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OXIDATIVE HYDROLYSIS OF PHOSPHORUS(V) ESTERS OF THIOLS BY PEROXYMONOSULFATE ION. REACTIONS OF PEROXYMONOSULFATE ION WITH PHOSPHORUS(V) ESTERS OF THIOLS

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Peroxymonosulfate ion, HSO_5^-, as Oxone, readily converts phosphorus(V) esters of thiols into the phosphorus(V) and sulfonic acids. The esters were $Ph_2PO \cdot SC_6H_4R(p)$ with R = MeO (1a), Me (1b), H (1c), Cl (1d) and NO_2 (1e), $(EtO)_2PO \cdot SPh$ (2), $Ph_2OI \cdot SEt$ (3) and PhPO(OEt)SEt (4). Reactions are first order in each reactant and second-order rate constants, k_2, for 1a–e fit the Hammett equation with $\rho = -0.46$. The rate constants increase markedly with increasing water content of H_2O–MeCN, the activation enthalpies are low and the entropies are negative. Despite the low value of $-\rho$, these esters are much less reactive than thiol ethers, but the rate constants of reactions of these compounds and acyl thiols qualitatively follow the ionization potentials of the ethers and the esters. © 1997 by John Wiley & Sons, Ltd.

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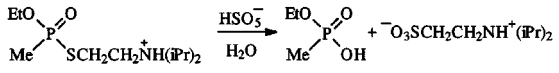
INTRODUCTION

Some chemical nerve agents, e.g. the fluorophosphonates, are readily detoxified by reaction with HO^-,[1,2] but the exceedingly toxic agent VX [*O*-ethyl *S*-(2-diisopropylamino)ethyl methylphosphonothioate] reacts at room temperature with both P—S and P—O cleavage and the latter reaction gives a toxic phosphonothioate ion. Therefore, other methods have to be considered for detoxification of VX.[2,3] Aqueous peroxymonosulfate ion, HSO_5^-, rapidly converts VX into phosphonic and sulfonic acids:[2,4a]



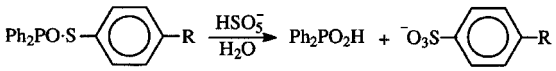
The reaction of peroxyacids is general for phosphorus(V) thiol esters,[4] and the first step appears to be oxidation at sulfur, followed by attack of water and P—S cleavage. Further oxidation at sulfur gives the sulfonic acid. Similar oxidative reactions of phosphorus(V) compounds have been identified in non-aqueous media.[5]

Peroxymonosulfate ion is most conveniently used as Oxone ($2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$), which is also a convenient reagent for the oxidation of sulfides to sulfoxides and then, more slowly, to sulfones.[6,7] Acyl thiols are also cleaved by HSO_5^- giving carboxylic and sulfonic acids and these reactions appear to be mechanistically similar to those of the phosphorus(V) thiol esters:

$$R'CO \cdot SR \xrightarrow[H_2O]{HSO_5^-} R'CO_2H + RSO_3^-$$

These reactions are fastest in polar solvents of high water content and are accelerated by electron-releasing substituents.[7] Solvent and substituent effects are similar to those on oxidations of sulfides by periodate ion.[7a,8]

We examined reactions of a series of thiol phosphinates (**1**) with HSO_5^- in H_2O–MeCN with the aim of determining kinetic electronic substituent effects:



1a-e; R = 1a, OMe; 1b, Me; 1c, H; 1d, Cl; 1e, NO_2

These reactions can be followed spectrophotometrically with dilute **1** ($<10^{-4}$ mol dm^3). Reactions of **VX** are generally followed by NMR spectrometry and because of its high toxicity this compound is inconvenient for systematic kinetic work.[2–4a] Most work therefore involves use of model

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compounds.[2–4a] However, NMR spectrometry is extremely useful in product identification.

A few measurements were made with other model compounds: thiophenyl diethyl phosphate [$(EtO)_2PO \cdot SPh$, **2**] and thioethyl diphenyl phosphinate ($Ph_2PO \cdot SEt$, **3**) and their reactions in D_2O–CD_3CN were followed by ^{31}P NMR spectrometry at 25·0 °C with 0·08 mol dm^{-3} HSO_5^-. Reaction of $Ph_2PO \cdot SPh$ (**1c**) was also followed by NMR spectrometry. Reactions of **1a**, **1c**, **2**, **3** and *O*,*S*-diethyl phenylphosphonothioate (**4**) with HSO_5^- were also followed spectrophotometrically in water (**4** is a better simulant for **VX** than the other esters[9]). Mechanistic evidence on the use of Oxone as decontaminant for toxic sulfur compounds is useful in indicating optimum reaction conditions, e.g. of temperature or solvent.

PhPO(OEt)SEt
4

RESULTS

Kinetics and products

Formation of phosphorus(V) and sulfonic acids has been demonstrated quantitatively by NMR spectrometry (see Experimental and Ref. 4a). Reactions of **1a**–**e**, **2**, **3** and **4** were followed spectrophotometrically and first-order rate constants, k_ψ, with respect to substrate, varied linearly with $[HSO_5^-]$. Except for reaction of the *p*-nitro derivative **1e**, plots of k_ψ against $[HSO_5^-]$ had zero intercepts (Figure 1). Second-order rate constants, $k_2 = k_\psi/[HSO_5^-]$ (Table 1), fit the Hammett equation,[10] with negative values of ρ. Electronic effects were small, $\rho = -0{\cdot}46$, and with these low values of ρ either σ_p or σ^+ parameters fit the data, but we base our values of ρ on the former.

The positive intercept observed with the *p*-nitro derivative **1e** (Figure 1) indicates that there is also hydrolysis followed by rapid oxidation of the thiol (see Experimental).

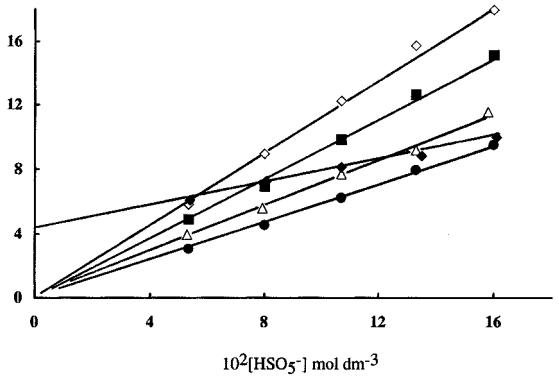


Figure 1. Plots of first-order rate constants, k_ψ, vs $[HSO_5^-]$ for reactions of $Ph_2PO \cdot SC_6H_4R(p)$ with $[HSO_5^-]$ in 95 vol.% aqueous MeCN at 25 °C. R = OMe (◇), Me (■), H (△), Cl (●) and NO_2 (◆)

This spontaneous hydrolysis should be assisted by a strongly electron-withdrawing substituent. The first-order rate constant of hydrolysis in the absence of HSO_5^- was $4{\cdot}3 \times 10^{-4}$ s^{-1}, and the intercept in the plot of k_ψ against $[HSO_5^-]$ is $4{\cdot}2 \times 10^{-4}$ s^{-1}. Reaction rates are very sensitive to the water content of the solvent (Table 2) and follow the Grunwald–Winstein equation (eq. 1)[11, 12] with high *m* values:

$$\log(k/k_0) = mY \quad (1)$$

These kinetic solvent effects are very similar to those on periodate oxidations of sulfides[8] and oxidations of sulfides and acyl thiols by HSO_5^-,[7] all of which follow the Grunwald–Winstein equation with $m \approx 1$.

The activation enthalpies are low and the activation entropies are negative (Table 1). These solvent and temperature effects are similar to those for reactions of HSO_5^- with sulfides and acyl thiols and for periodate ion oxidation of sulfides.[7, 8] Added salts and small changes in

Table 1. Second-order rate constants and activation parameters for reactions with HSO_5^- [a]

Substrate	$10^3 k_2$ (dm^3 mol^{-1} s^{-1}) 25·0 °C	35·0 °C	450 °C	50·0 °C	$\Delta H^{\neq}$ (kJ mol^{-1})	$\Delta S^{\neq}$ (J K^{-1} mol^{-1})[b]
1a $Ph_2PO \cdot SC_6H_4OMe(p)$	11·2	20·4	38·8	56·6	49·0	−110
1b $Ph_2PO \cdot SC_6H_4Me(p)$	9·10					
1c $Ph_2PO \cdot SC_6H_5$	7·10	14·6	29·7	40·6	53·1	−99
1d $Ph_2PO \cdot SC_6H_4Cl(p)$	5·81	11·4	22·6	32·0	50·6	−109
1e $Ph_2PO \cdot SC_6H_4NO_2(p)$	3·50					
2 $(EtO)_2PO \cdot SPh$	3·63[c]					
3 $Ph_2PO \cdot SEt$	38·3[c]					
4 PhPO(OEt)SEt	58·2[c]					
4 PhPO(OEt)SEt[d]	80·0	129	223	300	42·3	−124

[a] In 95 vol% H_2O–MeCN unless specified otherwise.
[b] Calculated at 25·0 °C.
[c] Interpolated values in 95 vol.% H_2O from data in Table 2.
[d] In 99·6 vol.% H_2O.

Table 2. Solvent effects on second-order rate constants of reactions with HSO_5^- [a]

	H_2O (wt%)								
	99·6	99·3	96·6	96·1	92·9	90·1	88·0	83·7	*m*
	Y[b]								
Substrate	3·53	3·51	3·39	3·37	3·25	3·14	3·05	2·88	
1a $Ph_2PO \cdot SC_6H_4OMe(p)$		14·8		11·2	7·58		3·78	2·57	1·34
1c $Ph_2PO \cdot SC_6H_5$		10·5		7·10	5·28		3·00	1·71	1·30
1d $Ph_2PO \cdot SC_6H_4Cl(p)$				5·81	4·21		2·26	1·38	1·32
2 $(EtO)_2PO \cdot SPh$	5·25			3·63				1·11	1·03
3 $Ph_2PO \cdot SEt$	54·3			38·3					1·0
4 PhPO(OEt)SEt	80·0		60·0			32·7		19·9	1·08

[a] Values of $10^3 k_2$ ($dm^3\ mol^{-1}\ s^{-1}$) at 25·0 °C in H_2O–MeCN.
[b] Interpolated from values in Ref. 12.

pH have little effect on rates, consistent with the oxidant being HSO_5^- without acid or base catalysis under our conditions. Some reactions were also followed by ^{31}P NMR spectrometry in D_2O–CD_3CN (Table 3) with higher substrate concentrations than those used for reactions followed spectrophotometrically. The only ^{31}P signals seen during reaction were those of the esters and the phosphorus(V) acids. Rate constants for reactions of **1c**, **2** and **3** determined in these conditions are given in Table 3.

Reaction of the *p*-nitro derivative (**1e**) was followed at a relatively high wavelength (see Experimental) and because of this red shift the absorbance by Oxone was small. We observed an isosbestic point at 250 nm, supporting our assumption that intermediates do not build up during reaction. We could not make this test with the other substrates because the absorbance of Oxone swamped that of the products.[7b]

Solvent hydrogen isotope effects are small. With 0·7 wt% MeCN as cosolvent and $8{\cdot}32\times10^{-2}$ mol dm^{-3} HSO_5^-, $k_{H_2O}/k_{D_2O} = 1{\cdot}30$ and 1·4 at 25·0 °C for reactions of $Ph_2PO \cdot SC_6H_4R(p)$, R = MeO and H (**1a** and **c**), respectively (see Experimental). These effects are similar to those on reactions of acyl thiols[7b] and on oxidations by other peroxy acids.[13]

The rate constants of reactions followed by NMR spectrometry agree reasonably well with those followed spectrophotometrically (Tables 1–3). For reaction of $Ph_2PO \cdot SPh$ (**1c**), the second-order rate constant, k_2, in 68% (v/v) D_2O–CD_3CN is $2{\cdot}5\times10^{-4}$ $dm^3\ mol^{-1}\ s^{-1}$. The value in 68% (v/v) H_2O–MeCN from extrapolated spectrophotometric values of k_2, based on the relationship between log k_2 and Y [equation (1)], is *ca* 3×10^{-4} $dm^3\ mol^{-1}\ s^{-1}$, in reasonable agreement, considering uncertainties in the extrapolation and the solvent isotope effect.

Table 3. Reactions of HSO_5^- as followed by ^{31}P NMR spectrometry[a]

Substrate	D_2O (vol.%)	$10^3 k_2$ ($dm^3\ mol^{-1}\ s^{-1}$)
1c $Ph_2PO \cdot SPh$	68	0·25
2 $(EtO)_2PO \cdot SPh$	68	0·23
3 $Ph_2PO \cdot SEt$	68	2·1
3 $Ph_2PO \cdot SEt$	80	7·3

[a] At 25·0 °C in D_2O–CD_3CN and 0·08 mol dm^{-3} HSO_5^-.

The kinetic forms and activation parameters (Table 1) of these reactions of HSO_5^- are qualitatively similar to those of sulfides and acyl thiols, where $\Delta H^{\neq}$ values are in the ranges 15–20 and 40–60 kJ mol^{-1} for the sulfides and esters, respectively, and the corresponding values of $-\Delta S^{\neq}$ are in the ranges 116–145 and 92–130 J K^{-1} mol^{-1}, respectively.[7b]

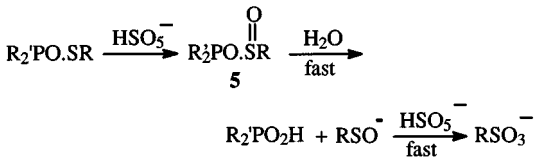
Solvent effects, as given by *m* values [equation (1)], increase from *ca* 0·9 for the sulfides[7b] to *ca* 1·3 for the esters (Table 2) but the $-\rho$ values decrease from 1 for the sulfides to 0.6 for the acyl thiols[7b] and 0·46 for the phosphorus(V) esters, based on data in Table 1. The solvent effect upon reaction of $Ph_2PO \cdot SEt$ (**3**) in H_2O–MeCN (Table 2) gives $m \approx 1{\cdot}0$, based on two data points, in reasonable agreement with other values (Table 2).

DISCUSSION

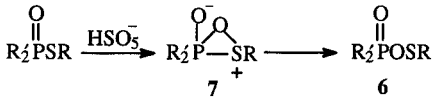
The initial reaction step is oxidation, although the final products are similar to those formed by nucleophilic attack by HO_2^- on phosphorus(V).[3] Several pieces of evidence exclude initial nucleophilic attack. (i) Electronic effects ($\rho \approx -0{\cdot}46$ are inconsistent with nucleophilic attack, for which ρ should be positive. (ii) Some peroxyanions are strong α-effect nucleophiles,[3] but HSO_5^- is a weak nucleophile[14] and SO_5^{2-}, which is a better nucleophile, is in very low concentration at the mild acidity of Oxone solutions. (iii) Intermediates generated by oxidation have been identified or postulated in reactions of peroxy acids with substrates similar to ours in non-aqueous media.[5] (iv) Reactions of HSO_5^- in $H_2{}^{18}O$ lead to incorporation of the

isotopic label on phosphorus but, in reactions with HO_2^-, oxygen is derived from the hydroperoxide ion.[9]

Oxidation by HSO_5^- or other peroxy acid can be regarded as an S_N2 displacement on oxygen[15] generating a labile *S*-oxide[5, 7b] (**5**), which breaks down rapidly with attack by H_2O on phosphorus followed by further oxidation:



An alternative path involves the formation of a mixed phosphinic sulfenic anhydride (**6**) by insertion and rearrangement of **7**:



Isotopic evidence is inconsistent with this mechanism because $H_2{}^{18}O$ should attack on sulfur and in the products the label is on phosphorus.[9] However, anhydrides have been identified in reactions of thiol phosphorus(V) esters by peroxy acids in non-aqueous media.[5]

The high sensitivity to solvent polarity, as shown by $m \approx 1{\cdot}3$ (Table 2), is typical of reactions with considerable charge development in the transition state,[16] but with the thioaryl derivatives (**1a**–**e**) electronic substituent effects are small, e.g. $\rho \approx -0{\cdot}46$, indicating only slight charge development. Electronic substituent effects at sulfur or phosphorus centers are also small, e.g. second-order rate constants for reactions of **3** and **4** are similar (Tables 1–3). For PhPO(OEt)SEt (**4**), $k_2 = 0{\cdot}08\ dm^3\ mol^{-1}\ s^{-1}$ in 99·6 vol% H_2O. This compound and **3** are, as expected, more reactive than $Ph_2PO \cdot SPh$ (**1c**), $k_2 = 0{\cdot}0105\ dm^3\ mol^{-1}\ s^{-1}$ (Table 2), due to inductive electron withdrawal by Ph as compared with Et. Based on reactions in water with small amounts of MeCN and in 68% (v/v), D_2O–CD_3CN replacement of Ph by EtO on phosphorus has little effect on reactivity, because $k_2 = 2{\cdot}5 \times 10^{-4}$ and $2{\cdot}3 \times 10^{-4}\ dm^3\ mol^{-1}\ s^{-1}$ in the latter solvent for $Ph_2PO \cdot SPh$ (**1c**) and $(EtO)_2PO \cdot SPh$ (**2**), respectively. Replacement of PhS by EtS increases k_2 by a factor of *ca* 8, based on $k_2 = 21 \times 10^{-4}\ dm^3\ mol^{-1}\ s^{-1}$ for reactions of $Ph_2PO \cdot SEt$ (**3**) (Table 3). For these esters, as for thiol esters,[7b] replacement of a thiophenyl by a thioalkyl group increases the reactivity towards HSO_5^- by approximately one order of magnitude. Any mechanistic description has to accommodate these paradoxical results, because in many nucleophilic reactions at alkyl and acyl centers high sensitivity to solvent polarity is associated with extensive charge development and high sensitivity to electronic substituent effects.[16]

The kinetic solvent isotope effects, $k_{H_2O}/k_{D_2O} \approx 1{\cdot}3$, are similar to those for reactions of HSO_5^- with acyl thiols.[7b] These effects are much smaller than those associated with reactions in which transition-state formation involves slow proton transfer, e.g. where the proton is 'in flight.'[17] The proton is lost from the transferred oxygen, but not in an initial equilibrium which would generate the weakly electrophilic SO_5^{2-}. Therefore, the proton must be lost after transition-state formation, as in other oxidations by peroxy acids.[7b, 13]

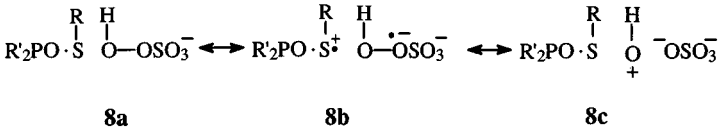
The small electronic effects of substituents in the thioaryl leaving group indicate that transition-state formation does not involve extensive S—O bond making. Electronic substituent effects are also small ($\rho \approx -0{\cdot}66$) for reactions of HSO_5^- with thiols coordinated to ruthenium(III) and cobalt(III).[18] Reactions of peroxy acids with nucleophiles can formally be written as if heterolysis generates HO^+ and an anion,[15] but isotopic evidence shows that HO^+ is not an intermediate with a finite lifetime. In addition, there is little build up of positive charge on the transferred oxygen in the transition state because it would generate a very acidic center, and therefore give a large solvent hydrogen isotope effect.[19] These results point to an 'early' transition state with little charge development on sulfur, but the high *m* values and the negative values of $\Delta S^{\neq}$ are evidence that the transition state is much more hydrated than the initial state, even though HSO_5^- it itself hydrophilic.

The reactions can be regarded as S_N2-like displacements on oxygen by sulfur, but it is necessary to account for the apparently contradictory structural and solvent effects on rates. We therefore consider mechanistic models that have been applied to bimolecular reactions of nucleophiles at alkyl, acyl and carbocationic centers.[20–22]

The transition state can be written as a resonance hybrid of **8a**, **b** and **c**, where the classical structures are reactant-like, **8a**, or involve electron transfer, **8b**, or heterolysis of the peroxy group, **8c** (Scheme 1).

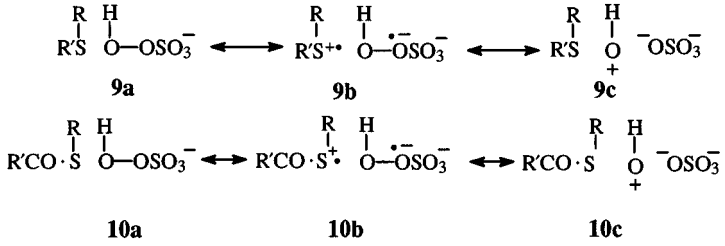
The corresponding transition states for reactions of sulfides and acyl thiols can be written as in Scheme 2.[7b]

There is no evidence for build-up of an intermediate in these reactions in aqueous solvents, and therefore species formed in the initial oxidation go rapidly to products, i.e. the rate is controlled by the ease of oxidation of the phosphorus(V) thioester. Based on values of $\rho \approx -0{\cdot}5$, $-0{\cdot}6$ and $-1{\cdot}0$ for reactions of phosphorus(V) esters, acyl thiols and



8a **8b** **8c**

Scheme 1



Scheme 2

sulfides, respectively, the less reactive the substrate, the lower are the electronic effects of substituents in the phenyl groups. This paradoxical result indicates that the cationic character on sulfur is lowest with the least reactive substrates. In addition, although inductive electronic substituent effects at phenyl groups or at phosphorus are small,[10] the sulfides are much more reactive than the esters. Relative reactivities depend upon solvent, substituents and temperature, but for RSMe (or RSEt) they are approximately R = Ph, 1, PhCO, 10^{-4} and Ph_2PO, 2×10^{-5} at 25·0 °C, contrasting sharply with the low (negative) values of ρ (Table 1 and Ref. 7b).

Solvent effects, as given by *m* values, increase in going from the reactive sulfides to the much less reactive esters. To this extent it appears that charge development in the oxidant increases as substrate reactivity decreases. Therefore, as reactivity decreases there is more heterolysis of the peroxy group in the transition state, which would become more like **8c**–**10c**, and interact more strongly with water. The small hydrogen isotope effects show that proton transfer does not contribute significantly to the free energy barrier to reaction (cf. Ref. 17) or to the high solvent sensitivity.

It is difficult to reconcile this evidence and the strong inhibition by heteroatoms at sulfur as evidenced by the much higher reactivities of sulfides as compared with the esters in terms of the qualitative physical organic treatments that are often used to rationalize structural effects upon nucleophilic reactions. However, to the extent that the classical structures **8b**–**10b** contribute to transition-state structures, the energy barrier to reaction should be related to ionization potentials, *IP*, of the thiol derivatives,[20, 21] consistent with recent discussions of reaction mechanisms.[22]

Substituent effects on reactivity

Differences in reactivities of sulfides and esters are much larger than expected in view of the small electronic effects of substituents in thiophenyl group.[7b] Acyl groups are inductively electron withdrawing, but not markedly so, e.g. $\sigma_I = 0{\cdot}55$ and 0·21 for COCN and $CONH_2$, respectively,[10] and phosphinyl groups probably behave similarly. Therefore, we cannot ascribe reactivity differences to inductive electron withdrawal by acyl or phosphinyl groups. Dr D. H. Aue pointed out to us that for epoxidation of alkenes by peroxyacids free energies of activation are linearly related to the *IP* of the alkenes.[23] There are few experimental values of *IP* for sulfides and acyl thiols, but *IP* = 8·67 and 9·65 eV for Me_2S[24] and MeCO · SMe,[25] respectively, estimated by photoelectron spectroscopy. Other experimental[26] and calculated[27] values are given in Table 4. Values of *IP* calculated with AM1 parameters (see Experimental) tend to be slightly higher than those estimated by photoelectron spectroscopy where comparisons can be made, but the differences do not obscure the relationship between reactivities and *IP*.

Replacement of a methyl group in Me_2S by phenyl does not increase *IP*, despite the $-I$ effect of phenyl. For reactions of sulfides and phosphorus(V) esters with HSO_5^- replacement of Me or Et by Ph at sulfur does not strongly inhibit reaction (Tables 1 and 3 and Ref. 7b). Inhibitions, which are generally less than an order of magnitude, may be due to steric hindrance by the bulky phenyl group rather than to electronic effects. Calculated values of *IP* are similar for MeCO · SMe and Me_2PO · SMe (Table 4), consistent with acyl thiols and phosphorus(V) esters having similar reactivities towards HSO_5^-, although we note that these comparisons neglect steric effects of substituents and solvent effects. Relationships between ionization potentials and free energies of activation are only qualitative, especially for reactions of HSO_5^- where rates are very sensitive to solvent composition, but the sequence of reactivities of sulfides and esters (Tables 1 and 3 and Ref. 7b) is that expected in terms of variations in *IP* (Table 4).

Nucleophilicities are often related to basicities based on Brønsted relationships.[28, 29] The fits are reasonably good if

Table 4. Ionization potentials of thiol derivatives[a]

Me_2S	8·67[b]	8·69[c]	9·10[d]	9·32[e]
MeCO · SMe	9·65[f]	9·92[d]	9·49[e]	
Me_2PO · SMe	9·74[d]			
PhSMe	8·60[g]	8·65–8·98[d, h]		8·45[e]

[a] Vertical ionization potentials in eV; experimental values are from photoelectron spectroscopy or photoionization.
[b] Ref. 24a.
[c] Ref. 24b.
[d] Calculated values, this work.
[e] Calculated values, Ref. 27.
[f] Ref. 25.
[g] Ref. 26.
[h] Value depends on the dihedral angle (see Experimental).

restricted to nucleophiles with common functional groups, but they fail when applied to a wide range of compounds, especially in strongly interacting solvents. Nucleophilicities towards activated carboxylic esters[20] and preformed carbocations[21] are related to ionization potentials and the relations cover a range of structures. This evidence supports the valence-bond, avoided-crossing mechanistic description as applied, for example, to S_N2 reactions at alkyl centers.[22] If oxygen transfers from peroxy acids are regarded as S_N2 displacements at oxygen,[7b, 8, 15] relationships between *IP* and nucleophilicity should apply to these oxidations at sulfur. The Hammett equation fits substituent effects on rates of oxidation by HSO_5^- and IO_4^- (Table 1 and Refs 7b and 8), but only within a very limited class of compounds, i.e. it is satisfactory only for minor structural perturbations. For a limited class of compounds with substituents on aryl groups the Hammett substituent parameters, and also basicities, are probably related to *IP*, but these relationships break down if structures and electronic distributions are significantly changed.

We conclude that the contributions of the classical 'electron-transfer' and 'heterolytic' transition-state structures **8b** and **c**, **9b** and **c** and **10b** and **c** change in favor of the 'heterolytic structures' on going from a sulfide to an acyl thiol to a thiol phosphorus(V) ester. This change can be envisaged in terms of the free energy diagrams developed by Thornton, Jencks and More O'Ferrall.[30] In a Jencks–More O'Ferrall free energy diagram the corners can be represented by the classical structures for electron transfer, **b**, and heterolysis, **c** (Schemes 1 and 2). The transition-state structure will move towards corner **b** as the *IP* of the substrate is reduced, as shown qualitatively in Figure 2. This change in transition-state structure is consistent with

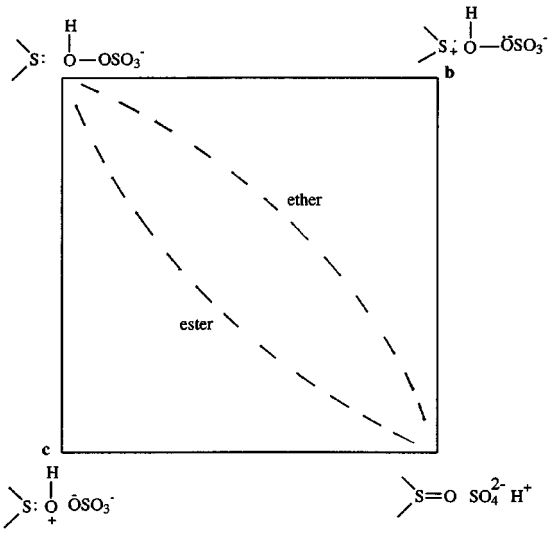


Figure 2. Jencks and More O'Ferrall free energy diagram for classical structures **b** and **c**

electronic substituent effects on phenyl as given by values of $-\rho$ being larger for the sulfides ($-\rho \approx 1$) than for the esters ($-\rho \approx 0{\cdot}46$–$0{\cdot}63$), and the greater sensitivity to solvent for the esters ($m \approx 1{\cdot}3$) than for the sulfides ($m \approx 0{\cdot}9$).

As regards transition-state structures, the solvent effects on reactions of HSO_5^- with the esters and ethers indicate that classical reactant-like structures **8a**, **9a** and **10a** are not major contributors to the resonance hybrid (Schemes 1 and 2). The importance of electron donation from substituents on the phenyl group increases ($-\rho$ increases) as the transition-state structure moves towards that represented by corner **b**, with charge development on sulfur (Figure 2) consistent with the values of ρ for reactions of the esters and ethers. The importance of solvation of the transition state, as indicated by values of m [equation (1)] should increase as the transition-state structure moves towards that represented by the heterolytic-like structure, corner **c** (Figure 2), consistent with the observation of higher values of m for reactions of the esters as compared with the more reactive ethers (Table 2 and Ref. 7). Therefore, consideration of changes in transition-state structure orthogonal to the reaction coordinate (anti-Hammond behavior) rationalizes the decrease in electronic effects, as given by values of $-\rho$, and the increase in sensitivity to solvent, as given by m [equation (1)] on going from reactions of the ethers to those of the esters. At the same time, the decrease in *IP* on going from the ethers to the esters (Table 4) follows the Hammond postulate in fitting the higher reactivity of the ethers as compared with the esters (Table 2 and Ref. 7).

CONCLUSIONS

Transition-state formation in oxygen transfer from peroxymonosulfate ion to thioethers and esters does not involve extensive build-up of positive charge on sulfur. Rate constants increase significantly with increasing solvent polarity, indicating strong interactions with solvent molecules consistent with negative entropies of activation. These observations and correlations of free energies of activation with ionization potentials of the substrates are consistent with a degree of electron transfer from sulfur to oxygen in formation of the activated complex. Kinetic substituent and solvent effects are explained in these terms based on recent treatments of nucleophilicity.

EXPERIMENTAL

Materials. The esters were prepared by standard methods.[28b, 31, 32] Samples **1c**, **2** and **3** were those used in earlier work.[31c] The other thioaryl diphenyl phosphinates (**1a**, **b**, **d**, **e**) were prepared on an 8 mmol scale by adding $Ph_2PO \cdot Cl$ in CH_2Cl_2 dropwise to equimolar aryhl thiol and Et_3N in CH_2Cl_2 with stirring for 1 h as described for the preparation of aryl diphenylphosphinates.[28b] The crude products were recrystallized twice from 2-PrOH, Et_2O–C_6H_{14} or Et_2O. All samples gave single spots in TLC (1:1 EtOAc–C_6H_{14}) and

had the expected ^{1}H NMR spectrum (200 MHz). The m.p.s generally agreed with literature values, as indicated; the substituent group is identified: **1a**, *p*-OMe, 140 °C (140–142 °C); **1b**, *p*-Me, 112 °C (112–114 °C); **1d**, *p*-Cl, 107 °C (110 °C); **1e**, *p*-NO_2, 152 °C (121–123 °C). The literature values in parentheses are those of Cook and Rahhal-Arabi,[32] and they noted that their sample of the *p*-NO_2 derivative (**1e**) contained some acid. The purity of our sample of **1e** was confirmed by GLC, which gave a single peak, and GLC–MS, which gave a peak of the molecular ion. *O*,*S*-Diethyl phenylphosphonothioate (**4**) was synthesized by L. J. Szafraniec and we are grateful for this donation.

Reactions with Oxone (Aldrich) were followed in redistilled, deionized H_2O with MeCN as cosolvent. Oxone solutions were freshly prepared and were standardized iodimetrically. In most experiments, specified volumes of H_2O (D_2O) and MeCN (CD_3CN) were mixed. For determination of *m* values solvents were made up by volume[12] and, where necessary, were converted into wt% from the densities of H_2O and MeCN at 25 °C.

Kinetics. Reactions were generally followed spectrophotometrically (by using 2 mm quartz cells) with Hewlett-Packard Model 8450 or 8451 diode-array spectrophotometers. The wavelengths were 235–245 nm for reactions of **1a**–**d**, **2**, **3** and **4** and 310–320 nm for **1e** and the general method is described elsewhere.[7, 31c] We had problems when we followed reactions of $Ph_2SO \cdot SEt$ (**3**) in the single-beam spectrophotometer because the absorbances at nominally complete reaction drifted with time and the calculated first-order rate constants depended on wavelength. We did not have this problem when the reactions were followed on the double-beam diode-array spectrophotometer. We saw similar behavior in reactions of some acyl thiols with HSO_5^- in dilute H_2SO_4, although not in the absence of H_2SO_4.[7b] We assume that the high light flux in the single beam spectrophotometer promotes photochemical reactions with some compounds. Except as noted above, rate constants (s^{-1}) obtained with both spectrophotometers were in satisfactory agreement and independent of wavelength [e.g. in 95 vol.% aqueous MeCN: for reaction of **1c** with 0·132 mol dm^{-3} HSO_5^-, $10^4 k_\psi$ = 9·17 (240 nm), 9·14 (245 nm); for reaction of **2** with 0·0832 mol dm^{-3} HSO_5^-, $10^3 k_\psi$ = 2·96 (240 nm), 2·95 (245 nm); for reaction of **3** with 0·0277 mol dm^{-3} HSO_5^-, $10^3 k_\psi$ = 1·53 (240 nm), 1·49 (245 nm); and in 99·6 vol% aqueous MeCN for reaction of **4** with 0·0261 mol dm^{-3} HSO_5^-, $10^3 k\psi$ = 2·04 (235 nm), 2·10 (240 nm), 2·07 (245 nm)]. Solutions of Oxone have the tail of an absorbance up to *ca* 250 nm and we used these solutions as a reference. We saw an isosbestic point at 250 nm in reaction of the *p*-nitro derivative (**1e**). The pH of the reaction solutions was usually not controlled, but for reactions of **1a**, **c** and **d** in 95 vol.% H_2O we varied it between 1·9 and 3·6 and the rate constants agreed within ±3% with no systematic variation. This insensitivity to small changes in pH was observed earlier in oxidations of sulfides and acyl thiols.[7b] We obtained similar results on addition of K_2SO_4–$KHSO_4$ equimolar to HSO_5^-.

The hydrolysis of the *p*-nitro derivative (**1e**) was followed in the absence of HSO_5^- in 95 vol.% aqueous MeCN with 5×10^{-2} mol dm^{-3} K_2SO_4–$KHSO_4$.

For reactions followed spectrophotometrically, [substrate] $\approx 5 \times 10^{-5}$ mol dm^{-3}, although for reaction of **1a** in 80 vol.% H_2O–MeCN at 25·0 °C [**1a**] was varied from 1×10^{-5} to 10×10^{-5} mol dm^{-3} and the values of k_ψ were within ±5%.

A few reactions were followed by ^{31}P NMR spectrometry on a GN 500 spectrometer at 25·0 °C, with [HSO_5^-] = 0·08 mol dm^{-3} and *ca* 0·02 mol dm^{-3} substrate in D_2O–CD_3CN made up by volume. Values of k_ψ were calculated from the decrease in the ^{31}P signal of the esters with time. The ^{31}P chemical shifts, rellative to external H_3PO_4, were 44·2, 23·9 and 46·3 ppm for **1c**, **2** and **3**, respectively, in D_2O–CD_3CN. The corresponding chemical shifts for the derived acids and anions in the reaction conditions were 28·8, −0·5 and 28·8 ppm.

Solvent hydrogen isotope effects for reactions of **1a** and **c** were calculated from values of k_ψ (s^{-1}) in 99·3 vol.% H_2O (D_2O) with 0·0823 mol dm^{-3} HSO_5^- at 25·0 °C. For reaction of **1a** values of $10^3 k_\psi$ were 1·22 and 0·936 s^{-1} in H_2O and D_2O, respectively, and corresponding values for reaction of **1c** were 0·865 and 0·620 s^{-1}.

Ionization potentials. Vertical *IP*s were estimated from the HOMO–LUMO gap calculated by using AM1 parameters.[33] The calculated values of *IP* for PhSMe depend on the dihedral angle between the phenyl and SMe groups and are 8·65, 8·75 and 8·98 eV for dihedral angles of 180, 150 and 120°, respectively. The predicted ground-state energies are insensitive to changes in this angle. Hanebeck and Gasteiger[27] noted problems in the interpretation of photoelectron spectra for compounds in which a π-system is bonded to sulfur. They also gave an extensive compilation with other examples of the effects of acyl groups on *IP* values of thiol derivatives.

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