Oxidation of Organic Sulphides by Chlorine and Iodosylbenzene Diacetate: Kinetics and Mechanism

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Chlorine oxidises diphenyl sulphide and a range of cyclic analogues, and also the corresponding sulphoxides, in a reaction which is first order with respect to both chlorine and substrate; the order with respect to chloride ion is −1. These results are consistent with a mechanism similar to that usually accepted for oxidation by bromine or iodine. Oxidation of the same substrates by iodosylbenzene diacetate is acid catalysed, but zero order with respect to oxidant. A mechanism is proposed, involving rate-determining rehybridisation of a tetrahedral protonated sulphide, or sulphoxide, to a trigonal pyramidal form from which the oxidant abstracts a hydride ion simultaneously with nucleophilic attack by water. The same mechanism can account for the formation of sulphonium salts as by-products from the more reactive sulphides. Structural influences on reactivity can be rationalised in terms of electronic and steric effects.

As an extension of our earlier studies on the anodic oxidation of diaryl sulphides,[1,2] we report kinetic measurements on the oxidation of a range of sulphides using two different chemical oxidants, chlorine and iodosylbenzene diacetate. Detailed kinetic studies of bromine [3] and iodine [4] as sulphide oxidants have been described, but the high rates resulting from the greater reactivity of chlorine, the inability to control the free chlorine concentration through trihalide formation, as with Br_3^- and I_3^-, and the possibility of simultaneous ring chlorination have limited the number of kinetic studies using chlorine as oxidant; reported results for dibenzothiophen,[5] however, are consistent with the mechanism proposed [3,4] for bromine and iodine as oxidants. Despite its potential as a reagent for the oxidation of sulphides to sulphoxides uncontaminated by sulphones, as revealed in the synthesis of thioxanthone sulphoxide,[6] no kinetic measurements appear to have been made for iodosylbenzene diacetate as an oxidant of sulphur compounds, although its use for the oxidation of glycols [7,8] and substituted anilines [9] has been extensively investigated.

The range of substrates included in our study permits evaluation of the effects on reactivity of ring closure, ring size, and the inclusion of carbonyl, sulphoxide, and sulphone groups in cyclic sulphides and sulphoxides, as well as the relative reactivities towards oxidation of sulphides and the corresponding sulphoxides. A stereochemical study of the reactions of thianthren with various oxidants is reported elsewhere.

EXPERIMENTAL

The sulphides and diphenyl sulphoxide were commercial reagents, all other sulphoxides and sulphones being prepared by published methods.[2,6] All were purified by procedures such as vacuum distillation (diphenyl sulphide), recrystallisation (all sulphoxides and sulphones), zone refining (thianthren and dibenzothiophen), vacuum sublimation (thioxanthone), and, if necessary, preparative h.p.l.c. (Altex h.p.l. chromatograph, 5 µm Spherisorb silica gel column, methylene dichloride–propan-2-ol eluant) until analytical h.p.l.c. showed the presence of one component only in each substrate sample. Iodosylbenzene diacetate was prepared and purified by Pausacker's method.[8] Perchloric acid was AnalaR grade. Constant boiling HCl was diluted with distilled water and AnalaR acetic acid to produce a solution 1.00M in HCl and containing 20.0% water by volume.

Kinetic Procedures.—(a) *Chlorine oxidation.* Kinetic measurements were performed by the coulometric method,[10] using the vessel and recording system previously described,[11] with an applied potential difference of 200 mV between the indicating electrodes. Chlorine was generated at an additional platinum electrode, the cathode being separated from the kinetic solution by a sintered glass disc. Experiment confirmed previous reports [12,13] that chlorine could be generated anodically at a platinum electrode with 100% current efficiency in the above solvent system. Constant generating currents in the range 50×10^{-6}—50×10^{-3} A were controlled by a circuit based on that described by Carter,[14] but employing a µA723 linear integrated circuit, and the generating charge measured by a Wenking SST 70 integrator. For the less reactive substrates, pseudo-first-order conditions were employed, with excess substrate, the concentrations of which ranged from 10^{-2} to 0.2M, depending on reactivity (and solubility). The recorder sensitivity was adjusted so that full scale deflection corresponded to initial chlorine concentrations in the range 10^{-6}—10^{-4}M. In all kinetic runs an initial deflection of at least 95% was obtained, and the recording continued until the deflection was <5%, *i.e.* covering 3—4 half lives for the chlorine. Rate constants k_{obs} were obtained from the slopes of linear plots of log (recorder reading) against time, and converted into second-order rate constants k_2 by dividing by the substrate concentration. For the slowest reactions, k_{obs} was corrected by subtracting the rate constant measured for the slow, first-order decrease in $[Cl_2]$ with time, due to reaction with trace impurities or to evaporation, in a blank solution containing chlorine but no substrate. In no case was the correction >10% of k_{obs}. It proved to be impossible to measure the rate of oxidation of thianthren trioxide by chlorine; for a saturated solution of the substrate in acetic acid, the rate of decrease in $[Cl_2]$ differed insignificantly from that of the blank. The more reactive substrates required second-order conditions, for which the recorder trace was analysed by the method of Janata and Zyka,[10] but using the measured charge instead of the product of current and time. Diphenyl sulphide and thianthren proved too reactive to measure by this method in the solvent containing 20.0% water; no recorder deflection was observed until the amount of generated chlorine exceeded that of sulphide, the subsequent decay of $[Cl_2]$ giving rate constants equal to those obtained with the corresponding sulphoxides. Reduction of the water content to 2.0% and replacement of the HCl by 1.00M-LiCl, however, permitted measurements to be made on these two sulphides, together with dibenzothiophen and thianthren monoxide for comparison. Assuming a linear free-energy relation for oxidation in the two solvent systems, the rate constants for dibenzothiophen and thianthren (k_{80} in 80% acetic acid, k_{98} in 98% acetic acid) define equation (1). The

$$\log k_{80} = 1.69 \log k_{98} + 2.01 \qquad (1)$$

values quoted in Table 1 for diphenyl sulphide and thianthren in 80% acetic acid were calculated from this equation and the experimental k_{98} values.

(b) *Iodosylbenzene diacetate oxidation.* Stock solutions, in 99% acetic acid–1% water (v/v) of iodosylbenzene diacetate and the substrate were thermostatted, then mixed and a portion transferred to a 1 cm spectrophotometer cell, mounted in an electronically controlled, electrically heated cell block. The absorbance, at a wavelength chosen for each substrate to give maximum change in optical density, was measured as a function of time in a Hilger Uvispek spectrophotometer. Initial measurements were made at equal concentrations of oxidant and substrate, but, in order to minimise oxidation of sulphides beyond the sulphoxide stage, most measurements were performed with an excess of substrate (not exceeding two-fold for spectrophotometric measurements). Kinetic measurements were also performed with an initial ratio [oxidant] : [substrate] of 0.05; for these, the decrease in [oxidant] was followed by quenching samples in excess potassium iodide solution and titrating the liberated iodine with sodium thiosulphate solution. Perchloric acid was used to catalyse the slower reactions, rate measurements being made, for each substrate, at no fewer than five acid concentrations, covering at least a seven-fold concentration range. Kinetic measurements were performed at two temperatures at least 15 °C apart.

Products from each substrate and from both oxidants were identified and measured by h.p.l.c. Microanalyses were performed by CSIRO Microanalytical Services, Melbourne.

RESULTS AND DISCUSSION

(a) *Chlorine Oxidation*.—All kinetic measurements were performed at 25 ± 0.05 °C. Apart from diphenyl sulphide and thianthren, discussed above, in no case was more than one mole of chlorine generated per mole of substrate. Product analyses indicated only sulphoxide (and unchanged sulphide) from sulphides, and sulphone (with unchanged sulphoxide) from sulphoxides. In the case of thianthren monoxide, only the unoxidised sulphur atom reacted, *i.e.* no thianthren sulphone was detected. Thianthren *cis*- and *trans*-dioxides were produced in the ratio 15.6 : 1.

Second-order rate constants are listed in Tables 1 and 2, in which the substrates are regarded formally as diphenyl sulphide or sulphoxide having undergone *ortho,ortho'*-ring closure in various ways. All rate constants are mean values from at least five measurements; reproducibility between replicates was ±3%.

Constancy of the k_2 values for varying initial reactant concentrations confirms the reactions to be overall second order, and first order with respect to substrate and chlorine. Measurements on thianthren sulphone (chosen for its convenient rate) at constant ionic strength 1.0M, maintained by $HClO_4$, and at chloride ion concentrations of 1.0, 0.5, and 0.25M, gave rate constants in the ratio 1 : 1.8 : 3.8, *i.e.* the order of the reaction with respect to chloride ion, at constant ionic strength, is −1.

TABLE 1

Rate constants for oxidation of diphenyl sulphide and its cyclic analogues by chlorine at 25 °C in 80% acetic acid

Compound	k_2/l mol^{-1} s^{-1}
Diphenyl sulphide	1.3×10^{9} [a] (1.59×10^{4}) [b]
Dibenzothiophen	9.0×10^{3} (14.0) [b]
Thianthren	1.8×10^{5} [a,c] (82.5) [b,c]
Thianthren monoxide	7.2×10^{2} (3.16) [b]
Thianthren sulphone	2.75
Thioxanthone	3.0×10^{3}

[a] Estimated from results in 98% acetic acid. [b] Measured in in 98% acetic acid. [c] Per S atom.

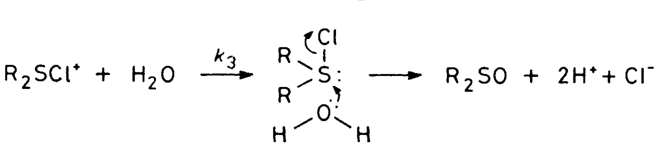
The rate increase with increasing water concentration for dibenzothiophen and thianthren monoxide probably arises partly from solvation and dielectric constant changes, but is also consistent with water being involved as a reactant in or before the rate-determining step. The rate of oxidation of diphenyl sulphide by bromine has also been shown to increase rapidly with increasing water content of the solvent.[10] The kinetic results are consistent with rate-determining nucleophilic attack by water on an ionised sulphur–chlorine adduct, proceeding through a trigonal bipyramidal transition state, as previously proposed for bromine [3] and iodine [4] oxidation of sulphides (Scheme 1).

TABLE 2

Rate constants for oxidation of diphenyl sulphoxide and its cyclic analogues by chlorine at 25 °C in 80% acetic acid

Compound	k_2/l mol^{-1} s^{-1}
Diphenyl sulphoxide	0.79
Dibenzothiophen sulphoxide	0.11
Thianthren dioxide (*cis*)	0.11 [a]
Thianthren dioxide (*trans*)	0.039 [a]
Thioxanthrone sulphoxide	1.02

[a] Per SO group.



SCHEME 1

Application of the steady state treatment leads to the rate expression (2) so that, at constant $[Cl^-]$ and $[H_2O]$, the observed second-order rate constant is given by equation (3). At the large $[Cl^-]$ employed, the second term in the denominator is negligible with respect to the

$$\text{rate} = \frac{k_2k_3K_1[R_2S][Cl_2][H_2O]}{k_{-2}[Cl^-] + k_3[H_2O]} \qquad (2)$$

$$k_{obs} = \frac{k_2k_3K_1[H_2O]}{k_{-2}[Cl^-] + k_3[H_2O]} \qquad (3)$$

first, leading to inverse first-order dependence on chloride ion concentration.

Baciocchi and Mandolini [5] found no difference in rate for the oxidation by chlorine of dibenzothiophen at initial chloride ion concentrations of zero and 10^{-2}M. At such low $[Cl^-]$ the first term in the denominator could well be smaller than the second, so that ionisation of the chlorine–sulphide adduct becomes rate determining. Alternatively, a positive salt effect, increasing the rate at the higher ionic strength, could compensate, in part at least, for the increased $[Cl^-]$; such positive salt effects have been observed in the oxidation of sulphides by bromine.[15]

The kinetically indistinguishable rate-determining attack by HOCl formed in a pre-equilibrium (Scheme 2),

$$Cl_2 + H_2O \rightleftharpoons HOCl + H^+ + Cl^-$$

$$R_2S + HOCl \longrightarrow R_2S(OH)Cl \longrightarrow R_2SO + H^+ + Cl^-$$

SCHEME 2

is much less likely in view of the low [HOCl] prevailing in 1M-HCl.

Two features of the results in Tables 1 and 2 are evident: (1) the greatly reduced reactivities of the sulphoxides compared with the corresponding sulphides, diphenyl sulphoxide being particularly affected in this way and (2) the small range of rate constants exhibited by the sulphoxides in contrast to the wide range for the sulphides.

Diphenyl sulphide is by far the most reactive substrate. The rate constant is reduced by at least four order of magnitude in all the cyclic analogues. This is understandable in terms of the lower charge density on sulphur,[16] leading to smaller K_1 values [equations (2) and (3)], and the lower rehybridisation rate constant k_2 because of the rigidity arising from cyclisation. Direct *ortho-ortho'*-closure in dibenzothiophen, and closure through S (thianthren) have very similar effects in decreasing reactivity, while the effect of ring closure by C=O (thioxanthone) is only slightly greater. Closure by SO (thianthren monoxide) or SO_2 (thianthren sulphone) cause progressive lowering of reactivity, reflecting the greater polarity of these groups, and to some extent, a steric effect involving non-bonding repulsion from the oxygen to the Cl attached to the other S in the initial chlorine adduct, or to the approaching water molecule in the rate-determining step. This interaction is of the same type as that which prevents the *cis*-dioxide of thianthren from existing in the *syn-cis*-configuration,[17-19] and would not be observed in thioxanthone because of the coplanarity of the C=O group and the aromatic rings.

In the sulphoxides, the polarised SO link leads to reduced electron availability on the sulphur atom, persisting also when the sulphoxide is protonated in 1M-HCl, and to increased solvation (all the sulphoxides are much more soluble in aqueous solvents than are the corresponding sulphides). The lower reactivity of sulphoxides can be attributed to both of these features together with greater difficulty in rehybridising to form the trigonal bipyramidal R_2SOCl_2 and the transition state, because of the necessity for oxygen to move. The small spread in rate constants for the sulphoxides is consistent with this latter factor being of predominant importance. Structural effects on reactivity are generally similar to those observed for the sulphides. Thioxanthone sulphone has the highest rate constant, that for diphenyl sulphoxide evidently being lowered by steric hindrance from the rotating phenyl groups. The lower rate constants for thianthren dioxides confirm that the sulphoxide group withdraws electrons from the oxidising sulphur atom more than does the carbonyl group in thioxanthone, as observed with the sulphides. The *cis*-dioxide, with its *anti-cis*-structure,[17-19] suffers less steric hindrance than does the *trans*-isomer. For the latter, an attacking reagent must either approach the S atom from within the dihedral angle, or experience non-bonding interaction with the oxygen of the other sulphoxide group, as discussed above for thianthren monoxide and thianthren sulphone. Further confirmation of these effects of structure on reactivity is provided by the results obtained with iodosylbenzene diacetate.

(b) *Iodosylbenzene Diacetate Oxidation*.—Product analyses indicated only sulphoxide (and unchanged sulphide) from sulphides, or sulphone (and unchanged sulphoxide) from sulphoxides; however, in the presence of perchloric acid, products eluted from the column after the oxidation of thianthren accounted for only 65—80% of the substrate taken, and for dibenzothiophen, up to 38% of a crystalline product of empirical formula $C_{24}H_{18}ClO_6S_2$, m.p. 283 °C, was isolated. This appears to be a sulphonium salt, as previously reported for anodic oxidation of sulphides.[20,21] The sulphonium perchlorate from dibenzothiophen has an empirical formula $C_{24}H_{15}ClO_4S_2$, which, as a dihydrate would be $C_{24}H_{19}ClO_6S_2$. The material unaccounted for in the oxidation of thianthrene is presumably of a similar nature. It was strongly held on the h.p.l.c. column, and attempts to elute it with strongly polar solvents were not carried out, for fear of destroying the activity of the column. Thianthren monoxide gave *cis*- and *trans*-thianthren dioxides in the ratio 8.5 : 1, together with *ca.* 1.5% of sulphone.

Rate measurements performed with equal initial concentrations of oxidant and substrate in all cases gave curved second-order plots but linear first-order ones. Rate constants were evaluated from the slopes of plots of $\ln [(D_0 - D_\infty)/(D_t - D_\infty)]$ against time, where D_0, D_t, and D_∞ are the absorbances at time zero, t, and after at least ten half-lives respectively. Figure 1 shows a typical first-order plot. The measurements performed by titrating the remaining oxidant, on solutions having an initial 20-fold excess of substrate, gave curved first-order plots, but linear zero-order ones (see Figure 2). These results imply that the reactions are first order with respect to substrate, and zero order with respect to oxidant. Confirmation follows from the linear plots obtained, with unequal initial reactant concentrations *a* (substrate) and *b* (oxidant) ($a > b$) when $\ln\{(D_0 - D_\infty)/[D_0 - D_\infty - b(D_0 - D_t)/a]\}$ was plotted against time (Figure 3), and from the excellent agreement between the rate constants evaluated from the slopes of the latter plots, and those from first-order plots at equal initial concentrations of the same reactants. [With unequal initial concentrations, $a > b$, $(D_t - D_\infty)$ is a measure of $(b - x)$, but a linear zero-order plot of $(D_t - D_\infty)$ *versus* time will result, for a reaction zero order in *b* and first order in *a*, only if $(a - x) \approx a$ throughout, *i.e.* for $a \gg b$. However, a linear first-order plot will result if $a/(a - x)$ is evaluated in terms of the measured absorbances and the known initial ratio a/b. Thus equation (4) results. Simplification leads to the expression given above.]

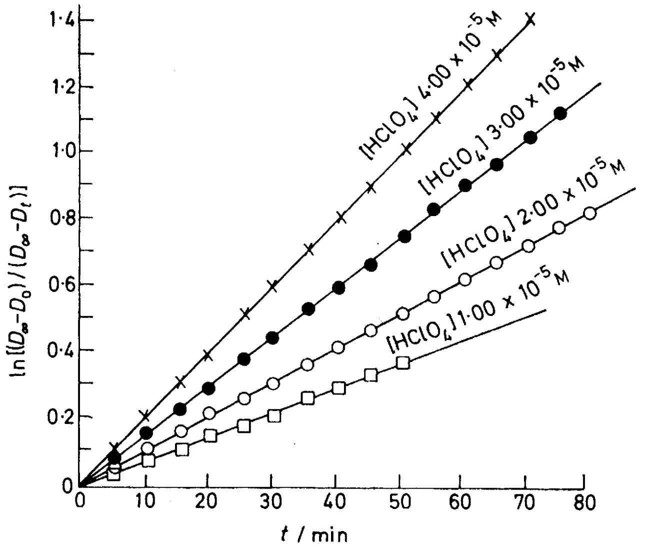


FIGURE 1 Linear first-order plots for oxidation of thianthren (Th) by iodosylbenzene diacetate at 50 °C, and effect of perchloric acid on the rate. $[\mathrm{Th}]_0 = [\mathrm{PhI(OAc)_2}]_0$ in each case

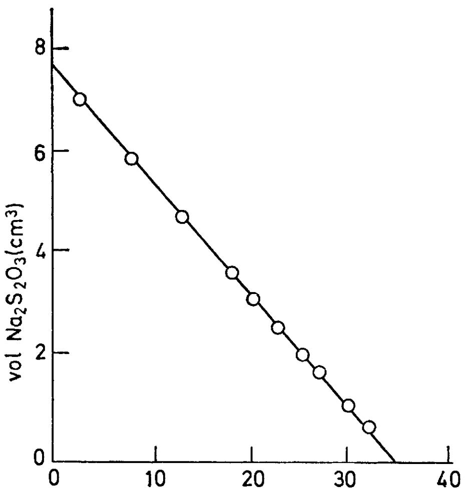


FIGURE 2 Linear zero-order plot for oxidation of diphenyl sulphide by iodosylbenzene diacetate at 25 °C. $[\mathrm{Ph_2S}]_0$ 0.21M, $[\mathrm{PhI(OAc)_2}]_0$ 0.011M

$$\frac{a}{a - x} = \frac{\frac{a}{b}\cdot b}{\frac{a}{b}\cdot b - x} = \frac{\frac{a}{b}(D_0 - D_\infty)}{\frac{a}{b}(D_0 - D_\infty) - (D_0 - D_t)} \quad (4)$$

Measurements on all substrates except the most reactive, diphenyl sulphide, in the presence of perchloric acid showed rates directly proportional to the concentration of added perchloric acid (see Figure 1). Thus the reactions are first order with respect to hydrogen ion, and the overall rate law is rate = k_2[substrate][H$^+$].

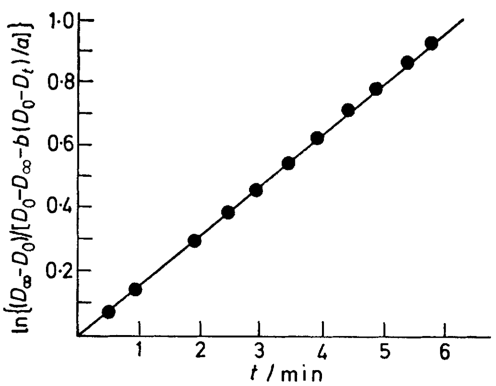


FIGURE 3 Linear first-order plot for oxidation of diphenyl sulphide by iodosylbenzene diacetate at 50 °C. $[\mathrm{Ph_2S}]_0$ 0.421M, $[\mathrm{PhI(OAc)_2}]_0$ 0.261M

The second-order rate constants k_2 in Tables 3 and 4 were evaluated by least squares from the slopes of plots of observed pseudo first-order rate constants against (HClO$_4$]. Diphenyl sulphide, thianthren, thianthren monoxide, and thioxanthone had measurable rates in the absence of perchloric acid, leading to pseudo-first-order rate constants k_{obs}. The latter three substrates were also measured in solutions containing known concentrations of perchloric acid, leading to second-order rate

TABLE 3

Rate constants and activation parameters for oxidation of diphenyl sulphide and cyclic analogues by iodosylbenzene diacetate

Compound	k_2/l mol^{-1} s^{-1} at 323 K	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K^{-1} mol^{-1}
Diphenyl sulphide	3.4×10^2	71.3	23.6
Dibenzothiophen	8.7	59.6	−43.1
Thianthren	8.9	80.2	20.9
Thianthren monoxide	0.89	67.7	−36.9
Thianthren sulphone	0.27	74.4	−26.2
Thioxanthone	1.10	72.4	−20.6

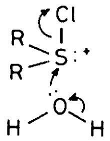
constants k_2. The hydrogen ion concentration in 99% acetic acid was then evaluated in each case as k_{obs}/k_2. Values obtained for 10^6 [H$^+$] in 99% acetic acid were 8.1 (thianthren), 7.6 (thianthren monoxide), and 7.9M (thioxanthone) giving a mean value for [H$^+$] of 7.9×10^{-6}M. This value, together with k_{obs} for diphenyl sulphide permits evaluation of a second-order rate constant k_2 for the latter. This kinetic procedure for evaluating [H$^+$] in 99% acetic acid was judged to be preferable to attempted direct measurement with its attendant errors, *e.g.* liquid junction potentials in potentiometry. Agreement between the values obtained with three substrates is satisfactory, and the value obtained is reasonable in relation to that reported in 100% acetic acid.[22]

TABLE 4

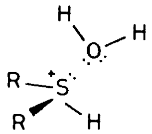
Rate constants and activation parameters for oxidation of diphenyl sulphoxide and cyclic analogues by iodosylbenzene diacetate

Compound	k_2/l mol^{-1} s^{-1} at 323 K	$\Delta H^\ddagger$/ kJ mol^{-1}	$\Delta S^\ddagger$/ J K^{-1} mol^{-1}
Diphenyl sulphoxide	2.3×10^{-2}	71.5	−55.5
Dibenzothiophen sulphoxide	8.2×10^{-3}	62.8	−91.1
Thianthren dioxide (*cis*)	2.1×10^{-3}	79.9	−43.6
Thianthren dioxide (*trans*)	2.1×10^{-3}	76.7	−53.6
Thianthren trioxide	3.8×10^{-3}	80.5	−41.8
Thioxanthone sulphoxide	6.1×10^{-2}	80.6	−19.3

Although protonation of the substrate would, if rate determining, lead to the observed rate law, such a process should be fast, involving as it does only minimal electronic reorganisation of substrate and hydrogen ion, and insignificant steric hindrance. *A priori*, protonation and development of a positive charge on sulphur would be expected to be unfavourable for oxidation, as this involves, formally at least, removal of an electron pair from sulphur. Protonation, however, undoubtedly enhances the reactivity of sulphur towards nucleophiles, *e.g.* H_2O. Considerable evidence exists[23] that nucleophilic attack on sulphur proceeds through a trigonal bipyramidal transition state (A), *e.g.* in the hydrolysis of sulphide–halogen adducts to produce sulphoxides.



(A)



(B)

N.m.r. measurements indicate[24] a tetrahedral structure (B) for protonated sulphides; nucleophilic attack by water on this would presumably be hindered by interaction with the lone pair on sulphur, since the fourth tetrahedral axis would provide the least sterically hindered approach direction.

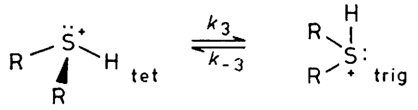
The mechanistic sequence (5)—(8), involving rate-determining rehybridisation of a tetrahedral to a trigonal pyramidal protonated substrate, followed by simultaneous nucleophilic attack by water and hydride ion abstraction by the oxidant leads to a rate law in accord with observations.

(a) Pre-equilibrium protonations

$$\mathrm{PhI(OAc)_2 + H^+ \overset{K_1}{\rightleftharpoons} PhIOAc^+ + HOAc} \quad (5)$$

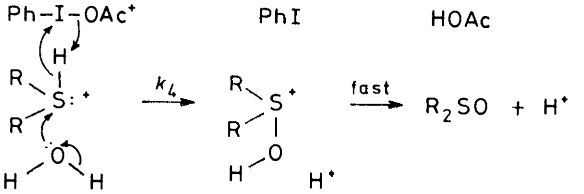
$$\mathrm{R_2S + H^+ \overset{K_2}{\rightleftharpoons} R_2SH^+_{tet}} \quad (6)$$

(b) Rehybridisation



(7)

(c) Nucleophilic attack by H_2O, simultaneously with hydride ion abstraction by PhIOAc$^+$ [alternatively, but less likely, by PhI(OAc)$_2$, *i.e.* omitting step (5)]



(8)

Application of the steady state treatment to R$_2$SH$^+_{trig}$ (omitting the subscript for simplicity) gives equation (9).

$$[\mathrm{R_2SH^+}] = \frac{k_3K_2[\mathrm{R_2S}][\mathrm{H^+}]}{k_{-3} + k_4[\mathrm{PhIOAc^+}][\mathrm{H_2O}]} \quad (9)$$

The rate of oxidation is given by equation (10). Substituting for [R$_2$SH$^+$] from (9) and for [PhIOAc$^+$] from

$$\text{rate} = k_4[\mathrm{R_2SH^+}][\mathrm{PhIOAc^+}][\mathrm{H_2O}] \quad (10)$$

(5) gives (11).

$$\text{rate} = \frac{k_4k_3K_2K_1[\mathrm{R_2S}][\mathrm{H^+}]^2[\mathrm{H_2O}][\mathrm{PhI(OAc)_2}]}{k_{-3}[\mathrm{HOAc}] + k_4K_1[\mathrm{PhI(OAc)_2}][\mathrm{H^+}][\mathrm{H_2O}]} \quad (11)$$

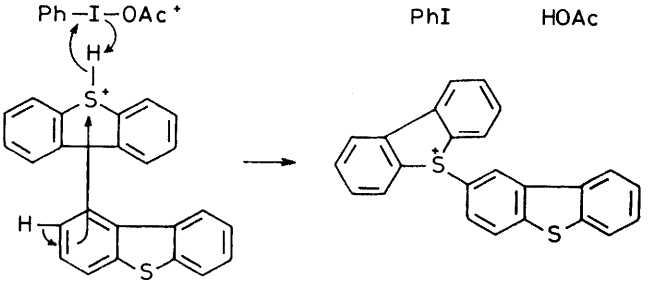
If the first term in the denominator is negligible with respect to the second, *i.e.* the rehybridisation step (7) is effectively irreversible, this simplifies to (12) in accordance with observed kinetic results, and

$$\text{rate} = k_3K_2[\mathrm{R_2S}][\mathrm{H^+}] \quad (12)$$

deducible directly by considering step (7) to be rate determining. A similar sequence may be written for sulphoxide substrates, except that the pre-equilibrium protonation reaction (6) must involve O rather than S protonation. The lower rates observed for oxidation of sulphoxides arise from the greater hindrance to rehybridisation [step (7)], because of the requirement to move OH, not just H in this step (Scheme 3).

SCHEME 3

Only a minor modification to the mechanistic sequence is required to explain the formation of a sulphonium salt at the same time as sulphoxide from dibenzothiophen (and possibly from thianthren). This requires the role of nucleophile in step (8) to be taken by the sulphide itself, *e.g.* for dibenzothiophen as in Scheme 4.



SCHEME 4

It is evident that, if the rehybridisation step (7) is rate determining, neither the rate, nor the rate law, depend on the relative amounts of each product formed. Only the two most reactive cyclic sulphides exhibited this behaviour; diphenyl sulphide was too reactive for rate measurements to be performed in the presence of perchloric acid, and all the other cyclic substrates have lower charge densities on the ring carbons,[16] leading to lower reactivity as nucleophiles.

The mechanism proposed has obvious similarities to that for anodic oxidation [1] and for oxidation by chlorine. In the former case,[1] nucleophilic attack by water is assisted by removal of an electron pair from S by the anode; in the latter, by removal of an electron pair as the stable anion Cl^-. The oxidant, iodosylbenzene diacetate, is required to assist the nucleophilic attack by water, because of the instability of the leaving group, hydride ion.

The general effects of structure on reactivity are thus similar for the two oxidants, chlorine and iodosylbenzene diacetate. The sulphides show a wide range of reactivities, the sulphoxides a much smaller range; the most reactive sulphide is diphenyl sulphide, while thioxanthone sulphoxide is slightly more reactive than diphenyl sulphoxide. For the sulphides the correlation between the rates of the two reactions is somewhat better than that for the sulphoxides, thus equations (13) and (14) hold. for the sulphides

$$\log k_{\mathrm{Cl_2(298\ K)}} = 2.57 \log k_{\mathrm{PhI\ OAc)_2(323\ K)}} + 2.60 \qquad (13)$$
r 0.975

for the sulphoxides

$$\log k_{\mathrm{Cl_2(298\ K)}} = 0.90 \log k_{\mathrm{PhI(OAc)_2(323\ K)}} + 1.19 \qquad (14)$$
r 0.916

Tables 3 and 4 show a wider spread in $\Delta S^{\ddagger}$ values than in $\Delta H^{\ddagger}$ values, hence relative rates are largely determined by the former. Specific solvation effects are likely to be more important for the sulphoxides than for the sulphides, and probably contribute to the poorer correlation for the sulphoxides.

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