

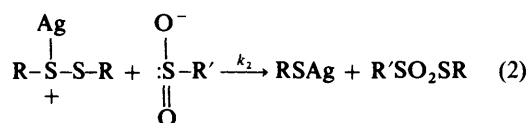
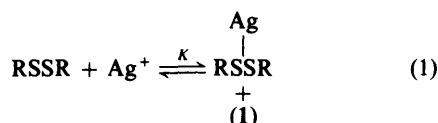
## A Kinetic Study of the Silver(I) Ion-assisted Synthesis of Thiosulphonate Esters from Aliphatic Disulphides

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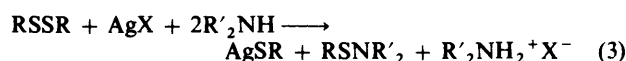
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Kinetic studies confirm that the silver(I) ion-promoted reaction of disulphides with sulphinate ions proceeds *via* formation of a disulphide-Ag<sup>+</sup> complex. Nucleophilic attack by sulphinate sulphur at the sulphenyl centre of the complex leads to silver alkyl sulphide and thiosulphonate. Under favourable conditions the 1:1 disulphide-silver complex can be isolated.

Kice has reviewed the large rate enhancements observed in cooperative electrophilic and nucleophilic assistance in the cleavage of sulphur-sulphur bonds.<sup>1,2</sup> Bentley and co-workers have apparently utilised such catalysis to provide a convenient 'one-pot' synthesis of thiosulphonate esters in good yield (>90%) from the silver(I) ion-assisted reaction of alkyl disulphides with sodium methanesulphinat.<sup>3</sup> Although they did not study the kinetics of the reaction, they proposed the concomitant mechanism shown in equations (1) and (2), where R = Me, Et, or Pr<sup>i</sup>; R' = Me.



A similar mechanism was proposed for the silver(I) ion-assisted synthesis of sulphenamides from disulphides [equation (3)].<sup>4</sup>



The isolation of solid silver nitrate-dialkyl disulphide 1:1 complexes has been reported<sup>5</sup> and Bentley and co-workers noted the appearance, in several reactions, of a white precipitate that they assumed indicated complex formation.<sup>3</sup> An earlier kinetic study of the reaction of disulphides with silver nitrate gave inconclusive results.<sup>6</sup> In an attempt to confirm the mechanism proposed by Bentley and co-workers,<sup>3</sup> we now report a detailed kinetic study of the reaction of silver nitrate and sodium toluene-*p*-sulphinat with diethyl and dibutyl disulphides in 60% (v/v) ethanol-water. Although it was not possible to follow the rate of formation of the complex, the rates of product formation could be conveniently followed by a conventional u.v. spectroscopic method.

### Experimental

**Materials.**—Diethyl and dibutyl disulphides were commercially available samples, which after fractionation had b.p. 46 °C at 14 mmHg (lit.,<sup>7</sup> 45 °C at 13 mmHg) and 73 °C at 2 mmHg (lit.,<sup>8</sup> 85 °C at 3 mmHg), respectively. Silver nitrate was BDH Chemicals AnalaR grade material and sodium toluene-*p*-sulphinat was a recrystallised commercial sample.

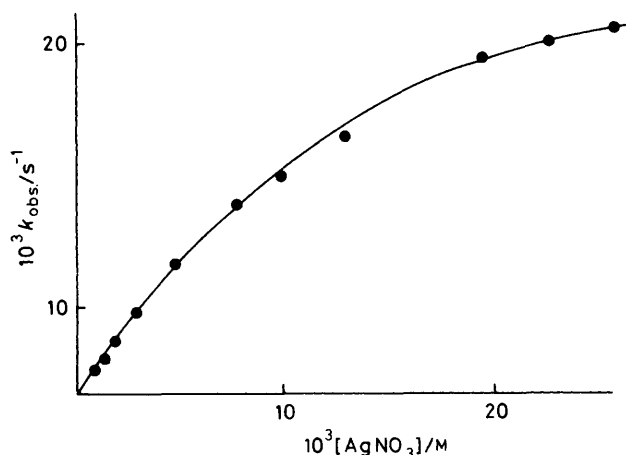


Figure 1. The effect of added silver nitrate on the rate of reaction of diethyl disulphide with sodium toluene-*p*-sulphinat

**Kinetic Measurements.**—Typically the disulphide (30  $\mu\text{l}$  of  $1.03 \times 10^{-2}\text{M}$  stock solution in ethanol) was added to a 60% (v/v) aqueous ethanol solution of sodium toluene-*p*-sulphinat (3.0 ml) in a thermostatted ( $\pm 0.2$  °C) u.v. cell. After thermal equilibration, silver nitrate (20  $\mu\text{l}$ ) was added, the resulting mixture shaken and the increase in absorption at 295 nm was continuously monitored using a Perkin-Elmer model 554 u.v. spectrometer. Both products absorb significantly at this wavelength. [Values of  $\log \epsilon_{295}$  for ethyl toluene-*p*-thiosulphonat and silver ethyl sulphide in 60% (v/v) aqueous ethanol are 2.76 and 3.56, respectively.] Values of the first-order rate coefficients,  $k_{\text{obs}}$ , were calculated from the standard equation and are shown in Figure 1 and the Table and were reproducible to  $\pm 5\%$ .

**Complex Isolation.**—Diethyl disulphide (0.28 g, 0.0023 mol) in 60% (v/v) ethanol-water was added slowly to a solution of silver nitrate (0.43 g, 0.0025 mol) in 60% (v/v) ethanol-water which had been cooled to 0 °C. The white crystals that formed were filtered off and recrystallised from absolute ethanol at 0 °C to give 0.35 g of product whose elemental analysis corresponded satisfactorily to  $\text{AgNO}_3 \cdot (\text{C}_2\text{H}_5)_2\text{S}_2$ .

**Reaction Products.**—These were isolated using the conditions described earlier by Bentley and co-workers<sup>3</sup> except that the solvent used was 60% (v/v) aqueous ethanol. From diethyl disulphide (2.44 g, 0.02 mol), silver nitrate (4.25 g, 0.025 mol), and sodium toluene-*p*-sulphinat (4.27 g, 0.025 mol) were obtained silver ethyl sulphide (3.12 g, 95%) and 0.74 g (86%) of a colourless oil: n.m.r. spectrum,  $\delta_{\text{H}}$  ( $\text{CDCl}_3$ ) 1.25 (3 H, t, Me),

**Table.** Values of the pseudo-first-order rate coefficients for the silver(I) ion-promoted reaction of dibutyl disulphide with sodium toluene-*p*-sulphinat in 60% (v/v) ethanol-water at 25.0 °C

(a) Effect of silver ion concentration.  $[R'SO_2^-] = 1.97 \times 10^{-3} M$

$10^3[Ag^+]/M$	1.97	2.94	4.87	7.72	9.80	13.0
$10^3k_{obs}/s^{-1}$	2.66	3.81	5.67	8.32	9.41	11.5
$10^3[Ag^+]/M$	16.2	19.4	22.6	25.7	32.0	47.2
$10^3k_{obs}/s^{-1}$	12.7	14.6	15.8	16.8	18.6	21.7

(b) Effect of ionic strength.  $[R'SO_2^-] = 1.97 \times 10^{-3} M$ ;  $I = 3.19 \times 10^{-2} M$  maintained with  $NaClO_4$

$10^3[Ag^+]/M$	13.0	16.2	19.4	22.6
$10^3k_{obs}/s^{-1}$	11.3	12.9	14.6	15.8

(c) Effect of nucleophile concentration.  $[Ag^+] = 1.97 \times 10^{-3} M$

$10^3[R'SO_2^-]/M$	1.97	3.93	5.90	7.87	9.84
$10^3k_{obs}/s^{-1}$	2.66	3.63	6.08	7.83	8.98

(d) Effect of temperature-derived parameters.  $[R'SO_2^-] = 1.97 \times 10^{-3} M$

$T/^\circ C$	24.2	30.4	35.2	40.1
$k_2/s^{-1}$	15.8	18.1	21.2	23.8

$\Delta H^\ddagger = 4.3 \pm 0.3 \text{ kcal mol}^{-1}$ ;  $\Delta S^\ddagger = -38.7 \pm 1.0 \text{ cal K}^{-1} \text{ mol}^{-1}$

2.43 (3 H, s, Me), 3.0 (2 H, q,  $CH_2$ ), 7.2–7.8 (4 H, AB, ArH); and mass spectrum ( $m/z$  216,  $M$ ) were consistent with those expected for ethyl toluene-*p*-thiosulphonate.

## Discussion

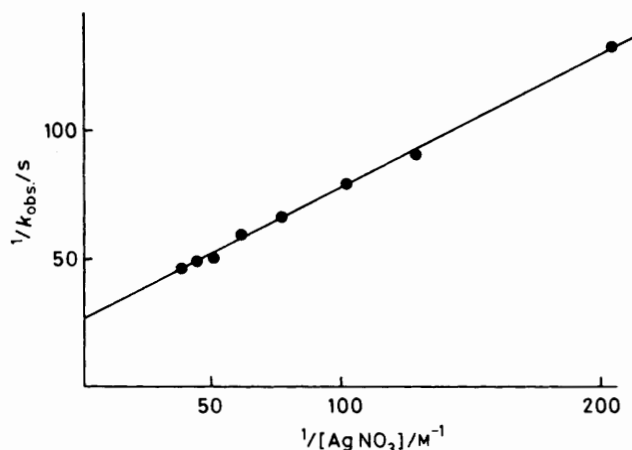
The kinetic results obtained for both compounds were so similar that they can conveniently be discussed together. Under pseudo-first-order conditions maintaining a large excess of the nucleophile ( $1.97 \times 10^{-3} M$ ) and silver nitrate over that of the disulphide ( $9.87 \times 10^{-5} M$ ), the observed first-order rate constant for product formation,  $k_{obs}$ , depends on  $[Ag^+]$ , as shown in Figure 1 and the Table, (a). At low values of  $[Ag^+]$ ,  $k_{obs}$  is approximately proportional to  $[Ag^+]$ , whilst at higher values,  $k_{obs}$  becomes independent of  $[Ag^+]$  and approaches a limiting value for both disulphides. This value is difficult to measure directly because of solubility problems at the higher values of  $[Ag^+]$ . Such kinetic behaviour, however, is consistent with the mechanism shown in equations (1) and (2). These observations indicate that when  $[Ag^+]$  is *ca.* equal to  $[R'SO_2^-]$ ,  $k_2$  exceeds  $k_{obs}$ , and the first step of the reaction is followed, whilst if  $[Ag^+]$  is raised sufficiently so that  $[Ag^+] \gg [R'SO_2^-]$ , the second step eventually becomes rate determining.

Only small effects of ionic strength on  $k_{obs}$  were observed for the reaction of added  $Ag^+$  ions at constant nucleophile concentration for the reaction of dibutyl disulphide [Table, (b)]. Rather larger ionic strength effects were noted for the reaction of dibutyl disulphide when  $[Ag^+]$  was kept constant and  $[R'SO_2^-]$  was varied from 1.97 to  $9.84 \times 10^{-3} M$ ;  $k_{obs}$  increased by *ca.* three times. Such kinetic behaviour could alternatively arise from a contribution to  $k_{obs}$  of a background  $Ag^+$ -catalysed solvolysis of the disulphide. No such reaction could, however, be detected.

If a rapid pre-equilibrium formation of the complex (1) from disulphide and  $Ag^+$  ions occurs as in equation (1), then provided that  $[Ag^+]$  and  $[R'SO_2^-] \gg [RSSR]$  [equation (4)], we obtain equations (5) and (6).

$$d[P]/dt = k_2[(1)][R'SO_2^-] \quad (4)$$

$$k_{obs} = k_2K[Ag][R'SO_2^-]/(1 + K[Ag^+]) \quad (5)$$



**Figure 2.** Test of equation (6) for the silver(I) ion-promoted reaction of diethyl disulphide with sodium toluene-*p*-sulphinat

$$\frac{1}{k_{obs}} = \left( \frac{1}{k_2K[R'SO_2^-]} \right) \frac{1}{[Ag^+]} + \frac{1}{k_2[R'SO_2^-]} \quad (6)$$

Hence the reaction scheme predicts that a plot of  $1/k_{obs}$  versus  $1/[Ag^+]$  whilst  $[R'SO_2^-]$  is kept constant allows the values of both  $k_2$  and  $K$  to be determined. Such a plot is illustrated in Figure 2 for diethyl disulphide. The data lead to values of  $K = 52$  and  $40 \text{ l mol}^{-1}$  and  $k_2 = 3.6 \times 10^{-2}$  and  $3.3 \times 10^{-2} \text{ s}^{-1}$  for diethyl and dibutyl disulphides, respectively. Thus the complex formed by diethyl disulphide with silver ions is both more stable and reacts with a nucleophile slightly faster than the corresponding complex derived from dibutyl disulphide.

The rate of reaction of dibutyl disulphide was also determined at a number of different temperatures. Double reciprocal plots [equation (6)] gave the derived values of  $k_2$  shown in the Table (d), and values of  $\Delta H^\ddagger = 4.3 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger = -38.7 \text{ cal K}^{-1} \text{ mol}^{-1}$  for the silver ion-promoted reaction. Very similar Arrhenius parameters ( $\Delta H^\ddagger$  *ca.*  $4 \text{ kcal mol}^{-1}$  and  $\Delta S^\ddagger$  *ca.*  $-45 \text{ cal K}^{-1} \text{ mol}^{-1}$ ) were obtained by Satchell and Weil for the silver ion-promoted hydrolysis of the *S*-acetal 2,2-diphenyl-1,3-oxathiolane.<sup>9</sup> In both cases the large negative values of  $\Delta S^\ddagger$  are associated with bimolecular rate-determining steps.

Using diethyl disulphide as a typical example we were able to confirm, using semi-preparative conditions, that in favourable cases the disulphide-silver complex can be isolated. The identity of the products and general stoichiometry of the reaction are also consistent with the general scheme [equations (1) and (2)] proposed by Bentley *et al.*<sup>3</sup> Although the toluene-*p*-sulphinat ion can behave as an ambident species,<sup>10</sup> we also were unable to detect any attack occurring *via* sulphinat oxygen. Presumably the soft sulphenyl centre of the complex is more susceptible to attack by the relatively soft sulphinat sulphur.<sup>11</sup>

## Acknowledgements

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