Oxidation of Thiones to Sulphines (Thione *S*-Oxides) with *N*-Sulphonyloxaziridines: Synthetic and Mechanistic Aspects

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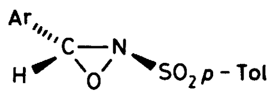
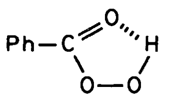
The kinetics of the two-step oxidation of diarylthiones by *N*-sulphonyloxaziridines to sulphines and then to ketones have been investigated and the results compared with those for reactions with perbenzoic acid. The synthetic utility of the oxaziridine and peracid oxidations has been compared for a few aliphatic thiones.

N-Sulphonyloxaziridines[1,2] have recently gained considerable importance as mild and selective reagents for the oxidation of a variety of substrates.[1a–d] In particular, they oxidize sulphides and disulphides to sulphoxides and thiolsulphinates without overoxidation.[1a]

The best method to produce thione *S*-oxides[3] is the controlled oxidation of thiones by peracids.[4] However, further oxidation of the sulphinyl group may occur to give in part the corresponding ketone (see Scheme). Previously,[5,6] we have shown that the selectivity of oxidation as expressed by the ratio k_1/k_2 is sufficiently high to allow the formation of thione *S*-oxides (**4**) without contamination by ketones (**5**), when unreactive aromatic peracids are employed.



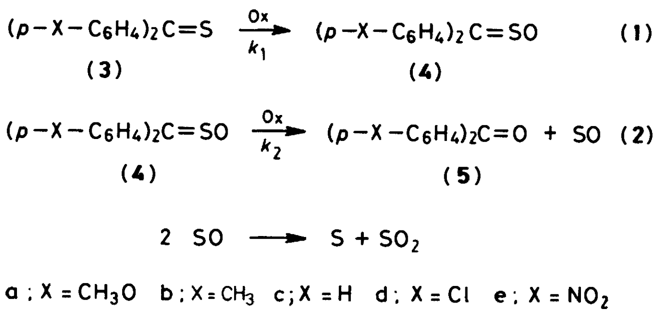
(1)



(2)

a ; Ar = 2-Cl,5-$NO_2C_6H_3$
b ; Ar = 3-$NO_2C_6H_4$

In a search for more selective oxidants, we have now investigated thione oxidation by oxaziridines (**1a,b**). We report here our kinetic data, along with some preparative applications.



$$(p\text{-X-}C_6H_4)_2C{=}S \xrightarrow[k_1]{Ox} (p\text{-X-}C_6H_4)_2C{=}SO \qquad (1)$$

(3) (4)

$$(p\text{-X-}C_6H_4)_2C{=}SO \xrightarrow[k_2]{Ox} (p\text{-X-}C_6H_4)_2C{=}O + SO \qquad (2)$$

(4) (5)

$$2\ SO \longrightarrow S + SO_2$$

a ; X = CH_3O b ; X = CH_3 c ; X = H d ; X = Cl e ; X = NO_2

Scheme.

Results and Discussion

Conversion of Thiones into S-Oxides.—*N*-Sulphonyloxaziridines (**1a,b**) cleanly oxidize thiones (**3a**—**e**) to the corresponding *S*-oxides (**4a**—**e**); all experiments were performed in the dark under an inert gas to avoid photo-oxidation.[7] Kinetic measurements were carried out by spectrophotometric analysis in the visible region, by following the disappearance of thiones (**3a**—**e**). Owing to the overlap of the spectra of thiones and sulphines[5] in the u.v. region, it was not possible to follow simultaneously the formation of sulphines (**4a**—**e**) and the disappearance of thiones: nevertheless, quantitative conversion of thione (**3b**) into sulphine (**4b**) was established by measuring the absorbance of the sulphine in the u.v. region as soon as the disappearance of the thione in the visible region was complete (see Experimental section). Second-order rate constants were obtained by varying the initial concentration of the reactants by a factor of *ca.* 5. Rate constants appeared to increase with the electron-releasing ability of the thione substituents (Table 1). This clearly indicates that the thiocarbonyl compound acts as the electron donor in oxygen transfer from the oxaziridine to the thiocarbonyl function. A Hammett plot of log k_1 *versus* 2σ values for the *p,p'*-disubstituted thiones (**3a**—**e**) (linear regression: log k_1 $-1.2784(2) + 1.973$; ρ -1.28) gave a very poor linear correlation (r 0.965). A better fit was obtained using the $2\sigma^+$ values (ρ -0.75; r 0.990). This result parallels that obtained in the oxidation of thione *S*-oxides to ketones[6] by perbenzoic acid (ρ -0.88). Activation parameters for the oxidation of (**3b**) with (**1a**) in CH_2Cl_2 were: E_a 10.48 kcal mol^{-1}, log A (20 °C) 8.12, $\Delta G^‡$ (20 °C) 16.75 kcal mol^{-1}, $\Delta S^‡$ (20 °C) -23.35 cal K^{-1} mol^{-1}. This suggests a very similar mechanism for thione oxidation by oxaziridines (**1**) and peracids (**2**). However, significant differences between the reactions with (**1**) and (**2**) appeared from a study of solvent effects. In the case of (**1**), k_1 increased slightly with solvent polarity (as indicated by dielectric constant) giving the highest rate in methanol (Table 2), while in the case of (**2**) the lowest rate was found in alcohols.[5] This has been interpreted as due to the interference of the protic solvent with the intramolecular hydrogen-bonded form of (**2**), which has been proved[8] to be the 'active' electrophilic form of the peracid.

On the other hand oxaziridines (**1**), with their covalent-bonded oxygen, are insensitive to the specific medium effect, whereas the rate is affected positively by an increase in the medium polarity. Oxidations with (**1**) were also carried out in the presence of acids of varying strength (Table 2), as it was expected that protonation of (**1**) could favour oxygen transfer. This expectation proved to be invalid since experiments with picric and acetic acid (Table 2) did not show a significant variation in the oxidation rate.†

Finally, a comparison between the absolute second-order rate constants for the oxidation of (**3b**) with (**1a**) and with acid (**2**)

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† Stronger acids, such as CF_3COOH, alter significantly the oxidation rate, but this can be attributed to a formation of a charge-transfer complex rather than to protonation of (**1**).[9]

at 25 °C in CCl_4 showed the higher reactivity of the latter, the ratio k_1 (**2**):k_1 (**1a**) being 69:1.

Conversion of Thione S-*Oxides into Ketones*.—The kinetics of the second oxidation step (see Scheme) were also investigated. The concentration of the reactants and their molar ratios are collected in Table 3; the kinetic experiments were performed in the dark in a Pyrex ampoule sealed under vacuum and containing a trace of *p*-benzoquinone as scavenger and followed by spectrophotometric analysis of the sulphine at 407 nm. In our first assumption, based on some qualitative data of Davis[10] about the relative rates of sulphoxide *versus* sulphide oxidation, the oxaziridine (**1**) was expected to be more selective than acid (**2**). Upon using (**2**), the selectivity, as expressed by the ratio $k_1:k_2$, ranged between 3×10^3 and 1.5×10^5, depending on the solvent employed.

In the second oxidation stage the standard deviation from the mean value of k_2 was *ca.* 10% due to the difficulty in determining the absorbance of the *S*-oxide (**4b**) in the presence of oxaziridine (**1a**) (see Table 3 and Experimental section). Nevertheless, k_2 (measured in CH_2Cl_2 at 20 °C) was 7.3×10^{-4} on average (see Table 3).

If we compare the ratio $k_1:k_2$, 2.7×10^3 when (**1a**) is the oxidant in CH_2Cl_2, with that obtained when (**2**) is the oxidant in the same solvent ($k_1:k_2$ 1.46×10^5), we can see that (**1a**) is a less selective oxidant than perbenzoic acid in the present oxidations.

Additionally, we noted a systematic deviation of the stoicheiometry from a rigorous 1:1 consumption ratio for (**1a**) and (**4b**), our results indicating a 30% excess of consumption for (**1a**). This affected the true value of k_2 to a lesser extent than the 10% deviation found for the mean value. Blank experiments showed that this excess of consumption of oxidant could not be attributed to reaction with S or SO_2. A possible explanation is oxidation of transient SO.

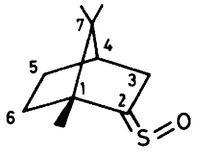
Table 1. Second-order rate constants k_1* (l mol^{-1} s^{-1}) for the oxidation of thiones (**3a**—**e**) to sulphines (**4a**—**e**) with (**1a**) in CH_2Cl_2

	Thiones				
Temperature (°C)	(**3a**)	(**3b**)	(**3c**)	(**3d**)	(**3e**)
1		0.59			
20	8.81	2.02	0.548	0.252	0.0113
25		2.81			

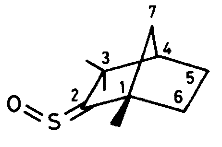
* Correlation coefficient always ≥0.999.

In conclusion, though (**1**) displays lower kinetic selectivity in thiocarbonyl oxidation than perbenzoic acid, its use gives some practical advantages: a larger variety of solvents (*i.e.* protic ones) can be employed, reaction is fast and quantitative, and a 1:1 stoicheiometric ratio of thione and oxidant creates no problem, as for perbenzoic acid.

Synthetic Applications.—The oxaziridine (**1**) is a neutral oxidizing agent which does not need a final aqueous work-up as always required by peracids. Moreover, a clean and good separation can be achieved by selective precipitation of the reduction product (*N*-sulphonylimine); final chromatography of the filtrate gives the *S*-oxide cleanly. For all these reasons we chose (**1b**) for the synthesis of two aliphatic *S*-oxides, thiocamphor *S*-oxide (**6**) and thiofenchone *S*-oxide (**7**).



(**6**)



(**7**)

Both products (**6**) and (**7**) were prepared previously in low yields by ozonization[11] or photochemical oxidation[7] of the corresponding thiones. *S*-Oxide (**6**) was also prepared by oxidation of thiocamphor with *m*-chloroperbenzoic acid; the product obtained was described as a liquid.[12] Starting from optically pure thiones we obtained optically pure *S*-oxides (**6**) and (**7**), in very good yield, when (**1b**) was employed as oxidant; both (**6**) and (**7**) are solids, produced with high stereoselectivity which we believe to be *E* for (**6**) and *Z* for (**7**). The absolute configuration of *S*-oxides (**6**) and (**7**) has been tentatively assigned on the basis of the well known n.m.r. behaviour of protons *syn* to the sulphinyl oxygen. We assigned *E* stereochemistry to compound (**6**) on the basis of the following evidence. The ^1H n.m.r. spectrum (300 MHz) of (**6**) showed two resolved signals for 3-H_2, one at δ 3.03, the other at δ 2.55: both were shifted downfield with respect to the parent thione[7] whereas the signal of the methyl group in position 1 was practically unaffected. This signal lies, together with those of the

Table 2. Solvent and added acid effect on the oxidation of (**3b**) to (**4b**) with (**1a**) (dielectric constants of the solvents employed in parentheses)

		CCl_4 (2.24)	$CHCl_3$ (4.81)	CH_2Cl_2 (9.08)	CH_3OH (32.7)	CH_3CN (37.5)
Added acid	Molar ratio [Acid]:[(**3b**)]	k_1/l mol^{-1} s^{-1} at 20 °C				
None		0.755	1.86	2.02	4.62	3.43
Picric	43			2.06		
Acetic	500			2.33		

Table 3. Second-order rate constants k_2 for the reaction of (**4b**) with (**1a**) in CH_2Cl_2 at 20 °C

Run	10^3 [(**4b**)]/mol l^{-1}	10^3 [(**1a**)]/mol l^{-1}	[(**1a**)]:[(**4b**)]	10^4 k_2/l mol^{-1} s^{-1}	*r*
1	4.87	101.9	20.92	6.26	0.993
2	5.42	68.1	12.56	7.88	0.987
3	6.07	33.8	5.57	7.22	0.990
4	9.37	85.1	9.08	6.80	0.990
5	5.87	50.9	8.68	8.03	0.994
6	5.69	25.7	4.51	7.70	0.994
				7.31 ± 0.8 (mean value)	

Table 4. Selected λ/nm and molar extinction coefficients (ε) employed in the kinetic runs for the oxidation of thiones (**3a**—**e**) and sulphine (**4b**) with oxaziridine (**1a**) in CH_2Cl_2

Compound	λ/nm	ε
(**3a**)	580	401
(**3b**)	592	260
(**3c**)	596	214
(**3d**)	603	260
(**3e**)	633	202
(**4b**)	407	160
(**4b**)	335	14 400
(**1a**)	407	3.35
(**1a**)	335	182

two methyls at position 7, in the δ 0.8—1.1 region. This means that the sulphinyl oxygen is *syn* to the protons in position 3 and *anti* to the methyl in position 1. For thiofenchone *S*-oxide (**7**) we propose that the sulphinyl oxygen occupies the same relative position. In this case the oxygen is very close to the *gem*-dimethyl group in position 3. In the ^1H n.m.r. spectrum two methyl groups are shifted downfield with respect to the parent thione[7] whereas the third methyl group is practically unaffected. This configuration is also favoured by the results of a high-field ^1H n.m.r. analysis based on lanthanide-induced shifts with $Yb(fod)_3$.

Experimental

Spectra.—^1H N.m.r. spectra were recorded with a Varian EM-360L spectrometer and on a high-field (300 MHz) Bruker instrument; ^{13}C n.m.r. spectra were recorded with a Varian XL-100 spectrometer; the shift reagent was tris-(6,6,7,7,8,8,8-heptafluoro-2,2-dimethyl-3,5-octanedionato)ytterbium. I.r. spectra were obtained with a Perkin-Elmer 177 spectrophotomer. Mass spectra were taken at 70 eV with a JEOL JMS D-100 spectrometer. Specific rotations were obtained with a JASCO DIP-360 polarimeter.

Kinetics.—U.v. and visible spectra were recorded on a Perkin-Elmer 323 model spectrophotometer. Molar extinction coefficients at the wavelength selected for kinetic runs in CH_2Cl_2 are collected in Table 4.

Kinetic runs for the oxidations of thiones (**3a**—**e**) to *S*-oxides (**4a**—**e**) were performed as previously described.[5]

For the oxidation of the *S*-oxide (**4b**), exact amounts (2—3 ml) of (**4b**) and (**1a**) solutions (see Table 3) were mixed in a Pyrex ampoule whose pathlength had been determined by use of standard solutions of the thiobenzophenone (**3b**). The solution was quickly frozen in liquid air and then degassed by the freeze–thaw technique under vacuum (10^{-3} Torr). Finally the ampoule was sealed and thermostatted (20 ± 0.2 °C). Kinetic data as a mean value of three independent measurements were obtained by monitoring, at intervals, the sulphine through its absorbance at 407 nm. The wavelength of 407 nm was chosen as a compromise between the large differences in this region of the molar extinction coefficients of (**4b**) (ε 160) and (**1a**) and sulphonylimine (ε 3.35 and 3.54 respectively) and the slope of the shoulders of their spectral curves. Other spectral regions were less suitable owing to the high concentration of reactants required.

The kinetics were followed to at least two half-lives and rate constants were calculated from the second-order rate equation, taking into account the additional absorption of the oxaziridine and sulphonylimine. Because of the almost identical value of their molar extinction coefficients (Table 4) and the large excess of (**1a**) with respect to the sulphonylimine, the concentration of the *S*-oxide (**4b**), at a given time, was calculated by the simple equation: $[C]^t_{CSO} = (A^t - A_{\infty})/\varepsilon_{CSO}$.

Stoicheiometry of the Oxidation of Thione (**3b**) *to* S-*Oxide* (**4b**) *by Oxaziridine* (**1a**).—In a kinetic experiment (**3b**) (0.0069 g, 0.031 mmol) was treated with oxaziridine (**1a**) (0.0436 g, 0.123 mmol [molar ratio (**1a**):(**3b**) 4] in CH_2Cl_2 (8 ml) at 25 °C. As soon as the absorbance of the thione in the visible region disappeared, an exact amount (1 ml) of the reaction mixture was diluted with cyclohexane (87 ml) and the absorbance of sulphine (**4b**) was recorded at 335 nm and compared with the value calculated on the basis of the molar extinction coefficients of (**4b**), (**1a**), and of the corresponding sulphonylimine (ε 347) (see Table 4). An experimental absorbance of 0.66 for pure (**4b**) was found. The calculated value is 0.63 for a 1 : 1 consumption ratio of (**1a**) to (**3b**).

Stoicheiometry of the Oxidation of S-*Oxide* (**4b**) *to Ketone by Oxaziridine* (**1a**).—In a kinetic experiment (**4b**) (0.0066 g, 0.027 mmol) was treated with oxaziridine (**1a**) (0.04555 g, 0.128 mmol) [molar ratio (**1a**):(**4b**) 4.74] in CH_2Cl_2 at 20 °C for 1 week ($t_{\frac{1}{2}}$ 800 min). The ampoule was opened, the solvent evaporated, and the mixture quantitatively redissolved in $CDCl_3$. The ratio of oxaziridine (**1a**) to sulphonylimine was evaluated by ^1H n.m.r. measurements of the intensities of the signals at δ 5.93 and 9.5. An experimental ratio of (**1a**) to sulphonylimine of 2.72 was found. That expected from a 1:1 consumption ratio for stoicheiometric conversion of (**4b**) into (**5b**) was 3.74. This showed a 27% excess of consumption of (**1a**). We excluded reaction of (**1a**) with sulphur dioxide and sulphur (co-products of oxidation) by means of blank runs with a large excess of SO_2 or S.

In a second kinetic run, (**4b**) (0.0068 g, 0.028 mmol) was treated with (**1a**) (0.003 014 g, 0.085 mmol) [molar ratio (**1a**):(**4b**) 3.03] and a 32% excess was found. Based on the hypothesis of an instantaneous, partial (30%) reaction of (**1a**) with SO, the kinetic constant of run 6 of Table 3 was calculated according to stoicheiometry of the type: 1 C=S=O + 1.3 (**1a**). Run 6 was chosen on the basis of its (**1a**):(**4b**) ratio of 4.5, which is identical to that used for stoicheiometry purposes, and thus the most sensitive, in terms of kinetic constants, to deviations from 1 : 1 stoicheiometry.

Oxidation of Thione (**3b**) *to Sulphine* (**4b**) *and of* (**4b**) *to Ketone* (**5b**) *by Perbenzoic Acid* (**2**).—Following the procedures already described,[5,6] the kinetic constants k_1 and k_2 were measured for CH_2Cl_2 solutions at 25 °C; k_1 was 144.4 l mol^{-1} s^{-1} (*r* 0.998) as a mean value of five independent runs, and k_2 was 9.89×10^{-4} l mol^{-1} s^{-1} (*r* 0.996). The stoicheiometry of these oxidations was confirmed as described above.

Materials.—Oxaziridines (**1a,b**),[13] thiones[5] (**3a**—**e**), (−)-thiocamphor,[14] and (+)-thiofenchone[15] were prepared according to published procedures. Optically active thiofenchone showed a higher specific rotation than previously reported: (−)-enantiomer $[\alpha]_D^{25}$ −422°, $[\alpha]_{546}^{25}$ −760° (*c* 1.2 in AcOEt); (+)-enantiomer $[\alpha]_D^{25}$ 393°. Both are >95% pure (^{13}C n.m.r. and gas-chromatography on 5% SP-1000, 6 ft × $\frac{1}{4}$ in, oven programme 2′ at 55 °C, then to 225 °C at 30 ° min^{-1}).

(1R)-(+)-*Thiocamphor* S-*Oxide* (**6**).—A solution of (**1b**) (0.40 g, 1.25 mmol) in anhydrous CH_2Cl_2 (15 ml; distilled from CaH_2) was dropped onto a solution of (−)-thiocamphor (0.20 g, 1.19 mmol) in CH_2Cl_2 (3.0 ml) cooled at 0 °C and under N_2 with magnetic stirring. After 30 min the colour had turned from orange to pale yellow, solvent was removed, and the residue was taken up in anhydrous n-hexane (15 ml). A solid was filtered off (0.36 g), m.p. 128—131 °C, identified from i.r. and ^1H n.m.r. as the *N-p*-tolylsulphonylimine of 3-nitrobenzaldehyde (95%). The remaining solution was evaporated to dryness under CO_2 giving an oil which was chromatographed on silica gel, eluant light petroleum–ethyl acetate (8:2 v/v), affording (**6**) (0.20 g, 91%), m.p. 118—120 °C; $[\alpha]_D^{25}$ $-71.2 \pm 0.5°$, $[\alpha]_{546}^{25}$ $-90.7 \pm 0.5°$ (*c* 2.0 in n-hexane); $\nu_{max.}(CS_2)$ 1 060 cm^{-1} (CSO); *m/z* 184 (M^+), 167 ($M^+ - OH$), 135 ($M^+ - OH - S$), 128, 107, 105, 93, and *91*; $\delta_C(CDCl_3)$ 12.0, 18.2, 19.2, 26.9, 35.5, 38.1, 44.3, 50.1, 56.1, and 210.2 p.p.m.; δ_H ($CDCl_3$; 300 MHz) 0.85 (s, 3 H), 0.96 (s, 3 H), 1.13 (s, 3 H), 1.28 (t, *J* 8 Hz, 1 H), 1.47 (t, *J* 8 Hz, 1 H), 1.89 (m, 2 H), 2.07 (m, 1 H), 2.55 (d, *J* 20 Hz, 1 H), and 3.03 (dm, J_1 20 Hz, 1 H).

When the oxidation was performed in anhydrous $CHCl_3$ by the same procedure, the yield was 79%.

(1S)-(−)-*Thiofenchone* S-*Oxide* (**7**).—This was obtained as described above from (**1b**) (0.36 g, 1.13 mmol) in anhydrous CH_2Cl_2 (10 ml) and (−)-thiofenchone (0.18 g, 1.08 mmol) in CH_2Cl_2 (3.0 ml). After 1.5 h at 0 °C the same work-up gave the sulphonylimine (0.28 g, 82%), m.p. 128—131 °C. Chromatography of the filtrate on silica gel, eluant light petroleum (b.p. 40—60 °C)–ethyl acetate (10:1 v/v), afforded an oil (0.15 g, 76%) which, on the basis of ^{13}C n.m.r. analysis, was a mixture of (**7**) (> 80%) and another product (very likely the *E*-isomer). Crystallization from n-pentane at −10 °C gave pure (**7**), m.p. 47—49 °C; $[\alpha]_D^{25}$ $+55 \pm 0.5°$, $[\alpha]_{546}^{25}$ $+65.5 \pm 0.5°$ (*c* 1.2 in n-hexane); $\nu_{max.}(CS_2)$ 1 045 cm^{-1} (CSO); *m/z* 184 (M^+), 167 ($M^+ - OH$), 142, 135 ($M^+ - OH - S$), 128, 107, 93, 91, and 69; δ_H ($CDCl_3$; 300 MHz) 1.33 (s, 3 H), 1.48 (s, 3 H), 1.52 (s, 3 H), and 1.2—1.9 (m, 7 H); δ_C 17.9 (q), 22.5 (q), 23.9 (q), 25.1 (t), 37.0 (t), 45.0 (t), 48.8 (d), 51.2 (s), 53.8 (s), and 214.1 p.p.m. (s).

When the oxidation was performed by the same procedure in anhydrous $CHCl_3$, the yield was 60%.

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