Studies on the Chemistry of Halogen and of Polyhalides. XVI. Voltammetry of Bromine and Interhalogen Species in Acetonitrile

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The voltammetric behavior of a number of halogen species in acetonitrile solution has been observed employing a rotating platinum indicator electrode. The compounds studied were: tetraethylammonium bromide, tetra-n-butylammonium tribromide, bromine, tetramethylammonium-iododibromide, -iododichloride, -iodobromochloride, -diiodobromide, iodine monobromide and iodine monochloride. Where possible electrode reactions have been postulated to account for the observed voltammetric behavior.

Introduction

A previous paper has reported a voltammetric study of iodine species in acetonitrile.[2] A similar study, also employing a rotating platinum indicator electrode, has been carried out on bromine species and a number of interhalogen and interhalide species.

Experimental

The experimental apparatus, electrode and solvent have been described previously.[2] All potential measurements are referred to the acetonitrile silver, silver nitrate (0.01 M) primary reference electrode. Current values on figures are expressed in the dimensions, microampere liter/millimole. Since the same rotating platinum electrode and stirring conditions were employed in this work as in the previous investigation,[2] current comparisons may be made directly. Data were obtained after preanodization of the electrode at 2.4 v. in the sample solution.

Bromine was purified by distillation from potassium bromide and barium oxide. Iodine monobromide was purified by fractional recrystallization with a final melting point of 41.5°. Iodine monochloride was furnished by Dr. W. A. Deskin. Its purification is described elsewhere.[3] Concentrations of stock solutions were obtained by iodometric titration. The bromine, iodine monobromide and iodine monochloride solutions, which show a slow conversion to tribromide, iododichloride and iododibromide ions, respectively, were examined spectrophotometrically before the voltammetric data were obtained. Bromine solutions showed no more than 3–4% conversion to tribromide ion, while iodine monobromide solutions in the concentration range 8–3 × 10⁻⁴ M showed 3–8% conversion. Acetonitrile solutions of iodine monochloride, which have been studied in detail by Popov and Deskin,[4] evidenced 3–7% conversion to iododichloride ion over a 2–0.4 × 10⁻³ M concentration range.

Tetra-n-butylammonium tribromide was prepared by allowing bromine vapor to come in contact with tetra-n-butylammonium bromide in a closed container. The product was recrystallized from ethanol and gave a melting point of 70–72° in agreement with the literature value.[5]

Tetrapropylammonium dibromoiodide, tetramethylammonium iododichloride, tetramethylammonium iodobromochloride and tetramethylammonium diiodobromide were prepared by the method of Chattaway and Hoyle.[6] Tetraethylammonium bromide (Eastman Kodak Company) was recrystallized from ethanol and dried over phosphorus pentoxide.

A supporting electrolyte of 0.1 M lithium perchlorate was employed throughout.

Results

Bromine Species.—The voltammetric behavior of bromide ion is shown in the lower portion of Fig. 1.

(1) (a) Abstracted from the Ph.D. Thesis of David H. Geske. State University of Iowa, 1957. (b) National Science Foundation Predoctoral Fellow, 1955–1957.

(2) A. I. Popov and D. H. Geske, THIS JOURNAL, 80, 1340 (1958).

(3) A. I. Popov and W. A. Deskin, J. Org. Chem., 22, 1732 (1957).

(4) A. I. Popov and W. A. Deskin, THIS JOURNAL, 80, 2976 (1958).

(5) R. E. Buckles, A. I. Popov, W. F. Zelezny and R. J. Smith, ibid., 73, 4525 (1951).

(6) F. D. Chattaway and G. Hoyle, J. Chem. Soc., 123, 654 (1923).

Half-wave potential and current constants are given in Table I, along with the corresponding electrode reactions. Kolthoff and Coetzee[7] reported half-wave potentials of 0.4 and 0.7 v. (recalculated to the Ag, AgNO₃ electrode) for waves I and II, respectively, for the bromide ion oxidation; these values agree satisfactorily with those found in Table I.

The occurrence and shape of wave III required further consideration. In degassed solutions the wave has the anomalous "hump" appearance. When the solution was saturated with oxygen the wave assumed the normal shape. Added to this peculiar dependence on the presence of oxygen is the fact that the current at wave III is not directly proportional to the bromide ion concentration but shows a deviation to higher values at lower concentrations.

The same behavior was observed for wave III in the current–voltage curve of tribromide ion (middle portion of Fig. 1). Voltammetric data for the tribromide ion are given in Table I. It was possible to obtain well-defined cathodic traces (preanodized electrode) only on the forward trace. When a reverse trace was started at −0.64 v., a c–v curve similar to that indicated by the dashed line in Fig. 1 was obtained. This hysteresis effect, which is similar to that observed in a study of iodine species, has been discussed elsewhere.[2]

The voltammetric behavior of bromine in acetonitrile is given in the top portion of Fig. 1. Half-wave potentials and current constants are given in Table I. When the reverse trace (with a preanodized electrode) was started at −0.6 v. satisfactory agreement with the forward trace obtained.

Iododibromide Ion.—The c–v curve for tetramethylammonium iododibromide is given in Fig. 2 expressed in terms of current constants. Voltammetric data are summarized in Table I. Anodic wave III probably corresponds to the electrode reaction

$$IBr_2^- - e^- \longrightarrow IBr + \tfrac{1}{2}Br_2$$
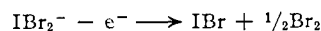
The current constant, −4.86 μa. l./mmole, is comparable to the constant for other one-electron oxidations.

Wave IV shows similarities to wave III in the bromide ion oxidation; the half-wave potential, 1.42 v., is essentially the same as that for wave III in the oxidation of bromide ion, and the current concentration relationship is similarly non-linear.
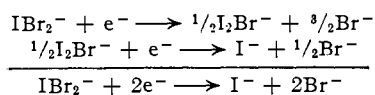
(7) I. M. Kolthoff and J. F. Coetzee, THIS JOURNAL, 79, 1852 (1957).

TABLE I

(0.1 M lithium perchlorate supporting electrolyte)

	$E_{1/2}$ vs. Ag, AgNO₃	I, μa. l./mmole (anodic processes given negative sign)	Electrode reaction
Et₄NBr			
Wave I	0.42ᵃ	-2.69 ± 0.08	$6Br^- - 4e \rightarrow 2Br_3^-$
II	0.71	-1.50 ± 0.09	$2Br_3^- - 2e \rightarrow 3Br_2$
III	1.42	-0.5ᵇ	?
Bu₄NBr₃			
Wave I	0.2ᶜ	9.19 ± 0.61	$2Br_3^- + 4e \rightarrow 6Br^-$
II	0.67	-5.32 ± 0.18	$2Br_3^- - 2e \rightarrow 3Br_2$
III	1.43	-1.2ᵇ	?
Br₂			
Wave I	(0.0)ᵈ	6.01 ± 0.23	$2Br_3^- + 4e \rightarrow 6Br^-$
II	0.58	4.24 ± 0.14	$3Br_2 + 2e \rightarrow 2Br_3^-$
Me₄NIBr₃			
Wave I	(-0.7)ᶜ,ᵉ	(1.5)ᵉ	Over-all reaction.
II	-0.08ᶜ	1.47 ± 0.07	$IBr_2^- + 2e \rightarrow I^- + 2Br^-$
III	0.81	-4.86 ± 0.03	$IBr_2^- - e \rightarrow IBr + \frac{1}{2}Br_2$
IV	1.42	-0.6ᵇ	?
Me₄NI₂Br			
Wave I	-0.12ᶜ	7.80 ± 0.16	$I_2Br^- + 2e \rightarrow 2I^- + Br^-$
II	0.34	-2.38 ± 0.08	$I_3^- - e \rightarrow \frac{3}{2}I_2$
III	0.75	-2.77 ± 0.13	$IBr_2^- - e \rightarrow IBr + \frac{1}{2}Br_2$
IV	1.88ᶠ	-9.5ᵇ	Same as wave IV, iodine system (see ref. 2)
V	1.34ᵇ	-0.7	?
IBrᶜ			
Wave I	-0.11	2.43 ± 0.24	Over-all reaction
II	0.26	1.53 ± 0.14	$IBr + 2e \rightarrow I^- + Br^-$
III	0.53	2.10 ± 0.10	
IClᶜ			
Wave I	-0.15	1.88 ± 0.12	Over-all reaction
II	0.26	1.81 ± 0.04	$ICl + 2e \rightarrow I^- + Cl^-$
III	0.59	2.53 ± 0.07	
Me₄NICl₂ᶜ			
Wave I	-0.21	1.07 ± 0.08	Over-all reaction
II	0.12	1.09 ± 0.10	$ICl_2^- + 2e \rightarrow I^- + 2Cl^-$
III	1.14	-3.82 ± 0.09	$ICl_2^- - e \rightarrow ICl + \frac{1}{2}Cl_2$
Me₄NIBrCl			
Wave I	(-0.03)ᶜ,ᵍ	(3.4)ᵍ	$IBrCl^- + 2e \rightarrow I^- + Br^- + Cl^-$
II	0.97	-4.53 ± 0.08	$IBrCl^- - e \rightarrow ICl + \frac{1}{2}Br_2$
III	1.49	-0.35	?

ᵃ $E_{1/2}$ for 1 mM solution. Plot of log (Br⁻) vs. $E_{1/2}$, approximate straight line with slope of -62 mv. ᵇ Current constant for 1 mM solution. Current-concentration relationship was non-linear, showing deviation to higher current constants at lower concentrations. ᶜ Data obtained on forward trace. ᵈ Wave I badly drawn out, $E_{1/2}$ only approximate. ᵉ Approximate data, "peak" quite irreproducible, overlaps with current decrease. ᶠ Data for reverse trace. ᵍ Approximate data, wave badly drawn out.

Data given in Table I were obtained on the forward trace with a preanodized electrode. Data for wave I are only approximate since the wave overlapped with the beginning of the current decrease and actually had a "peak" appearance. Despite the approximate nature of the data for wave I, it is clearly evident that the sum of the observed current constants for waves I + II is smaller than expected for the electrode reactions

$$IBr_2^- + e^- \longrightarrow \frac{1}{2}I_2Br^- + \frac{3}{2}Br^-$$
$$\frac{1}{2}I_2Br^- + e^- \longrightarrow I^- + \frac{1}{2}Br^-$$
$$\overline{IBr_2^- + 2e^- \longrightarrow I^- + 2Br^-}$$

Thus, from previous experience with the iodine system,[2] a two-electron reduction wave would be

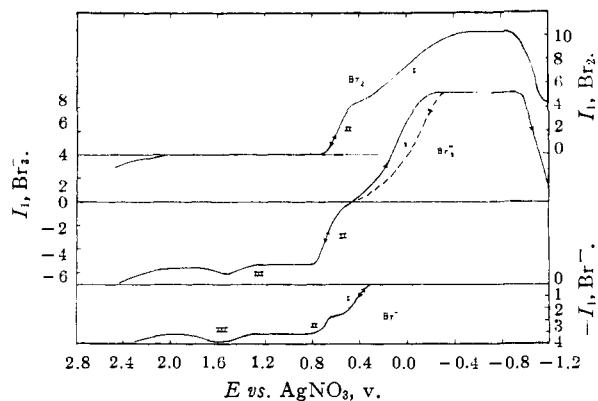

Fig. 1.—Voltammetry of the bromine system: top, bromine; middle, tribromide ion; bottom, bromide ion. Current constant, μa. l./mmole vs. potential of RPE, volts vs. Ag, AgNO₃ electrode.
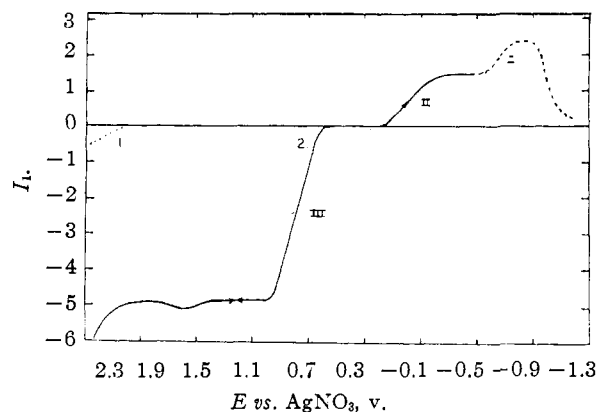

Fig. 2.—Voltammetry of tetramethylammonium iododibromide (0.1 M lithium perchlorate supporting electrolyte). Current constant, μa. l./mmole vs. potential of RPE, volts vs. Ag, AgNO₃ electrode. 1, residual current; 2, Me₄NIBr₂.

expected to have a current constant of 9–10 μa. l./mmole, rather than the value of about 3 μa. l./mmole that was observed. This pronounced lowering of the reduction current is considered in more detail in the Discussion section.

Diiodobromide Ion.—Data for the voltammetric study of tetramethylammonium diiodobromide are summarized in Table I. The c-v curve is given in Fig. 3. The cathodic electrode reaction probably is

$$I_2Br^- + 2e^- \longrightarrow 2I^- + Br^-$$
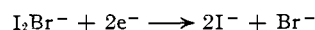
The observed current constant, 7.80 μa. l./mmole, is lower than observed for the two-electron reduction of triiodide ion, 9.52 μa. l./mmole. However, the cathodic current constant for diiodobromide ion does not appear to be grossly lowered as was the case with the iododibromide and iododichloride ions.

It is significant that only one reduction wave is observed. This indicates that diiodobromide ion is of approximately the same stability as the triiodide ion. This is further borne out by the similarity between the half-wave potential for the triiodide ion reduction, -0.15 v., and that for the reduction of diiodobromide ion, -0.12 v.
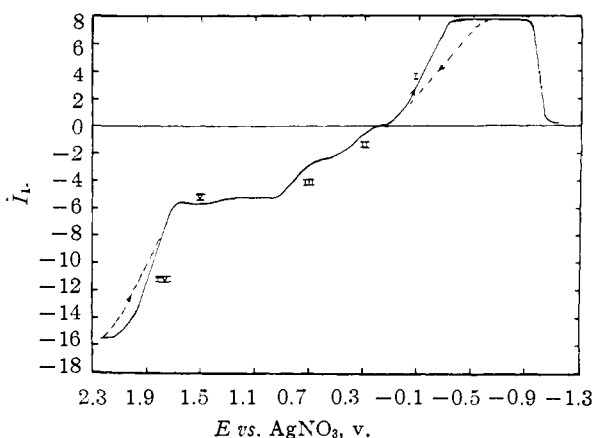
Evaluation of the anodic behavior of diiodobro-

Fig. 3.—Voltammetry of tetramethylammonium diiodo-bromide (0.1 M lithium perchlorate supporting electrolyte). Current constant, μa. l./mmole $vs.$ potential of RPE, volts $vs.$ Ag, AgNO$_3$.
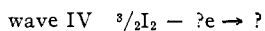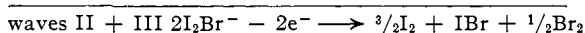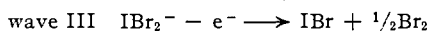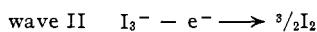
mide ion is a more complex problem. The current constants for waves II and III, -2.34 and -2.77 μa. l./mmole, respectively, are approximately equivalent to the current constant for a one-half electron oxidation. Wave IV has a half-wave potential and a non-linear current concentration relationship which are similar to those observed for oxidation wave IV in the iodine system.[2] Wave V has a half-wave potential (1.34 v.) only somewhat more negative than the half-wave potential (1.42 v.) for wave IV in the iododibromide ion oxidation and wave III in the bromide ion oxidation, both of which are anomalous waves apparently involving nascent bromine.

Correct assignment of electrode reactions for these oxidation waves should present a reasonable explanation for the following conditions: (a) occurrence of two anodic waves (II and III) of approximately equal magnitude; (b) anomalous wave V, apparently characteristic of bromide ion oxidation; and (c) wave IV, assumed to be analogous to the iodine oxidation (wave IV, iodine system) previously noted.[2]

It is known[8] that diiodochloride ion can undergo a disproportionation reaction to iododichloride and triiodide ions. If one assumed that the disproportionation equilibrium can be established in the

$$2I_2Br^- \longrightarrow I_3^- + IBr_2^-$$
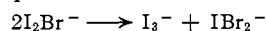
case of diiodobromide ion, the following electrode reactions can be assigned

wave II $I_3^- - e^- \longrightarrow \ ^3/_2I_2$
wave III $IBr_2^- - e^- \longrightarrow IBr + \ ^1/_2Br_2$

waves II + III 2I$_2$Br$^-$ $-$ 2e$^-$ $\longrightarrow$ $^3/_2$I$_2$ + IBr + $^1/_2$Br$_2$
wave IV $^3/_2$I$_2$ $-$?e $\rightarrow$?

The postulations for waves II and III seem valid since the observed half-wave potentials 0.34 and 0.75 v., coincide rather well with the half-wave potentials of 0.30 and 0.81 v. found for the oxidation of triiodide ion[2] (wave II) and the oxidation of iododibromide ion (wave III), respectively. Furthermore the magnitude of waves II and III, -2.34 and 2.77 μa. l./mmole, shows reasonable

(8) A. I. Popov and R. F. Swensen. THIS JOURNAL, 77, 324 (1955).

agreement with one-half of the current constant for the triiodide ion oxidation, -2.43 μa. l./mmole and for the iododibromide ion oxidation, -2.42 μa. l./mmole.

The ratio of the current constant for wave IV for oxidation of diiododibromide ion to wave IV in the iodine oxidation is approximately 0.6. When the electrode reaction scheme postulated above is expressed on a molar basis, it is seen that three-fourths of a mole of iodine per mole of diiodobromide ion oxidized should undergo the reaction corresponding to wave IV. Thus the observed ratio of 0.6 is somewhat lower than the anticipated value of 0.75.

An alternate electrode reaction is $I_2Br^- - e^- \rightarrow I_2 + \ ^1/_2 Br_2$. This would account for the anomalous wave V but not for the occurrence of the *two* oxidation waves, II and III. In addition the predicted iodine oxidation current for this reaction (corresponding to a value of 1.00 for the ratio defined in the preceding paragraph) is considerably *larger* than the observed current.

Another possible electrode reaction, $I_2Br^- - e^- \rightarrow IBr + \ ^1/_2 I_2$, does not account for the two-step oxidation wave, nor does it involve nascent bromine, which is assumed to be characteristic of wave V.

Iodine Monobromide and Iodine Monochloride.—The voltammetric behavior of iodine monochloride and iodine monobromide are given in Table I. The c–v curves for the two species are quite similar, $i.e.$, both involve a three-step wave, followed by a current decrease at more negative potentials. The over-all electrode reactions presumably are
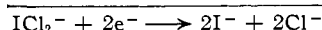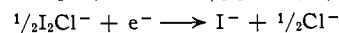
$$IBr + 2e^- \longrightarrow I^- + Br^-$$
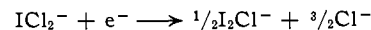
and

$$ICl + 2e^- \longrightarrow I^- + Cl^-$$
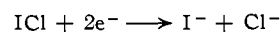
The observed total current constants, 6.06 and 6.22 μa. l./mmole, respectively, are, however, substantially lower than the constant for the two-electron reduction of iodine, 10.78 μa. l./mmole. It has not been possible to assign specific electrode reactions to the individual waves.

Iododichloride Ion.—Voltammetric data for tetramethylammonium iododichloride are given in Table I and Fig. 4. Anodic wave III corresponds to the electrode reactions

$$ICl_2^- - e^- \longrightarrow ICl + \ ^1/_2Cl_2$$
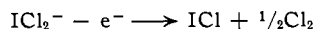
The limiting current constant, -3.82 μa. l./mmole is nearly identical with that observed for the oxidation of chloride ion, -3.64 μa. l./mmole.

The logical electrode reactions for the reduction of iododichloride ion are

$$ICl_2^- + e^- \longrightarrow \ ^1/_2I_2Cl^- + \ ^3/_2Cl^-$$
$$\ ^1/_2I_2Cl^- + e^- \longrightarrow I^- + \ ^1/_2Cl^-$$
$$ICl_2^- + 2e^- \longrightarrow 2I^- + 2Cl^-$$

These reactions do suggest waves of equal height; however, the observed waves with current constants of 1.07 and 1.09 μa. l./mmole, respectively, are much smaller than the 3 to 5 μa. l./mmole constants observed for other one-electron reductions. This situation is analogous to that observed for iododibromide and iodobromochloride ions.

Iodobromochloride Ion.—Voltammetric data for tetramethylammonium chloride are summarized in Table I. Cathodic wave I is drawn out and may involve more than one electrode reaction. The over-all cathodic reaction is assumed to be

$$IBrCl^- + 2e^- \longrightarrow I^- + Br^- + Cl^-$$

although the current constant, 3.4 μa. l./mmole, is abnormally small for a two-electron reduction. Anodic wave II is considered to be

$$IBrCl^- - e^- \longrightarrow ICl + {}^1/_2Br_2$$
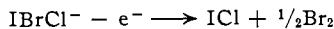
The small hump-shaped wave III corresponds closely in half-wave potential to the anomalous wave IV, $E_{1/2} = 1.42$ v., observed in the oxidation of iododibromide ion.

Discussion

Bromine Species.—The nature of the electrode reactions corresponding to waves I and II seems satisfactorily established as

wave I $6Br^- - 4e^- \longrightarrow 2Br_3^-$

wave II $2Br_3^- - 2e^- \longrightarrow 3Br_2$
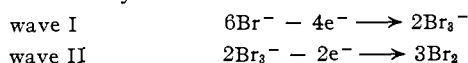
It should, however, be noted that the ratio of the current constants for waves I and II was not exactly 2.00 as indicated by the stoichiometry of the above reactions. The experimentally observed values were rather 1.69, 1.74 and 1.42 for bromide ion, tribromide ion and bromine, respectively. The shift of half-wave potentials for waves I and II in the same series, bromide ion, tribromide ion, bromine, to more negative potentials apparently indicates an irreversibility emphasized by the condition of the electrode surface.

The decrease of the limiting current in the reduction of tribromide ion and bromine is analogous to that encountered in the study of the iodine system.[2] It is only possible to say that the limiting current decrease involves either a repulsion of anionic species from the electrode or a specific electrode effect that permits one reaction to occur, but not another.

It has not been possible to characterize explicitly the electrode reaction corresponding to wave III. The fact that wave III is not observed in the c–v curve of molecular bromine may mean that nascent bromine is a prerequisite for the electrode reaction.

Interhalogen and Interhalogen Species.—The nature of the electrode reactions occurring in the oxidation of iododibromide, iododichloride and iodobromochloride ions seem to be satisfactorily established. Since the limiting ionic conductances for these ions are approximately equal, 104.3, 100.1 and 102.0,[9] the current constants for the respective oxidations should be essentially equal. It is seen from data in Table I that the current constant for oxidation of iododichloride ion is somewhat smaller than expected.

The grossly lowered cathodic current constants for these same three ions are indeed puzzling. The suggestion can be made that because of the limiting
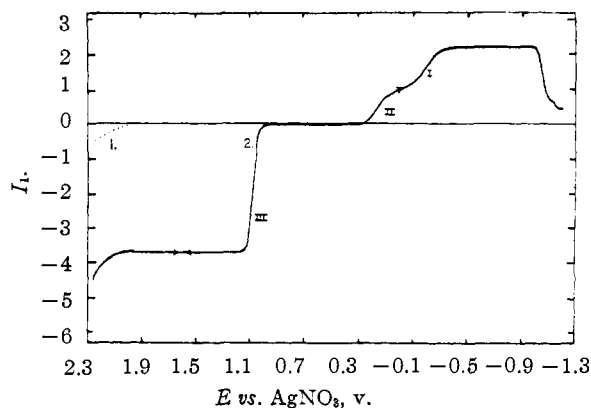
(9) A. I. Popov and N. E. Skelly. THIS JOURNAL, **77**, 5309 (1955).

Fig. 4.—Voltammetry of tetramethylammonium iododichloride (0.1 M lithium perchlorate supporting electrolyte). Current constant, μa. l./mmole vs. potential of RPE, volts vs. Ag, AgNO₃ electrode. 1, residual current; 2, Me₄NICl₂.

current decrease, the complete cathodic behavior of the ions was not observed. This possibility seems particularly likely in the case of iododibromide ion where, as was pointed out, wave I overlapped with the potentials at which the limiting current decrease occurred. On the other hand, the limiting current plateau in the reduction of iododichloride ion was fully 0.6 v. long. If one assumes that iododichloride and iododibromide ions have similar c–v curves, it is safe to conclude that the total reduction behavior of the iododibromide has been observed. Some abnormal effect must be responsible for the low cathodic current constants of the interhalide ions. It is possible that specific electrode surface effects are possible for these anomalous observations.

Comparison of the voltammetric behavior of iodine chloride and iodine bromide can be done by considering that the iodine has a partial positive charge and thus has a more positive reduction potential than iodine; or it can be done by considering that the chloride and bromide each have a partial negative charge and thus would have a more negative half-wave potential with respect to chlorine and bromine. On this basis it is not surprising to find that iodine chloride has a rather positive reduction half-wave potential (wave III). Further comment is not justified because of the apparent complexity of the reduction reactions.

The limiting current decrease which occurred in the iodine system[2] was encountered again with the interhalogen species. It is seen that in no case is the occurrence of the limiting current decrease inconsistent with the possibility that anionic repulsion takes place. This correlation does not, however, rule out the possible occurrence of a specific electrode effect. It is possible that chronopotentiometric studies may offer a further insight into the limiting current decrease.

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