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Stereochemistry of the Cathodic Reduction of Halogenated Organic Derivatives

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Investigations on the stereochemistry of the electrochemical reduction of organic halogeno-derivatives are reviewed, and a comparison is made of the behaviour of these compounds on mercury and on platinum. Specific interaction between the halogen and the mercury electrode is shown to occur during reduction: i.e. direct contact between the halogeno-derivative and mercury is a condition for production of the transition state. In the reduction of optically active halogenocyclopropanes electron transfer occurs from the halogen atom with formation of a carbanion having the same configuration as the original halogeno-compound, but subsequent reactions (protonation, inversion, sp^3–sp^2 transition, etc.) may have a substantial effect on the configuration of the final product. The simultaneous detachment of two halide anions in the reduction of vicinal dihalogeno-derivatives results in the formation of compounds containing multiple bonds. A list of 40 references is included.

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I. INTRODUCTION

The electrochemical reduction of the carbon–halogen bond is a heterogeneous process occurring on the electrode surface. Therefore the behaviour of organic halogeno-derivatives during such reduction depends not only on their structure but also on the factors which distinguish heterogeneous from homogeneous processes. Among such factors are primarily (1) the orientation of the transition state in the field of the electrode—i.e. the positions of the atoms and the direction relative to the electrode surface of the dipoles of the bonds undergoing rupture—and (2) the distance from the electrode surface to the point at which the transition state is located, i.e. the length of the path traversed by the electrons from the surface to the molecule of the halogeno-derivative.

From investigations on the effect of solution composition (nature and concentration of electrolyte, nature of solvent, etc.) on the form of the polarisation curves it has been concluded that, in the cathodic reduction of organic compounds, the transition state is adsorbed on the electrode[1].

The present Review will examine the relation between the three-dimensional structure and the electrochemical properties of halogenated organic compounds.

Most monohalogeno-derivatives are reduced at a mercury cathode irreversibly in two stages, which correspond to the successive transfer of two electrons:

$$\begin{aligned} R{-}X + e^- &\xrightarrow{\text{slow}} I \quad \text{(intermediate cpd.)} \\ I + e^- &\xrightarrow{\text{rapid}} R^- + X^- \end{aligned} \qquad (1)$$

Transfer of the second electron is usually rapid, and therefore only one two-electron wave is observed on the polarogram. It is difficult to establish the nature of intermediate compound (I) formed by transfer of the first electron, but it may be assumed to be either a radical-anion $(R{-}X)^\bullet$ or a combination of a radical $R^\bullet$ and a halide anion. The carbanion R^- formed as a result of the two-electron transfer is in most cases a very strong base, and therefore rapidly detaches a proton from a molecule of the solvent (HS), being thus converted into a hydrocarbon:

$$R^- + HS \xrightarrow{\text{rapid}} RH + S^- \qquad (2)$$

The stereochemical result of the formation of a hydrocarbon from a halogeno-derivative may be determined either by the electron transfer (1) or by the protonation (2). If the carbanion formed by reaction (1) has insufficient time to lose its original configuration before capture of a proton, the stereochemistry of the reduction will be determined by the electrochemical stage (1). Apart from structural factors, the configurational stability of the primary carbanion R^- may be promoted also by its interaction with the electrode surface.

A change in the original configuration may occur also at the stage of formation of the intermediate compound I (Eqn. 1), provided that this compound includes the radical $R^\bullet$ (in the case of a radical-anion the configuration would probably be maintained). This possibility creates additional difficulties in interpreting the stereochemical results of the reduction of halogeno-derivatives. In order to reduce to a minimum the effect of isomerisation at the stage of transfer of the first electron, compounds which are reduced at fairly negative potentials must be chosen for investigation of the stereochemistry. In other words, the rate of transfer of the second electron, which depends on the potential, should exceed considerably the potential-independent rate of isomerisation of the radical $R^\bullet$ into the thermodynamically more advantageous configuration. This aspect will be discussed in greater detail in Section III.

The mechanism of the cathodic reduction of organic halogeno-derivatives has already been discussed in several reviews[2–4]. The stereochemistry of the electrochemical reactions of organic compounds forms the subject of a recently published Review[5]. Few papers have been published on the stereochemistry of the cathodic reduction of halogeno-derivatives, almost all during recent years.

II. ORIENTATION OF CARBON–HALOGEN DIPOLE IN THE FIELD OF THE ELECTRODE

Most organic halogeno-derivatives are reduced with a mercury electrode at potentials at which the electrode surface is negatively charged. However, this does not mean that the $R^{\delta+}-X^{\delta-}$ dipole is necessarily arranged with its positive pole towards the electrode surface and the negative pole in the solution. On the contrary, many data show that, when halogeno-derivatives are adsorbed on a negatively charged mercury surface, this dipole is directed with its negative pole towards the electrode[2]: i.e. an electrostatically disadvantageous orientation is established. The reason is that halogens have a specific affinity for mercury. If the Hg←XR interaction energy on formation of the transition state exceeds the change in electrostatic energy accompanying reorientation, an electrostatically unfavourable orientation is established.

In this connection it is interesting to compare the behaviour of halogeno-derivatives on mercury and platinum electrodes. According to Vlček[6] cobalt(III) complexes containing as ligands anions which form with mercury stable complexes or insoluble salts (Cl^-, Br^-, I^-, CNS^-, etc.) are reduced on mercury at abnormally positive potentials. The variation in the reduction potentials of these compounds does not correspond to their position in the corresponding "structural" series which includes complexes with other anions. On a platinum electrode, however, no abnormalities are observed, which indicates "catalysis by the surface of the mercury electrode"[6]. Interaction of the halogenated derivatives with the surface of metallic mercury may lead to the formation of organomercury compounds. In the reduction of allyl iodide, benzyl iodide[8], ethyl α-bromophenylacetate, and several other compounds, which may give relatively stable radicals R$^\cdot$, organomercury compounds are already formed on contact with the electrode surface. In these cases the polarograms of the halogeno-derivatives exhibit two one-electron waves which are identical with the waves of the corresponding organomercury compounds, e.g.

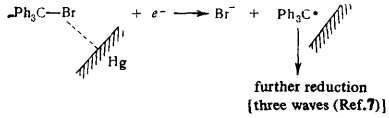
$$C_6H_5CH_2I + Hg \xrightarrow{\text{rapid}} C_6H_5CH_2HgI$$

$$C_6H_5CH_2HgI + e^- \rightarrow C_6H_5CH_2Hg^\cdot \quad (\text{or } C_6H_5CH_2^\cdot + Hg) \text{ (1st wave)}$$

$$C_6H_5CH_2Hg^\cdot + e^- + H^+ \rightarrow C_6H_5CH_3 + Hg \text{ (2nd wave)}$$

In most cases, however, the formation and reduction of organomercury compounds is merely a side-reaction accompanying the cathodic reduction of the halogeno-derivative and is due to interaction of RX with the electrode surface. Nevertheless, chloro-, bromo-, and iodo-derivatives of *o*-, *m*-, and *p*-barenes [1,2-, 1,7-, and 1,12-dicarbaclovododecaborane-12] are fairly easily reduced on mercury, the iodo-derivatives reacting the most readily, with reduction potentials close to the dissolution potentials of mercury. On platinum, however, these compounds are not reduced in the accessible potential range (to −1.8 V relative to the saturated calomel electrode, s.c.e. in anhydrous dimethylformamide. Diphenyliodonium salts behave similarly, being very easily reduced on mercury but not reduced on platinum[8–10].

Fig. 1 shows polarograms of triphenylbromomethane obtained on mercury and platinum electrodes in dimethylformamide. A "normal" two-electron wave is observed on platinum, whereas four waves are observed on mercury, the first of which is located at far less negative potentials †. This is probably due to interaction between the halogeno-derivative and mercury with formation of a triphenylmethyl radical[7]:



Similar phenomena are observed also with diphenylbromomethane and 9-bromofluorene.

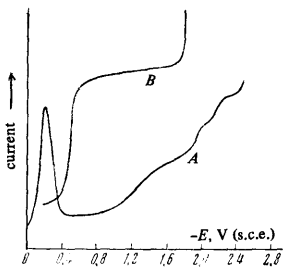


Figure 1. Polarograms for trimethylphenyl bromide in dimethylformamide containing 0.1 M tetraethylammonium bromide at 25°C on:
A) mercury; B) platinum.

These results confirm the earlier conclusion[11,12] that a transition complex involving the metal of the electrode surface is formed in the reduction of halogeno-derivatives. This means that the reducible molecule is tightly "clamped" to the electrode surface, the $R^{\delta+}-X^{\delta-}$ dipole being so arranged that the halogen atom is able to interact with the mercury. Such interaction is possible also with a "perpendicular" orientation of the dipole with its negative pole towards the electrode surface and with orientation parallel to the surface. The true orientation of the halogeno-derivative may be intermediate between these two extreme cases.

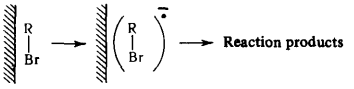
It has been found[13] with a large number of bromoalkanes RCH_2Br that the half-wave potentials do not correlate satisfactorily with the Taft σ^*-constants for the groups R. Correlation with the σ^*-constants of the groups RCH_2 is still less satisfactory. Substantial improvement is obtained by taking into account the steric hindrance due to the substituent R, i.e. by introducing the steric constants E_S into the correlation equation[14]:

$$E_{1/2} = 0.32\sigma^* + 0.12\,E_s - 2.16$$

It follows from this equation that the steric hindrance to electron transfer is considerably smaller than that resulting from an S_N2 reaction of RCH_2Br with such nucleophiles as OH^- or SCN^- (the coefficient of E_S in the above equation is unity). The steric hindrance in the

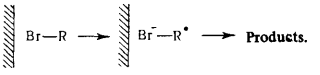
† The first wave exhibits a maximum whose nature is obscure. A similar maximum is always found in the reduction of mercury halides in anhydrous dimethylformamide.

cathodic reduction of these bromides is about the same as in the hydrolysis of esters, when the attacking nucleophile approaches the carbonyl carbon in a direction perpendicular to the C=O bond. It has been concluded[13] from these considerations that, in the cathodic reduction of alkyl bromides, the C–Br bond is oriented parallel to the electrode surface, and "perpendicular attack" takes place on the antibonding σ*-orbital of the molecule:



Such a mechanism involves the intermediate formation of an unstable radical-anion RBr•, which breaks down rapidly into the radical R• and the anion Br^-. Transfer of the second electron to R• occurs rapidly, and does not affect the half-wave potential.

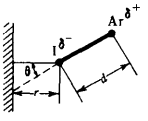
Sease et al.[15] consider that, in the reduction of bromides, the bromine atom is located at the surface of the mercury electrode, and the electron passes from the cathode to the carbon across the bridge formed by the bromine atom:



This hypothesis is based on the observation of reduction waves for compounds containing the bromine atom "in the bridgehead", e.g. 1-bromonorbornane, 1-bromobicyclo[2, 2, 2]octane, and bromotriptycene. If electrons had passed directly to the carbon atom, these compounds would not, in the opinion of the authors, have been reduced, owing to the considerable steric hindrance.

At the present time "perpendicular attack" and attack at the halogen atom are the most widely accepted views.

As the carbon–iodine bond in nuclear-substituted iodobenzenes becomes more ionic, the half-wave potential becomes more negative (the ionicity is determined from the nuclear quadrupole resonance spectra)[16,17]. It is impossible to explain this fact if the electron is assumed to pass to the carbon atom. Caldwell and Hacobian therefore supposed[17] that electron transfer occurs via the iodine atom. A somewhat modified spatial model of the reaction, as compared with that proposed by the authors, is given below:



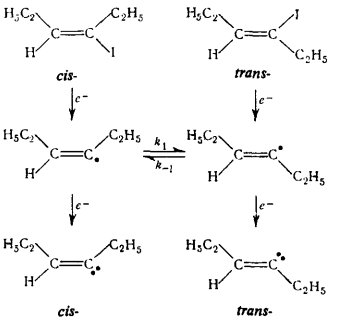
The ArI molecule is inclined at an angle $\frac{1}{2}\pi - \theta$ to the electrode surface, with the iodine atom closer than the carbon atom thereto. In passing to the iodine atom the electron traverses a distance r at an angle θ to the vector of the Ar–I bond. Accepting this orientation of the aryl iodide and putting $\cos\theta = 1$, these authors calculated the distance r between the iodine atom and the electrode surface from the slope of the linear plot of the ionic character of the bond against the half-wave potential. If the positive pole of the dipole is located on the carbon atom combined with the iodine, we have $\alpha = 2$ Å and the calculated value of $r = 1.2$ Å; if, however, the positive pole is located at the centre of the benzene ring ($d = 3.39$ Å), then $r = 1.4$ Å. The mean value of $r = 1.3$ Å agrees well with the van der Waals radius of iodine (1.33 Å). This was regarded as evidence, firstly that the iodobenzene molecule is perpendicular to the electrode surface during reduction, and secondly that the iodine atom is in close contact with the mercury surface[17]. However, the analogous calculation based on Lambert's model, in which the molecule of the halogeno-derivative is parallel to the electrode surface ($\cos\theta = 0$), gives $r = 1.05$ and 1.25 Å when $d = 2$ and 3.39 Å: i.e. the results are close to the values calculated by Caldwell and Hacobian and comparable with the half-thickness of the aryl iodide molecule.

Whatever the orientation of iodobenzene relative to the electrode surface, it follows from these calculations that reduction takes place with the molecule in close contact with the electrode, and electron transfer is effected at a distance less than 1.5 Å. It must be noted that the disposition of the transition state at the surface may depend on the potential of the electrode[1], but this question will not be examined here.

III. MONOHALOGENO- AND *gem*-DIHALOGENO-DERIVATIVES

As has already been remarked, a change in configuration of the group R during the cathodic reduction of halogeno-derivatives may occur either at the stage of formation of the radical R• or at the stage of formation of the carbanion. The possibility of isomerisation of the radical formed as a result of transfer of the first electron has been well illustrated by the work of Fry and Mitnich[18]. The electrolysis of *cis*- and *trans*-3-iodohex-3-enes in dimethylformamide with tetra-n-butylammonium bromide as supporting electrolyte yields a mixture of *cis*- and *trans*-hex-3-enes, in which the *trans*-isomer always predominates (70–94%) independently of the configuration of the initial iodide. The course of the reaction can be represented by Scheme 1.

Scheme 1



In this case *cis*–*trans*-isomerisation can take place only at the stage of formation of the radical, since the vinyl carbanions formed by transfer of the second electron, unlike the corresponding radicals, are configurationally stable owing to the disadvantageous character of the allene structure. The *trans*-radical is thermodynamically more stable (i.e. $k_1 \gg k_{-1}$), and therefore the *trans*-hydrocarbon predominates in the reaction products.

The possibility of a change in configuration at the stage of radical formation is one factor leading to the usually low optical purity of hydrocarbons obtained by the electrolysis of optically active halides (see below).

If the rate of inversion of the radical exceeds the rate of transfer of the second electron, and the radical is able freely to change its orientation relative to the electrode surface, the hydrocarbon formed by reduction of an

optically active halide will be a racemate. If, however, even a proportion of the radicals form a surface compound with the mercury, electron transfer between the electrode and the radical will lead to formation of an optically active product, whose configuration will be determined by the disposition of the transition state on the electrode surface.

It is easy to understand that, in the reduction of saturated halogeno-derivatives, the stereochemistry of transfer of first and second electrons should be the same: otherwise it would be necessary to suppose that, for some unknown reason, the molecule rotates through 180° about an axis parallel to the electrode surface in the interval of time between these two processes ‡, or that the electron moves along a trajectory skirting the molecule. In the subsequent discussion of the stereochemistry, therefore, we shall not divide the transfer of the two electrons into two one-electron stages.

If interaction is assumed to occur between the halogen atom and the surface of the mercury electrode, the initial configuration of the carbanion formed by two-electron reduction of the molecule RX should coincide with the configuration of the initial halogeno-derivative. If, however, the transfer of electrons occurs on the side opposite to the liberated halogen atom, inversion of configuration should be observed. Henceforward we shall term these two cases "attack on halogen" and "attack on carbon" (the former corresponds to the "parallel" or "perpendicular" arrangement of the $R^{\delta+}-X^{\delta-}$ dipole considered above).

A general scheme of the reaction for cases of attack on halogen and on carbon (Fig. 2) shows the following stages—(1) actual transfer of electrons, (2) diffusion of initially formed carbanion from electrode surface into solution, (3) inversion of carbanion in solution, (4) and (5) protonation in solution of uninverted and inverted carbanions respectively, (6) transition of carbanion from sp^3 to sp^2 configuration as a consequence of conjugation with the substituent *d* (e.g. NO_2, COR, CN, etc.), (7) diffusion into solution of carbanion after having assumed a planar configuration, and its subsequent protonation, and (8) protonation of planar carbanion which has been unable to lose its bond with the electrode. It can be assumed from Fig. 2 that the stereochemistry of the cationic reduction of the carbon–halogen bond will depend on the stereochemical direction of five different stages in the process.

Table 1 shows the changes in configuration of the hydrocarbon formed by protonation at different stages in the conversion of the carbanions, compared with the configuration of the initial halogeno-derivative. The overall stereochemical result of the electrode reaction is seen to depend on the relative rates of the different stages: i.e. it is closely connected with the chemical structure of the initial halogeno-derivative and the resulting carbanion. In general it is fairly difficult to predict which stage will determine the stereochemistry to a greater extent, and which to a smaller extent, so that it is difficult to distinguish "attack on halogen" from "attack on carbon". To settle this question it is necessary to choose an organic halogeno-derivative which will give a configurationally stable carbanion on reduction, i.e. a carbanion which will not contain substituents *d* capable of stabilising it by conjugation and localisation of a negative charge on a heteroatom, and which would possess a low rate of inversion.

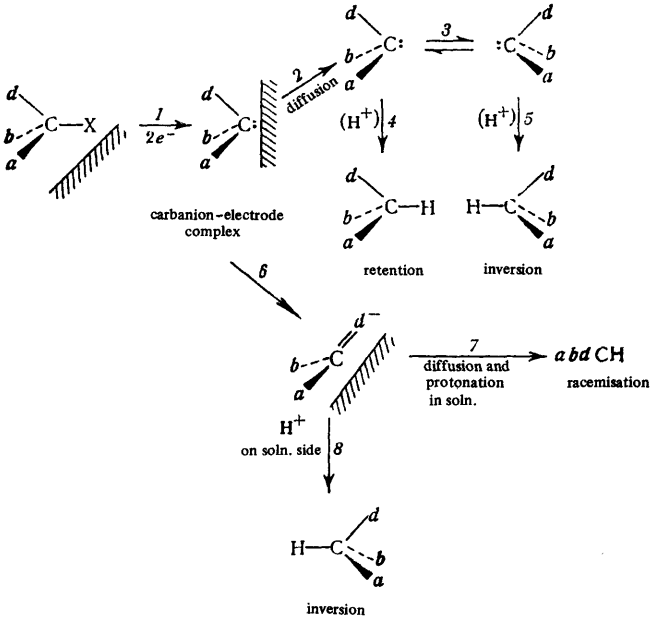


Figure 2. Events occurring during lifetime of carbanion formed by cathodic reduction of an optically active halogeno-derivative. The scheme shows the case in which electron transfer occurs with retention of configuration.

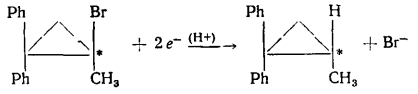
Table 1.

Stage of reaction	*1*	*4*	*3.5*	*6.7*	*6.8*
Attack "on halogen"	retention	retention	inversion	racemisation	inversion
Attack "on carbon"	inversion	inversion	retention	racemisation	retention

These requirements are satisfied by halogenated vinyl and cyclopropyl derivatives. Cyclopropyl anions are inverted at a very low rate [19]—less than twice a second—so that the stereochemical contribution of reactions (3) and (5)—and, in the absence of substituents capable of conjugation, also reactions (6–8) and (6–7)—is not so large. Thus it may be expected that the stereochemistry of the cathodic reduction of cyclopropyl halides will be determined in considerable measure by the stages of actual transfer of electrons (1) and of diffusion of the carbanion into the solution (2). Hence it is not surprising that almost all work on the stereochemistry of the cathodic reduction of halogeno-derivatives has been done on derivatives of cyclopropane. Study of the stereochemistry of these reactions shows that electron transfer occurs with retention of configuration, i.e. on the side of the halogen atom.

‡ This does not apply to the *cis*- and *trans*-iodohexenes discussed above, which by analogy with other π-systems probably have a horizontal orientation relative to the electrode surface. If a stage of isomerisation of the radical is involved, therefore, the stereochemistry of transfer of first and second electrons may be different.

Walborsky and his coworkers[20] electrolysed (+)-(S)-1-bromo-1-methyl-2,2-diphenylcyclopropane in acetonitrile at a mercury cathode at a potential of −2.7 V (s.c.e.). This gave a 93% yield of the corresponding hydrocarbon, which had the configuration of the original bromide (25% optical purity):



The current–time curve obtained at a stationary macroelectrode had an unusual form. A mercury-containing product appeared in the solution at the start of electrolysis, and the mean consumption of electrons per R–Br molecule was < 2. Results obtained by cyclic volt–amperometry suggested the mechanism of reduction

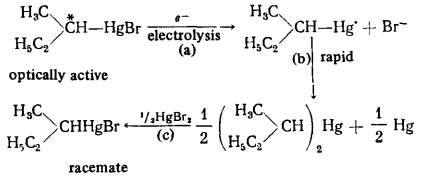
$$R{-}Br + e^- \rightarrow (R{-}Br)^{\cdot-} \qquad RHg_n^{\cdot} + e^- \rightarrow R^- + Hg_n$$

$$(R{-}Br)^{\cdot-} \rightarrow R^{\cdot} + Br^- \qquad RHg_n^{\cdot} + RHg_n^{\cdot} \rightarrow RHg_nR + RHgR + Hg_{n-1}$$

$$R^{\cdot} + e^- \rightarrow R^- \qquad R_2Hg + e^- \rightarrow R^- + RHg^{\cdot} \xrightarrow{Hg} RHg_n^{\cdot}$$

$$R^{\cdot} + Hg_n^{\cdot} \rightarrow RHg_n^{\cdot} \qquad R^- + H^+ \rightarrow RH$$

The retention of configuration in this case might have been explained by a double inversion of configuration at the stages of electrolysis of RBr and formation of R_2Hg[5]. According to Dessy et al.[21], however, optically active s-butylmercuric bromide is completely racemised during electrolysis. This is proved by the cycle of reactions



Electrolysis of optically active s-butylmercury bromide produces an organomercury radical, which then dimerises rapidly to di-s-butylmercury. The action of mercury(II) bromide on this last compound yields optically inactive s-butylmercury bromide. It has been duly proved that stage (*c*) occurs with retention of configuration[22], and therefore racemisation should take place at either stage (*a*) or stage (*b*). Disproportionation of RHg· radicals (reaction *b*) involves rupture of only one C–Hg bond: i.e. if stage (*a*) leads to the retention of configuration, the optical activity of RHgBr obtained from R_2Hg should be partly retained. Hence it may be concluded that the RHg· radicals are optically inactive: i.e. racemisation occurs at the stage of formation of RHg· from RHgBr.

This conclusion is consistent also with the fact that the reduction at a mercury electrode of phenylmercuric bromide containing the radioactive isotope ^{203}Hg is accompanied by rapid isotopic exchange between the organomercury compound and the metallic mercury of the electrode, whereas on open circuit such exchange is almost zero[21]. This implies that organomercury radicals are involved in the isotopic exchange:

$$Ph{-}^{203}Hg^{\cdot} + Hg \underset{}{\overset{rapid}{\rightleftharpoons}} PhHg^{\cdot} + {}^{203}Hg$$

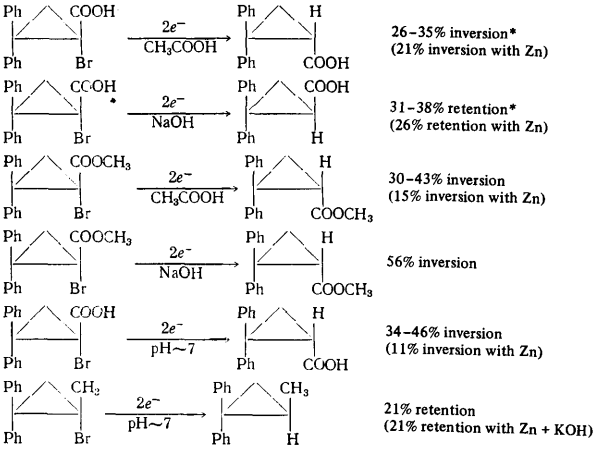
It is natural to expect that such exchange will be accompanied by racemisation, since the reaction involves fission of the carbon–mercury bond§.

§ Thus data on the stereochemistry of the reduction of organomercury compounds cannot be used in discussing the question of the distance between the depolariser and the electrode.

It is clear that the corresponding organomercury compound is not an intermediate product in the reduction of 1-bromo-1-methyl-2,2-diphenylcyclopropane. Besides the reason mentioned at the beginning of this Section, the incomplete retention of the configuration can be explained also by the partial occurrence of the reaction via the organomercury compound and partial inversion of the carbanion in solution (stages (2) and (3) in Fig. 2).

Annino et al.[23] have also investigated the cathodic reduction of optically active 1-bromo-1-methyl-2,2-diphenylcyclopropane in alcoholic medium at potentials of ~2.3 V (s.c.e.). The product was a hydrocarbon of 21% optical purity (retention of configuration), which agrees with Walborsky's results[20]. An investigation was made also of the stereochemistry of the reduction at a mercury electrode of optically active 1-bromo-2,2-diphenylcyclopropanecarboxylic acid and its methyl ester at various solution pH values produced by the addition of acetic acid or of sodium hydroxide to the alcoholic solutions. The results are shown in Scheme 2. The stereochemistry of the cathodic reduction of these bromo-derivatives corresponds qualitatively to that of their reduction with metallic zinc (these results are given in parentheses in Scheme 2).

Scheme 2

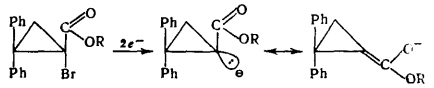


* The expression "30% inversion" means that the result of reduction is a hydrocarbon whose absolute configuration is opposite to that of the initial bromide, while the yield of this hydrocarbon is 30% of the initial bromide of 100% optical purity (the remaining 70% of the total quantity of cathodic reduction product comprises a racemate). The "percentage retention of configuration" is to be interpreted analogously.

The results are explained on the basis of two fundamental assumptions: (1) electron transfer to the cyclopropyl bromide molecule occurs on the side containing the bromine atom, with formation of a carbanion having the configuration of the original bromide; and (2) the general stereochemistry of the process is determined by the stereoselective reaction of the carbanion, either free or shielded by the electrode, with a proton donor.

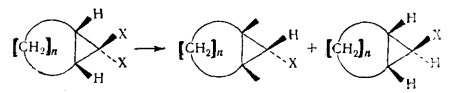
In the case of the brominated cyclopropanecarboxylic acids the carbanion formed by reduction is able to assume

a planar configuration as a consequence of conjugation with the carbonyl group:



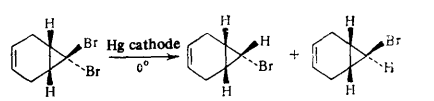
In contrast to 1-methyl-2,2-diphenylcyclopropyl bromide, therefore, such compounds are reduced with retention of configuration. In this case the stereochemistry of the reaction is probably determined by stages (6)–(8) (Fig. 2). The fact that in alkaline medium 1-bromo-2,2-diphenylcyclopropanecarboxylic acid is reduced with retention of configuration (Scheme 2) is probably due to the considerably diminished stabilisation of the planar anion owing to ionisation of the carboxy-group.

The cathodic reduction of *gem*-dihalogenocyclopropanes is highly stereoselective. Fry and Moore[24] have examined the composition of the products of the electrolysis of 1,1-dihalogeno-2,3-tetra(and hexa)methylenecyclopropanes in various solvents. The reaction results in detachment of one halogen atom with formation of a monohalogenocyclopropane, the main product in all solvents being the *cis*-isomer:



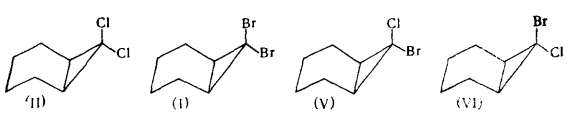
I: $n = 4$, X = Br
II: $n = 4$, X = Cl
III: $n = 6$, X = Br

cis- (*endo*-) *trans*-(*exo*-)



(IV) *cis*- *trans*-

Similar results have been obtained by Annino and his coworkers[25], who investigated the compounds



(II) (I) (V) (VI)

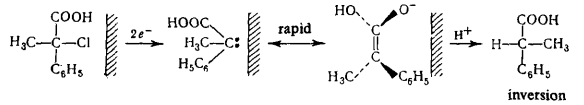
In compounds (V) and (VI), which contain both chlorine and bromine, the bromine is reduced. Table 2 gives the proportions of *cis*- and *trans*-monohalogeno-derivatives (the *endo/exo* ratios) determined by gas–liquid chromatographic analysis of the products of the electrolysis. The ratio of the isomers in the reaction product depends not only on the nature of the solvent but also on the inert electrolyte.

Three conclusions can be drawn from the above results: (1) *cis*-monohalogeno-compounds are the main products of the electrolysis of dibromo- and dichloro-derivatives; (2) the content of the *cis*-isomer increases with increase in the concentration of water in the solution; and (3) the stereospecificity of the reaction is greater with chloro- than with bromo-derivatives. The results can be explained by two alternative schemes: firstly, of two identical halogen atoms, that one is reduced which is located in the *cis*-position to the hydrogen atoms adjacent to the bond between the rings, in which case electron transfer occurs with retention of the configuration; or secondly the *trans*-halogen is reduced with inversion of the configuration.

If "attack on halogen" is supposed to occur (see above), steric hindrance on formation of the transition state is far greater for a halogen in the *trans*-position to the hydrogen atoms of the bridging bond. This is supported by the fact that the reduction of bromine in the two isomeric 7-bromo-7-chlorobicyclo[4,1,0]heptane occurs with greater difficulty in (VI) than in the isomer (V), in which the spatial position of the bromine is more favourable for approaching the electrode surface.

The stereospecificity of the cathodic reduction of different halogens (Cl > Br) is analogous to that observed in the preparation of Grignard reagents from cyclopropyl halides. This occurs with retention of configuration, the loss of optical activity falling in the sequence I > Br > Cl[26]. The mechanism of the reaction RX + Mg → RMgX is probably similar to that of the cathodic reduction of the halides[27]. Preferential formation of *endo*-isomers is observed also in the reduction of compounds (I), (II), and (V) with zinc or lithium amalgam in alcohol[25].

Optically active α-chlorohydratropic acid is reduced with inversion of configuration[28]. This result is explained by "attack on carbon" and accompanying inversion. However, as with the halogenated cyclopropanecarboxylic acids (Table 2), a better explanation is "attack on halogen" and rapid transition of the carbanion into a planar configuration. Owing to the shielding effect of the electrode, subsequent protonation occurs predominantly on the solution side:



inversion

Table 2. Stereochemistry of the electrolysis of *gem*-dihalogenocyclopropanes at a controlled potential.

Compound	Solvent-electrolyte*	Ratio of isomeric products (*endo/exo*)
I	DMF-LiCl	1.6
	96% DMF—4% H_2O—LiCl	3.0
	CH_3OH—LiCl	1.9
	95% CH_3OH—5% H_2O—LiCl	2.7
	95% CH_3OH—5% HCl—LiCl	3.5
	90% CH_3OH—10% H_2O—LiCl	5.3
	CH_3COOH—TEAB	4.0
II	DMF—LiCl	4.3
	96% DMF—4% H_2O—LiCl	5.3
	CH_3OH—LiCl	19.0
	95% CH_3OH—5% HCl—LiCl	only *endo*
	33% HMPTA—67% C_2H_5OH	only *endo*
III	CH_3OH—LiCl	only *endo*
	95% CH_3OH—5% HCl—LiCl	only *endo*
IV	CH_3OH—LiCl-	2.7
	90% CH_3OH—10% H_2O—LiCl	10.0
V	C_2H_5OH—TEAB	3.6
	C_2H_5OH—LiCl	2.6
VI	C_2H_5OH—LiCl	0.38
Mixture of V + VI (1:1)	C_2H_5OH—LiCl	1

* DMF = dimethylformamide; HMPTA = hexamethylphosphorotriamide; TEAB = tetraethylammonium bromide.

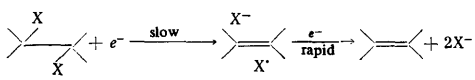
Reduction by zinc in acetic acid proceeds similarly. Ott and Kramer[29] reported that α-chlorohydratropic acid is reduced by this system with inversion of configuration, but by hydrogen–palladium with its retention. According to Brewster[30] inversion of configuration is a result of direct interaction between zinc and the chlorine atom: a carbanion is formed which is then rapidly protonated, before it is able to diffuse into the solution, i.e. to free itself from the metal surface.

Thus it may be concluded that, in the preparative electrolysis of optically active halogeno-derivatives, electron transfer to the molecule RX occurs on the side of the halogen atom in close contact with the electrode surface; this leads to the formation of a carbanion having the same configuration as the initial bromide. However, subsequent events occurring in the lifetime of the carbanion (inversion, resonance stabilisation, diffusion into the solution) may influence considerably the overall stereochemical result of the reaction. Depending on the properties of the organic halogeno-derivative, therefore, either retention, inversion, or complete racemisation of the configuration may be observed.

IV. VICINAL DIHALOGENO-DERIVATIVES

Most cases of the cathodic reduction of vicinal dihalogeno-derivatives involve the simultaneous detachment of two halide anions with the formation of a multiple bond. Thus the electrolysis of 1,2-dibromoethane yields ethylene and ethane[31]. This reaction recalls the formation of alkenes, which occurs when vicinal dibromides are treated with zinc or magnesium. The mechanism of the reduction of such compounds has already been considered in a review[5]. Here we shall discuss briefly only the stereochemical aspects of this reaction.

cis-1,2-Dibromocyclohexane is reduced at a potential of −1.85 V (s.c.e.) and the *trans*-isomer far more easily (−1.0 V)[32]. *meso*-2,3-Dibromosuccinic acid is more easily reduced than is the (±)-isomer[33], and this applies also to *meso*-2,3-dibromobutane-1,4-diol[34]. The greater ease of reduction of *meso*-dihalides implies that *trans*-elimination occurs preferentially. In the case of rigid bicyclic systems the *cis*-dibromides are more easily reduced, since a *trans*-coplanar configuration cannot exist[35,36]. Detachment of the two halogen atoms probably occurs simultaneously:



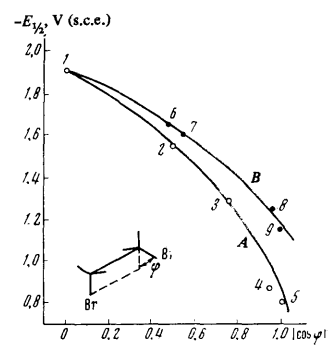
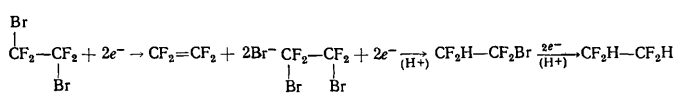


Figure 3. Dependence of half-wave potential of vicinal dibromides on dihedral angle between C−Br bonds:
A) compounds having an *anti*-planar configuration ($120° \leqslant \varphi \leqslant 180°$); B) compounds having a *syn*-planar configuration ($0° \leqslant \varphi \leqslant 60°$). It is clear that an *anti*-planar configuration is more favourable.

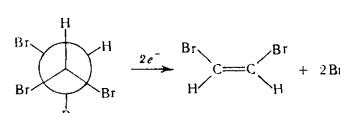
It can be shown that both halogen atoms are involved in formation of the transition state. Zavada et al.[36] determined half-wave potentials for a large number of vicinal dibromides and monobromides. In the series of dibromides $E_{\frac{1}{2}}$ varies from −0.82 to −1.67 V, but in the series of monobromides from −1.90 to −2.16 V (s.c.e.). The compounds were selected so that the steric hindrance was about the same in the two series, i.e. so that it made a relatively small contribution to variation in the reduction potentials. The main reason for the marked variation in the half-wave potentials in the vicinal dibromides is the variation in the dihedral angle φ between the planes formed by each bromine atom with the carbon–carbon bond. The graph in Fig. 3 shows that molecules having an *anti*- or *syn*-planar arrangement of the bromine atoms (φ = 180° or 0°) are reduced at more positive potentials than are molecules in which the angle φ lies between 60° and 120°.

Other evidence of the simultaneous detachment of two bromine atoms has been obtained by Feoktistov and Gol'din[37] in a study of the cathodic reduction of 1,2-dibromotetrafluoroethane. The product of reduction of the *anti*-isomer is tetrafluoroethylene, whereas the *syn*-isomer yields tetrafluoroethane¶:



Not only halogens but also other electronegative groups, e.g. hydroxyl and acetoxyl, may be split off together with a bromine atom[33]. In these cases reduction is also facilitated when the two groups are located in the same plane.

The electrolysis of tetrabromoethane yields a mixture of *cis*- and *trans*-dibromoethylene in the proportions 6 : 1[39,40]. These results show that *trans*-elimination predominates, since in polar solvents (50% aqueous ethanol was used in this example) tetrabromoethane exists predominantly as the staggered conformation:



cis- and *trans*-Dibromoethylenes are formed in the ratio 6 : 1, differing considerably from the proportions in the reduction of tetrabromoethane by zinc or by tin(II) chloride (1.2–2 : 1). The probable reason is that, during electrolysis within the potentials of the limiting diffusion current, i.e. with diffusion control of the reaction, the staggered conformation is unable to pass into the more reactive transoid conformation[40], whereas with kinetic control (dehalogenation by zinc) such conversion is possible.

¶ However, successive replacement of chlorine by hydrogen has been observed[38] in the electrolysis both of diethyl dichloromaleate and of diethyl dichlorofumarate. Reduction of the corresponding dibromo- and di-iodo-esters proceeds "normally": i.e. acetylenedicarboxylic ester is formed[38].

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