility to nucleophilic attack by sulphides [6] and their ability to act as nucleophiles is shown by their ability to decarboxylate α-oxo-carboxylic acids [7], suggests that they may have structures (C) or (D):

In order to test the first point, a study was made of the rose bengal sensitised oxidation of di-n-hexylsulphide in methanol-chloroform solution (1:1 v/v) containing compounds (1)-(5) (Table 2). Oxidative deselenation was observed, the reactivity of the addends (1)-(5) being that expected from a consideration of their susceptibility to nucleophilic attack. Control experiments, together with the foregoing evidence, showed that deselenation was not occurring via attack of singlet oxygen upon (1)-(5). We therefore propose the following mechanism (where X = Se):



X = S or Se

In accord with this mechanism, it was found that the addition of a compound such as (1) led to a decrease in rate of sulphoxide formation. When the

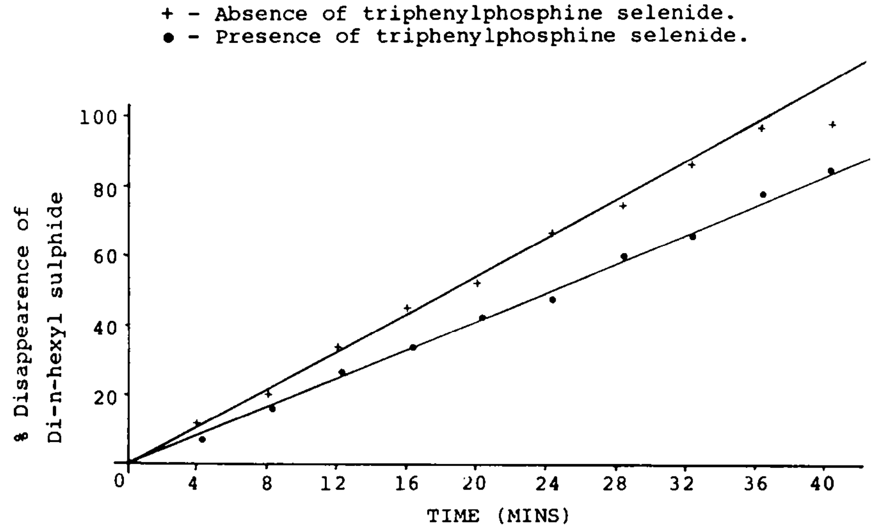
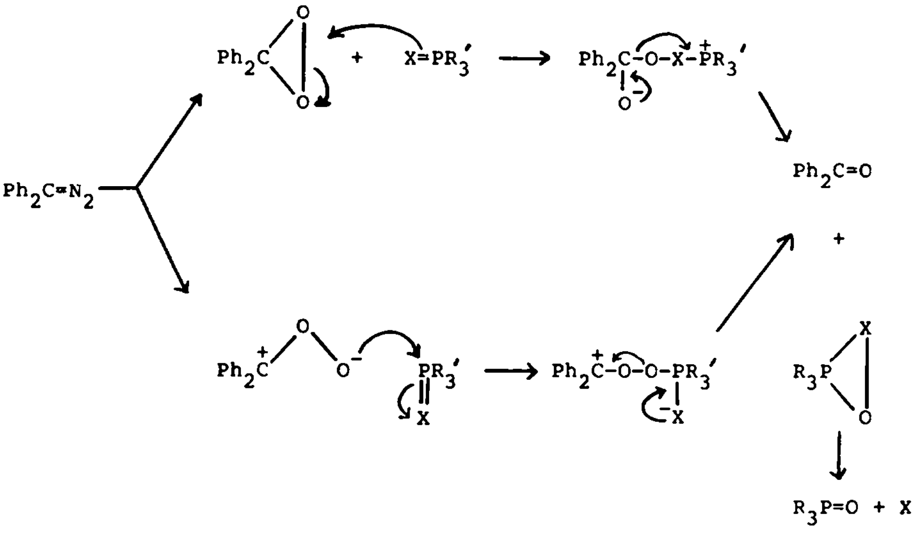


Figure % Disappearance of Di-n-hexylsulphide with time in the presence and absence of triphenylphosphine selenide.

sulphides (5)-(8) were used in place of the selenides (1)-(4), oxidative desulphurisation at phosphorus was observed but, based on product yield, this reaction is far less facile than the oxidative deselenation of (1)-(4) (i.e. in reaction (iii), compounds (5)-(8) compete less effectively for B than (1)-(4).

The ability of (1)-(8) to intercept peroxidic species generated by oxidation of sulphides suggested that they might also react with carbonyl oxides. The rose bengal photosensitised oxidation and direct photooxidation of diphenyldiazomethane were carried out and the effect of adding compound (1)-(8) upon the reactions determined. The results shown in Tables 3 and 4 demonstrate that compounds (1)-(7) can intercept the peroxidic species generated on oxidation of the diazo compound. The order of reactivity of (1)-(7) is similar to that found for the reaction of these compounds with the peroxidic compounds generated on oxidation of sulphides and therefore propose the following reaction mechanism:



X = S or Se

Benzophenone was found to be produced in all these reactions.

TABLE 2

Photosensitised[a] (rose bengal) oxidation of di-n-hexyl sulphide in the presence of compounds containing P=Se and P=S bonds.

COMPOUND	% OXIDISED PHOSPHORUS COMPOUND		% UNCHANGED PHOSPHORUS COMPOUND
$Ph_3P{=}Se$ (1)[b,c,d]	100		0
$Ph_2P(Se)OEt$ (2)[b,d]	96		4
$PhP(Se)(OEt)_2$ (3)[b,d]	64		36
$(EtO)_3P{=}Se$ (4)[b,d]	51		49
$(MeO)_3P{=}Se$ (5)[b,d]	41		59
$Ph_3P{=}S$ (6)[d]	22	37[f]	
$Ph_2P(S)(OEt)$ (7)[d]	11	29[f]	
$PhP(S)(OEt)_2$ (8)[d]	4	6[f]	
$(EtO)_3P{=}S$ (9)[e,d]	2	3[f]	

a - Rose bengal 2×10^{-4} M, solvent methanol-chloroform (1:1 v/v).
b - 30 min irradiation period, sulphide 1×10^{-2} M.
c - In the absence of sulphide, only 3% phosphine oxide obtained.
d - Organophosphorus compound, 2.5×10^{-3} M.
e - 60 min irradiation period, sulphide 1×10^{-2} M.
f - 60 min irradiation period, di-n-hexyl sulphide 5×10^{-2} M dm^{-3}

Table 3

Photosensitised[a] oxidation of diphenyldiazomethane in the presence of compounds containing P=Se and P=S bonds.

COMPOUND	YIELD OF OXIDISED ORGANOPHOSPHORUS COMPOUND (%)	
	A[b]	B[c]
$Ph_3P{=}Se$ (1)	98	
$Ph_2P(Se)OEt$ (2)	89	
$PhP(Se)(OEt)_2$ (3)	53	
$(EtO)_3P{=}Se$ (4)	46	
$(MeO)_3$ P=Se (5)	37	
$Ph_3P{=}S$ (6)	15	31
$Ph_2P(S)OEt$ (7)	6	10
$PhP(S)(OEt)_2$ (8)	0	0
$(EtO)_3PS$ (9)	0	0

a - Irradiation time 90 min, Rose bengal as sensitiser (2×10^{-4} M), organophosphorus compound 2.5×10^{-3} M, solvent - methanol/ chloroform (1:1 v/v).
b - Diphenyldiazomethane 1×10^{-2} M.
c - Diphenyldiazomethane 5×10^{-2} M.

Table 4

Direct photooxidation[a] of diphenyldiazomethane in the presence of compounds containing P=Se and P=S bonds

COMPOUND	YIELD OF OXIDISED[b] ORGANOPHOSPHORUS COMPOUND (%)
$Ph_3P{=}Se$ (1)	94
$Ph_2P(Se)OEt$ (2)	19
$PhP(Se)(OEt)_2$ (3)	14
$(EtO)_3P{=}Se$ (4)	13
$(MeO)_3P{=}Se$ (5)	10
$Ph_3P{=}S$ (7)	8
$Ph_2P(S)OEt$ (8)	0
$PhP(S)(CEt)_2$ (9)	0
$(EtO)_3P$	0

a - Irradiation time 24 hours, organophosphorus compound 2.5 x 10^{-3} M, solvent methanol - chloroform (1:1 v/v).

b - Diphenyldiazomethane used 1 x 10^{-2} M.

CONCLUSIONS

We have shown that the peroxidic species generated by oxidation of sulphides and diazoalkanes can cause oxidative desulphurisation and deselenation at pentacovalent phosphorus. Mechanistic interpretation of the results is bedevilled by the fact that the peroxidic species seem to be able to exist as zwitterionic species as well as a covalent cyclic structure and compounds containing P=X bonds (X = S or Se) can act as nucleophiles or suffer nucleophilic attack. The change in reactivity of the organophosphorus compounds observed when the aryl groups are successively replaced by alkoxyl groups, would favour the view that the phosphorus atom develops charge in the transition state and hence favouring the view that the compounds containing P=X bonds (X = S or Se) are acting as nucleophiles. Clearly a full interpretation demands a greater knowledge of the structure of the peroxidic species produced upon oxidation of sulphides and diazoalkanes.

EXPERIMENTAL

M.ps, which are uncorrected, were determined in capillary tubes. ^1H nmr spectra were measured on a JEOL 60 MHz spectrometer, in deuterochloroform solution with tetramethylsilane as internal standard. G.L.C. analyses were carried out using a Shimadzu GC-mini 2 gas chromatograph (F.I.D. detector) in conjunction with a Shimadzu chromatopac C-R1B integrator. The column used was a copper capillary 50 meter SX 0.31 SE54 021 JDF. Compounds were identified by comparison of their retention times with those of authentic samples. Rose Bengal di-n-hexylsulphide (Aldrich) were used as received, without further purification. Diphenyldiazomethane was prepared by the standard method [15] and characterised by its i.r. spectrum and melting point.

The solvents chloroform and methanol were refluxed over phosphorus pentoxide and calcium hydride respectively for several hours and then distilled and stored under nitrogen before use.

Preparation of compounds

Compounds (6)-(9) were prepared by the methods previously described [15] and their spectral properties confirmed their structures. The selenides were prepared from the appropriate tervalent organophosphorus compound which was treated with excess selenium, in dry benzene, and stirred at room temperature under nitrogen atmosphere for 24 hours. The excess selenium was filtered and the solvent removed to give the desired product. The selenides, if solids were purified by recrystallisation from ethanol or of liquids by fractional distillation under vacuum. Compound (1), m.p. 180-182°C (lit. 184-5°C [16]) was obtained in 88% yield. Analysis calculated for $C_{18}H_{15}PSe$: C, 63.34; H, 4.39; P, 9.09. Found: C, 63.49; H, 4.50; P, 9.02%. δ 7.3 (m, 9H, aromatic meta and para), 7.7 (ddd, 6H, $^3J_{HCCP}$ 11.5 Hz, $^3J_{HCCH}$ 7 Hz, $^4J_{HCCCH}$ 2Hz, H-ortho). Compound (2) m.p. 46-48°C, 93% yield. Analysis calculated for $C_{14}H_{15}OPSe$: C, 54.33; H, 4.85; P, 10.02. Found: C, 54.63; H, 5.00; P, 10.18%. δ 7.4 (m, 6H, aromatic meta and para), 7.8 (ddd, 4H, $^3J_{HCCP}$ 14 Hz, $^3J_{HCCH}$ 9 Hz, $^4J_{HCCH}$ 2 Hz, H-ortho), 3.9 (dq, 2H, $^3J_{HCOP}$ 9.5 Hz, $^3J_{HCCH}$ 8.5 Hz, $-OCH_2-$), 1.3 (t, 3H, $^3J_{HCCH}$ 7 Hz, $-CH_3$). Compound (3) b_{15} 125-8°C, 91% yield. Analysis calculated for $C_{10}H_{15}O_2$ PSe: C, 43.29; H, 5.41; P, 11.18. Found: C, 43.31; H, 5.53; P, 11.21%. δ 7.3 (m, 3H, aromatic meta and para), 7.6 (ddd, 2H, $^3J_{HCCP}$ 13 Hz, $^3J_{HCCH}$ 8.5 Hz, $^4J_{HCCCH}$ 2Hz, H-ortho), 3.9 (ddq, 4H, $^3J_{HCOP}$ 9 Hz, $^3J_{HCCH}$ 8.5 Hz, $-OCH_2$), 1.3 (t, 6H, $^3J_{HCCH}$ 6.5 Hz, $-CH_3$). Compound (4) b_{12} 93-5°C (lit. 14, b, 98.5°C [17]), 92% yield. Analysis calculated for $C_6H_{15}O_3PSe$: C, 29.37; H, 6.12; P, 12.65. Found: C, 29.59; H, 6.14; P, 12.69%. 3.9 (dq, 6H, $^3J_{HCOP}$ 9 Hz, $^3J_{HCCH}$ 8 Hz, OCH_2), 1.3 (t, 9H, $^3J_{HCCH}$ 7.5 Hz, $-CH_3$). Compound (5) b_{15} 85-88°C (Lit. b_{11} 73-74°C [17]), 90% yield. Analysis calculated for $C_3H_9O_3PSe$: C, 17.73; H, 4.43; P, 15.26. Found: C, 18.00; H, 4.47; P, 15.30%. δ 3.7 (d, 9H, $^3J_{HCOP}$ 14 Hz, $-CH_3$).

Irradiation Conditions

The reactions were carried out by irradiating in pyrex tubes (18 x 300 mm) known concentrations of the sensitised (rose bengal or diphenyldiazomethane), dissolved in chloroform: methanol (1:1 v/v) containing the organophosphorus compound and di-n-hexylsulphide. The solutions were flushed with oxygen through the reactions and irradiated with daylight fluorescent tubes (8 x 20 w), arranged in a circular array around the reaction vessel which was contained in a cylindrical glass vessel (8 x 20 cm) containing a 2% aqueous solution of potassium dichromate to filter out unwanted radiation.

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