

Mechanism of the Oxidation of Sulphides with Sodium Periodate

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The kinetics of the oxidation of RSAr , R_2S , and $(\text{CH}_2)_n\text{S}$ sulphides with NaIO_4 yielding sulfoxides were investigated in ethanol–water solutions, and the rate equation $v = k_2[\text{sulphide}][\text{IO}_4^-]$ was found to be valid. The observed substituent ($\rho = 1.40$ for $\text{YC}_6\text{H}_4\text{SMe}$; $\rho^* = 1.06$ and -0.60 for RSPH and R_2S , respectively) and solvent effects ($m = 0.722$ for MeSPh) are explained by an electrophilic attack of periodate oxygen on sulphide, leading to a polar transition state. The slight steric requirements of the reaction ($\delta = 0.27$ and 0.105 for RSPH and R_2S , respectively) and the lack of solvent isotope effect exclude the participation of water in an $\text{S}_\text{N}2$ -type nucleophilic displacement on a sulphonium centre, which might be considered to have been formed from sulphide and periodate in a fast pre-equilibrium. A moderate anchimeric assistance was observed for the conversion of $\text{XC}_6\text{H}_4\text{SMe}$ sulphides with $o\text{-X} = \text{CO}_2\text{Me}$, CO_2H , and CO_2^- (k_2^o/k_2^p ca. 1). From the results it is concluded that oxidation proceeds by a one-step electrophilic oxygen transfer from IO_4^- to sulphide through a polar product-like transition state that is stabilized by a polar neighbouring group or by the increasing polarity of the medium.

The mechanisms of the oxidation of sulphides to sulfoxides involving polar transition states have been studied extensively. Halogenating agents are known to convert sulphides primarily into halogenosulphonium salts,^{1,2} and intermediates with a positive sulphonium centre have also been proposed for reactions of sulphides with peroxydisulphate,³ peroxydiphosphate,⁴ pyridinium chlorochromate,⁵ and iodosylbenzene diacetate.^{2c,6} In these reactions sulfoxides are formed from sulphonium intermediates in a subsequent step by a nucleophilic attack of water on the positive sulphur atom. Oxidations carried out with peroxy compounds are electrophilic oxygen-transfer reactions proceeding through a less polar transition state. These latter involve a heterolytic splitting of the O–O bond, which is promoted by a concerted inter- or intramolecular proton transfer.⁷ A mechanism including the formation of diacyloxysulphurane intermediate has also been suggested recently for the conversion of sulphides by peroxyhexanoyl nitrate.⁸ The periodate oxidation of sulphides to sulfoxides under mild conditions is widely used in syntheses,⁹ but the reaction pathway has not been investigated in detail as yet. This paper reports a study on the mechanism of this reaction, based upon kinetic investigations.

Results and Discussion

Kinetic Equation.—The rates of reactions between NaIO_4 and the sulphides listed in Tables 1–6 were measured by the u.v. spectrophotometric method. The absorptivity of the reactants at $\lambda > 260$ nm was much higher than that of the sulfoxide and NaIO_3 products. Ethanol–water 1:1 (v/v) was used as the solvent, in which sulphides and periodate can be dissolved in the concentration ranges $[\text{S}] = 4 \times 10^{-3}$ – 5×10^{-4} and $[\text{IO}_4^-] = 2 \times 10^{-3}$ – $5 \times 10^{-4}\text{M}$, respectively. The reactions proved to be second-order overall, first-order with respect to each reactant, and rate equation (1) was valid with commensurable concentrations of the reactants.

$$v = k_2[\text{S}][\text{IO}_4^-] \quad (1)$$

Reactions were also studied under pseudo-first-order conditions, *i.e.*, taking the sulphide or periodate reactant in excess. Plotting $1/k_1$ against either $1/[\text{S}]$ or $1/[\text{IO}_4^-]$, straight lines passing through the origin were obtained (Figure 1). This

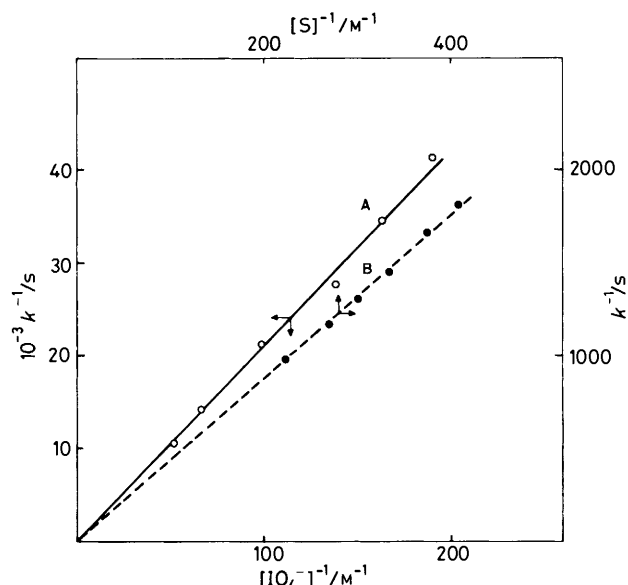


Figure 1. $1/k_1$ versus $1/[\text{IO}_4^-]$ (A) and $1/k_1$ versus $1/[\text{S}]$ (B) plots for the reactions of NaIO_4 with $m\text{-NO}_2\text{C}_6\text{H}_4\text{SMe}$ ($[\text{S}]_0 = 4.88 \times 10^{-4}\text{M}$) and Pr_2S ($[\text{IO}_4^-]_0 = 4.98 \times 10^{-4}\text{M}$), respectively, under pseudo-first-order conditions in 1:1 (v/v) ethanol–water at 25°C .

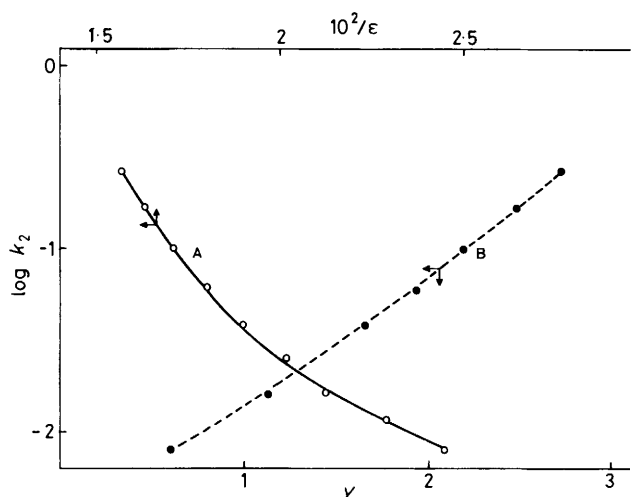
finding clearly shows that a reaction pathway including a fast equilibrium formation of an intermediate and its slow decomposition into the products can be excluded, although a mechanism of this type has been recognized formerly for other reactions of both sulphides⁵ and NaIO_4 .^{9b} The k_2 values calculated from the pseudo-first-order rate constants k_1 were, within experimental error, equal to those evaluated from the second-order rate equation. From Figure 1 and equation (1), respectively, $k_2 = 4.93 \times 10^{-3}$ and $4.89 \times 10^{-3}\text{M}^{-1}\text{s}^{-1}$ were obtained for the conversion of $m\text{-NO}_2\text{C}_6\text{H}_4\text{SMe}$, and $k_2 = 0.246$ and $0.237\text{M}^{-1}\text{s}^{-1}$ for that of Pr_2S .

In the product of the reaction of MeSPh with NaIO_4 only MePhSO was detected by i.r. spectroscopy. This suggests that, in case of experimental conditions used in the present study, there is no need to consider products other than sulfoxides.

Table 1. Rate constants for the reaction of MeSPh with NaIO₄ in ethanol-water solvent mixtures at 25 °C

EtOH:H ₂ O (v/v)	10 ² k ₂ /M ⁻¹ s ⁻¹
70:30	0.798
65:35	1.15
60:40	1.64
55:45	2.51
50:50	3.82
	3.82 ± 0.10 ^a
	3.81 ^b
	3.84 ^c
45:55	6.05
40:60	9.93
35:65	16.9
30:70	26.7

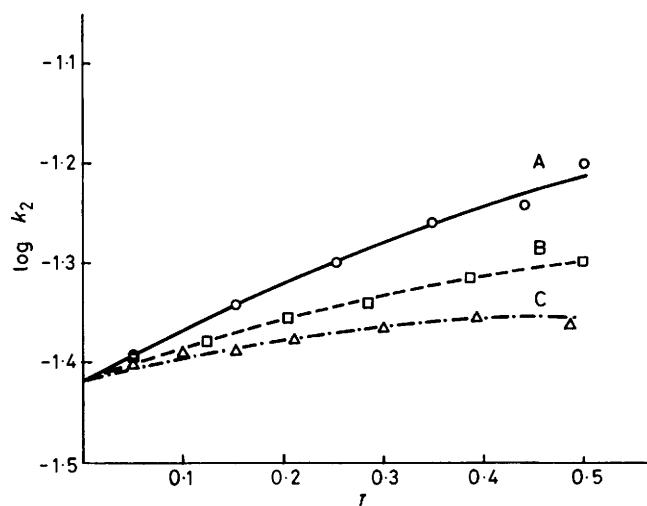
^a The solvent contained 0.05M Britton-Robinson buffer; pH was varied in the range 1.85–8.0. ^b In EtOD-D₂O solvent. ^c The solvent contained 10⁻³M of acrylonitrile.

**Figure 2.** log *k*₂ versus 1/ε (A) and log *k*₂ versus *Y* (B) plots for the reaction of MeSPh with NaIO₄ in ethanol-water solvent mixtures at 25 °C (ε and *Y* values were taken from references 10 and 11, respectively)

Medium Effects in the Oxidation of MeSPh.—The rate of conversion of MeSPh in 1:1 (v/v) ethanol-water proved to be independent of pH in moderately acidic and neutral solutions (Table 1). The range of measurement could not be extended, because the reaction mixture coloured and decomposed at pH < 1.5, while in the basic region (pH > 9) sodium periodate precipitated from the buffer containing 50% (v/v) ethanol.

The rate of conversion did not change either in deuterated solvent or in the presence of acrylonitrile used as radical scavenger (Table 1). These findings exclude both the participation of water in the rate-controlling step and the possibility of a radical mechanism.

The reaction rate increased with increasing water concentration in the solvent (Figure 2; the plot log *k*₂ against 1/ε is non-linear). It should be mentioned that just the opposite tendency would be expected for a reaction between a neutral species and a negative ion, if the latter were, as is usual, the nucleophilic reactant. Thus the experimentally observed solvent effect leads to the conclusion that the transition state is more polarized than the two reactants together in the initial state, *i.e.*, the sulphide suffers the electrophilic attack of the periodate anion. This results in a positive polarization of the sulphur atom

**Figure 3.** log *k*₂ versus *I* (ionic strength) plots for the reaction of MeSPh and NaIO₄ in 1:1 (v/v) ethanol-water containing LiClO₄ (A), NaClO₄ (B), or NaCl (C) in the concentration range 0.05–0.5M; *T* = 25 °C

and in an increase of the negative charge in the periodate moiety, both promoted by the ionizing power of the solvent. Since the reaction proved to be sensitive to the change in polarity of the solvent, we tried to describe the effect quantitatively by applying the Grunwald-Winstein equation, log *k*/*k*₀ = *mY*. The log *k*₂ versus *Y* plot was almost linear (Figure 2) with *m* = 0.722 calculated from the slope (*r* 0.998).

As had been expected for the reaction of a neutral molecule (MeSPh) with a negatively charged ion (IO₄⁻), the increasing ionic strength of the media increased the reaction rate only at higher salt concentrations. The effect was also influenced by the size of both the cations and anions of the added salt (Figure 3).

Substituent Effects.—Data in Table 2 show that the reactivity of different types of sulphides towards NaIO₄ follows the order of nucleophilicity: Pr₂S > MeSPh > Ph₂S. The activation parameters obtained are characteristic of bimolecular reactions (Table 2). Only Δ*H*[‡] values are appreciably influenced by the variation of S-substituents.

Hammett correlations. Using the log *k*₂ values for a series of *m*- and *p*-substituted aryl methyl sulphides (Table 3), a good correlation was obtained with the Hammett σ constants (ρ = 1.40; *r* 0.987). Only the rate constant of *p*-O₂CC₆H₄SMe showed a marked deviation in the Hammett plot. Although σ is zero for *p*-CO₂⁻, the reactivity of this sulphide towards IO₄⁻ is markedly smaller than that of MeSPh (*ca.* 3/7). This observation can be rationalized by a repulsion between the negatively charged carboxylate and periodate ions.

It follows from the observed negative ρ data that an electrophilic attack at the sulphur atom occurs in the reaction. However, |ρ| is much smaller than the values obtained for reactions proceeding through a halogenosulphonium ion intermediate (*cf.* ρ = 4.25^{1a} and -3.2^{2b} for reactions yielding RArSCI⁺ and RArSBr⁺, respectively). This suggests that for the periodate oxidation of sulphides the positive polarization of the sulphur atom in the transition state is not very high, similar to the electrophilic oxidation of sulphides by H₂O₂ (ρ = 1.13)^{7b} and by peroxyhexanoyl nitrate (ρ = 1.7)⁸ where the formation of a sulphurane intermediate has been supposed.

Taft correlations. When comparing the reactivities of RSPH and R₂S sulphides with different alkyl groups, no significant decrease in reaction rates was observed by increasing the bulkiness of alkyl substituent(s). Similarly, the reaction rates

Table 2. Temperature dependence of rate constants and activation parameters for reactions of sulphides with NaIO₄ in 1:1 (v/v) ethanol-water

Sulphide	10 ² k ₂ /M ⁻¹ s ⁻¹					ΔH [‡] / kJ mol ⁻¹	ΔS ^{‡a} / J mol ⁻¹ K ⁻¹
	20 °C	25 °C	30 °C	35 °C	40 °C		
Pr ₂ S	19.2	23.7	29.8	46.0	60.7	42.7	-113.4
MeSPh	2.70	3.82	5.34	7.23	10.12	47.2	-113.3
Ph ₂ S	0.208	0.316	0.454	0.612	0.914	52.8	-115.9

^a At 25 °C.**Table 3.** Substituent effect for reactions of *m*- and *p*-YC₆H₄SMe sulphides with NaIO₄ in 1:1 (v/v) ethanol-water at 25 °C

Y	10 ² k ₂ /M ⁻¹ s ⁻¹
<i>p</i> -MeO	8.97
H	3.82
<i>p</i> -CO ₂ ^{-a}	1.66
<i>m</i> -MeO	2.58
<i>p</i> -Cl	2.18
<i>m</i> -Cl	1.12
<i>p</i> -CO ₂ H	0.735
<i>p</i> -CO ₂ Me	0.708
<i>m</i> -NO ₂	0.489
<i>p</i> -NO ₂	0.300

^a The solvent contained 0.05M-Britton-Robinson buffer; pH 8.

were changed only slightly with change in the ring size of cyclic sulphides (Table 4).

Applying the Taft equation no fair correlations were obtained either with the original σ* and E_s [equation (2)]^{12a} or with the improved σ₁ and E_s^c substituent constants [equation (3)].^{12b} If σ₁ was neglected [equation (4)], the correlation became even poorer.

$$\log k_2 = \rho^* \sigma^* + \delta E_s + a \quad (2)$$

$$\log k_2 = \rho_1 \sigma_1 + \rho_s E_s^c + a \quad (3)$$

$$\log k_2 = \rho_s E_s^c + a \quad (4)$$

Nevertheless, the negative sign for polar reaction constants attests to the fact that the +I effect of alkyl groups enhances the reactivity of sulphides. In contrast, the steric effect is of minor importance, as it may be concluded from the low values of steric reaction constants (Table 4). In this respect the periodate oxidation and the reactions of sulphides with H₂O₂^{7c,d} or N-halogeno compounds^{1b,d} are comparable.

Neighbouring group effect. The rate constants in Table 5 obtained for *o*-XC₆H₄SMe sulphides with different *ortho*-X groups clearly point to the anchimerically assisted conversion of sulphides with *o*-X = CO₂Me, CO₂H, and CO₂⁻ groups. Assuming that the electronic effects of a substituent in both *ortho*- and *para*-position are approximately the same, the result of steric hindrance and anchimeric assistance caused by *ortho*-X substituents was estimated by calculating the ratio of the rate constants determined for the *ortho*- and *para*-substituted compounds (see k₂^o/k₂^p data in Table 5).

The relative rate values of ca. 0.3 obtained for *o*-MeO and *o*-NO₂ derivatives are commensurable with those found in oxidations with H₂O₂,^{7e} both reflecting not too large repulsive steric effects in these reactions. (cf. the much smaller k^o/k^p = 0.06 data observed for the Cl⁺ addition to *o/p*-MeOC₆H₄SMe,^{1c} where the formation of a chlorosulphonium intermediate seems to be more responsive to steric hindrance.) The decreased reactivity of the *ortho*-nitro compound may be attributed both

to the repulsion between the anion reactant and the negatively polarized nitro-oxygen atoms and to the shielding of the sulphur reaction centre by attractive sulphur(II)-oxygen(nitro) interaction in the initial state.¹³

In case of *o*-X = CO₂Me, CO₂H, and CO₂⁻ the k₂^o/k₂^p ratio is close to unity, suggesting that in the periodate oxidation of these *ortho*-derivatives the moderate steric hindrance is approximately compensated by a moderate anchimeric assistance. (Cf. the corresponding values of k₂^o/k₂^p = 6.5, 9.1, and 62.8, respectively, found for Cl⁺ addition.^{1c} Here the large repulsive steric effect is overcompensated by a very effective anchimeric assistance.) The similar and moderate neighbouring group activities of *o*-CO₂Me and *o*-CO₂H groups seems to be compatible with an attractive (Coulomb type) non-bonded interaction between the carbonyl-oxygen and the positively polarized sulphur atom in the transition state (see references 1c and 13a), rather than with the formation of a cyclic acyloxysulphonium intermediate. The decreased neighbouring group activity of *o*-CO₂⁻ group in the periodate oxidation of sulphides, as compared with the anchimerically assisted Cl⁺ addition, may be explained if the Coulomb repulsion between the reactants both bearing negative charge is also taken into account.

The electronic effect of *p*-Y groups in the periodate oxidation of *p*-Y-*o*-X-C₆H₃SMe sulphides (X = CO₂H and CO₂⁻) proceeding with neighbouring group participation was evaluated by the Jaffe 4-parameter equation (5),¹⁴ where ρ_s, σ_s

$$\log k_2^Y/k_2^H = \rho_s \sigma_s + \rho_o \sigma_o \quad (5)$$

and ρ_o, σ_o are the reaction and substituent constants referring to the sulphide-S and carboxyl(ate)-O reactive centres, respectively (Table 6). From the similar values of ρ and ρ_s it follows that the influence of *p*-Y groups on the sulphur reaction centre is not changed significantly by the neighbouring *ortho*-groups. In the same manner, the neighbouring group activity of an *o*-CO₂H group is not affected by *p*-Y groups, since ρ_o is close to zero. In contrast, electron-withdrawing *p*-Y substituents enhance the reactivity of the *o*-CO₂⁻ group, as can be seen from the positive ρ_o value. This effect may be attributed to the delocalization of the negative charge of *o*-CO₂⁻ in the aromatic ring, decreasing the Coulomb repulsion between the reactants charged negatively.

Oxidizing Species.—The dissociation equilibria of periodic acid in water, as it is shown in equation (6), had been extensively studied earlier;^{9b} the pK₁ 1.64, pK₂ 8.36, and pK_B -1.60 data point to the predominance of IO₄⁻ species.¹⁵

Using a u.v. technique, similar values of pK₁ 0.65 and pK₂ 10.80 were obtained by us for the acidity constants in 1:1 (v/v) ethanol-water, i.e., in a medium less able to hydrate ions. Thus IO₄⁻ may also be regarded as an oxidizing species in the mixed solvents used in our experiments. The pH-independent k₂ rate constants (Table 1) are also in agreement with the measured acidity constants. The participation of H₄IO₆⁻ ions in the

Table 4. Steric effect in reactions of RSPH, R₂S, and (CH₂)_nS sulphides with NaIO₄ in 1:1 (v/v) ethanol-water at 25 °C

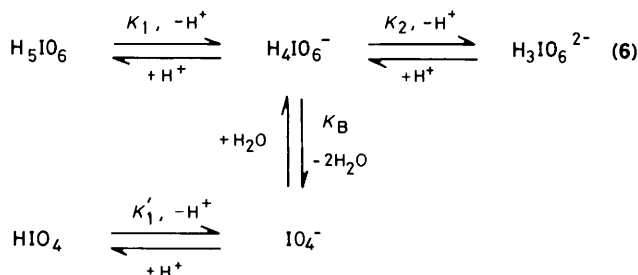
Sulphide		10 ² k ₂ /M ⁻¹ s ⁻¹	Taft equation	ρ [*] /ρ ₁	δ/ρ _s	a	r
R ¹	R ²						
Me	Ph	3.82	(2)	-1.06	+0.27	-1.43	0.960
Et	Ph	4.92					
Pr	Ph	3.62					
Pr ⁱ	Ph	4.58					
Bu ^t	Ph	3.01	(4)		+0.089 6	-1.26	0.742
Me	Me	26.7	(2)	-0.60	+0.165	-0.565	0.933
Et	Et	38.7					
Pr	Pr	23.7					
Pr ⁱ	Pr ⁱ	32.6					
Bu	Bu	29.1	(3)		+0.151	-0.696	0.868
Bu ^s	Bu ^s	20.6	(4)		+0.077 3	-0.303	0.760
Bu ⁱ	Bu ⁱ	20.5					
Bu ^t	Bu ^t	19.2					
-(CH ₂) ₃ -		24.3					
-(CH ₂) ₄ -		71.4					
-(CH ₂) ₅ -		39.9					
-(CH ₂) ₆ -		33.7					

Table 5. Neighbouring group effect in reactions of *o*-XC₆H₄SMe sulphides with NaIO₄ in 1:1 (v/v) ethanol-water at 25 °C

<i>o</i> -X	10 ² k ₂ /M ⁻¹ s ⁻¹	k ₂ ^o /k ₂ ^p
MeO	2.30	0.26
NO ₂	0.105	0.35
CO ₂ Me	0.697	0.99
CO ₂ H	0.829	1.13
CO ₂ ^{-a}	1.75	1.06

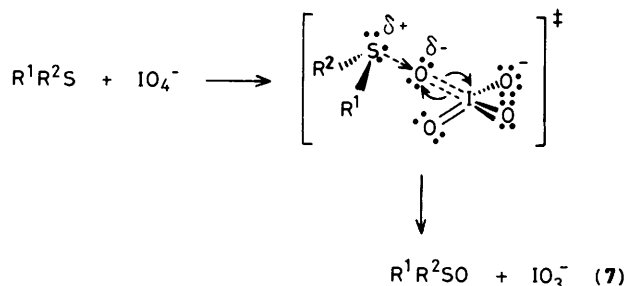
^a The solvent contained 0.05M-Britton-Robinson buffer; pH 8.**Table 6.** Substituent effect in reactions of *p*-Y-*o*-X-C₆H₃SMe sulphides with NaIO₄ in 1:1 (v/v) ethanol-water at 25 °C

<i>p</i> -Y	<i>o</i> -X	10 ² k ₂ /M ⁻¹ s ⁻¹	ρ _s	ρ _o
MeO	CO ₂ H	2.11	-1.51	+0.012
H	CO ₂ H	0.829		
Cl	CO ₂ H	0.381		
MeO	CO ₂ ^{-a}	5.19	-1.56	+0.481
H	CO ₂ ^{-a}	1.75		
Cl	CO ₂ ^{-a}	1.17		

^a The solvent contained 0.05M-Britton-Robinson buffer; pH 8.

oxidation process can be excluded, as no secondary isotope effect has been observed.

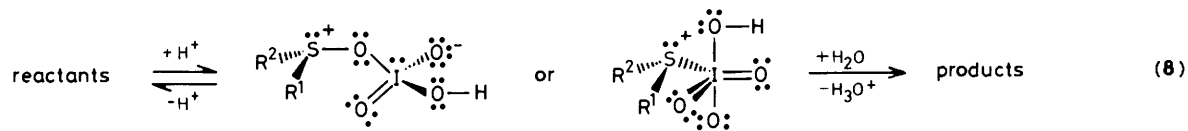
Mechanism.—All these experimental results have led us to the conclusion that the conversion of sulphides by periodate ion involves a rate-determining one-step electrophilic oxygen transfer from periodate ion to sulphide, similar to the reaction between I⁻ and IO₄⁻ ions,¹⁶ and the oxidation of sulphides with peroxy compounds.⁷ The oxygen transfer involving a nucleophilic attack of sulphur at periodate-oxygen may also be compared with reactions which proceed by the S_N2 mechanism. Low ρ values and moderate neighbouring group activities are consistent with the development of a polar transition state



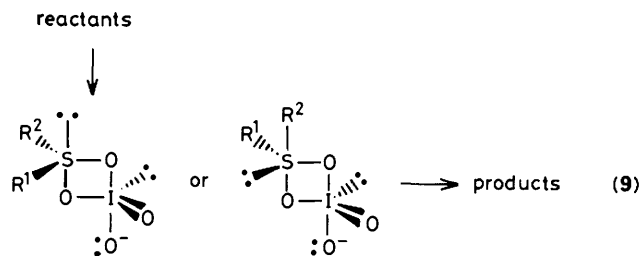
shown in equation (7) rather than with the formation of an intermediate with positive sulphonium centre, as shown, *e.g.*, in equation (8).

The former mechanism gained an additional support from the solvent effect observed. As to the possibility of the latter reaction pathway, both the lack of solvent isotope effect and the pH independence of the rate constants exclude the rate-controlling participation of water as a nucleophile and proton-transfer agent.

As an alternative, one might also assume that the periodate oxidation of sulphides, like the conversion of glycols,^{9b} proceeds through a cyclic intermediate, as has been proposed for the interpretation of stereoselective oxidation of several thiane



derivatives.^{9c} However, such cyclic intermediates should exhibit a sulphurane structure, as described in equation (9).



Such arrangements would be highly unfavourable owing to the apical position of a lone pair or an alkyl group. The formation of a cyclic sulphurane intermediate would also require a much higher entropy of activation than has been observed experimentally. The ΔS^\ddagger values given in Table 2 resemble the corresponding data measured for typical reactions involving oxygen transfer, e.g., for the oxidation of iodide ions by periodate¹⁶ and for that of sulphides by hydrogen peroxide^{7b} ($\Delta S^\ddagger = -96$ and $-115 \text{ J mol}^{-1} \text{ K}^{-1}$, respectively). In addition, the steric requirements in case of reaction (9) would be higher than those for (7). Thus the observed small values of steric reaction constants (see Table 4) also seem to be inconsistent with a cyclic sulphurane mechanism.

Experimental

Materials.—Sulphides were prepared by known methods and purified by distillation or crystallization. The purity of analytical grade NaIO_4 (Reanal, Budapest) was checked by iodimetric titration.

Kinetics.—Kinetic measurements were carried out at $25.00 \pm 0.05^\circ\text{C}$ in 1:1 (v/v) ethanol–water, unless otherwise stated. Initial concentrations of reactants were varied between 2×10^{-2} and $5 \times 10^{-4}\text{M}$. Under pseudo-first-order conditions the concentration of the reactant in excess was at least 10-times higher than that of the other one. Constant pH values (measured by the method of Bates *et al.*¹⁷) were maintained by 0.05M-Britton–Robinson buffer. The influence of ionic strength was investigated by varying the concentration of NaCl , NaClO_4 , and LiClO_4 in the range 0.05–0.5M. Reactions were followed by measuring the absorption of the mixture at various wavelengths in the region 260–430 nm, depending on the structure of the sulphide. At the given wavelengths the absorption of the sulphide and NaIO_4 reactants is much higher (usually more than ten-fold) than that of the sulphoxide and NaIO_3 products.

Product Analysis.—MeSPh (0.2mm) was treated in 1:1 (v/v) ethanol–water (10 cm^3) with NaIO_4 (0.2mm) at 25°C for 24 h. The solution was concentrated, diluted with water, then extracted with chloroform. The extract was dried, evaporated, and the residue was analysed by i.r. spectroscopy. The spectrum was identical with that of MePhSO. The peaks characteristic of MeSPh and MePhSO₂ could not be detected.

Dissociation of H_5IO_6 .—The dissociation equilibria of H_5IO_6 in 1:1 (v/v) ethanol–water were measured at 25°C by u.v. spectroscopy according to the method of Crouthamel *et al.*¹⁵

Acknowledgements

This work was supported by the Institute for Science Management and Information, Ministry of Education, Budapest, Hungary. The authors thank Miss Zs. Szigeti for technical assistance.

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Received 27th June 1984; Paper 4/1103