equation 1. From the fact that the main wave yielding the normal limiting current appears at both types of electrode at considerably more positive potentials than the prewave, it is evident that the film must break down at these more positive potentials. It is of interest to note (Fig. 2) that this breakdown potential is more positive at *p*H 5 than at *p*H 7, the reversible electrode reaction also occurring at more negative potentials with increasing *p*H. The breakdown potential, especially at *p*H less than 5, is more positive when the polarogram is run from negative to positive potentials than in the opposite direction indicating that the structure of the film is affected by conditions of its formation.[4] Cysteine and its mercury compounds are dipolar and oriented at the electrode. The adherence of the film to the mercury surface therefore may depend on the charge of the electrode and on the *p*H of the solution. Film formation is decreased by increasing temperature. No film formation and waves corresponding to a reversible one electron reaction are observed at 80° both at C.M.E. and the D.M.E. RSSR and TSST when present at high enough concentrations appear to be stronger adsorbed on mercury than HgRS and eliminate the prewave at room temperature. Apparently the adsorbed layer of disulfide is permeable to cysteine.

The thickness of the film of mercurous cysteinate at the C.M.E. can be found from the dissolution pattern. The number of HgRS molecules reduced (see equation 1) from right to left can be calculated from the quantity of electricity corresponding to the area of the dissolution patterns (Table II). From the known area of the electrode surface this number was calculated to be 11.6×10^{14} molecules HgRS per cm.^{2} of electrode surface and the area occupied by one HgRS molecule is therefore 8.6 Å.^{2}. From the density of mercury, the effective area of the electrode and the assumption of cubic structure of mercury the number of mercury atoms on the surface of the electrode at 25° is calculated to be also 11.7×10^{14} atoms per cm.^{2}, *i.e.*, one atom occupies 8.5 Å.^{2}. These results clearly indicate that the film at the C.M.E. is composed of a monomolecular layer of HgRS.

Attributing the prewave observed at the D.M.E. also to an adsorbed film of HgRS, its thickness can be calculated from the Brdicka[10] relation

$$i = nFZ\Delta q$$

where i is the current determined by the amount of adsorbed substance, F the faraday, Z the maximum number of adsorbed moles per cm.^{2} and Δq the average increase of the electrode surface per second. Expressing the characteristics of the dropping electrode m in g. per sec. and t in sec., Δq is given by

$$\Delta q = 0.85 m^{2/3} t^{-1/3} \text{ cm.}^2/\text{sec.}$$

Taking for i the value of the false diffusion current (0.62 μa. at -0.2 volt, see Fig. 2B) measured in a solution of a cysteine concentration greater than 2.5×10^{-4} *M* at *p*H 5.0 the value for Z was calculated to be 7.4×10^{-10} mole per cm.^{2} or 4.4×10^{14} adsorbed molecules per cm.^{2}, a value which is of the same order of magnitude as that (11×10^{14}) calculated for the film at the C.M.E. The agreement between these figures is rather striking, considering that the hydrodynamic conditions around the mercury are so different with both types of electrodes. It is reasonable, then, to conclude that the film at both electrodes is composed of a monomolecular layer of mercurous cysteinate which becomes the seat of a high electrical resistance.

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[10] R. Brdicka, *Z. Elektrochem.*, **48**, 278 (1942).

MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY OF THE UNIVERSITY OF MINNESOTA]

Polarographic Reduction of Cystine and of Dithiodiglycolic Acid in the Presence of Iron

BY I. M. KOLTHOFF, W. STRICKS AND NOBUYUKI TANAKA[1]

RECEIVED MAY 27, 1955

In alkaline medium (*p*H 9.2) iron has a great effect on the polarographic reduction of cystine. In the presence of sufficient iron only one wave of cystine is observed at fairly positive potentials which yields the normal diffusion current while in the absence of iron a relatively small prewave followed by a drawn out reduction wave is found. The potentials of the iron-catalyzed wave correspond to a reversible one-electron reaction, although the over-all reduction involves two electrons. The catalysis is explained by the reaction: $RSSR + Fe(II) \rightarrow Fe(III) + RS^{\cdot} + RS^-$ which is rapid and is followed by polarographic reduction of $RS^{\cdot}$ and Fe(III), of which the iron reduction is potential determining. An alternate mechanism accounts equally for the experimental facts. The iron catalysis is eliminated by Versene and much pyrophosphate, but tartrate has no effect. The oxidation potential measured at the dropping mercury electrode of the cystine–cysteine system in the presence of iron does no longer correspond to the reaction $RSSR + 2H^+ + 2e^- \rightleftarrows 2RSH$.

In studies of iron–cysteine–cystine systems[2] it was observed that iron increases the polarographic prewave of cystine. This effect has been studied in greater detail and the results are reported in the present paper. The first (prewave) of the double wave of cystine at the dropping mercury electrode in a *p*H range of 3 to 9 was found to be kinetic in

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[1] Tohoku University, Sendai, Japan.

[2] N. Tanaka, I. M. Kolthoff and W. Stricks, THIS JOURNAL, **77**, 1980, 1996 (1955).

nature and to correspond to the over-all reversible reaction[3]

$$RSSR + 2e^- + 2H^+ \rightleftarrows 2RSH \qquad (1)$$

in which RSSR denotes the cystine and RSH the cysteine. The first step of the reaction was attributed to an interaction between the mercury of the electrode and adsorbed RSSR

$$RSSR + Hg \rightleftarrows HgRS + RS^{\cdot} \rightleftarrows Hg(RS)_2 \qquad (2)$$

In the presence of small concentrations of ferrous or ferric iron in alkaline medium the height of the prewave of cystine increases and in the presence of sufficient iron attains a limiting value equal in height to the diffusion current of cystine in the absence of iron.

One possible explanation of this catalytic effect is that ferrous iron catalyzes reaction (2) by rapidly removing RS$^{\cdot}$ according to the reaction

$$Fe(II) + RS^{\cdot} \longrightarrow Fe(III) + RS^- \qquad (3)$$

The over-all reduction then occurs by the simultaneous reduction of Fe(III) and HgRS according to

$$Fe(III) + e^- \rightleftarrows Fe(II) \qquad (4)$$

$$HgRS + e^- \rightleftarrows Hg + RS^- \qquad (5)$$

Another interpretation is that Fe(II) reacts rapidly with RSSR at the surface of the electrode according to

$$RSSR + Fe(II) \rightleftarrows RS^{\cdot} + Fe(III) + RS^- \qquad (6)$$

followed by the reduction of Fe(III) (equation 4) and RS$^{\cdot}$

$$RS^{\cdot} + e^- \longrightarrow RS^- \qquad (7)$$

It has been shown[2] that ferrous iron in alkaline medium can reduce cystine. According to equation 4 ferrous iron is re-formed continuously and thus can exert its catalytic effect. After presentation of the experimentally determined characteristics of the catalyzed wave it will be shown that equations 6, 4 and 7 as well as equations 2, 3, 4 and 5 quantitatively account for the experimental facts.

Some data on the effect of iron on the polarographic reduction of dithiodiglycolic acid are also given in the experimental part.

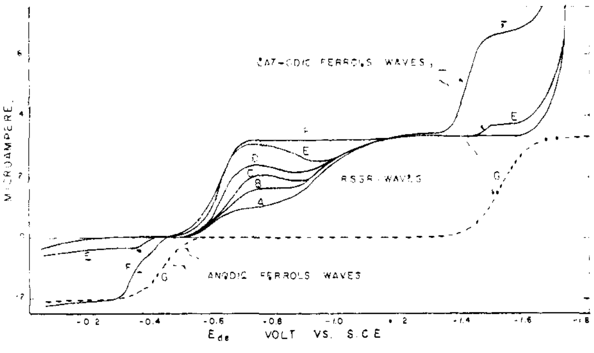

Fig. 1.—Current-voltage curves of 5×10^{-4} M cystine (0.05 M borax, 0.1 M sodium tartrate, pH 9.2) in the presence of: A, no iron; B, 2×10^{-6} M Fe(II); C, 5×10^{-6} M Fe(II); D, 10^{-5} M Fe(II); E, 10^{-4} M Fe(II); F, 6.7×10^{-4} M Fe(II); G, C-V curve of 6.7×10^{-4} M Fe(II) (0.05 M borax, 0.1 M sodium tartrate) in the absence of cystine (---). Currents are corrected for residual.

Materials and Experimental

All chemicals, instruments and experimental methods were the same as those described previously.[3]

Characteristics of the Cystine Wave in the Presence of Iron

Variation of Iron Concentration at Constant Cystine Concentration.—The effect of various concentrations of ferrous iron on the current-voltage curve of 5×10^{-4} M cystine in a 0.05 M borax buffer (0.1 M in sodium tartrate) is illustrated in Fig. 1. Tartrate was added in order to keep iron in solution at pH 9. Experiments at iron concentrations lower than 5×10^{-5} M in the absence and presence of tartrate indicated that the iron catalysis is not affected by tartrate. Even traces of ferrous iron increase the height of the prewave, the increase being considerably less than proportional to the iron concentration (see Fig. 1). When the concentration is sufficiently large (6×10^{-4} M in Fig. 1) the prewave attains the height of the diffusion current of cystine and only a single reduction wave of cystine is observed. The prewave or the single wave is shifted to more positive potentials as the iron concentration is increased.

The same results as in Fig. 1 were obtained with ferric (up to 10^{-4} M) instead of ferrous iron.

Figure 1 also shows the anodic and cathodic ferrous waves in the presence and absence of cystine. The anodic as well as the cathodic ferrous waves are shifted to more positive potentials in the presence of cystine. The shift of the anodic iron wave which cannot be explained by complex formation with cystine is attributed to an effect of adsorbed cystine which is strongly surface active and in solutions of pH 9 it displaces the electrocapillary maximum to more positive potentials. Several examples are found in the literature[4] of the displacement of polarographic waves by strongly capillary active substances. We found that thymol also shifts the anodic ferrous wave to more positive potentials. For example, the half-wave potential of 6.7×10^{-4} M ferrous iron in 0.05 M borax, 0.1 M tartrate and 10^{-5} M thymol was found to be -0.22 volt as compared to -0.42 volt in the absence of thymol. The cathodic ferrous wave which is not affected by thymol will be dealt with below.

Variation of Cystine Concentration at Constant Iron Concentration.—At a ferrous iron concentration of about 7×10^{-4} M and at cystine concentrations varying from 0.17 to 1.5×10^{-3} M (pH 9.2) the appearance of the cystine wave was found to be unchanged. From the data in Table 1 it is seen that the height of the wave is proportional to the cystine concentration while the half-wave potential is shifted to more negative values with increasing cystine concentration.

Table 1

Current at -0.75 Volt and Half-wave Potential of Cystine in the Presence of 6.7×10^{-4} M Fe(II) in 0.05 M Borax, 0.1 M Sodium Tartrate (pH 9.2)

Concn. RSSR $\times 10^3$, M	$\frac{Fe(II)}{RSSR}$	i, μa.	i/c[a]	$E_{1/2}$, v.[b] vs. S.C.E.
0.166	4.0	1.11	6.68	-0.572
0.50	1.23	3.32	6.64	-0.588
1.00	0.67	6.61	6.61	-0.607
1.50	0.45	9.90	6.60	-0.616

[a] i/c = μa./mmole/l. [b] Corrected for iR drop.

Effect of pH.—Polarograms of 5×10^{-4} M cystine in an acetate buffer of pH 4.7 in the presence of 10^{-4} M to 2×10^{-4} M ferrous iron revealed that the cystine wave is unaffected by iron at this low pH. The height of the prewave in this medium was found to be 1.10 μa. (measured at -0.4 volt) in the absence and presence of ferrous iron.

Effect of Cysteine, Versene, Pyrophosphate in a Borax Buffer of pH 9.2.—In order to gain some further insight into the mechanism of the iron-catalyzed electroreduction of cystine the effect of these three compounds which form complexes with ferrous and ferric iron was investigated.

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[3] I. M. Kolthoff, W. Stricks and N. Tanaka, This Journal, **77**, 5211 (1955).

[4] See I. M. Kolthoff and J. J. Lingane, "Polarography," Interscience Publishers Inc., New York, N. Y., 1952, p. 558, 785.

The cystine wave obtained in a mixture of 5×10^{-4} *M* cystine, 1.02×10^{-3} *M* cysteine and 6.7×10^{-4} *M* Fe(II) was equal in shape and height to that obtained in the absence of cysteine but its half-wave potential was shifted by about 30 mv. to a more negative value. Polarograms were also run of mixtures (borax-tartrate) of ferrous iron and cysteine in the absence of cystine. While the anodic waves in ferrous-cysteine-cystine and ferrous-cysteine mixtures were found to be badly distorted and not to give a well-defined diffusion region, the cathodic ferrous waves obtained from these mixtures appeared to be well-defined. Some data on the iron reduction waves are listed in Table II. It is seen that the half-wave potential of the ferrous reduction wave in a tartrate-borax solution is about 100 mv. more negative than that in the presence of either 10^{-3} *M* cysteine or 5×10^{-4} *M* cystine. The diffusion current of the ferrous wave was found the same in the presence and absence of cystine but larger in the presence of cysteine. These data indicate that the height of the ferrous reduction wave in the presence of cystine and absence of cysteine is controlled by diffusion of the ferrous tartrate complex while the potential corresponds to the reduction of the ferrous cysteinate complex which is formed on the surface of the electrode upon reduction of the cystine to cysteine.

TABLE II

HALF-WAVE POTENTIAL AND DIFFUSION CURRENT OF THE CATHODIC FERROUS WAVE

0.05 *M* borax, 0.1 *M* sodium tartrate, 6.67×10^{-4}*M* Fe(II)

Concn. RSH, *M*	Concn. RSSR, *M*	$E_{1/2}$, v. *vs.* S.C.E.	i_d, μa.	$i_d/cm^{2/3}t^{1/6}$
0	0	−1.52	3.42	2.24
1.02×10^{-3}	0	−1.42	3.80	2.48
0	5.0×10^{-4}	−1.41	3.43	2.25

In the presence of 3.3×10^{-3} *M* Versene the catalytic effect of iron at *p*H of 9.2 was found to be completely precluded. Thus at this Versene concentration a 5×10^{-4} *M* cystine solution (0.05 *M* borax, 0.1 *M* tartrate) gave a prewave of 0.92 μa. in the absence and presence of 2×10^{-4} *M* Fe(II), as compared to 3.12 μa. at the same iron concentration in the absence of Versene.

The halfwave potential of the composite ferrous-ferric iron wave (4.8×10^{-4} *M* in both Fe(II) and Fe(III)) in 4×10^{-3} *M* Versene (0.05 *M* borax, 0.1 *M* tartrate) in the absence of cystine was found to be −0.234 volt, while the i_d/c-values of the anodic and cathodic iron waves were 3.27 and 3.16, respectively.

The effect of pyrophosphate was investigated in 5×10^{-4} *M* cystine solutions in 0.05 *M* borax at ferrous iron concentrations varying from 2×10^{-6} to 10^{-3} *M* and at pyrophosphate concentrations between 0.004 and 0.05 *M*. Qualitatively the effect of pyrophosphate was similar to that of Versene, but considerably larger concentrations of pyrophosphate than of Versene are required to eliminate the iron catalysis. For example, in a 5×10^{-4} *M* RSSR solution which was 2×10^{-4} *M* in Fe(II) the height of the prewave was found to be 2.70, 2.08 and 0.91 μa. in the presence of 0.00, 0.004 and 0.05 *M* pyrophosphate, respectively. The height of the uncatalyzed prewave (in the absence of iron) was 0.78 μa. in the same media. While less than 3×10^{-3} *M* Versene was required to eliminate the iron catalysis, even 0.05 *M* pyrophosphate under the same experimental conditions did not eliminate the iron effect completely.

A polarogram of a mixture of 5×10^{-4} *M* Fe(II) and 5×10^{-4} *M* Fe(III) in 0.05 *M* pyrophosphate and 0.05 *M* borax consisted of a steep composite wave with a fully developed anodic wave ($i_d/c = 2.85$) and a small cathodic wave ($i_d/c = 0.36$) which was followed by a second drawn-out wave. The sum of the two cathodic waves ($i_d/c = 3.00$) corresponded to the reduction of total ferric iron. The half-wave potentials of the composite wave and of the second cathodic wave were −0.395 and −0.815 volt *vs.* S.C.E. Apparently more than one ferric iron pyrophosphate complex of widely different stabilities coexist in the solution.

The Dithiodiglycolic Acid Wave in the Presence of Iron.—Some characteristics of the wave of dithiodiglycolic acid (TSST) have been described previously.[3] Our present experiments indicate a marked difference in the effect of iron on the cystine and TSST waves. In 0.05 *M* borax, 0.1 *M* in KCl, the current-voltage curves of 5×10^{-4} *M* TSST were practically unaffected by iron at concentrations up to 2×10^{-5} *M* Fe(II), while 5×10^{-4} *M* iron increased the prewave of TSST from 0.08 μa. (in the absence of iron) to 0.24 μa. At the same iron concentration the cystine prewave attained the height of the diffusion current. The small effect of iron on the TSST wave was completely eliminated by TSH or tartrate, while cysteine and tartrate had no such effect on the RSSR-Fe(II) system.

Discussion

The fact that the prewave of cystine in the presence of sufficient ferrous iron attains a height which is equal to the diffusion current of cystine in the absence of iron and proportional to the cystine concentration suggests that the iron-catalyzed wave is controlled by diffusion of cystine and not by that of a ferrous cystine complex. Other evidence that under our experimental conditions no complex of ferrous iron with cystine exists in the solutions to any appreciable extent has been presented in a previous section.

A plot of $\log (i_d - i)/i^2$ *vs.* *E* for the one-step wave of 5×10^{-4} *M* RSSR in the presence of 6.7×10^{-4} *M* Fe(II) gave a straight line with a slope of 0.055 and the plot of $\log i_d/2$ *vs.* $E_{1/2}$ at cystine concentrations given in Table I ([Fe(II)] = 6.7×10^{-4} *M*) was also found to be a straight line with slope of 0.059. These data indicate that the potential of the cystine wave in the presence of iron is determined by a reversible one-electron transfer although the height is determined by an over-all two electron reaction.

Considering equations 6, 4 and 7 it is reasonable to assume that RS· is being reduced much more rapidly than the ferric iron which can only be in the solution in the form of a complex. Reaction (4) then would represent the potential-determining reaction.

Both ferric iron and cysteine are formed at the surface of the dropping mercury, the two components forming a very strong complex.[2] The iron reduction then may be represented by

$$\mathrm{Fe(RS^-)_3 + e^- \rightleftarrows Fe(RS^-)_2 + RS^=} \quad (4a)$$

Assuming reversibility of equation 4a the potential of the system is given by

$$E = E_s^\circ + 0.0591 \log \frac{K_{\mathrm{Fe(RS^=)3}}}{K_{\mathrm{Fe(RS^=)_2}}} - 0.0591 \log [\mathrm{RS^=}] \quad (8)$$

where the *K*'s are the dissociation constants of the ferric and ferrous cysteinates and E_s° the standard potential (+0.529[5] volt *vs.* S.C.E.) for the couple

$$\mathrm{Fe^{+++} + e^- \rightleftarrows Fe^{++}}$$

The value of *E* can be calculated at a given cysteine concentration from the known dissociation constants $K_{\mathrm{Fe(RS^-)_3}} = 8 \times 10^{-33}$ and $K_{\mathrm{Fe(RSS^-)_2}} = 1.7 \times 10^{-12}$ [2] and from the intrinsic dissociation constants of cysteine.[6] The value of *E* is the same for both the hydroxyl containing iron complexes $\mathrm{FeOH(RS^-)_2}$ and $\mathrm{FeOHRS^-}$ and for the complexes $\mathrm{Fe(RS^-)_3}$ and $\mathrm{Fe(RS^-)_2}$, the ratio of the dissociation constants of the two pairs of compounds being practically the same.[2] Thus

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(5) W. M. Latimer, "Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice-Hall, Inc., New York, N. Y., 1952, p. 223.

(6) W. Stricks and I. M. Kolthoff, THIS JOURNAL, **73**, 4569 (1951).

$$E = -0.735 - 0.0591 \log [RS^-] \qquad (9)$$

Mixtures which were 5×10^{-4} M in RSSR, 10^{-3} M in RSH, 0.05 M in borax, 0.1 M in tartrate and which were 6.7×10^{-4} M and 2×10^{-3} M in ferrous iron gave only one reduction wave of cystine with half-wave potentials of −0.63 and −0.60 volt and zero current potentials of −0.58 and −0.55 volt, respectively.

From equation 9 we calculate a half-wave potential of −0.56 volt for a cysteine concentration of 10^{-3} M, which is in reasonable agreement with the experimental value of 0.60 for the above solution with the larger iron concentration, the experimental values becoming closer to the calculated ones as the iron concentration increases.

In order to exert the catalytic effect the oxidation potential of the iron in the system must be such that reaction (6) can take place to an appreciable extent and this reaction must be rapid. The half-wave potential of the ferrous–ferric couple in Versene at *p*H 9.2 is −0.234 volt while that of the couple in a cysteine solution is −0.54 volt. The oxidation potential of the system in the presence of Versene is not negative enough to give any appreciable reaction to the right in equation 6. The partial elimination of the catalytic reduction in the presence of much pyrophosphate appears to be attributable to the same cause as in the presence of Versene.

Whereas in the absence of iron the reversible oxidation potential corresponding to equation 1 of the RSSR–RSH couple is measured at the dropping electrode this should be no longer true in the presence of iron if our interpretation is correct. Actually the zero current potential of the couple was found more positive in the presence than in the absence of iron. For example, in a mixture of 5×10^{-4} M RSSR and 10^{-3} M RSH(*p*H 9) the zero current potentials were found to be −0.614 and −0.55 volt in the absence and presence of 2×10^{-3} M Fe(II).

Finally it should be mentioned that the sequence of reactions (2), (5), (3) and (4) can account equally well for the observed facts as reactions (6), (4) and (7). It is difficult to develop experimental conditions under which one sequence of reactions is conclusively favored over the other.

From the few experiments with dithiodiglycolic acid in the presence of iron it is found that iron has little effect on the prewave of this disulfide. The small effect is eliminated by tartrate which has no effect on the iron catalysis in the reduction of cystine. It might be inferred that reaction (6) with TSST instead of RSSR does not occur or occurs more slowly than with RSSR.

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MINNEAPOLIS, MINNESOTA

[CONTRIBUTION FROM THE PENNSYLVANIA STATE UNIVERSITY AND THE UNIVERSITY OF MICHIGAN]

Effect of Structure and Hydrogen Bonding on the Stereochemistry of Electrode Reactions. The α,α'-Dibromosuccinates

BY PHILIP J. ELVING,[1] ISADORE ROSENTHAL AND AARON J. MARTIN

RECEIVED FEBRUARY 25, 1955

The diastereoisomers (*meso* and racemic (*d,l*) forms) of α,α'-dibromosuccinic acid have been electrolyzed at a mercury cathode at controlled potentials over the *p*H range of 0.4 to 8.5. Fumaric acid was produced quantitatively from the *meso* form at all *p*H levels. The racemic form was converted entirely to fumaric acid at low (below 0.4) and high (above 6.9) *p*H levels; between these *p*H values, the *cis*-acid (maleic) also was formed, with a maximum yield (70 ± 3% of the products) at about *p*H 4.0. Diethyl *meso*- and *rac*-dibromosuccinates gave only diethyl fumarate on electroreduction. The data are interpreted with regard to steric factors and the effect of *p*H on these factors. A mechanism capable of explaining the nature of the reduction products produced by the elimination reaction is presented. Extended data on the polarographic behavior of diethyl fumarate and maleate also are given. Large scale and polarographic reductions of the compounds studied are compared.

Winstein, Pressman and Young[2a] studied the elimination of bromine from the 2,3-dibromobutanes, using iodide ion as the reducing agent, and found that the *meso* diastereoisomer formed 96% *trans*-2-butene while the racemic (*dl*) isomer formed 91% *cis*-2-butene. These facts, together with the observed second-order kinetics,[2b] were explained by assuming that the bromine atoms are *trans*[3] to each other prior to reduction and that the dehalogenation process is initiated by the removal of one of the bromine atoms by combination with iodide ion.[2a] The mechanism of the iodide reduction was considered to be a frontal attack on a bromine atom by an iodide ion forming a negatively charged carbon atom (carbanion) and BrI. The free electrons attack the carbon face opposite the remaining bromine atom, freeing bromide ion with an inversion of the carbon atom to form the olefin. In actual reaction, both steps were thought to proceed simultaneously.

The *cis* effect in elimination reactions and stereochemical control of organic reactions has been reviewed recently.[2c]

In a polarographic study of *meso*[4a]-α,α'-dibro-

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[1] University of Michigan, Ann Arbor, Mich.

[2] (a) S. Winstein, D. Pressman and W. G. Young, THIS JOURNAL, **61**, 1645 (1939); (b) W. G. Young, D. Pressman and C. D. Coryell, *ibid.*, **61**, 1640 (1939); (c) D. Y. Curtin, *Record Chem. Prog.*, **15**, 111 (1954); (d) J. Hine and W. H. Brader, THIS JOURNAL, **77**, 361 (1955).

[3] In using the term *trans* with regard to the relative position of atoms or groups on two carbon atoms joined only by a single bond, we mean that the groups in question will be in, or close to, positions in which they will have the maximum possible separation from each other. The term *cis* is used in an opposite sense.