Reduction of Vicinal Dihalides. I The Electrochemical Reduction of *meso*and (±)-1,2-Dibromo-1,2-diphenylethane

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Abstract

The mechanism of the electrochemical dehalogenation of organic vicinal dihalides has been examined in acetonitrile by using *meso*- and (\pm)-1,2-dibromo-1,2-diphenylethane. Reduction potentials and product distributions obtained from the isomeric dibromides could not be accommodated within a mechanism involving a concerted addition of two electrons. However, these results can be explained by a stepwise addition of electrons, allowing the possibility of bond rotation at an intermediate stage. The product distributions obtained from the reduction of the (\pm)-dibromide were found to be potential-dependent, a result not previously observed for this compound, but consistent with a stepwise mechanism.

Introduction

Bromine may be eliminated from vicinal dibromides by a variety of nucleophiles to give an olefinic product.¹ Debromination may also be achieved electrochemically, as first noted by Stackelberg and Stracke,² who were able to reduce 1,2-dibromoethane on mercury in dioxan, achieving an 80% yield of ethene. Both the chemical and electrochemical debromination may be described by the same overall reaction (Scheme 1), with the two electrons being obtained either from an electrode surface or from a nucleophilic reagent.



Considerable confusion exists as to the precise mechanistic details of the electrochemical debromination. Previous investigations of the reaction may be divided essentially into two distinct schools of thought, offering contrasting views of the process. These are represented in Schemes 2 and 3.

¹ Saunders, W. H., and Cockerill, A. F., 'Mechanisms of Elimination Reactions' (Wiley–Interscience: New York 1973).

² Stackelberg, W., and Stracke, W., Z. Elektrochem., 1949, 53, 118.

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Scheme 2. Concerted mechanism.



Scheme 3. Stepwise mechanism.

Scheme 2 invokes a concerted transfer of two electrons, giving a transition state with synchronous $C \alpha$ -Br and $C \beta$ -Br bond rupture and a high degree of double-bond character. Scheme 3 involves a stepwise addition of electrons, which may produce a radical or carbanionic intermediate. The poor understanding of the mechanism for electrochemical dehalogenation is well illustrated in the reduction of the diastereomers of 1,2-dibromo-1,2-diphenylethane (1), for which both mechanisms have been proposed.³⁻⁵



A major aim of this work is to reinvestigate the electrochemical reduction of vicinal dihalides to determine which of these proposed mechanisms applies. The behaviour of *meso-* and (\pm) -(1) will be compared by using electrode potential measurements and product distributions from controlled-potential electrolysis.

Results and Discussion

Reduction Potentials

Dibromide reductions were examined on both platinum and mercury electrodes in acetonitrile (MeCN) solutions containing $0 \cdot 10$ M tetrabutylammonium perchlorate (Bu₄NClO₄). Fig. 1 shows the cyclic voltammogram obtained for *meso*-(1) on platinum. Only a single cathodic peak is observed, corresponding to a totally irreversible two-electron process for the reduction of the dibromide funtionality. Such a process is confirmed in the cyclic voltammogram by the anodic peaks present, which may be readily attributed to the oxidation of Br⁻ liberated in the elimination. Similar behaviour is also exhibited by (±)-(1). The reduction of the olefinic product cannot be detected within the solvent limit on platinum; however, the cyclic voltammogram of (±)-(1) at a hanging mercury

³ Inesi, A., and Rampasso, L., J. Electroanal. Chem., 1974, 54, 289.

⁴ Sokol, W. F., Ph.D. Thesis, Wayne State University, 1978.

⁵ Lund, H., and Hobolth, E., Acta Chem. Scand., Ser. B, 1976, 30, 895.



Fig. 2. Cyclic voltammogram of (\pm) -(1) at a hanging mercury drop electrode in MeCN, showing the reduction of stilbene at $-2 \cdot 6$ V.

drop electrode clearly shows a second cathodic peak at $-2 \cdot 6$ V, characteristic of (*E*)-stilbene (Fig. 2).

The electrode potentials measured for the reduction of the diastereomers of (1) in MeCN show that the (±)-dibromide is approximately $0 \cdot 1$ V more difficult to reduce than its *meso*-isomer on both mercury and platinum (Table 1). This is in conflict with Inesi and Rampasso,³ who found both isomers to be reduced at identical potentials in dimethylformamide. However, a difference in $E_{1/2}$ of $0 \cdot 17$ V was obtained by Lund and Hobolth⁵ for the direct-current polarograms of *meso*- and (±)-(1) in dimethylformamide. For voltammograms on mercury in butanenitrile this difference was $0 \cdot 50$ V.⁶ Interestingly, Sokol⁴ claimed similar behaviour to that observed by Inesi and Rampasso,³ but his voltammetric

⁶ O'Connell, K. M., and Evans, D. H., J. Am. Chem. Soc., 1983, 105, 1473.

results measured at a hanging mercury drop electrode in dimethylformamide show a difference in peak potentials for the isomers of 0.09 V.

Table	1.	Electrode	potential	data	for	the	reduction	of	meso-	and	(±)-(1)
in MeCN											
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Compound	Electrode	Parameter	Electrode potential ^A
meso-(1)	platinum	Ep ^B	-1.14
	dropping mercury	$E_{1/2}$	-0.596
(±)-(1)	platinum	Ep	-1.23
	dropping mercury	$E_{1/2}$	-0.690
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^B Scan rate 0.20 V s^{-1} . ^A V ν . Ag/0·1 M AgNO₃.

The observations of Inesi and Rampasso are difficult to reconcile with those made here and in other studies $^{4-6}$ of these compounds. Indeed, the majority of studies performed on other dibromides also suggest that diastereomers show different behaviour. The (±)-isomers of substituted and unsubstituted 2,3-dibromobutanes^{6,7} and 3,4-dibromobutanes^{6,8} all have reduction potentials more cathodic of their *meso*-forms in several solvents. The magnitudes of these potential differences are generally 0.04-0.30 V, although larger values have been observed.8

The preference for an antiperiplanar (*anti*) arrangement of halogens in the electrochemical reduction of vicinal dibromides has been established by Zavada et al.⁹ using $E_{1/2}$ values for cyclic dibromides with known dihedral angles. In the case of *meso-(1)* the *anti-conformer* is clearly the dominant species. While the equilibrium population of the *anti*-conformer for the (\pm) -dibromide is expected to be only 20% at 300 K,¹⁰ the Curtin-Hammett principle^{11,12} suggests that such a low value does not necessarily hinder the reaction. This principle states that, provided the activation energy of the reaction is large compared to that for bond rotation, the relative amounts of products are independent of the relative population of the ground-state conformations, but, rather, depend only on the activation energies of the processes leading to these products. The barrier to rotation for the stilbene dibromides has been shown to be low.⁶ and so the *anti*-arrangement of bromines should be readily attained during reaction.

The differences in reduction potentials between diastereomers are often attributed to the relative stabilites of their *anti*-conformers.^{6,7} Clearly, the phenyl groups cannot be coplanar either in the *anti*-conformation for the (±)-dibromide or in the expected anti-elimination product (Z)-stilbene,¹³ thus reducing the possibility of any delocalization of charge or double-bond character. Any transition state for this isomer would also suffer from steric interactions of

- ⁸ Brown, O. R., Middleton, P. H., and Thelfall, T. L., J. Chem. Soc., Perkin Trans. 2, 1984, 955. ⁹ Zavada, J., Krupicka, J., and Sicher, J., Collect. Czech. Chem. Commun., 1963, 28, 1664.
- ¹⁰ Ivanov, P., and Pojarlieff, I., J. Mol. Struct., 1977, 38, 259.
- ¹¹ Curtin, D. Y., Rec. Chem. Prog., 1954, 15, 111.
- ¹² Eliel, E. L., 'Stereochemistry of Carbon Compounds' (McGraw-Hill: New York 1962).
- ¹³ Wolf, A., Schmidtke, H. H., and Knop, J. V., Theor. Chim. Acta, 1978, 48, 37.

⁷ McKeon, M. G., J. Electroanal. Chem., 1963, 3, 402.

the bulky phenyl groups. Such eclipsing effects are not observed in the case of *meso*-(1).

Product Distributions

While determining the stereochemical course of a reaction can provide useful information, and indeed is essential for the debromination reaction to be fully understood, the results from such experiments can often be ambiguous. In the case of vicinal dibromides, product distributions thought by some authors to indicate a concerted reduction mechanism (Scheme 2) can also be considered as consistent with a stepwise process (Scheme 3) involving bond rotation at an intermediate stage.

Two fundamental assumptions must be made when proposing a concerted dihalide reduction mechanism. The first is that all conformers are reducible, although the rate of reduction for each conformer may be different. The second requirement is for the stereochemical integrity of the conformer to be maintained during the course of the reduction process.

The first of these assumptions follows from the dependence, observed by Zavada *et al.*,⁹ of the reduction potential upon the dihedral angle between carbon-bromine bonds, and has been conclusively demonstrated by O'Connell and Evans.⁶ Arguments in favour of the second assumption are far less convincing. Clearly the preservation of conformer stereochemistry through a concerted process rules out the possibility of bond rotation. However, few instances are known where only the products of pure *anti*-elimination are achieved. In almost all cases the reduction of isomeric dibromides results in the formation of either the more stable (*E*)-product or a mixture of (*E*)- and (*Z*)-olefins.



Such results may be rationalized in terms of the first assumption, as illustrated in Scheme 4 for the diastereomers of dibromide (1). While the conformer of (\pm) -(1) with bromines in a synclinal (*syn*) arrangement is expected to be the most populated, if an *anti*-arrangement of bromines is favoured for elimination, then by applying the Curtin–Hammett principle the relative reaction rates will be $k_3 > k_2$. However, conditions may exist where k_2 becomes significant. Inesi and Rampasso³ claim that the *syn*-arrangement allows both bromine atoms to approach the electrode surface; this may assist electron transfer, negating the effect of the leaving groups not being coplanar. As they obtained only (*E*)-stilbene from the reduction of (\pm)-(1) they concluded that for this substrate $k_2 > k_3$.

Scheme 4

Results obtained here for controlled-potential electrolysis of the dibromide meso-(1) at mercury in MeCN (Table 2) show that this substrate is reduced exclusively to (*E*)-stilbene. Such results are consistent with either a concerted or a stepwise reduction mechanism, as the *anti*-elimination product from meso-(1) is also the more stable olefin.

Table 2.	Reduction of dibromides meso- and (±)-(1) at a stirred mercury pool electrode
	in various electrolyte solutions in MeCN

Compound	Applied potential ^A	Electrolyte	(Z)-:(E)-Stilbene	
meso-(1)	-1.00	0.10 м Bu4NClO4	0:100	
	-2.00	0.10 м Bu4NClO4	0:100	
(±)-(1)	$-1 \cdot 80$	0.10 м Bu4NClO4	41:59	
	$-1 \cdot 80$	0·30 м Bu4NClO4	44:56	
	$-1 \cdot 80$	0·10 м Bu4NBr	36:64	
	-1.80	0·30 м Bu4NBr	43:57	

^A V ν . Ag/0 · 1 M AgNO₃.

Controlled-potential electrolysis of (\pm) -(1) under the same conditions indicates that, while (*E*)-stilbene is the major product, a significant fraction of the (*Z*)-olefin is formed. This is in agreement with results obtained in dimethylformamide by Lund and Hobolth.⁵ Once again it is not easy to rationalize the observations of Inesi and Rampasso. A possible explanation lies in the way these authors relied on u.v.-visible spectroscopy alone to determine product mixtures. While the spectra of the two isomers are substantially different, these authors chose to work at substrate concentrations which gave absorbances in the order of 1 · 5 on electrolysis. Under such conditions it is questionable that the analysis would have allowed the detection of (*Z*)-stilbene at low levels.

Lund and Hobolth obtained a constant (Z)/(E) ratio when (\pm) -(1) was reduced at two distinct potentials.⁵ However, Fig. 3 shows that the product distribution for the reduction of this isomer on mercury in MeCN is clearly dependent on the electrode potential. The fraction of (*Z*)-stilbene increases from 7 to 40% as the electrolysis potential becomes more negative. A constant product mixture is obtained at the more cathodic potentials. This may in part explain the results of Lund and Hobolth, who performed their electrolyses at two potentials which were both well cathodic of $E_{1/2}$. While comparisons with results obtained in dimethylformamide and under different electrolysis conditions should be viewed with caution, the two potentials used by these authors correspond to approximately $-1 \cdot 3$ and $-2 \cdot 2$ V against the $Ag/0 \cdot 1$ M $AgNO_3$ reference electrode used in this work. Product distributions measured at these potentials would therefore be expected to fall within the upper half of Fig. 3.

Can these results be explained in terms of a concerted reduction? Potentialdependent olefin mixtures have been observed previously for the reduction of simple vicinal dibromoalkanes,⁸ with a concerted mechanism similar to Scheme 4 being used to describe this effect. At mild potentials $k_3 > k_2$, as expected for this scheme. However, at more negative electrode potentials it was felt that the activation energies for the two reduction processes become lower than the barrier to rotation, resulting in simultaneous reduction of *syn*- and *anti*-conformers. At these potentials the product distibutions would be expected to reflect the relative solution populations of the substrate conformers.

From Fig. 3 it can be seen that entirely the reverse behaviour is displayed by (\pm) -(1). The fraction of the *anti*-elimination product, (*Z*)-stilbene, clearly increases as the electrode potential is made more negative, until a limiting value is reached. Less than 10% *anti*-elimination is achieved at mild potentials. A concerted mechanism for the reduction of this dibromide must therefore be ruled out.



The observed product distributions may, however, be readily accommodated within a stepwise reduction mechanism. As shown in Scheme 3, a radical intermediate may be formed following the transfer of one electron and loss of the β -halogen. At mild potentials this radical may be sufficiently long lived to allow bond rotation to the more stable (*E*)-stilbene. As the electrode potential becomes more cathodic the transfer of a second electron and loss of the α -hologen is likely to occur at a faster rate, giving less bond rotation and hence a higher yield of (*Z*)-stilbene.

Supporting Electrolyte Effects

The background electrolyte, while electrochemically inert under the conditions of most reactions, may still exert an influence on the stereochemical course of the reductions and therefore cannot be ignored in discussing mechanisms. Product distributions obtained from the controlled-potential electrolysis of the dibromide (\pm)-(1) show that a lower fraction of (*Z*)-stilbene is formed when the electrolyte is Bu₄NBr, compared with the use of Bu₄NClO₄ at the same concentration (Table 2). Such an effect cannot be explained in terms of a concerted mechanism, for which the presence of Br⁻ should have no effect on product distributions. It is, however, entirely consistent with a stepwise reduction process, as a high concentration of Br⁻ in solution may result in slower loss of Br⁻ from the substrate, allowing a higher degree of bond rotation and hence more (*E*)-stilbene. Lund and Hobolth⁵ have made a detailed examination of the effect of electrolyte cations on the distribution of products from controlled-potential electrolysis of (\pm) -(1) in dimethylformamide. They found that the fraction of (*Z*)-stilbene increases with the size and concentration of the cation. To explain these results they proposed ion-pair formation between the electrolyte cation and a carbanionic intermediate, with the size of the cation determining the extent of bond rotation.

These authors rule out any influence of the double layer at the mercury/dimethylformamide interface. They assume the adsorption of tetraalkylammonium ions on mercury in dimethylformamide is greater for ions with shorter alkyl chains, and argue that smaller quaternary cations should therefore displace larger cations from the electrode surface. However, they obtained almost the same product distribution in the presence of $0.1 \text{ M Bu}_4\text{N}^+$ and $0.01 \text{ M Me}_4\text{N}^+$ together as for the Bu $_4\text{N}^+$ alone.

Double-layer structure has been examined in detail at the interface of mercury with dimethylformamide¹⁴ and MeCN,¹⁵⁻¹⁷ and found to be similar in both solvents. While the adsorption of tetralkylammonium ions on mercury may be weak in dimethylformamide, it becomes more pronounced with increasing length of the alkyl chain, the reverse of the behaviour presumed by Lund and Hobolth.⁵ In fact, the results they obtained in the presence of Me_4N^+ demonstrate the stronger adsorption of Bu₄N⁺, since the addition of a small amount of Me_4N^+ had almost no effect on product distributions. Another observation used by these authors to argue against cation adsorption is the constant fraction of (Z)-stilbene formed when (\pm) -(1) is electrolysed at two distinct potentials. Fawcett and Loutfy¹⁵ have shown that the concentration of quaternary cations in the double layer increases as the electrode becomes more negative. In contrast to Lund and Hobolth, a clear potential dependence was observed in this work for reductions in MeCN, with an increase in the fraction of the (Z)-olefin at cathodic potentials (Fig. 3). However, it should be noted that the magnitude of this increase is too large to be explained by double-laver effects alone.

While the possibility of ion-pairing can by no means be ignored, such a mechanism does imply the formation of a carbanionic intermediate that is relatively long lived. The results obtained with different cations can be explained more simply in terms of the structure at the electrode interface. If the first step in dihalide reduction produces a radical intermediate, this species may then interact with the mercury electrode. Such interactions may stabilize this radical, giving a slower loss of the α -halogen. Adsorption of cations at mercury may limit the approach of the intermediate and, in the absence of interactions with the electrode, a lower degree of bond rotation may occur. This is supported by controlled-potential electrolysis product distributions obtained at different electrolyte concentrations (Table 2), with a significantly higher fraction of (*Z*)-stilbene formed on electrolysis of (±)-(1) in either $0.3 \\ M Bu_4NClO_4$ or $0.3 \\ M Bu_4NBr$.

¹⁴ Fawcett, W. R., Ikeda, B. M., and Sellan, J. B., Can. J. Chem., 1979, 57, 2268.

¹⁵ Fawcett, W. R., and Loutfy, R. O., Can. J. Chem., 1973, **51**, 230.

¹⁶ Gambert, R., and Baumgartel, H., J. Electroanal. Chem., 1985, 183, 315.

¹⁷ Nielaba, P., Knowles, T., and Forstmann, F., J. Electroanal. Chem., 1985, 183, 329.

Reduction Mechanism

It is often argued that electrochemical dehalogenations must follow a concerted mechanism, as such processes occur at far less negative potentials than the corresponding monohalide reductions.^{18,19} This observation can be explained with the molecular orbital calculations performed by Beland *et al.*²⁰ for the reduction of chlorinated organic compounds. They suggest that the first electrochemical step involves the addition of an electron to a σ antibonding orbital of a carbon-chlorine bond, and, the greater the electron density of this bond, the greater the bond weakening. For y-1,2,3,4,5,6-hexachlorocyclohexane, or Lindane (2), the greatest electron density is concentrated about the axial chlorines on C3, C4 and C5, and the product obtained on electrochemical reduction is consistent with *anti*-elimination of chlorines. The presence of an axial hydrogen (C2 and C6) does not appear to enhance electron density on its neighbouring chlorine in any way.



An important point to be drawn from the work of Beland *et al.*²⁰ is that they were only discussing the addition of a single electron. Their results cannot be considered as indicative of a concerted mechanism. A stepwise reduction may also be envisaged, where the addition of the first electron is influenced by the vicinal halogen. While Beland *et al.*²⁰ have only considered chlorinated substrates, similar behaviour may be expected for bromine derivatives; in fact bromine, having a lower electronegativity than chlorine, may be capable of greater enhancement of electron density of a neighbouring halogen.



Scheme 5

¹⁸ Rosenthal, I., and Lacoste, R. J., J. Am. Chem. Soc., 1959, **81**, 3268.
¹⁹ Fry, A. J., 'Synthetic Organic Electrochemistry' (Harper & Row: New York 1972).
²⁰ Beland, F. A., Farwell, S. O., Callis, P. R., and Geer, R. D., J. Electroanal. Chem., 1977, **78**, 145.

The results obtained in this work are consistent with a stepwise reduction of the dibromide functionality. Scheme 5 represents the likely mechanism for the debromination of (\pm) -(1). The reaction can be postulated to proceed through an initial addition of one electron to the substrate, with the bromines in an antiperiplanar conformation. While the solution population of this conformer is low, the *anti*-arrangement is favoured for electron transfer, and the ease of bond rotation ensures that this is the only reduction pathway.

Loss of the first halogen produces a radical intermediate which may then react in several ways. It may accept a second electron directly and expel the remaining halogen to give (Z)-stilbene. Alternatively the radical may allow rotation about the central carbon–carbon bond prior to second electron transfer, resulting in the formation of the more stable product, (E)-stilbene. The possibility of some interaction between the radical intermediate and the electrode surface must also be allowed for in the reduction scheme. The distribution of the product olefins is dependent upon both the electrolyte composition and the applied electrode potential.

Experimental

Acetonitrile (A.R. grade) was dried over activated 4A molecular sieve for 48 h prior to distillation under nitrogen. Preparation and purification of tetrabutylammonium salts and dibromides *meso-* and (\pm) -(1) have been described previously.^{5,21,22}

All solutions for electrochemical experiments were 0.10 M Bu₄NClO₄ in MeCN, unless otherwise stated. Potentials were measured relative to the Ag/0.1 M AgNO₃ reference electrode in MeCN. Substrate concentrations of 3×10^{-3} and 1×10^{-3} M were used for cyclic voltammetry and polarography, respectively.

In cyclic voltammetry experiments an EG & G PARC universal programmer 175 was used with a 173 potentiostat. The working electrode was a 3 mm diameter platinum disc set inside a 17 mm diameter Kel-F rod, while the counter electrode was a 0.5 mm diameter platinum wire. The cell and Luggin capillary were prepared as described previously.²³ The working electrode surface was cleaned and pretreated by the procedure outlined by Bailey and Ritchie.²⁴ Polarography was performed on a Metrohm Polarecord E506 with an E505 stand. For controlled-potential electrolysis an Amel 551 potentiostat and an H-cell with a sintered glass separator were employed, with a stirred mercury pool as working electrode. All experiments were performed at ambient temperature ($23\pm1^\circ$ C).

Analysis of samples was carried out as follows. The reaction mixture was poured into 4 M HCl, and products were separated from the salts by extraction with ether or light petroleum. The organic layer was dried over magnesium sulfate, and then concentrated. All solutions were analysed on a Hewlett–Packard 25 m fused-silica capillary column containing a bonded phenyl methyl silicone stationary phase at 200°C. A Hewlett–Packard 5790A gas chromatograph was used, with flame ionization detection and helium as carrier gas.

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²² Avraamides, J., and Parker, A. J., Aust. J. Chem., 1983, **36**, 1705.

- ²³ Power, G. P., Ritchie, I. M., and Sjepcevich, G., Chem. Aust., 1981, 48, 468.
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