Nucleophilic Substitution of Nitroaromatic Halides by Electrogenerated Polysulphide Ions in Dimethylacetamide

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Electrogenerated polysulphide ions $S_3^{\cdot-}$ and S_8^{2-} readily react with haloaromatics, ArX, activated by nitro electron-withdrawing substituents in dimethylacetamide. Nucleophilic substitutions on fluoro-2,4-dinitrobenzene (**1a**; X = F), halo-4-nitrobenzenes (**2a**; X = F, Cl, Br, I) and 2-nitrobenzenes (**3a**; X = F, Cl, Br, I) lead to the coloured arylmonosulphide (**1b**; X = S^-) and aryldisulphide (**2c**–**3c**; X = S_2^-) ions. From the reaction kinetics studied by UV–VIS spectrophotometry, the order of reactivity is ArF > ArBr, ArI > ArCl. The proposed S_NAr mechanism implies that the dianions S_6^{2-} and S_8^{2-} are the nucleophilic agents ($S_6^{2-} \gg S_8^{2-}$) rather than the $S_3^{\cdot-}$ and $S_4^{\cdot-}$ radical anions.

The nucleophilic reactivity of polysulphide ions on alkyl halides in protic media has been the subject of several reports.[1] In dipolar aprotic solvents, stabilization of the ions S_8^{2-} and $S_3^{\cdot-}$ [2,3] leads chiefly to dialkyl tri- and tetra-sulphides, according to the overall reactions that take place in dimethylacetamide[4] (DMA) [reactions (1) and (2)].

$$2\,RX + 2\,S_3^{\cdot-} \longrightarrow RS_3R + 3/8\,S_8 + 2X^- \qquad (1)$$

$$2\,RX + S_8^{2-} \longrightarrow RS_4R + 1/2\,S_8 + 2X^- \qquad (2)$$

These reactions are analogous to those occurring with the superoxide ion $O_2^{\cdot-}$ in the same type of medium[5] [reaction (3)].

$$2\,RX + 2\,O_2^{\cdot-} \longrightarrow RO_2R + O_2 + 2X^- \qquad (3)$$

In the case of halo aromatics activated by electron-withdrawing groups, the displacement of halide ions by $O_2^{\cdot-}$ has been shown in several instances.[6–9] Initial attack occurs *via* an S_NAr mechanism,[9] for an overall process leading to phenolate ions [reaction (4)].

$$ArX + 2\,O_2^{\cdot-} \longrightarrow ArO^- + 3/2\,O_2 + X^- \qquad (4)$$

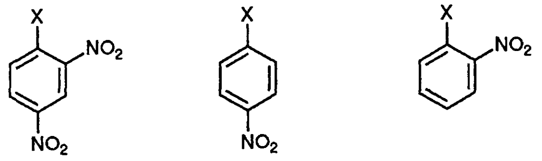
We have recently described the general formation of stable aryl disulphide ions ArS_2^- in DMA by the direct reaction of sulphur on aromatic thiolates[10,11] [reaction (5)]. It should

$$ArS^- + 1/8\,S_8 \rightleftharpoons ArS_2^- \qquad (5)$$

thus be possible to obtain ArS^-/ArS_2^- solutions by nucleophilic substitution of polysulphide ions on aryl halides. We report here on the reactivity of $S_3^{\cdot-}$ and S_8^{2-} ions electrogenerated from sulphur towards a series of activated halo compounds ArX [fluoro-2,4-dinitrobenzene (**1a**; X = F), fluoro-, chloro-, bromo-, iodo-4-nitrobenzene (**2a**) and -2-nitrobenzene (**3a**) based on a kinetic study of these reactions in DMA. 4-Bromobenzophenone, 2-bromopyridine, bromobenzene and 1-bromonaphthalene were also tested.

Results

Reactions and their rates were followed at 20 °C by UV–VIS absorption spectrophotometry coupled with classic voltammetry, after the addition of ArX derivatives to $S_3^{\cdot-}$ and S_8^{2-} solutions, initially obtained by electrolysis of a defined concentration of sulphur (see the Experimental section).



1 **2** **3**

a; X = halogen
b; X = S^-
c; X = S_2^-

In the case of compounds reacting with $S_3^{\cdot-}$ ions a simplified reaction balance was established, analogous to that for $O_2^{\cdot-}$ ions[7,9] [reaction (6)]. In order to process the results quantitatively, it was necessary to take into account the equilibria of the sulphur/polysulphide[3] and aryl disulphide/thiolate[11] systems, as well as the characterization of the different chemical species, eqns. (7) and (8).

$$ArX + 2\,S_3^{\cdot-} \longrightarrow ArS^- + 5/8\,S_8 + X^- \qquad (6)$$

Dimerization[3] of $S_3^{\cdot-}$:

$$2\,S_3^{\cdot-} \rightleftharpoons S_6^{2-} \qquad (7)$$

$$K_1 = [S_3^{\cdot-}]^2[S_6^{2-}]^{-1} = 0.07\ \text{mol dm}^{-3}$$

Disproportionation[3] of S_8^{2-}:

$$S_8^{2-} \rightleftharpoons 2\,S_3^{\cdot-} + \tfrac{1}{4}S_8 \qquad (8)$$

$$K_2 = [S_3^{\cdot-}]^2[S_8]^{1/4}[S_8^{2-}]^{-1} = 6.0 \times 10^{-5}\ (\text{mol dm}^{-3})^{5/4}$$

When thiolate ions (**2b**) or (**3b**) react with sulphur, ArS_2^- ions (**2c**–**3c**) are obtained according to equilibrium (5) defined by the constant $K_3 = [ArS_2^-][ArS^-]^{-1}[S_8]^{-1/8}$ with $K_3 = 0.53$ $(\text{mol dm}^{-3})^{-1/8}$ (**2**) and $K_3 = 14.0$ (**3**).[11] The stability of ArS_2^- ions decreases when the electron attraction effect is enhanced in the aromatic ring[11] and 2,4-dinitrophenyl disulphide ions (**1c**) were not observed from the evolution of spectra when sulphur was added on ArS^- ions (**1b**).

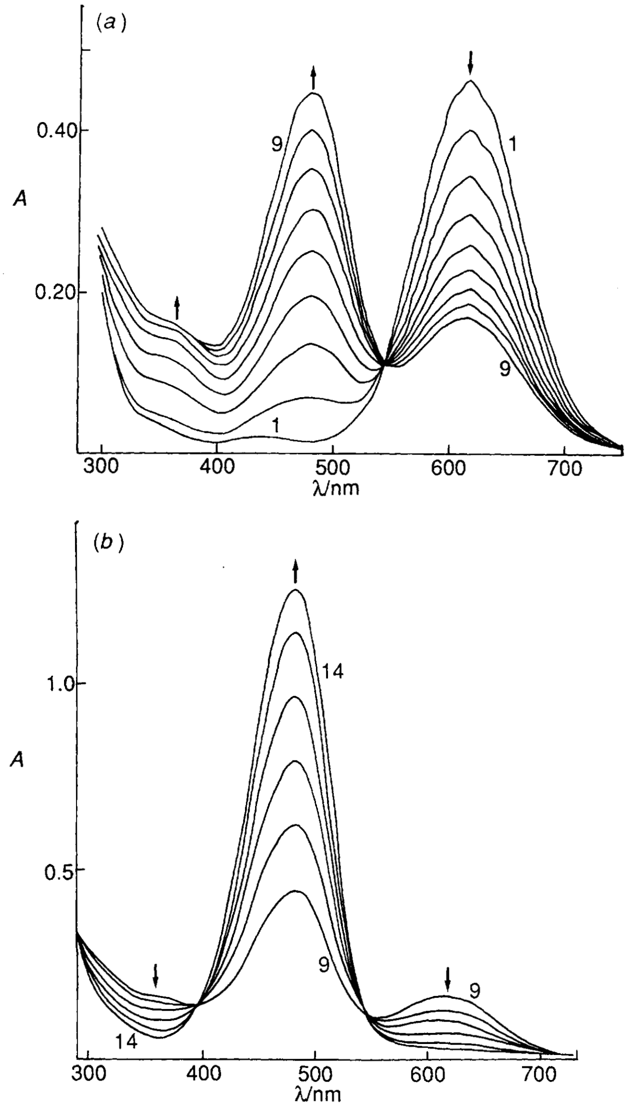


Fig. 1 (*a*) Evolution of UV–VIS absorption spectra during the addition of fluoro-2,4-dinitrobenzene to an S(−1/3) solution $C_0 = 1.15 \times 10^{-3}$ mol dm^{-3}. The thickness of the cell was 0.1 cm; $y = [\mathrm{ArX}]/C_0 = 0$ (1); 1/54 (2); 1/27 (3); 1/18 (4); 1/13.3 (5); 1/10.5 (6); 1/8.9 (7); 1/7.6 (8); 1/6.7 (9). (*b*) Reaction ArX (**1a**) + S(−1/3). y = 1/6.7 (9); 1/4.5 (10); 1/3.4 (11); 1/2.8 (12); 1/2.3 (13); 1/2.1 (14).

Spectrophotometric (λ_{max}, ε_{max}) and electrochemical characteristics (half-wave potentials of oxidation, O, or reduction, R) are summarized in Table 1.

In the concentration range chosen and with the experimental set-up used, reaction rates could be followed when the kinetic constants were within a defined interval (see the Experimental section). Under these conditions, the equilibrium states between species $S_6^{2-}/S_3^{\cdot -}$ [eqn. (7)], $S_8^{2-}/S_3^{\cdot -}$ [eqn. (8)] and ArS_2^-/ArS^- [eqn. (5)] were reached 'instantaneously'.

Stoichiometry of ArX + $S_3^{\cdot -}$ *Reactions*.—Non-activated substrates such as bromobenzene and 1-bromonaphthalene were unreactive towards polysulphide ions. Similarly, when 2-bromopyridine or 4-bromobenzophenone were added to $S_3^{\cdot -}$ solutions in the ratio $[\mathrm{ArX}]/[S_3^{\cdot -}]_0 = 10$, reaction did not occur to any appreciable extent. It occurred with a significant rate only in the case of halo(nitro)aromatic compounds **1a**, **2a** and **3a**.

The reaction is fast with fluoro-2,4-dinitrobenzene. When this derivative was added to a solution of $S_3^{\cdot -}$ ions in the proportion $y = [\mathrm{ArX}]/[S_3^{\cdot -}]_0$, the stoichiometric study was based on the spectral changes shown in Figs. 1(*a*) and (*b*) and on the voltammetry recordings (Fig. 2).

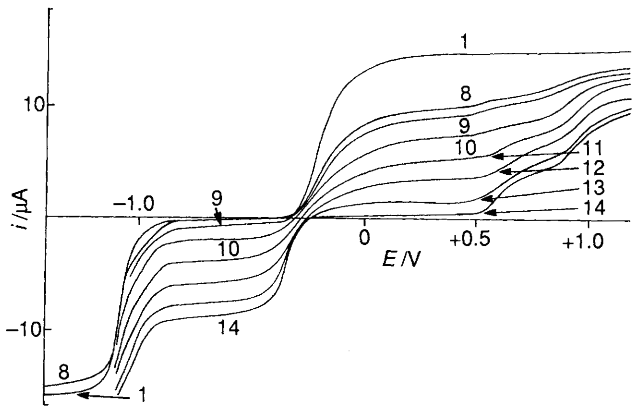


Fig. 2 Evolution of voltammograms during the reaction of ArX (**1a**) with S(−1/3). Same conditions as for Figs (1(*a*)–(*b*). Rotating gold-disc electrode Ω = 1000 rev min^{-1}, diameter = 2 mm; *E vs.* reference Ag/AgCl, KCl sat. in DMA/N(Et)$_4$ ClO$_4$ 0.1 mol dm^{-3}.

For values of y less than 1/7 (curves 1–8, Fig. 1), the absorption of $S_3^{\cdot -}$ ions (λ_{max} = 617 nm) decreased, whilst the absorption of ArS^- ions at λ = 480 nm increased; there was an isosbestic point at 540 nm. The consumption of S_8 arising from reaction (6) leads to S_8^{2-} ions according to eqn. (8) and is practically quantitative because of the excess of $S_3^{\cdot -}$ ions and the value of K_2. The presence of S_8^{2-} ions, masked by ArS^- ions at 515 nm, was detected at 360 nm (see Table 1). The spectral changes correspond to the balance (9) of reactions (6) + (8):

$$\mathrm{ArX} + 7\, S_3^{\cdot -} \longrightarrow \mathrm{ArS}^- + 5/2\, S_8^{2-} + X^- \qquad (9)$$

The molar absorption coefficients at 540 nm calculated for $S_3^{\cdot -}$ (1400 dm^3 mol^{-1} cm^{-1}), ArS^- (2000) and S_8^{2-} (3400) justify the isosbestic point at this wavelength. For $1/7 < y < 1/2$, [Fig. 1(*b*)] the absorption of ArS^- at 480 nm continued to increase at the expense of the residual absorption of $S_3^{\cdot -}$ ions and especially that of S_8^{2-} ions which were consumed (decrease in A_{360} and λ_{is} at 390 nm). Sulphur was then detected on the voltammograms (Fig. 2) by the appearance and increase of its reduction wave R_1 ($E_{1/2} = -0.34$ V *vs.* reference). For $0 < y < 1/2$, the oxidation currents of ArS^- ($E_{1/2} = +0.92$ V and +0.60 V) increased while that of the $S_3^{\cdot -}$ and S_8^{2-} ions ($E_{1/2} = -0.20$ V) decreased.

There was no spectral change when y was greater than 1/2, in compliance with the final balance (6), except for a slight decrease in A_{480}. The fact that the diarylsulphide Ar_2S could be obtained by reaction (10) could explain the slow decrease of

$$\mathrm{ArX} + \mathrm{ArS}^- \xrightarrow{k_1} \mathrm{Ar_2S} + X^- \qquad (10)$$

the ArS^- concentration. The study of the rates of these reactions will be discussed below.

In the case of ArX derivatives **2a** and **3a**, substitutions of $S_3^{\cdot -}$ were slow. ArS_2^- ions are among the products expected from the simultaneous presence of sulphur and thiolate ions in solution. Spectral changes occurring when fluoro-2-nitrobenzene was added are shown in Fig. 3; at the beginning of the reaction (curve 2) the absorption at $\lambda \sim 500$ nm increased at the expense of A_{617} ($S_3^{\cdot -}$), as a result of the formation of ArS^- (λ_{max} = 502 nm) and S_8^{2-} ions (λ_{max} = 515 nm) rather than ArS_2^- based on the values of K_2 and K_3. At the end of the

Table 1 Spectrophotometric and electrochemical characteristics of sulphur polysulphide ions[3,11] and aryldisulphide/thiolate ions[11] in DMA. Half-wave potentials at a rotating gold-disc electrode *vs.* reference[12] Ag/AgCl, KCl sat. in DMA/Et_4NClO_4 0.1 mol dm^{-3}.

					ArS^-			ArS_2^-		
Parameter	S_8	S_8^{2-}	S_6^{2-}	$S_3^{\bullet -}$	**1b**	**2b**	**3b**	**1c**	**2c**	**3c**
λ_{max}/nm ($\varepsilon/10^3$ $dm^3\ mol^{-1}\ cm^{-1}$)	262 (8.0)	360 (7.8) 515 (4.1) 617[a] (0.9)	460 (3.2) 345 (11.6)	617 (3.8)	480 (27.0)	502 (30.0)	502 (2.0)	— 617[a] (10.0)	600 (11.0) 617[a] (3.6)	681 (5.0)
Wave ($E_{1/2}$/V)	R_1 (−0.34) R_2 (−1.10)	R_2 (−1.10) O_1 (−0.20)	R_2 O_1	R_2 O_1	O (+0.92)	O (+0.67)	O (+0.55)	O (0.60)[b]	O (+0.27)	O (0.05)

[a] Absorption of the species at $\lambda = 617$ nm. [b] In the presence of sulphur, the catalytic oxidation of ArS^- ions (**1b**) is observed at 0.60 V because of the formation of ArS_2^- ions **1c** in the lone diffusion layer (see Fig. 2).

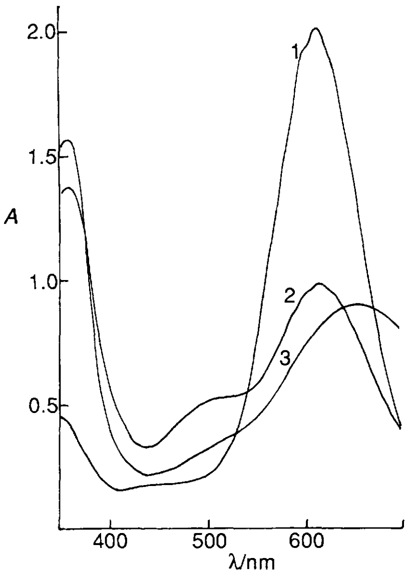


Fig. 3 Visible spectral changes during the reaction of fluoro-2-nitrobenzene with $S_3^{\bullet -}$ ions. $C_0 = 6.0 \times 10^{-3}$ mol dm^{-3}; $\xi_t = 0$ (1); 0.21 (2); 0.91 (3).

reaction (curve 3), only products ArS^- and above all ArS_2^- ($\lambda_{max} = 681$ nm) were detected. Regardless of the nature of X and the progress of the substitutions, these two types of ion were localized on the voltammograms by the same catalytic oxidation wave of ArS^- ions by sulphur, described elsewhere[11] [$E_{1/2} = +0.05$ V with **3** and +0.27 V with **2**].

$$ArS^- + 1/8\ S_8 \longrightarrow ArS_2^- \qquad (5)$$

$$ArS_2^- - e^- \longrightarrow 1/2\ Ar_2S_2 + 1/8\ S_8 \qquad (11)$$

Reactivity of ArS^- *and* ArS_2^- *Ions on* ArF *Derivatives*.—The fact that ArS^-/ArS_2^- solutions were obtained with derivatives **2** and **3** predicts that the reactions of ArS_x^- ions ($x = 1$ or 2) on aromatic halides occur very slowly in comparison with the substitution of polysulphide ions. This was verified by a study of their reactivity towards ArF compounds, fluorine generally being the best nucleofugic leaving group in S_NAr processes.[13] When the reactions occurred, the method was identical with that we recently described when comparing the nucleophilicities of nitrophenyl mono- and di-sulphides towards alkyl halides;[14] ArF compounds were first added to the solutions of thiolate ions arising from the electroreduction of diaryl disulphides Ar_2S_2 (**1c**–**3c**) and the changes in maximum absorption of ArS^- ions were recorded. Fluoro derivatives were also added to ArS^-/ArS_2^- solutions with defined initial composition, for Ar = *o*-, *p*-nitrophenyl (see the Experimental section); in this case, the competitive reactions (10) and (12) were followed by recording the evolution of the maximum absorptions of ArS^- (**2b**, **3b**) or ArS_2^- (**3c**) ions.

$$ArS_2^- + ArF \xrightarrow{k_2} ArS_2Ar + F^- \qquad (12)$$

Processing of the results[14] (Table 2), reveals that the reactions are second order. With compounds **3**, the determination of k_1 easily led to that of k_2 according to the model of concurrent reactions.

From the kinetic studies of the reactions with fluoro-2-nitrobenzene, the reactivity of aryldisulphide ions **2c**, **3c** appears to be higher than that of the corresponding thiolates **2b**, **3b**. These results agree with the enhanced nucleophilicities of ArS_2^- ions towards alkyl halides.[14] However, ArS_x^- ions ($x = 1,2$) generated by substitution of polysulphide ions on haloaromatics **2a**, **3a** are only slightly (Ar = *o*-nitrophenyl) or not at all (Ar = *p*-nitrophenyl) reactive towards the corresponding substrates ArX.

Kinetic Studies of the Reactions of Polysulphide Ions S(− 1/3) *with Halo(nitro)benzenes* **2a** *and* **3a**.—The kinetic study was carried out with initial solutions of substrate ArX at concentration $[ArX]_0$ and of sulphur S(−1/3) such that $C_0 = [S_3^{\bullet -}]_0 + 2[S_6^{2-}]_0$, based on the recording of the absorbance at the wavelength of the $S_3^{\bullet -}$ ions ($\lambda_{max} = 617$ nm) as a function of time. The progress ξ_t of the reaction is defined by eqn. (13).

$$\xi_t = \frac{[ArX]_0 - [ArS]_t}{0.5C_0} \qquad (13)$$

The order of the reaction concerning $S_3^{\bullet -}$ ions was initially determined for derivatives (**2**) by the initial-rate method. For $0 < \xi_t < 0.1$, the overall reaction (9) can be considered alone, since the formation of ArS_2^- is negligible in comparison with that of S_8^{2-} ions as a first approximation.

$$ArX + 7\ S_3^{\bullet -} \longrightarrow ArS^- + 5/2\ S_8^{2-} + X^- \qquad (9)$$

$$v_t = -\frac{d[ArX]_t}{dt} = -\frac{1}{7}\frac{dC_t}{dt} = -\frac{1}{7}\left(1 + \frac{4[S_3^{\bullet -}]}{K_1}\right)\frac{d[S_3^{\bullet -}]_t}{dt} = k_{obs}[ArX]_t[S_3^{\bullet -}]_t^n \qquad (14)$$

The initial rate v_0 was easily deduced from the absorption changes of $S_3^{\bullet -}$ ions at 617 nm, corrected by that of S_8^{2-} ions. For each ArX (**2a**) derivative (X = F, Cl, Br, I) the determination of v_0 for five pairs of values (C_0, $[ArX]_0$) with $4 \times 10^{-4} < C_0 < 3 \times 10^{-3}$ mol dm^{-3} led to the determination

Table 2 Rate constants $k_x{}^a$ (dm^3 mol^{-1} s^{-1}) of the reactions between thiolate or disulphide ions (**1b/c**–**3b/c**) with ArF compounds in DMA at 20.0 ± 0.5 °C. Ionic strength = 0.1 mol dm^{-3}.

ArS_x^-	x	**1a** (X = F)	**2a** (X = F)	**3a** (X = F)
1	1	2.3	—	—
2	1	f^b	Nr^c	Nr
	2	f	Nr	0.7 × 10^{-3}
3	1	f	—	0.12 × 10^{-2}
	2	f	—	2.20 × 10^{-2}

[a] Mean values ±8% from duplicate runs. [b] f = fast with respect to experimental conditions ($k_x > 100$). [c] Nr = no reaction after addition of [ArF] = 5.0 × 10^{-2} mol dm^{-3} in $[ArS_x^-] = 10^{-3}$ mol dm^{-3}.

Table 3 Experimental values of order relative to $S_3^{\cdot -}$ and rate constants $k_{obs}{}^a$ (dm^6 mol^{-2} s^{-1}) of the reactions between halo-4-nitrobenzene **2a** and S(−1/3) ions at 20.0 ± 0.5 °C. Ionic strength = 0.1 mol dm^{-3}.

X	n	k_{obs}
F	2.06	120
Cl	1.95	30
Br	1.98	67
I	2.00	90

[a] k_{obs} values ±10%.

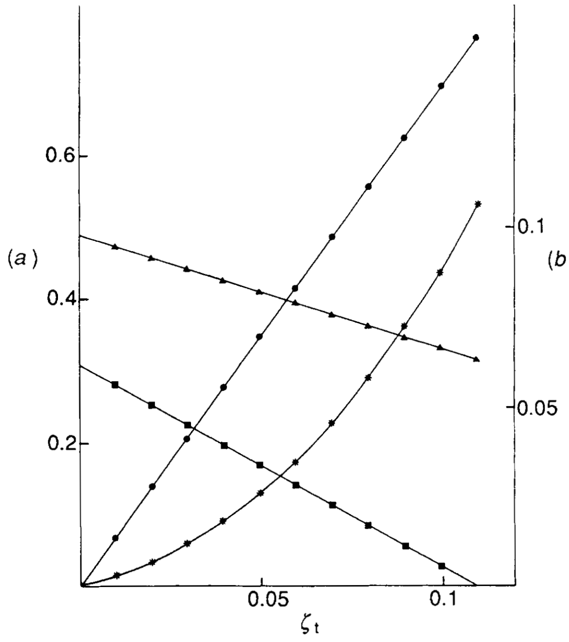


Fig. 4 Variation of ArI, $S_3^{\cdot -}$, S_8^{2-} and ArS_2^- concentrations during the progress of the reaction of iodo-4-nitrobenzene with $S_3^{\cdot -}$ ions. $[ArI]_0 = 0.300 \times 10^{-3}$ mol dm^{-3} $[S_3^{\cdot -}]_0 = 4.82 \times 10^{-3}$ mol dm^{-3}. (*a*) [ArI] × 10^3 mol dm^{-3} ■, $[S_3^{\cdot -}] \times 10^2$ mol dm^{-3} (▲); $[S_8^{2-}] \times 10^3$ mol dm^{-3} (●); (*b*) $[ArS_2^-] \times 10^4$ mol dm^{-3} (✱). Calculated a_j^i coefficients for this typical experiment: $a_0^{Ar} = -0.548 \times 10^{-3}$; $a_1^{Ar} = 0.176$; $a_0^8 = 0.211 \times 10^{-2}$; $a_1^8 = -0.437$; $a_0^2 = 0.75 \times 10^{-4}$; $a_1^2 = -0.0304$; $a_2^2 = 3.07$.

of n and the evaluation of k_{obs}, eqn. (15). The results are listed in Table 3.

$$\log v_0/[ArX]_0 = \log k_{obs} + n \log [S_3^{\cdot -}]_0 \quad (15)$$

The second order obtained for $S_3^{\cdot -}$ led us to propose that the S_6^{2-} ions are effective nucleophilic agents in the substitution of polysulphide ions (S(−1/3) on activated aromatic halides. The hypothesis of a trimolecular process in the rate-determining step is relatively improbable. The rate is thus characterized by eqn. (16) with $k_3 = k_{obs} K_1$.

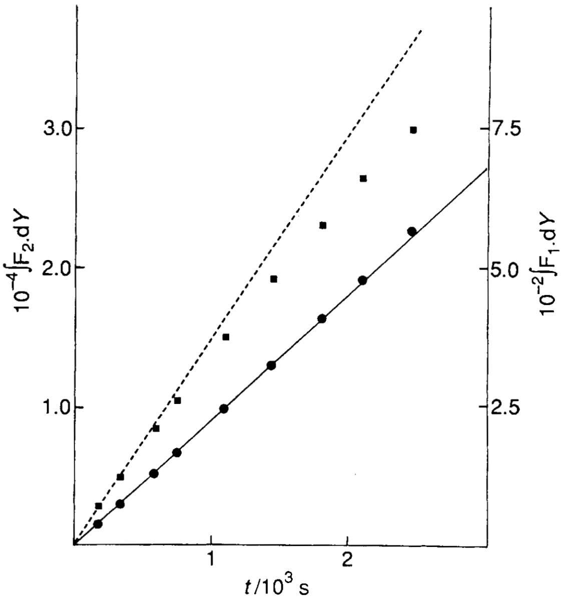


Fig. 5 Kinetic studies of the reaction of iodo-4-nitrobenzene with $S_3^{\cdot -}$ ions. Same conditions as for Fig. 4. Calculations assuming first order (■) and second order (●) with respect to $S_3^{\cdot -}$ ions. $k_{obs} = 9.08$ dm^6 mol^{-2} s^{-1}.

$$v_t = k_3[ArX]_t[S_6^{2-}]_t \quad (16)$$

A precise kinetic study was then carried out with the halo-nitrobenzene series (**2a**) and (**3a**). At $\lambda = 617$ nm, only the absorptions of the $S_3^{\cdot -}$, S_8^{2-} and ArS_2^- ions need be considered (Table 1).

$$A_{617}^t/1 = \varepsilon_3[S_3^{\cdot -}]_t + \varepsilon_8[S_8^{2-}]_t + \varepsilon_2[ArS_2^-]_t \quad (17)$$

For $0 < \xi_t < 0.1$, side reactions of ArX with the S_8^{2-}, ArS^- and ArS_2^- ions were neglected. In these conditions, the concentrations of species in solution are linked by 'instantaneously' established equilibria (7), (8) and (5), with constants K_1, K_2 and K_3, and by the conservation equations of charges and of the initial concentrations of Ar derivative and sulphur. The concentrations were determined for each reaction by a calculation program using a dozen values chosen for ξ_t. A_{617}, calculated by means of eqn. (17), led to time t, noted on the experimental curve and corresponding to ξ_t. Concentrations $[ArX]_t$, $[S_8^{2-}]_t$ and $[ArS_2^-]_t$ could be expressed as a simple polynomial, as a function of $[S_3^{\cdot -}]_t$ (noted Y_t), from their changes with time; one example is shown in Fig. 4.

$$[ArX]_t = a_0^{Ar} + a_1^{Ar} Y_t \quad (18)$$

$$[S_8^{2-}]_t = a_0^8 + a_1^8 Y_t \quad (19)$$

$$[ArS_2^-]_t = a_0^2 + a_1^2 Y_t + a_2^2 Y_t^2 \quad (20)$$

The combination of eqns. (17)–(20) enabled $[S_3^{\cdot -}]_t = f(t)$ to be obtained. A simple kinetic equation was then deduced from eqn. (16) for v_t and tested by assuming first or second order with reference to $S_3^{\cdot -}$ (see Fig. 5 linked to the experimental

$$\int_{Y_0}^{Y_t} F(Y_t)\, dY = k_{obs} t \quad (21)$$

Table 4 Rate constants $k_3{}^a$ and $k_4{}^a$ ($dm^3\ mol^{-1}\ s^{-1}$) of the reactions of S_6^{2-} and S_8^{2-} ions on halo-4-nitrobenzenes **2a** and -2-nitrobenzenes **3a** at 20.0 ± 0.5 °C. Ionic strength = 0.1 mol dm^{-3}.

Ar		F	Cl	Br	I
2	k_3	9.1	2.2	5.5	6.4
	k_4	0.13	0.021	0.11	0.11
3	k_3	10.8	1.3	2.3	2.1
	k_4	0.13			

[a] Mean values of k_3 and k_4 ± 5% from deviation of several kinetic runs.

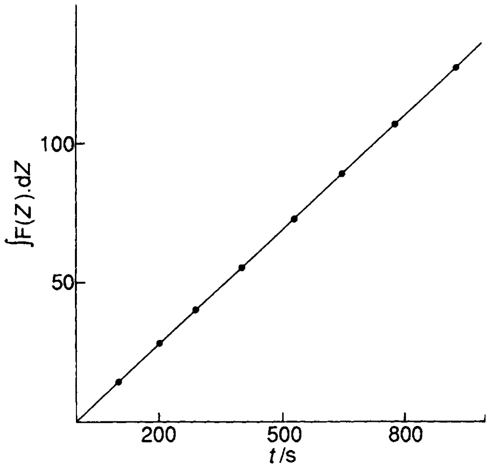


Fig. 6 Kinetic studies of the reaction of bromo-4-nitrobenzene with S_8^{2-} ions. $[ArX]_0 = 1.03 \times 10^{-3}$ mol dm^{-3}; $[S_8^{2-}]_0 = 1.72 \times 10^{-3}$ mol dm^{-3}; $[S_3^{\cdot -}]_0 = 0.50 \times 10^{-3}$ mol dm^{-3}; $[S_8]_0 = 5.0 \times 10^{-3}$ mol dm^{-3}. Calculated a'^{i}_{j} coefficients: $a'^{8}_{0} = 1.72 \times 10^{-3}$; $a'^{8}_{1} = -1.20$. $k'_{obs} = 0.1375\ dm^3\ mol^{-1}\ s^{-1}$.

$$F_n(Y_t) = -a_1^{Ar}[(a_0^{Ar} + a_1^{Ar}Y_t)Y_t^n]^{-1} \qquad (22)$$

conditions of Fig. 4) eqns. (21) and (22) with $n = 1$ or 2, depending on the assumed order.

That the reaction was second order with respect to $S_3^{\cdot -}$, as previously deduced from the study of the initial rates, was confirmed in all cases and no significant autoacceleration, caused by the possible reaction of S_8^{2-} ions with ArX, was observed. The rate constants k_3 of the reactions of S_6^{2-} ions with aromatic halides **2a** and **3a** are listed in Table 4.

Kinetic Studies of the Reactions of S_8^{2-} *Ions with Some Halo(nitro)benzenes.*—Solutions of S_8^{2-} ions were obtained by partial electrolysis of concentrated solutions of sulphur, close to saturation (see the Experimental section). The concentrations $[S_3^{\cdot -}]_0$ and $[S_6^{2-}]_0$ calculated from constants K_1 and K_2, were always very small in comparison with $[S_8^{2-}]_0$ deduced from the spectrum ($\lambda_{max} = 515$ nm). The study of the reactivity of S_8^{2-} ions with halo-4-nitrobenzenes **2a** was carried out in a manner similar to that of S(−1/3) ions, based on $A_{502} = f(t)$ recordings. At 502 nm, only the absorptions of S_8^{2-} and ArS^- need be taken into consideration (Table 1).

$$A^t_{502}/1 = \varepsilon_8[S_8^{2-}]_t + \varepsilon_1[ArS^-]_t \qquad (23)$$

Concurrent reactions (24) and (25) should also be considered

$$ArX + S_6^{2-} \xrightarrow{k_3} ArS^- + 5/8\ S_8 + X^- \qquad (24)$$

$$ArX + S_8^{2-} \xrightarrow{k_4} ArS^- + 7/8\ S_8 + X^- \qquad (25)$$

These correspond to the same formation balance for the mixture ArS^-/ArS_2^-, since the sulphur concentration remained practically constant. From eqns. (5) and (8), we obtain eqns. (26) and (27).

$$[ArS_2^-]_t = \gamma[ArS^-]_t \quad \text{with} \quad \gamma = [S_8]^{1/8}K_3 \qquad (26)$$

$$[S_8^{2-}]_t = \beta[S_3^{\cdot -}]_t^2 \quad \text{with} \quad \beta = [S_8]^{1/4}K_2^{-1} \qquad (27)$$

Assuming that the reactions are first order with respect to S_8^{2-}, as for S_6^{2-}, the rate of substitution of polysulphide ions is expressed by formula (28).

$$v_t = -\frac{d[ArX]_t}{dt} = (1 + \gamma)\frac{d[ArS^-]_t}{dt} = (k_3[S_6^{2-}]_t + k_4[S_8^{2-}]_t)[ArX]_t \qquad (28)$$

$$v_t = k'_{obs}[ArX]_t[S_8^{2-}]_t \qquad (29)$$

with $$k'_{obs} = k_4 + k_3(K_1\beta)^{-1}$$

and $$[ArX]_t = [ArX]_0 - [ArS^-]_t(1 + \gamma)$$

On the basis of the conservation of mass equations, $[ArS^-]_t$ and $[S_8^{2-}]_t$ can be easily calculated for different chosen values of ξ_t and a simple expression of $[S_8^{2-}]_t$ as a function of $[ArS^-]_t = Z_t$ is accessible in the form of eqn. (30). $[ArS^-]_t$

$$[S_8^{2-}]_t = a'^{8}_{0} + a'^{8}_{1}Z_t \qquad (30)$$

was then deduced from the experimental variation of $A_{502} = f(t)$ and the following kinetic equation [eqn. (31)] could be

$$\int_{Z_0}^{Z_t} F(Z_t)dZ = k'_{obs}t \qquad (31)$$

established with $(1 + \gamma)\ F(Z_t)^{-1} = a'^{8}_{0}R_0 + [a'^{8}_{1}R_0 - a'^{8}_{0}(1 + \gamma)]Z_t - a'^{8}_{1}(1 + \gamma)Z_t^2$ and $R_0 = [ArX]_0$.

Calculations confirmed first order with reference to S_8^{2-} for all the substitutions of aromatic halides **2a** (see Fig. 6 for one example) and led to the constants k_4 listed in Table 4. The same method was applied with fluoro-2-nitrobenzene, based on changes in $A_{681} = f(t)$. In this case, the competitive reaction $ArX + ArS_2^-$ ($k_2 = 2.2 \times 10^{-2}\ dm^3\ mol^{-1}\ s^{-1}$ from Table 2) caused an autoacceleration phenomenon shown on the integrations for $\xi_t >$ *ca.* 1/6, and the decrease in absorption of ArS_2^- when ArF was in excess.

Discussion

There is no reaction in DMA between $S_3^{\cdot -}$ ions and non-activated ArX substrates, such as bromobenzene or 1-bromonaphthalene. This enables the probability of an $S_{RN}1$ mechanism[15,16] to be eliminated, where the initial step involves electron transfer, leading to the anion radical $ArX^{\cdot -}$.

$$ArX + S_3^{\cdot -} \longrightarrow ArX^{\cdot -} + 3/8\ S_8 \qquad (32)$$

The fact that reactions are observed only with haloaromatics activated by strong electron-withdrawing NO_2 substituents is consistent with an S_NAr mechanism, often observed in dipolar aprotic media.[13] In the course of substitution of $O_2^{\cdot -}$ ions, the formation of the σ complex $ArXO_2^{\cdot -}$ was revealed by cyclic voltammetry.[9] The $S_8^{2-}/S_4^{\cdot -}$ equilibrium has been proposed for polysulphide ions S(−1/4),[17] as established for S(−1/3) between S_6^{2-} and $S_3^{\cdot -}$.[2,3] The analogy of the reactivity of $O_2^{\cdot -}$

Table 5 Calculated charge distribution on anionic sulphur chains S_x^{y-} from Meyer *et al.*[18]

S–S–S ---
1 2 3

x	y	S(1)	S(2)	S(3)	S(4)
3	−1	−0.38	−0.24		
4	−1	−0.34	−0.16		
6	−2	−0.50	−0.30	−0.20	
8	−2	−0.47	−0.27	−0.15	−0.11

ions with S(−1/3) or S(−1/4), observed particularly in the case of alkyl halides,[4] is consistent with the initial addition of anion radicals $S_3^{\cdot -}$ or $S_4^{\cdot -}$ and obtaining intermediate complexes $ArXS_3^{\cdot -}$ and $ArXS_4^{\cdot -}$. Based on our study, order 2 for $S_3^{\cdot -}$ and order 1 for S_8^{2-} led us to propose that the dianions S_6^{2-} and S_8^{2-} were effective nucleophiles during substitutions, with the following order of reactivity: $S_6^{2-} > S_8^{2-} \gg S_3^{\cdot -}, S_4^{\cdot -}$. This observation may be perhaps interpreted in terms of electron-density distribution on the sulphur atoms of the different ions. The results of calculations carried out by Meyer *et al.*,[18] using the extended Hückel method (Table 5), show that the charge is more diffuse in the anion radicals.

The mechanism can thus be summarized by eqns. (33)–(35).

$$ArX + S_x^{2-} \xrightarrow{k} ArS_x^- + X^- \quad \text{slow} \qquad (33)$$

$$ArS_x^- \longrightarrow ArS_2^- + \frac{(x-2)}{8} S_8 \quad \text{fast} \qquad (34)$$

$$ArS_2^- \rightleftharpoons ArS^- + 1/8\, S_8 \quad \text{fast} \qquad (35)$$

Arylpolysulphide ions arising from the initial slow step are rapidly transformed into the stable ions ArS_2^- and ArS^- in the equilibrium.

Of all the ArX derivatives studied, fluorine is the best nucleofuge of the halogens, as is generally the case for S_NAr reactions. The order of reactivity, F > Br, I > Cl, is the same as that noted during the reaction between halo(nitro)benzenes and the KO_2–crown ether complex in benzene.[6]

The nucleophilicity of S_6^{2-} ions towards activated aryl halides in DMA is equivalent to that noted for $O_2^{\cdot -}$ ions in DMF[7] (at 20 °C k = 9.0 dm^3 mol^{-1} s^{-1} for the reactions $4\text{-}NO_2C_6H_4F + O_2^{\cdot -}$ and $k < 2.0$ with $4\text{-}NO_2C_6H_4Cl$). Their reactivity is higher than that of benzenethiolate ions[19] considered to be among the most powerful nucleophilic agents (k = 4.0 dm^3 mol^{-1} s^{-1} with $4\text{-}NO_2C_6H_4F$ and 0.25 with $4\text{-}NO_2C_6H_4I$ in DMF at 25 °C).

Experimental

Materials and Equipment.—Aryl halides, diaryl disulphides, sulphur and dimethylacetamide were commercially available reagent-grade products. Sulphur and diaryl disulphides were recrystallized from benzene. DMA distilled under reduced nitrogen pressure was added to 0.1 mol dm^{-3} tetraethylammonium perchlorate as the supporting electrolyte, stored over 4 Å molecular sieves and used within one week of distillation.

Electrochemical equipment, electrodes and the thermostatted flowthrough cell have been described previously.[3] Absorption spectra were obtained with a Kontron Uvikon 930 spectrophotometer.

Generation of $S_3^{\cdot -}$, S_8^{2-} *and* ArS^-/ArS_2^- *Solutions.*—All initial anionic solutions were prepared by controlled-potential electrolysis. The course of the reaction was followed by classic voltammetry with a rotating gold-disc electrode. Their composition was determined precisely from the UV–VIS spectra, using known spectrophotometric characteristics (Table 1) and the values of constants K_1, K_2 and K_3. Electrolysis was carried out in the cell with a large gold grid electrode as the cathode on 35 cm^3 of sulphur or diaryl disulphide solutions. The cathodic and anodic compartments were separated by No. 4 sintered porous glass.

$S_3^{\cdot -}$ solutions were prepared by the electroreduction of S_8[3] on the plateau of its second reduction wave R_2 (at E = −1.3 V *vs.* reference), up to 8/3 F mol^{-1} S_8, according to eqn. (36).

$$S_8 + 8/3\, e^- \longrightarrow 8/3\, S_3^{\cdot -} \qquad (36)$$

All initial concentrations, C_0 used for the kinetic runs were included between 5 × 10^{-4} and 6 × 10^{-3} mol dm^{-3}. As an example, for C_0 = 5 × 10^{-3} mol dm^{-3}, $[S_3^{\cdot -}]_0$ = 4.44 × 10^{-3} mol dm^{-3} and $[S_6^{2-}]_0$ = 0.28 × 10^{-3} mol dm^{-3}.

Solutions of S_8^{2-}, the concentration of which was always close to 2 × 10^{-3} mol dm^{-3}, were obtained by partial electrolysis of concentrated sulphur solutions[3] (of the order of 8 × 10^{-3} mol dm^{-3}) on the plateau of its first reduction wave R_1 (at E = −0.7 V *vs.* reference) according to eqns. (37) and (8).

$$S_8 + 2\, e^- \longrightarrow S_8^{2-} \qquad (37)$$

$$S_8^{2-} \rightleftharpoons 2\, S_3^{\cdot -} + 1/4\, S_8 \qquad (8)$$

The presence of an excess of sulphur shifts the disproportionation equilibrium to the left. Thus, the reactivity of S_8^{2-} ions with fluoro-4-nitrobenzene was studied using a solution of initial composition $[S_8^{2-}]_0$ = 1.43 × 10^{-3} mol dm^{-3}, $[S_3^{\cdot -}]_0$ = 0.39 × 10^{-3} mol dm^{-3}, $[S_6^{2-}]_0$ = 2.2 × 10^{-6} mol dm^{-3} and $[S_8]_0$ = 6.0 × 10^{-3} mol dm^{-3}.

Solutions of ArS^- ions (**1b**–**3b**) such as 6 × 10^{-4} mol dm^{-3} (**1b** and **2b**) < $[ArS^-]_0$ < 5 × 10^{-3} (**3b**) were generated in a similar way by reduction of symmetrical disulphides at a fixed potential on their bielectronic wave,[20] according to the overall reaction (38).

$$Ar_2S_2 + 2\, e^- \longrightarrow 2\, ArS^- \qquad (38)$$

The addition of defined quantities of a sulphur solution at 9 × 10^{-3} mol dm^{-3} in the case of derivatives **2** and **3** led to solutions ArS^-/ArS_2^-.

Rate Measurements.—A small volume of concentrated solution of ArX compounds (V_{max} = 1 cm^3) was added to solutions S(−1/3), S(−1/4) or ArS^-/ArS_2^- at 20.0 ± 0.5 °C. Changes in absorbance were recorded *vs.* time at 617 nm ($ArX + S_3^{\cdot -}$), 502 nm ($ArX + S_8^{2-}$), or at λ_{max} for the ions ArS^- **1b**, **3b** or ArS_2^- **3c** (reactions $ArS^- + ArX$). This enabled the kinetic characteristics reported in this study to be deduced. The precision of results was assigned for the 'fast' reactions by the transfer of the solution from the reaction medium to the spectrophotometric cell (l = 1 mm pathlength), which took about 8 s. In addition, solutions of $S_3^{\cdot -}$ and S_8^{2-} ions were slightly sensitive to reoxidation and their concentrations diminished by 2 to 3% per hour. In these conditions, the rate constants of the reactions $ArX + S_6^{2-}$ (k_3) and $ArX + S_8^{2-}$ (k_4) can be evaluated in the intervals

$$5000 > k_3/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} > 3 \times 10^{-4}$$

$$20 > k_4/\text{dm}^3\,\text{mol}^{-1}\,\text{s}^{-1} > 3 \times 10^{-4}$$

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