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A Kinetic Study of the Reactions of Dialkyl Disulphide with Benzene Sulphinic Acid Sodium Salt in Aqueous Dimethyl Disulphoxide Promoted by Silver Ions

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Abstract. Substituent effects on the kinetics of the silver (1) ion catalysed reaction of dialkyl disulphides with sulphinates ions in aqueous dimethylsulphoxide (DMSO) have been investigated. The results are consistent with the previous proposed mechanism involving a bimolecular rate-determining step.

Introduction

Kice has reviewed the large rate enhancements observed in co-operative electrophilic and neucleophilic assistance in cleavage of sulphur-sulphur bonds [1-2]. Bentley and his co-workers have utilized such catalysis to provide a convenient "one-pot" synthesis of thiosulphate esters in good yield (>90%) from the silver(I) ion-assisted reaction of alkyl disulphides with sodium methane sulphinate [3]. Bentley and his co-workers also noted the appearance of white precipitate in several reactions assuming as the indications of complex formation [3]. The isolation of solid silver nitrate-dialkyl disulphide 1:1 complexes has been reported [4].

Diethyl disulphide reacts with aryl sulphinates in aqueous ethanol solvents in the presence of silver nitrate to give the thiosulphonate ester [3]. The kinetics of the silver (1) catalysed reaction of sodium toluene-p-sulphinate with diethyl and dibutyl disulphides in 60% (v/v) ethanol water have been reported and a mechanism involving a bimolecular rate-determining step has been proposed [5].

More recently, Satchell and his co-workers reported a kinetic study on the reaction of diphenyl disulphide with toluene-p-sulphinate ions in 60% aqueous ethanol in the presence of silver ions and proposed that complexes involving both one and two silver ions were involved [6]. The present study of substituent effects on the silver (I) ions catalysed reactions on the mechanism of such reactions with sulphinate ions was undertaken to provide further information on the mechanism of such reactions. The rates of reactions at various concentration of silver and sulphinate ions at different temperatures were followed by conventional uv spectroscopy.

Experimental

Materials

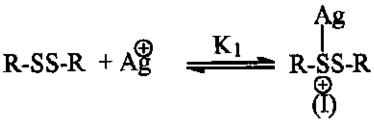
Dimethyl disulphide [DMDS], diethyl disulphide[DEDS], dipropyl disulphide [DPDS], dibutyl disulphide [DBDS],and diisopropyl disulphide [DIPDS],were commercially available samples which after fractionation had b.p 109.0°C at 760 mmHg for DMDS, 46.0°C at 14 mmHg (lit[7], 45.0°C at 13 mmHg) for DEDS , 71.0°C at 8 mmHg (lit[7]. 195.0°C at 760 mmHg) for DPDS.73.0°C at 1.8 mmHg (lit [7], 85.0°C at 3 mmHg) for DBDS, and 70.0°C at 10 mmHg (lit [8], 175.0°C at 760 mmHg) for DIPDS. Silver nitrate was obtained from BDH (Analar grade) and commercially available benzene sulphinic acid sodium salt was recrystallized before use.

Kinetic measurements

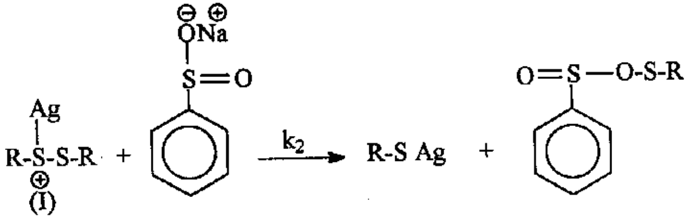
Typically the disulphide (30 μl of 1.03×10^{-2} M stock solution in ethanol) was added to 70% (v/v) aqueous DMSO solution of benzene sulphinic acid sodium salt (3.0 ml) in thermostatted (± 0.2°C) u.v. cell. After thermal equilibration, silver nitrate (30 ml of a 0.3 M stock solution to give a final concentration of 3.0 × 10-3 M) was added. The resulting mixture was shaken and increase in absorption at 315 nm was continuously monitored using a Perkin-Elmer Model 330 u.v. spectrometer. Values of the first-order rate coefficients, k_{obs} , were calculated from the standard equation.

Results and Discussions

Aliphatic disulphides were found to be so similar in their kinetic behavior that they could be conveniently discussed together. Under pseudo-first-order conditions with a large excess of the nucleophile (2×10^{-3} M) and silver ions over that of the disulphide (1.00×10^{-4}M) the observed first-order rate constant for product formation, k_{obs}, depends on the concentration of silver ions, as shown in Table 1 and Fig. 1. At low values of silver concentration, k_{obs} is approximatley proportional to the concentration, of silver ions, while at higher values k_{obs} becomes independent of the concentration of silver ions and approaches a limiting value for alkyl disulphides. This value is difficult to measure directly because of solubility problems at the higher values of silver concentration. In order to discuss such kinetic behavior, it has been assumed [6] that at low silver ion concentration reaction of 1:1 complexes with the nucleophile forms the net major reaction pathway (equation 1 and 2) and complex formation between silver and benzene sulphinate ions is regarded as a side reaction as in (equation 3). The overall mechanism is shown in equations (1), (2) and (3).



(1)



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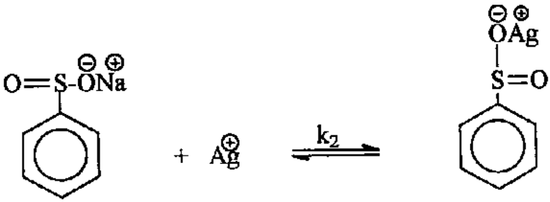

(3)

Table 1. Values of the pseudo- first-order rate cofficient for the silver (I) ion-promoted reactions of dialkyldisulphides with benzene sulphinic acid sodium salt in 70% DMSO-H_2O at 25.0°C

10^3[Ag]/M	DMDS $10^2k_{obs}/s^{-1}$	DEDS $10^2k_{obs}/s^{-1}$	DPDS $10^2k_{obs}/s^{-1}$	DBDS $10^2k_{obs}/s^{-1}$	DIPDS $10^2k_{obs}/s^{-1}$
1	2.1	1.8	1.2	0.9	0.15
3	4.3	3.3	2.8	1.91	0.50
5	6.5	6.0	3.9	3.30	1.0
7	8.0	7.5	5.0	4.3	2.01
10	9.5	9.0	6.2	5.5	2.9
13	11.0	10.5	7.3	6.5	3.7
14	12.5	12.2	9.0	8.4	4.55
15	13.2	12.8	10.5	9.5	5.6
17	14	13.4	11.2	10.2	6.1
20	14.5	13.8	11.4	10.9	6.3

When the concentration of silver ions to the concentration of benzene sulphinic acid sodium salt, k_2 exceeds k_{obs} and equation (1) is rate-determining. If the concentration of the silver ions is raised higher to the concentration of benzene sulphinic acid sodium salt, the second step becomes the rate determining step.

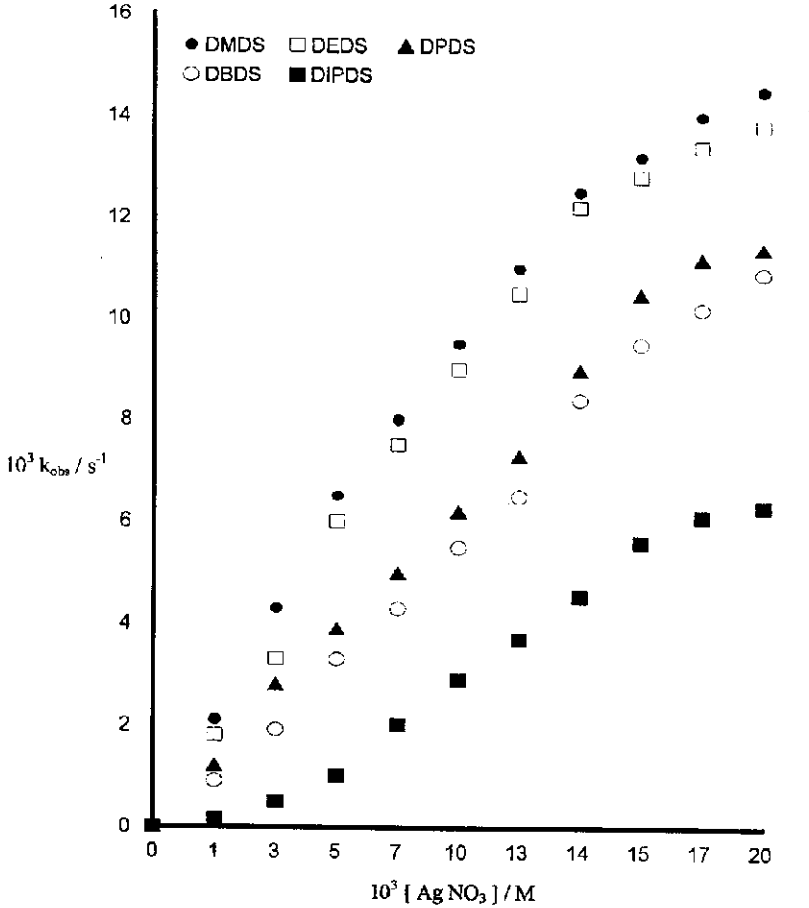

Fig. 1. The effect of added silver nitrate on the rate of the reactions of alkyl disulphide with benzene sulphinic acid sodium salt in 70% DMSO-H_2O(v/v)at25.0°C.

The following equations (4), (5) and (6) can be derived based on: pre-equilibrium formation of the complex (I) from disulphide and silver ions in equation (1), concentration of the silver ions and concentration of benzene sulphinic acid sodium salt being at least ten-fold excess ones that of the disulphide. Silver benzene sulphinate does not form a complex with alkyldisulphides.

$$d[p]/dt = k_2[(I)][C_6H_5SO_2Na] \tag{4}$$

$$K_{obs.} = K_2K_1 = [Ag] + [C_6H_5SO_2Na]/1 + K_1[Ag+] + K_2[C_6H_5SO_2Na] \tag{5}$$

$$\frac{1}{K_{obs.}} = \left[\frac{1}{k_2K_1[C_6H_5SO_2Na} + \frac{K_2}{k_2K_1}\right]\frac{1}{[Ag+1]} + \frac{1}{k_2[C_6H_5SO_2Na]} \tag{6}$$

The stability constant (K_2 =355 mol^{-1} dm^3 at 25.0°C) of the complex silver benzene sulphonate (equation 3) was determined by the Benesi-Hidebrand method [9] using the following equation:

$$1/[Ag^+]_{total} = A_{max} K_2 \, 1/A\text{-}k_2$$

The approximate values of k_2 and K_1 for alkyldisulphides were determined by using equation (6), a plot of $1/k_{obs.}$ versus $1/[Ag^+]$ while $[C_6H_5SO_2Na]$ was kept constant Table 2 and Fig. 2. The values of k_2 and K in Table 2 show a gradual decrease for the reactions of disulphide with benzene sulphinic acid sodium salt promoted by silver ions from dimethyl disulphide to dibutyl disulphide and a much more dramatic decrease going to diiso-propyl disulphide which could be probably because of the greater steric bulk of the isopropyl group which could make access to the S-S group more difficult. A similar steric effect for attack at a sulphur-sulphur bond has been observed by Fava and his co-workers on the rate of exchange of labelled sulphite ions with a series of alkyl thiosulphates [10].

$$^{*}SO_3^{2-} + RS - SO_3^{-} \quad RS - SO_3^{*} + SO_3^{2-}$$

for which the relative rates of exchange were: Me, 100; Et, 50; Isopropyl, 0.7.

Table 2. Approximate values of K_1 and k_2 derived from the equation (6) for reactions of dialkyldisulphide with benzene sulphinic acid sodium salt in 70% DMSO-H_2O (v/v) at 25.0°C promoted by silver ions

$[C_6H_5SO_2Na]$ = 1.97 × 10^{-3} M
[RSSR] = 1.00 × 10^{-4} M

Disulphide	K_1 mol^{-1} dm^3	k_2 mol^{-1} dm^3 s^{-1}
DMDS	285.5	69.3
DEDS	258.0	67.1
DPDS	218.1	58.9
DBDS	160.3	54.8
DIPDS	920.0	13.3

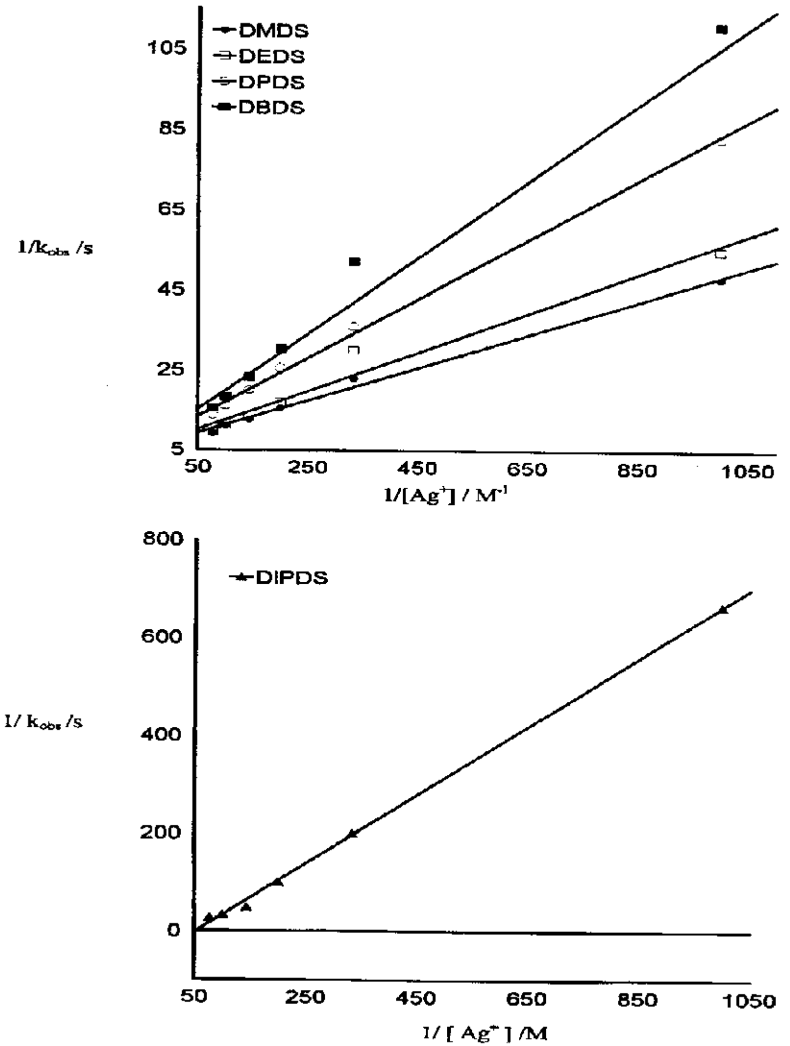

Fig. 2. Plot of equation (6) for the silver ions promoted reaction of alkyldisulphide with benzene sulphinic acid sodium salt in 70% DMSO-H_2O (v/v) at 25.0°C.

The rates of reaction of dialkyl disulphides were also determined at various temperatures. Double reciprocal plots (equation 6) gave the derived values of k_2 as shown in Table 3 and the values of Ea, ΔH* and ΔS* as shown in Table 4 are consistent with the propose mechanism.

Table 3. Values of k_2 (mol^{-1} dm^3 s^{-1}) for the reaction of open chain disulphides with benzene sulphinic acid sodium salt in 70% DMSO-H_2O at different temperatures

$[C_6H_5SO_2Na] = 1.97 \times 10^{-3}$ M
[R SS R] $= 1.00 \times 10^{-4}$ M
$[Ag^+] = 5 \times 10^{-3}$ M

Disulphide	25.0°C	35.0°C	45.0°C	50.0°C
DMDS	69.3	102.5	200.1	280
DEDS	67.1	99.8	190	258
DPDS	59.0	79.1	157.1	201.5
DBDS	54.8	70.0	151.7	193.5
DIPDS	13.3	22.1	35.3	51.4

Table 4. Arrhenius parameters for the reactions of dialkyl disulphides with benzene sulphinic acid sodium salt promoted by Ag^+ in 70% DMSO-H_2O(v/v)

$[C_6H_5SO_2Na] = 1.97 \times 10^{-3}$ M
[R-SS-R] $= 1.00 \times 10^{-4}$ M
$[Ag^+] = 5.00 \times 10^{-3}$ M

Disulphide	E_a(kJ mol^{-1})	ΔH*(kJ mol^{-1})	-ΔS*(JK-1 mol^{-1})
DMDS	45.2	42.7	327.9
DEDS	43.4	41.5	323.8
DPDS	43.0	41.2	320.5
DBDS	42.8	40.0	316.3
DIPDS	41.0	39.7	304.7

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دراسة حركية لتفاعلات ثنائي الكيل ثنائي السلفيد مع أملاح الصوديوم لحامض البنزين سلفونيك في المحاليل المائية لثنائي ميثيل السلفوكسيد والمحفز بواسطة أيونات الفضة

عادل بن محمد السليم

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ملخص البحث. تأثير الاستبدال على حركيات أيونات الفضة (١) المحفزة لتفاعل ثنائي الكيل السلفيد مع أيونات السلفيت في المحاليل المائية لـ (DMSO) وكانت النتائج تتفق مع الميكانيكية المتوقعة التي تتضمن الخطوة المحددة لتفاعل ثنائي الجزئية.