Dehalogenation of Vicinal Dibromides by Electrogenerated Polysulfide Ions in Dimethylacetamide

Gérard Bosser and Jacky Paris *
Laboratoire de Synthèse et d'Etudes Physico-chimiques Organiques, UFR Sciences, Parc de Grandmont, 37200 Tours, France

Dehalogenation reactions of vic-dibromides by electrogenerated S_6^{2-} ($\rightleftharpoons S_3^{\bullet -}$), S_4^{2-} or S_3^{2-} polysulfide ions have been investigated in dimethylacetamide by use of spectroelectrochemistry on a series of dibromides: methyl *erythro*-2,3-dibromo-3-phenylpropanoate (**1**), diethyl *meso*-2,3-dibromosuccinate (**2**), *meso*-1,2-dibromo-1,2-diphenylethane (**3**), DL-1,2-dibromo-1,2-diphenylethane (**4**), 1,2-dibromobutane (**5**), 1,2-dibromophenylethane (**6**), DL-2,3-dibromobutane (**7**), *erythro*-3,4-dibromoheptane (**8**), *threo*-3,4-dibromoheptane (**9**), *meso*-5,6-dibromodecane (**10**), *trans*-1,2-dibromocyclohexane (**11**). Substitution and elimination are competing mechanisms with **5**–**7** while the quantitative formation of alkenes is observed with the other substituted dibromides. In dilute solutions, indirect electrochemical reductions of vic-dibromides have been performed in the presence of small amounts of sulfur as catalyst at potentials leading to $S(-\frac{1}{3})$ ions with **1**–**3**, or at more cathodic potentials (formation of S_4^{2-}/S_3^{2-} ions) for **8**–**11**. On a preparative scale, stereospecific *anti* debrominations afford only *E* alkenes from chemical reaction with **3** or mediated electrolysis of **1**, **2** or **10**. Kinetic studies of the reactions between $S(-\frac{1}{3})$ ions and compounds **4**, **8**–**10** imply that the dianions S_6^{2-} are the eliminating agents rather than $S_3^{\bullet -}$ radical ions for the concerted *anti* dehalogenations.

Dehalogenation of vic-dibromides to alkenes using a very large number of reagents such as metal or transition-metal complexes, anions and other nucleophiles, has been recently reviewed.[1] Among the many possible anionic species, sulfide ions have been proposed in aqueous media under phase-transfer conditions[2] or in dimethylformamide.[3]

Vicinal dibromides are also converted into the parent alkenes by electrochemical reduction in aprotic media[1,4] according to an overall two-electron reaction. Indirect reductions have been

$$\text{–CHBr–CHBr–} + 2e^- \longrightarrow \text{–}\underset{|}{\text{C}}\text{H=}\underset{|}{\text{C}}\text{H–} + 2Br^- \qquad (1)$$

performed at lower cathodic overpotentials by using electrogenerated aromatic anion radicals[1,4c] or reduced states of metalloporphyrins.[1,4f]

Polysulfide ions S_8^{2-}, S_6^{2-} ($\rightleftharpoons S_3^{\bullet -}$), S_4^{2-} can be generated in dipolar aprotic media *via* a cathodic reduction of sulfur.[5] In previous papers, we reported on the nucleophilic properties of the stable species S_8^{2-} and S_6^{2-}: with alkyl halides, the S_N2 substitutions lead to dialkyl tri- and tetra-sulfides[6] whereas aryldisulfide ions are obtained from S_NAr processes on activated haloaromatics.[7]

We examine here the reductive debromination of vic-dibromides using electrogenerated polysulfide ions in dimethylacetamide (DMA). Reactions of the stable solutions of S_6^{2-} ($\rightleftharpoons S_3^{\bullet -}$) ions with a series of eleven vic-dibromides, which are listed in Table 1, have been directly studied. UV–VIS absorption spectrophotometry coupled with classic voltammetry enables the reactions or their kinetics to be followed. Indirect electrolysis of dibromides in the presence of small amounts of sulfur at potentials corresponding to the formation of S_6^{2-} or S_4^{2-}/S_3^{2-} ions, have been performed at the preparative scale on several substrates.

Results and Discussion

Characteristics of Sulfur/Polysulfide Ions and vic-Dibromoalkanes in DMA.—The reactivity of polysulfide ions towards dibromides in DMA was determined by use of the known electrochemical and spectrophotometric characteristics of the sulfur/polysulfide ions system[5,7] and those of the dibromide species which we determined.

The electrochemical reduction of sulfur on a rotating gold, platinum or glassy carbon microelectrode occurs in two two-electron steps shown by two waves of equal intensity (R_1 and R_2). Overpotentials were lowest with the gold electrode, which was chosen for this work. The stable product of the first step of electrolysis of sulfur at controlled potential is the intense blue anion-radical $S_3^{\bullet -}$ (λ^3_{max} = 617 nm, ε^3_{617} = 3800 dm^3 mol^{-1} cm^{-1}; ε^3_{515} = 280), resulting from the disproportionation of the carmine red S_8^{2-} ion (λ^8_{max1} = 515 nm, ε^8_{515} = 4100; λ^8_{max2} = 357 nm, ε^8_{357} = 7800; ε^8_{617} = 900) generated at the electrode surface (R_1, $E_{\frac{1}{2}} = -0.34$ V *vs.* ref.).†

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

$$K_1 = [S_3^{\bullet -}]^2[S_8]^{\frac{1}{4}}[S_8^{2-}]^{-1} = 5.0 \times 10^{-5}\ (\text{mol dm}^{-3})^{5/4}$$

The complete elimination of sulfur leads to $S_3^{\bullet -}$ ions in equilibrium with their dimer S_6^{2-} (λ^6_{max1} = 465 nm; ε^6_{465} = 3000; λ^6_{max2} = 345 nm; ε^6_{345} = 11 000).

$$S_6^{2-} \rightleftharpoons 2S_3^{\bullet -} \qquad (3)$$

$$K_2 = [S_3^{\bullet -}]^2[S_6^{2-}]^{-1} = 0.07\ \text{mol dm}^{-3}$$

The $S(-\frac{1}{3})$ and S_8^{2-} ions were in turn oxidised to sulfur (O_1, $E_{\frac{1}{2}} = -0.20$ V *vs.* ref.) and reduced to S_3^{2-} and S_4^{2-} ions (R_2, $E_{\frac{1}{2}} = -1.10$ V). The latter, highly reactive species, reoxidised slowly in the solvent to $S_3^{\bullet -}$ ions. The concentrations of S_8^{2-}, $S_3^{\bullet -}$ and S_6^{2-} ions could be easily determined by using their spectrophotometric characteristics and constants K_1 and K_2. The sulfur concentration was generally deduced from the limit

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† All potentials are expressed in comparison to the reference electrode[5] Ag/AgCl, KCl saturated in DMA/Et_4NClO_4 0.1 mol dm^{-3}.

Table 1 Reduction half-wave potentials[a,b] *vs.* ref. at a rotating gold-disc electrode and spectrophotometric characteristics[c] of vic-dibromides in DMA

Dibromide	$E_{\frac{1}{2}}$/V	λ_{max}/nm	ε/dm³ mol⁻¹ cm⁻¹
Methyl *erythro*-2,3-dibromo-3-phenylpropanoate (**1**)	−0.96	260	3300
Diethyl *meso*-2,3-dibromosuccinate (**2**)	−0.88	262	500
meso-1,2-Dibromo-1,2-diphenylethane (**3**)	−1.10	268	5000
DL-1,2-Dibromo-1,2-diphenylethane (**4**)	−1.30	262	4000
1,2-Dibromobutane (**5**)	−1.52		
1,2-Dibromophenylethane (**6**)	−0.88	261	2000
DL-2,3-Dibromobutane (**7**)	−1.65		
erythro-3,4-Dibromoheptane (**8**)	−1.48		
threo-3,4-Dibromoheptane (**9**)	−1.55		
meso-5,6-Dibromodecane (**10**)	−1.42		
trans-1,2-Dibromocyclohexane (**11**)	−1.40		

[a] Mean value ±0.10 V. [b] Prewaves (pw) are generally noted at 0.30–0.50 V lower cathodic potentials with $i_{pw}/i_T \simeq \frac{1}{3}$. [c] ε ± 15%.

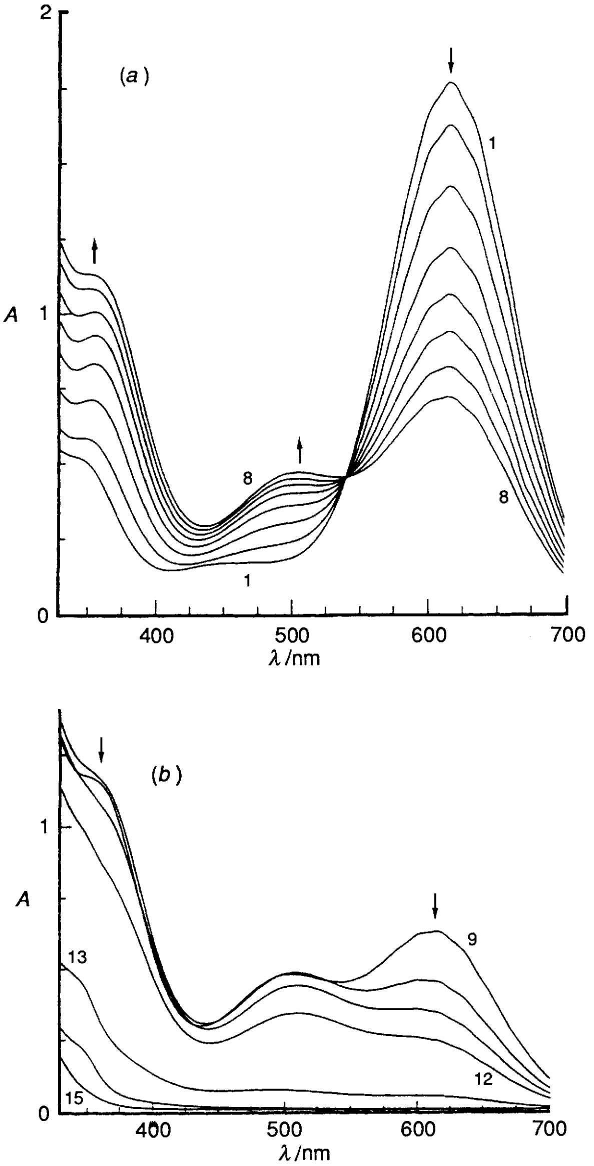

Fig. 1 (*a*) Evolution of UV–VIS absorption spectra during the addition of diethyl *meso*-2,3-dibromosuccinate (**2**) to an S($-\frac{1}{3}$) solution C_0 = 5.28 × 10⁻³ mol dm⁻³. The thickness of the cell was 0.1 cm; y = $[RBr_2]/C_0$ = 0 (1); 1/81 (2); 1/41 (3); 1/27 (4); 1/20 (5); 1/16 (6); 1/13.5 (7); 1/11.5 (8). (*b*) Reaction RBr_2 (**2**) + S($-\frac{1}{3}$): y = 1/10 (9); 1/7.8 (10); 1/6.2 (11); 1/4.5 (12); 1/2.7 (13); 1/2.3 (14); 1/2.0 (15).

intensity of its diffusion wave R_1 ($E_{\frac{1}{2}} = -0.34$ V) after calibration, or from its maximal absorption at 262 nm (ε = 8000 dm³ mol⁻¹ cm⁻¹) if there were no interferences.

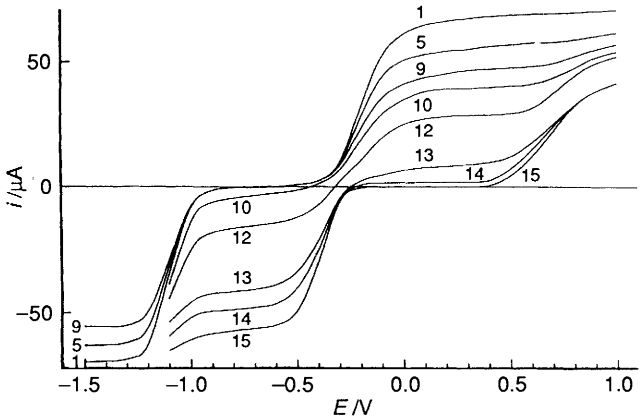

Fig. 2 Evolution of voltammograms during the reaction of dibromide **2** with S($-\frac{1}{3}$). Same conditions as for Figs. 1(*a*)–(*b*). Rotating gold-disc electrode, Ω = 1000 rev min⁻¹, diameter = 2 mm; *E vs.* reference Ag/Ag Cl, KCl sat. in DMA/NEt_4ClO_4 0.1 mol dm⁻³.

The reduction of vic-dibromides in an aprotic medium was shown by an irreversible wave whose reproducibility on platinum or gold electrodes is often approximate.[4e] The same was true in DMA, where currents and potentials on the voltammograms changed with successive plots. Table 1 lists the mean values of measured $E_{\frac{1}{2}}$ potentials and the characteristics of any maximal absorptions of the vic-dibromides studied.

The easier reduction of *meso*-**3** and *erythro*-**8** forms in comparison to that of the respective DL-**4** and *threo*-**9** forms agrees with the general observation[1] summarised by Brown *et al.*[4e] that 'species which can most readily assume an *anti*-conformation are most easily reduced'.

Reactivity of Polysulfide Ions S($-\frac{1}{3}$) *with vic-Dibromides.*—This study was carried out in the same way with each compound **1**–**11**: a concentrated solution of vic-dibromide (noted RBr_2) in DMA was progressively supplemented with an S($-\frac{1}{3}$) solution of concentration, $C_0 = [S_3^{\cdot -}]_0 + 2[S_6^{2-}]_0$ close to 5 × 10⁻³ mol dm⁻³.

In the case of species **1**, **2** and **3** the reactions were fast under our experimental conditions (see Experimental section, kinetic studies) and changes in the spectra and the curves $i = f(E)$ were used to determine their stoichiometry [examples in Figs. 1 and 2 of the addition of diethyl *meso*-2,3-dibromosuccinate (**2**) to a solution of C_0 = 5.28 × 10⁻³ mol dm⁻³]: as long as the ratio $y = [RBr_2]/C_0$ remained less than 0.12, A_{617} ($S_3^{\cdot -}$) decreased while A_{515} (S_8^{2-}), (λ_{is} = 543 nm), and A_{357} (S_8^{2-}) increased. For $0.12 < y < 0.5$ A_{515} began to decrease and sulfur was detected on the voltammograms by its reduction wave R_1 ($E_{\frac{1}{2}} = -0.34$ V), while the first oxidation wave of bromide ions ($3Br^- \longrightarrow Br_3^- + 2e^-$) increased ($E_{\frac{1}{2}} \simeq +0.70$ V). At the stoichiometry of $[RBr_2]/C_0 = 0.5$, the solution was bleached.

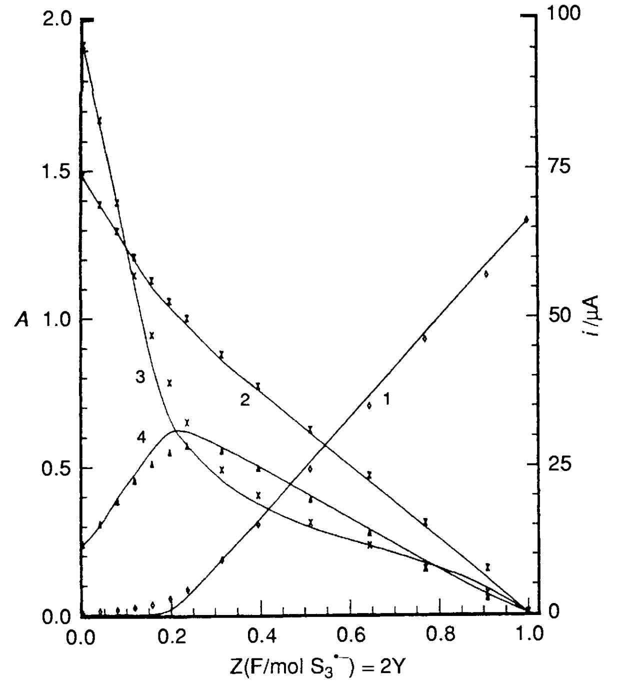

Fig. 3 Calculated curves of iR_1 (1), iO_1 (2), A_{617} (3), A_{515} (4) as a function of z(F/mol $S_3^{\cdot -}$) compared to the experimental values during the addition of methyl *erythro*-2,3-dibromo-3-phenylpropanoate to a $S(-\frac{1}{3})$ solution, $C_0 = 5.25 \times 10^{-3}$ mol dm^{-3}

Table 2 Composition (mol%)[a] of the reaction products obtained by addition of dibromides **5**, **6**, **7** to $S(-\frac{1}{3})$ solutions at C_0 values close to 5×10^{-3} mol dm^{-3}

Dibromide	$[S_8]_f/[S_8]_0$	%C=C	$\%RS_3$
5	0.60	20	80
6	0.75	50	50
7	0.88	76	24

[a] Mol% ± 10% from the uncertainty on iR_1 measurements.

Sulfur, assayed by measuring iR_1 corresponded to the concentration having generated $S(-\frac{1}{3})$ ions at the initial moment ($[S_8]_0 = \frac{3}{8}C_0$). The concentration of bromide ions, determined by measuring their limit oxidation current after calibrating with a solution of NBu_4Br was compatible with that of added dibromide.

The quantitative reoxidation of $S(-\frac{1}{3})$ ions and the generation of halide ions complied with the formation of an alkene according to the overall process in eqn. (4).

$$\text{-CHBr–CHBr-} + 2S_3^{\cdot -} \longrightarrow \underset{|}{\text{-CH}}{=}\underset{|}{\text{CH-}} + \tfrac{3}{4}S_8 + 2Br^- \quad (4)$$

At the beginning of dibromide addition ($y < 0.12$), reaction (5) = (4) + (2) was observed because of the intermediate formation of S_8^{2-} ions by reaction (2*b*) ($8S_3^{\cdot -} \longrightarrow 3S_8^{2-}$, $\lambda_{is} = 543$ nm).

$$\text{-CHBr–CHBr-} + 8S_3^{\cdot -} \longrightarrow \underset{|}{\text{-CH}}{=}\underset{|}{\text{CH-}} + 3S_8^{2-} + 2Br^- \quad (5)$$

The changes in the spectra and the $i = f(E)$ curves (iR_1 and iO_1) throughout redox chemical reactions (4) and (5) were identical to those determined during the electrochemical oxidation of ions $S(-\frac{1}{3})$ at constant potential on the O_1 plateau. Thus, Fig. 3 shows the changes in currents and characteristic absorptions during the experimental oxidation of an $S(-\frac{1}{3})$ solution, $C_0 = 5.25 \times 10^{-3}$ mol dm^{-3} by dibromide **1**. It is compared to the simulated electrochemical oxidation curves, function of z(F/mol $S_3^{\cdot -}$), from constants K_1 and K_2 and equations of conservation of sulfur and of charges ($y = [RBr_2]/C_0 = z/2$).

The reactions with derivatives **4**–**11** were slow. Overall stoichiometry could be determined after adding an excess of dibromoalkane to $S(-\frac{1}{3})$ solutions (in general $[RBr_2]/C_0 = 10$, with $5.0 \times 10^{-3} < C_0 < 5.5 \times 10^{-3}$ mol dm^{-3}), causing their bleaching. Compounds **4**, **8**–**11** led to the total recovery of sulfur equivalent to C_0 and thus to the formation of an alkene according to the process described above. At the beginning of the reactions, the 'simultaneous' recording of absorptions A_{617} ($S_3^{\cdot -}$), A_{543} (λ_{is}) and A_{515} (S_8^{2-}) as a function of time complied with the balance $8S_3^{\cdot -} \longrightarrow 3S_8^{2-}$ of the intermediate eqn. (5).

In the case of 1,2-dibromobutane (**5**), 1,2-dibromophenylethane (**6**) and 2,3-dibromobutane (**7**), however, 60% (**5**), 75% (**6**) and 88% (**7**) of the initial sulfur concentrations were recovered on completion of the reaction, based on comparative measurements of iR_1. $S(-\frac{1}{3})$ ions led to the formation of trisulfides RS_3R with alkyl monohalides according to an S_N2 reaction.[6] The partial formation of cyclic trisulfides by substitution on species **5**–**7**, where the weakness of α-branching generally decreases elimination in favour of substitution[8] can be envisioned in dilute solutions according to reaction (6).

$$\text{-CHBr–CHBr-} + 2S_3^{\cdot -} \longrightarrow R{\equiv}S_3 + \tfrac{3}{8}S_8 + 2Br^- \quad (6)$$

In this case, S_8^{2-} ions would be generated as intermediates according to the overall reaction (7) = (2) + (6).

$$\text{-CHBr–CHBr-} + 5S_3^{\cdot -} \longrightarrow R{\equiv}S_3 + \tfrac{3}{2}S_8^{2-} + 2Br^- \quad (7)$$

The initial consumption of $S_3^{\cdot -}$ ions after the addition of 1,2-dibromobutane (**5**) to a solution at $C_0 = 4.90 \times 10^{-3}$ mol dm^{-3} was in relatively good agreement with this hypothesis, since at equilibrium $\Delta[S_3^{\cdot -}]/\Delta[RBr_2] \simeq 5.9$.

$R{\equiv}S_3$ compounds are generally unstable and polymerise when extracted from the reaction medium, as shown by attempts to synthesise derivatives with relatively unsubstituted groups, such as $(CH_2)_nS_3$ ($n = 2,3,4$).[8] Under our conditions of concentration ($C_0 \simeq 5 \times 10^{-3}$ mol dm^{-3}), the final proportion of alkene (%C=C) and of trisulfide ($\%RS_3$) could be estimated (Table 2) from the sulfur concentration at the end of the reaction ($[S_8]_f$), resulting from competitive reactions (4) and (6), in comparison to $[S_8]_0 = \frac{3}{8}C_0$ [eqn. (8)].

$$100[S_8]_f/[S_8]_0 = \tfrac{1}{2}(\%RS_3) + (\%C{=}C) \quad (8)$$

Indirect Electrochemical Reduction of vic-Dibromides.—When diethyl *meso*-2,3-dibromosuccinate (**2**) was added to an $S(-\frac{1}{3})$ solution at values of $y > 0.5$ (conditions of Fig. 1), the limit current of sulfur reduction iR_1 continued to increase, while the oxidation current of bromide ions remained constant. The direct addition of compounds **1**, **2** to a 2.0×10^{-3} mol dm^{-3} solution of sulfur led to a considerable increase of iR_1 in proportion to $[RBr_2]$, without changing the limit current of R_2. In both cases, iR_1 doubled for $[RBr_2]/[S_8]_0 \simeq 1.7$. In the presence of *meso*-1,2-dibromo-1,2-diphenylethane (**3**), the effect was lower, since under the same conditions iR_1 increased by only 18%. During the electrochemical reduction of these solutions at a potential set to the plateau of R_1 ($E = -0.5$ V), iR_1 decreased and the solution remained colourless, while dibromide was not completely eliminated. Only the oxidation

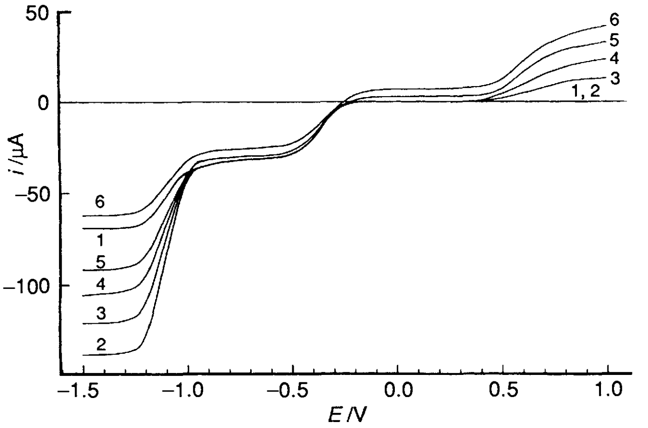

Fig. 4 Evolution of voltammograms during the electrolysis of a solution $[S_8]_0 = 10^{-3}$ mol dm^{-3} (1), in presence of DL-1,2-dibromo-1,2-diphenylethane $[RBr_2] = 3.0 \times 10^{-3}$ mol dm^{-3} (2), at $E = -1.2$ V *vs.* ref. z(F/mol RBr$_2$) = 0.5 (3); 1.0 (4); 1.5 (5); 2.2 (6)

wave of the bromide ions ($E_{\frac{1}{2}} = +0.70$ V) increased. This phenomenon is consistent with proposing sulfur as mediator for the catalytic reduction of such dibromoalkanes as **1–3** by polysulfide ions $S(-\frac{1}{3})$ or S_8^{2-} [eqns. (9) and (10)].

$$S_8 + 2e^- \longrightarrow S_8^{2-} \qquad (9)$$

$$\text{-CHBr-CHBr-} + S_8^{2-} \longrightarrow \text{-}\underset{|}{\mathrm{C}}\mathrm{H}\text{=}\underset{|}{\mathrm{C}}\mathrm{H}\text{-} + S_8 + 2Br^- \qquad (10)$$

Concerning compounds **4**, **8**, **11**, their addition to a solution of sulfur at 2.0×10^{-3} mol dm^{-3} caused the current iR$_2$ of the second reduction wave to increase ($E_{\frac{1}{2}} = -1.10$ V), while iR$_1$ remained constant. When $[RBr_2]/[S_8]_0 \simeq 1.4$, iR$_2$ doubled. The indirect electrolysis of these derivatives, for which the reduction overpotential (see Table 1) is greater than that of $S_3^{\bullet -}$ (or S_8^{2-}) ions by *ca.* 0.2 (**4**) to 0.45 V (**9**), can be proposed. Thus the reduction of a solution of sulfur at 1.0×10^{-3} mol dm^{-3} containing DL-dibromodiphenylethane at 3.0×10^{-3} mol dm^{-3} at a potential set to the plateau of R$_2$ ($E = -1.20$ V) (Fig. 4) led to a decrease in iR$_2$ and an increase in the oxidation current of bromide ions according to processes (11) + (12).

$$\tfrac{3}{4}S_8 + 4e^- \longrightarrow 2S_3^{2-} \qquad (11)$$

$$\text{-CHBr-CHBr-} + 2S_3^{2-} \longrightarrow \text{-}\underset{|}{\mathrm{C}}\mathrm{H}\text{=}\underset{|}{\mathrm{C}}\mathrm{H}\text{-} + 2S_3^{\bullet -} + 2Br^- \qquad (12)$$

The blue colour of the solutions resulted from the formation of $S_3^{\bullet -}$ ions [$\lambda^3_{\max} = 617$ nm, $E_{\frac{1}{2}}$ (O$_1$) = -0.20 V], but their concentration remained low during electrolysis, since they reacted fairly rapidly with **4** (see kinetic study). In this case, the overall process (13) is again observed.

$$\text{-CHBr-CHBr-} + S_8 + 2e^- \longrightarrow \text{-}\underset{|}{\mathrm{C}}\mathrm{H}\text{=}\underset{|}{\mathrm{C}}\mathrm{H}\text{-} + S_8 + 2Br^- \qquad (13)$$

The reducing properties of polysulfide ions and the possibility of homogeneous redox catalysis by the mediator pair sulfur/polysulfide ions for the dehalogenation of vic-dibromides was applied on a preparative scale with derivatives methyl *erythro*-2,3-dibromo-3-phenylpropanoate (**1**), diethyl *meso*-2,3-dibromosuccinate (**2**), *meso*- and DL-1,2-dibromo-1,2-diphenylethane (**3**, **4**) and *meso*-5,6-dibromodecane (**10**).

S_6^{2-} ions could be generated chemically from the quantitative oxidation of Na$_2$S$_4$ by sulfur[9] [eqn. (14)]. The debromination reaction of **3** added to a solution of S_6^{2-} yielded exclusively (E)-stilbene.

$$S_4^{2-} + \tfrac{1}{4}S_8 \longrightarrow S_6^{2-} \qquad (14)$$

Other compounds were indirectly reduced at a controlled potential set to the plateau of the first wave of sulfur (**1**, **2**) or to that of the second (**4**, **10**). The results of syntheses and the operating conditions used are described in Table 3.

The generation of a mixture of Z:E stilbenes (75:25) from DL-1,2-dibromo-1,2-diphenylethane (**4**) is consistent with all the results on the particular debromination of this compound in protic or aprotic media:[2,3,4c,10] depending on the reducing agent used, the proportion of (Z)-stilbene in Z–E mixtures varies from 0 to 96%, while elimination from the *meso* isomer is always stereospecific. As in our case, more than 70% of (Z)-stilbene in generally obtained with 'two-electron reductants' such as I$^-$, RS$^-$ or Pt(II).[10] In this particular example, the reaction mechanism has not been clearly elucidated, even though it is a subject of considerable discussion.[4c,10]

Complete stereospecificity is found for all the other dehalogenation reactions we have performed: only E alkenes are obtained from **1–3** and **10**. Reductive dehalogenations can be classified as one- or two-electron processes: reagents which transfer electrons singly as aromatic anion radicals generally proceed *via* β-bromoalkyl radicals[1,11] ('outer-sphere process'[1]) and lead to mixtures of alkenes with a predicted equilibrium E:Z ratio of 75:25 for *meso*- and DL-4,5-dibromooctane.[1] The two-electron processes (E2 type elimination) normally result in stereospecific dehalogenation *via* a conformation with antiperiplanar bromine atoms, as has been shown with a very large number of reducing anions.[10] Our results strongly support this concerted reduction E2 mechanism; the *anti* conformation is favoured in the case of **1** and **2**, as for **3**, where it accounts for 92% of the conformers at equilibrium at 300 K.[12] This type of species, highly reactive as a result of their structure, have often—if not exclusively—been used as models for reactions with a large number of anions or nucleophiles. The formation of only E alkenes from **1**, **2**, **3** and **10** is analogous to what is obtained with *meso*-4,5-dibromooctane,[1] with iron and cobalt(I) porphyrins[1] ('inner-sphere process').

Equilibria $S_{2x}^{2-}/S_x^{\bullet -}$ (x = 2,3,4) have been proposed for polysulfide ions,[13] but have been clearly established only between S_6^{2-} and $S_3^{\bullet -}$, the anion-radical representing $S(-\frac{1}{3})$, predominant in dilute solution.[6,13a] As we have found, the reactions are slow between $S(-\frac{1}{3})$ ions and compounds **4**, **8–11**, for which concurrent substitutions have not been detected. The study of their kinetics may lead to a better understanding of the reducing species: the anion-radical $S_3^{\bullet -}$ or the dianion S_6^{2-}.

Kinetic Studies of the Reactions of $S(-\frac{1}{3})$ *Ions with vic-Dibromides* **4**, **8–11**.—The kinetic study was carried out on the 'simultaneous' recording of absorptions A_λ^1 at 617 nm ($S_3^{\bullet -}$) and 515 nm (S_8^{2-}) as a function of time after the addition of one of the selected dibromides to a solution at $C_0 = [S_3^{\bullet -}]_0 + 2[S_6^{2-}]_0$, as long as $\Delta[RBr_2]/C_0 < \frac{1}{8}$ [eqn. (15)].

$$A_\lambda^1/l = \varepsilon^3[S_3^{\bullet -}] + \varepsilon^8[S_8^{2-}] \qquad (15)$$

When sulfur is not detected in the voltammograms, the overall process (5) = (4) + (2) is a satisfying description of the spectra, as we have reported previously.

Table 3 Mediated electrolysis of vic-dibromides **1**, **2**, **4** and **10**

Dibromide	[Sulfur]/mmol dm^{-3}	[RBr$_2$]/mmol dm^{-3}	Potential/V	*n*F/mol RBr$_2$	*E*:*Z*
1	1.04	32	−0.50	1.82	100:0
2	1.44	52	−0.50	1.74	100:0
4	3.20	88	−1.20	2.0	25:75
10	4.0	88	−1.20	1.84	99:1

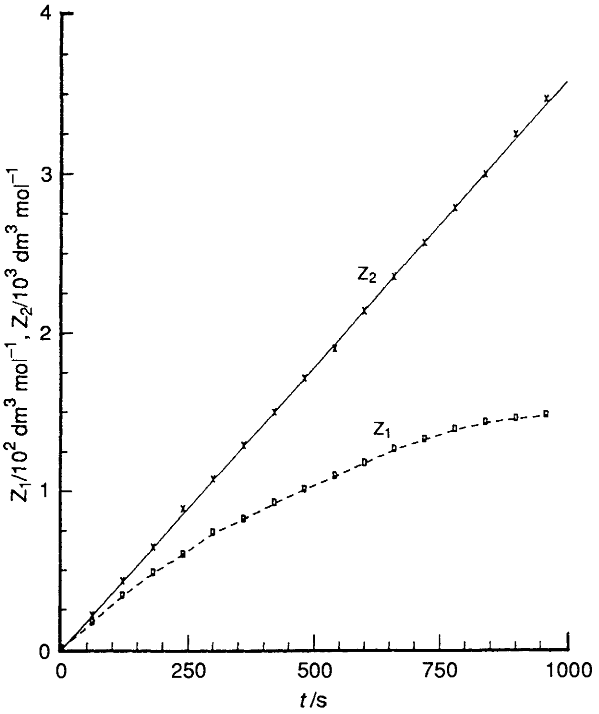

Fig. 5 Kinetic studies of the reaction of *meso*-5,6-dibromodecane with $S(-\frac{1}{3})$ ions. $C_0 = 4.86 \times 10^{-3}$ mol dm^{-3}; $[RBr_2]_0 = 1.31 \times 10^{-3}$ mol dm^{-3}. Calculations assuming first-order (Z_1) and second-order (Z_2) behaviour with respect to $S_3^{\bullet -}$ ions.

In these conditions, reaction (2) is quantitative and fast, while equilibrium (3) is considered to obtain at all times. The rate equation is expressed by presuming a bimolecular process involving RBr$_2$, $S_3^{\bullet -}$ or S_6^{2-} [eqns. (16) and (17)].

$$v_t = -\frac{d[RBr_2]_t}{dt} = k_1[RBr_2]_t[S_3^{\bullet -}]_t \qquad (16)$$

$$v_t = k_2[RBr_2]_t[S_6^{2-}]_t = \frac{k_2}{K_2}[RBr_2]_t[S_3^{\bullet -}]_t^2 \qquad (17)$$

The equations of conservation of charge and the initial concentrations of dibromide and sulfur enable $[RBr_2]_t$ (denoted R_t) to be expressed as a function of $[S_3^{\bullet -}]_t$ (denoted X_t).

$$C_0 = X_t + 2\frac{X_t^2}{K_2} + 2[S_8^{2-}] + 2[R_0 - R_t]$$

$$3C_0 = 3X_t + 6\frac{X_t^2}{K_2} + 8[S_8^{2-}]$$

A rate equation $Z_n(t)$ can now be established easily and tested, supposing an order $n = 1$ [eqn. (16)] or $n = 2$ [eqn. (17)] with respect to $S_3^{\bullet -}$ (*e.g.* Fig. 5):

Table 4 Rate constants $k_2{}^a$ (dm^3 mol^{-1} s^{-1}) for the reaction of $S(-\frac{1}{3})$ ions with vic-dibromides at 20.0 ± 0.5 °C. Ionic strength = 0.1 mol dm^{-3}

Dibromide	k_2
4	45
8	4.8
9	1.3
10	3.6
11	2.3

[a] Mean values ±5% from duplicate runs except for **4**, ±10%.

$$Z_n(t) = \int_{X_0}^{X_t} F_n(X_t)\mathrm{d}X = k_n t$$

with

$$F_1 = F_2\frac{X_t}{K_2}$$

$$F_2 = \frac{1 + 4X_t/K_2}{\left(\frac{2}{K_2{}^2}X_t^2 + \frac{X_t}{K_2} + \frac{8R_0 - C_0}{K_2}\right)X_t^2}$$

In all cases, order 2 relative to $S_3^{\bullet -}$ is deduced from integrations, leading us to select S_6^{2-} ions as the $S(-\frac{1}{3})$ agents involved in reaction (4), if we eliminate the improbable hypothesis of a trimolecular process in the rate-determining step. The nature of the sulfur-containing intermediate in the transition state cannot be proposed from our analytical results but, as for S$_N$Ar reactions of $S(-\frac{1}{3})$ on nitroaromatic halides,[7] it appears that S_6^{2-} dianions are the effective reducing agents, the charge being more diffuse in the $S_3^{\bullet -}$ radical anions according to Meyer *et al.*[14] calculations. The rate constants k_2 of the reactions of S_6^{2-} ions with **4**, **8**–**11** are listed in Table 4.

The reactivity of the least reducing[15] polysulfide ions S_8^{2-} can be neglected in comparison to that of S_6^{2-}, since no significant modification of rates was observed from the $Z_2 = f(t)$ curves, even when the advancement of the reactions approached stoichiometry (Fig. 5). This observation had been made previously in the case of S$_N$Ar substitutions on nitroaromatic halides $[v(S_6^{2-}) \gg v(S_8^{2-})]$.[7] The reaction rates observed with the *meso*-**3** *and erythro*-**8** species were higher than the respective rates of DL-**4** and *threo*-**9**. This is consistent with the easier dehalogenations of molecules whose *anti* arrangement of the two bromines is favoured[2b,16] and which are also easier to reduce electrochemically (Table 1).

The reactivity of S_6^{2-} ions in DMA can be situated with respect to that of I$^-$ ions in DMF[16] at 36 °C on *meso*-dibromodiphenylethane (**3**), where $k = 1.1 \times 10^{-2}$ dm^3 mol^{-1} s^{-1} and on DL-dibromodiphenylethane (**4**), where $k = 0.34 \times 10^{-4}$ dm^3 mol^{-1} s^{-1} ($k_{DMA}{}^{20\,°C} = 45$ with S_6^{2-}).

Conclusions

The dehalogenation of vic-dibromides with non-primary groups, leading to alkenes, can be easily carried out at laboratory temperatures in aprotic dipolar media such as dimethylacetamide, using polysulfide ions which are chemically or electrochemically accessible. The catalytic current at the second wave of sulfur reduction with dibromides whose corresponding alkenes are not stabilised by resonance indicates that S_4^{2-} (or S_3^{2-}) ions are remarkable elimination agents.

The kinetic study of the reactions between $S(-\frac{1}{3})$ ions and vic-dibromides is consistent with proposing that the S_6^{2-} dianions—and probably S_4^{2-} as well—are the reducing agents rather than the anion-radicals $S_3^{\cdot -}$ (or $S_2^{\cdot -}$). Stereospecific syntheses by electrolysis in the presence of sulfur confirm that eliminations occur according to a concerted mechanism of the E2 type rather than by initial one-electron transfer.

Experimental

Materials and Equipment.—Sulfur, dimethylacetamide, alkenes (used as received) and vic-dibromides **5**, **6**, **7** and **11** were obtained from Aldrich. Bromine and the supporting electrolyte NEt_4ClO_4 were Fluka products.

Solvent purification, electrochemical equipment, electrodes and the thermostatted flow-through cell have been described elsewhere.[5] UV–VIS spectra were recorded on a Kontron Uvikon 930 spectrophotometer. M.p.s were determined on a Köfler block and were uncorrected. Analysis and identification of the synthesised alkenes (**1**–**4**) were performed by ^1H NMR spectroscopy (Varian EM 360–60 MHz, $CDCl_3$ as solvent, $SiMe_4$ as internal standard, J values in Hz) by using commercial alkenes or their mixtures for comparison. 5,6-Dibromodecane (**10**) and the product of its preparative dehalogenation were analysed by ^{13}C NMR (JEOL SX 90 Q, 22.49 MHz, $CDCl_3$) and GC–MS for the alkene (Hewlett-Packard 5989 A, EI 70 ev, OVI column 50 m).

Synthesis of the vic-Dibromides **1**–**4** *and* **8**–**10**.—The DL- and *meso*-1,2-dibromodiphenylethane (**3**, **4**) were prepared from (*Z*)- and (*E*)-stilbene respectively, by addition, in acetic acid, of pyridinium hydrobromide–perbromide according to the method of Fieser.[17] vic-Dibromides were recrystallised from xylene (*meso*-**3**, m.p. 237–239 °C; lit.,[18] m.p. 240–241 °C) and ethanol (DL-**4**, m.p. 111–112 °C; lit.,[19] m.p. 114 °C).

The other dibromoalkanes **1**, **2**, **8**–**10** were prepared according to the same general procedure for *trans* bromination:[20] to a solution of 30–40 mmol of the alkene in 100 cm^3 of dichloromethane a slight excess of bromine was progressively added. The mixture was refluxed for 1 h. The organic layer was then washed three times with 50 cm^3 of water and dried over anhydrous sodium sulfate. Compounds **1** and **2** precipitated and were recrystallised from hexane–benzene (**1**, m.p. 114–116 °C, lit.,[21] m.p. 115–116 °C) and ethanol–water respectively (**2**, m.p. 56–58 °C; lit.,[22] m.p. 58 °C). In the case of **8**–**10**, the crude products were further passed through a short silica gel column with light petroleum (b.p. range 35–60 °C) as eluent and distilled under reduced pressure; *meso*-5,6-dibromodecane (**10**): purity > 97%, by ^{13}C NMR spectroscopy; δ_C 13.88 (C-1), 21.82 (C-2), 29.02 (C-3), 36.52 (C-4), 59.53 (C-Br).

Chemical Synthesis of (E)-*Stilbene.*—The S_6^{2-} ions ($\rightleftarrows S_3^{\cdot -}$) used for the dehalogenation of *meso*-1,2-dibromodiphenylethane (**3**) were generated by heating a dimethylacetamide solution of Na_2S_4 (6 mmol) and S_8 (1.5 mmol) at 70 °C in an inert atmosphere (N_2) for 2 h. The addition of derivative **3** (5.8 mmol) bleached the orange–blue solution of polysulfide ions in less than 2 min, while NaBr and sulfur precipitated. After filtration, the reaction medium was diluted with three times its volume of water in order to permit the extraction of the reaction product with diethyl ether, which is partially miscible with DMA. The organic phase was washed with water until residual DMA was eliminated and was dried over anhydrous sodium sulfate. The (*E*)-stilbene obtained after evaporating the ether (89% yield) was recrystallised from hexane, m.p. 122–124 °C (lit.,[23] 124–125 °C); $\delta_H(CDCl_3)$ 7.1 (s, 2 H), 7.2–7.6 (m, 10 H).

Preparative Electrolyses.—Preparative scale experiments were performed at room temperature in a cell with two compartments separated by a sintered glass frit n°4. The cathode compartment contained a large gold grid electrode, a magnetic stirring bar and the reference electrode. The counter electrode was a platinum foil of 20 cm^2 in area. Each of the cell compartments was filled with 125 cm^3 of 0.5 mol dm^{-3} solution of NEt_4ClO_4 in DMA deaerated by nitrogen bubbling.

Indirect electrolysis of vic-dibromides **1**, **2**, **4**, **10** under an inert atmosphere with sulfur as mediator were carried out according to the procedure reported on the typical example, **1**: 4 mmol of methyl *erythro*-2,3-dibromo-3-phenylpropanoate and 0.13 mmol of sulfur were dissolved in the catholyte. The reduction at −0.5 V was performed as long as the solution became coloured as a result of the formation of S_x^{2-} ions after the overall reduction of RBr_2 (4 h). The solid reaction product (85% yield) was obtained by treatment of the catholyte after filtration of NEt_4Br evolved by the electrolysis in the same way as for the chemical synthesis, and recrystallised from EtOH at −10 °C (lit.,[24] m.p. 36 °C); $\delta_H(CDCl_3)$ 3.85 (s, 3 H), 6.5 (d, 1 H, *J* 17), 7.3–7.6 (m, 5 H), 7.8 (d, 1 H, *J* 17) identical with commercial (*E*)-methyl cinnamate spectrum.

The electrolysis of diethyl *meso*-2,3-dibromosuccinate (**2**) (6.5 mmol) in the presence of sulfur (0.18 mmol) at $E = -0.50$ V *vs.* ref. gave only diethyl fumarate (74% yield), b.p. ≃ 100 °C (12 mmHg), lit.,[25] 95–96 °C (10 mmHg); $\delta_H(CDCl_3)$ 1.36 (t, 6 H, *J* 7), 4.3 (q, 4 H, *J* 11), 6.86 (s, 2 H).

The electrolysis of DL-1,2-dibromo-1,2-diphenylethane (**4**) (11 mmol) in the presence of sulfur (0.4 mmol) at $E = -1.20$ V afforded a mixture of *Z*/*E*-stilbene (80% yield). The relative intensities of ^1H NMR signals at δ 6.6 (s, 2 H) for (*Z*)-stilbene and δ 7.1 (s, 2 H) for (*E*)-stilbene as a measure of the *Z*:*E* ratio gave 75:25.

The indirect electrolysis of 5,6-dibromodecane (**10**) (11 mmol) with sulfur as mediator (0.5 mmol) at $E = -1.20$ V yielded, after extraction, 65% of (*E*)-dec-5-ene (≃99%) and (*Z*)-dec-5-ene (≃1%); (*E*)-dec-5-ene: δ_C 13.89 (C-1), 22.25 (C-2), 31.91 (C-3), 32.37 (C-4), 130.31 (C-5, C=C), *m*/*z* 140 (M^+, 12%); (*Z*)-dec-5-ene: δ_C 129.79 (C-5, C=C).

Rate Measurements.—$S(-\frac{1}{3})$ solutions (35 cm^3 or 40 cm^3) were prepared by the electroreduction of sulfur (concentrations *ca.* 2×10^{-3} mol dm^{-3}) at a controlled potential on the plateau of the second wave R_2 ($E = -1.5$ V) up to $\frac{8}{3}$F mol^{-1} according to eqn. (18).

$$S_8 + \tfrac{8}{3}e^- \longrightarrow \tfrac{8}{3}S_3^{\cdot -} \qquad (18)$$

A small volume of a concentrated solution (in DMA) of RBr_2 derivatives **4**, **8**, **9**, **10** or **11** ($v_{max} = 1$ cm^3) was then added at 20.0 ± 0.5 °C. Changes in absorbance *vs.* time at 617 nm ($S_3^{\cdot -}$) and 515 nm (S_8^{2-}) as long as $\Delta[RBr_2]/Co < \frac{1}{8}$ enabled the kinetic characteristics to be deduced. The transfer of the solution from the reaction medium to the spectrophotometric cell (1 mm pathlength) took *ca.* 8 s. With $C_0 = 5 \times 10^{-3}$ mol dm^{-3}, $[RBr_2]/Co = \frac{1}{20}$, $t_{\frac{1}{2}} \geq 20$ s, the rates can be studied for $k_2 < 130$ dm^3 mol^{-1} s^{-1}.

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