Studies on the Chemistry of Halogen and of Polyhalides. XIII. Voltammetry of Iodine Species in Acetonitrile

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Voltammetric studies of iodine, sodium iodide and tetramethylammonium triiodide were made with acetonitrile as solvent and a rotating platinum indicator electrode. Two of the waves observed for these species are well-characterized as involving iodide ion–triiodide ion and triiodide ion–iodine electrode reactions. The two waves occurring at more positive potentials probably involve oxidation of iodine to cationic iodine species. From the voltammetric data for equimolar mixtures of triiodide ion and iodide ion, and iodine and triiodide ion, the formal electrode potentials for the respective half-reactions were calculated. A study was made of the oxidation of iodide ion in the presence of pyridine, 2,6-lutidine, 2-picoline, 2,2'-bipyridine, 4,4'-bipyridine, 2,2',2''-tripyridine and 1,10-phenanthroline. The voltammetric reduction of dipyridine iodine (I) perchlorate also was studied.

Introduction

The aqueous iodine system has been the subject of a number of voltammetric studies.[2-5] The physical and chemical properties of acetonitrile make it an excellent solvent for a voltammetric study of the iodine species. Recently Kolthoff and Coetzee[6] made a preliminary study of the oxidation of chloride, bromide and iodide ions at a rotating platinum electrode in acetonitrile. In the present work a comprehensive study of the iodine system in acetonitrile was undertaken using a rotating platinum indicator electrode.

Experimental Part

Apparatus.—The same polarograph, polarographic cell and saturated silver chloride reference electrode were used as previously described.[7] Once again, *all potential measurements refer to the acetonitrile silver, silver nitrate (0.01 M) primary reference electrode*.

The indicator electrode was a platinum bead, with an area of 0.29 mm.[2], fused into a soft glass tube. When rotated at 594 r.p.m., the linear peripheral velocity was 15.6 cm./sec. The platinum electrode was cleaned by immersion in hot concentrated nitric acid, repeated rinsing with distilled water, immersion in acidic ferrous ammonium sulfate solution for several minutes and further rinsing with distilled water.[6] This procedure gave a "clean" electrode which was subjected to prepolarization as indicated in later sections, usually preanodization in the test solution at ÷2.4 v. for one minute.

Limiting currents observed with the rotating electrode are conveniently expressed in terms of the limiting current constant I_1, where $I_1 = i_{1(\text{obs.})}/C_{\text{mM}}$, and has the dimensions, microampere liter/millimole. The I_1 value is an arbitrary constant for a particular electrode reaction and is dependent upon the area of the electrode and the hydrodynamic conditions existing at the electrode. Since the same electrode and rate of rotation were used throughout, comparison of various electrode reactions was made by means of the limiting current constant I_1.

A number of runs also were made with a gold-plated platinum bead electrode. An adherent deposit of gold was obtained by electrodeposition at 70° from a solution of auric chloride containing potassium cyanide and sodium dihydrogen phosphate.

Electrodes were rotated with a Sargent S-76485 Synchronous Rotator, at 594 r.p.m. Where variable stirring velocities were desired, the Eberhard Governed Power-Stir, No. 77-836D, was employed.

Reagents.—Acetonitrile was purified as previously described,[7] except that it was not necessary to carry out the final distillation in a nitrogen atmosphere, since oxygen in acetonitrile is not reduced at the rotating platinum electrode (hereafter referred to as the RPE).

Anhydrous lithium perchlorate, used as supporting electrolyte, was obtained by dehydration of lithium perchlorate trihydrate (G. F. Smith & Company) at 170–180° in an air oven. The resulting material was recrystallized from acetonitrile and redried at 170°. Reagent grade iodine was resublimed from a mixture of calcium oxide and potassium iodide. The concentration of a stock solution of iodine was determined by iodimetric titration. Reagent grade sodium iodide was dried over phosphorus pentoxide *in vacuo*. Tetramethylammonium triiodide and pentaiodide were prepared as described by Chattaway and Hoyle.[8] Purity was verified by iodometric titration.

Dipyridine iodine (I) perchlorate was prepared by the reaction of iodine with dipyridine silver perchlorate in chloroform.[9] The melting point was 185° compared with the value of 180° reported by Carlsohn. The iodometric equivalent was 192 in agreement with the calculated value of 192.7. Diphenyliodonium perchlorate was prepared by reaction of alcoholic solutions of silver perchlorate and diphenyliodonium iodide. The melting point was 173° in comparison with the value of 170–171° reported by Beringer.[10] Diphenyliodonium iodide, prepared by the usual method,[11] was furnished by Dr. S. Wawzonek of this Laboratory.

Pyridine was kept over barium oxide for several days, and then distilled with a boiling point of 113.0–113.5° at 730.8 mm.; 2-picoline was distilled at 37 mm. with a boiling point of 52°, and 2,6-lutidine had a boiling point of 53° under a pressure of 23 mm. The melting point of 4,4'-bipyridine was 110–111° in agreement with the value of 111.0–112.0° reported by Dimroth and Frister.[12] The three amines, 2,2'-bipyridine, 2,2',2''-tripyridine and 1,10-phenanthroline monohydrate were used as obtained from G. F. Smith & Company.

A sample of iron(III) tris-1,10-phenanthroline perchlorate dihydrate, $Fe(1,10\text{-phenan})_3(ClO_4)_3 \cdot 2H_2O$ was kindly supplied by Mr. W. Ward of this Laboratory.

Millicoulometric Studies.—Millicoulometric studies were made using the RPE as the working electrode and the polarograph as a constant voltage source and at the same time as a coulometer. Current readings were recorded every 15 minutes on the polarograph chart paper. Graphical integration of a plot of current in microamperes *versus* time in seconds gave the total quantity of electricity in microcoulombs. In order to eliminate the possibility of contamination of the sample solution with chloride ion from the refer-

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

(2) W. Nernst and E. J. Merriam, *Z. physik. Chem.*, **53**, 235 (1905).

(3) E. Brunner, *ibid.*, **56**, 321 (1906).

(4) According to Bibliography of Publications Dealing with the Polarographic Method, J. Heyrovsky, *Collection of Czech. Chem. Comms.*, **21**, Supplement 1, 5 (1956). the oxidation of iodide. bromide and chloride ions was studied by E. M. Skobets, N. N. Atamanenko and V. D. Ryabokon. *Zavodskaya Lab.*, **17**, 899 (1951). However. to date it appears that this particular publication is not available in the United States.

(5) I. M. Kolthoff and J. Jordan, THIS JOURNAL, **75**, 1571 (1953).

(6) I. M. Kolthoff and J. F. Coetzee, *ibid.*, **79**, 1852 (1957).

(7) A. I. Popov and D. H. Geske, *ibid.*, **79**, 2074 (1957).

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

(9) H. Carlsohn, "Über eine neue Klasse von Verbindungen des positiv einwertigen Iods." Verlag von S. Hirzel, Leipzig, 1932.

(10) F. M. Beringer, unpublished results. see *Iodine Abstracts and Reviews*, **3**, No. 3. 30 (1956).

(11) H. J. Lucas and E. R. Kennedy, *Org. Syntheses*, **22**, 52, 70, 72 (1942).

(12) O. Dimroth and F. Frister, *Ber.*, **55**, 3963 (1922).

ence electrolyte over the course of the three to four-hour electrolysis, a saturated calomel electrode with an agar bridge was used as a reference electrode in a procedure similar to that of previous workers.[6]

Results

Residual Current.—One of the most remarkable features of voltammetry with a RPE in acetonitrile is the wide range of potentials available for study. It is seen from the residual current for a 0.1 M lithium perchlorate solution (Fig. 1, trace I) that the potential range extends from approximately 2.2 v. to −3.3 v. The limiting cathodic reaction appears to be the deposition of lithium. Observation of a stationary wire electrode with a binocular telescope while the limiting reaction was occurring clearly showed formation of a metallic deposit. The identity of the limiting anodic reaction is not as well defined. No *gross* oxidation of solvent or electrode was observed. A study of the variation of current with rate of rotation gave an α-value of 0.19, from $i = KR^{\alpha}$, where i is the current, R is the rate of rotation in r.p.m., and K is an arbitrary constant. An α-value of zero would indicate an electrode process completely independent of mass transfer processes. Electrode processes at the RPE controlled by rate of mass transfer have an α-value of approximately 0.6 (*vide infra*).

Although the limiting anodic reaction is not completely understood, highly oxidizing conditions certainly are in effect.[12a] It seems reasonable that any water present in the acetonitrile would be oxidized to hydrogen ion and oxygen. In fact the coulometric studies of Hanselman and Streuli[13,14] employed such a reaction.

The effect of increasing amounts of water on the residual current is shown in Fig. 1. These data were obtained by first tracing from 0.64 to 2.5 v. (reverse trace) and then from 0.64 to −3.5 v. (forward trace). The solution containing 0.36% water showed an anodic residual current (reverse trace) only slightly greater than with pure solvent. The forward trace showed a "bump" at −0.6 v.; however, when a retrace was made over the same potentials, the "bump" was absent. Behavior of solutions of higher water content was similar. The acetonitrile solutions without added water showed only a very slight "bump."

It is possible to interpret these results in view of the work of Kolthoff and Tanaka[15] on the formation of an oxide film on the RPE. Polarization to the potentials at which the anodic limiting reaction occurred, placed an oxide film on the electrode. Forward polarization resulted in a dissolution pattern as the oxide layer was reduced. With the oxide layer reduced, the retrace showed no "bump" or dissolution pattern. Further evidence that the current at −0.7 v. was due to oxide reduction was

(12a) NOTE ADDED IN PROOF:—The recent work of H. Schmidt, *Angew. Chemie*, **69**, 638 (1957), on the electrolysis of silver perchlorate in acetonitrile with platinum electrodes is of particular interest here. The anodic reaction was found to be

$$ClO_4^- \rightarrow ClO_4 + e^-$$
$$ClO_4 + CH_3CN \rightarrow CHlO_4 + CH_2CN$$
$$2CH_2CN \rightarrow NCCH_2CH_2CN$$
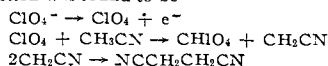
This is undoubtedly the limiting anodic reaction in the present study.
(13) R. B. Hanselman and C. A. Streuli, *Anal. Chem.*, **28**, 916 (1956).
(14) C. Streuli, *ibid.*, **28**, 130 (1956).
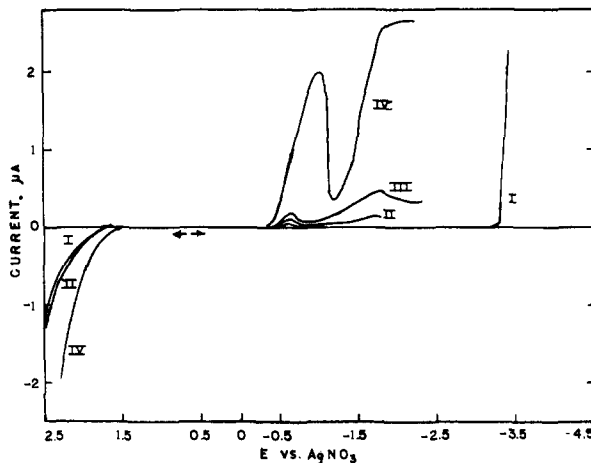(15) I. M. Kolthoff and N. Tanaka, *ibid.*, **26**, 632 (1954).

Fig. 1.—Effect of water on residual current: I, 0% water; II, 0.36% water; III, 1.08% water; IV, 4.3% water. Current, μa *vs.* potential of RPE, volts *vs.* Ag, AgNO₃ electrode.

found by pretreating the "clean" electrode with hot nitric acid to place an oxide layer on the electrode. A forward trace showed a dissolution pattern at −0.7 v.

Since the cathodic dissolution pattern actually is a current–time curve, it was possible to measure the total quantity of electricity consumed in the oxide reduction. The dissolution pattern for the oxide film formed on the electrode after anodization at positive potentials corresponded to approximately 7×10^{-4} coulombs/cm.², whereas Kolthoff and Tanaka[15] have calculated a dissolution pattern of 4.3×10^{-4} coulombs/cm.² for a monomolecular oxide layer. From these data it is concluded that an oxide film of at least monomolecular thickness is formed on the platinum electrode when it is traced to extremely positive potentials in "anhydrous" acetonitrile.

The presence of an oxide film on the platinum electrode has a pronounced effect on the observed current–voltage curves. In general, current–voltage curves obtained with a "clean" electrode (no oxide film) had a higher overvoltage than those obtained with an anodized electrode. As will be pointed out below, the presence of the oxide film is also related to the limiting current decrease.

Limiting Current Decrease.—Figure 2 (trace 1) shows an example of the phenomenon that will be termed the limiting current decrease. The current–voltage curve of an iodine solution shows a two-step reduction wave, *i.e.*, formation of triiodide ion (wave II) and then iodide ion (wave I). However at approximately −0.9 v. the cathodic current decreases to approximately the level of the iodide to triiodide ion reduction. This abrupt current decrease is anomalous because the current had arrived at a limiting value at −0.3 v. and there would seem to be no reason why a cathodic reaction should cease as the potential is increased to more negative values.

Nikolaeva, *et al.*,[16,17] have observed current de-

(16) N. V. Nikolaeva, N. S. Shapiro and A. N. Frumkin, *Doklady Akad. Nauk S.S.S.R.*, **86**, 581 (1952).
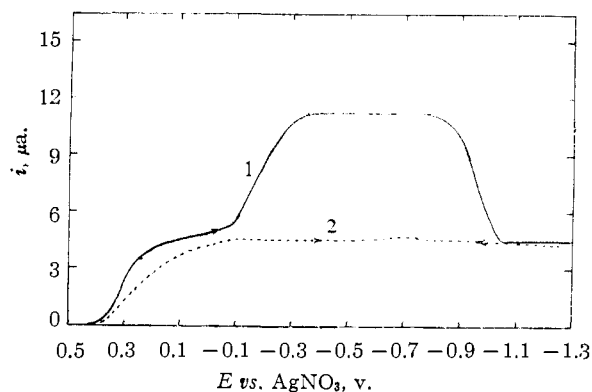(17) N. V. Nikolaeva and A. A. Grossmann, *ibid.*, **95**, 1013 (1954).

Fig. 2.—Voltammetry of 1.15 mM iodine solution. (1) Forward trace, preanodized electrode; (2) forward retrace following trace 1; reverse trace starting at −1.3 v. coincides with trace 2. Current, μa. vs. potential of RPE, volts vs. Ag, AgNO$_3$ electrode.

creases in the reduction of certain anions on various solid electrodes including platinum. They found that indifferent electrolytes in sufficiently high concentrations eliminated the minima. Their results were explained by the suggestion that anions were repelled from the negatively-charged electrode surface. This was supported by correlation of the potential at which the limiting current decrease occurred with the null potential of the solid metal electrode.

The experimental observations given below offer evidence on the nature of the limiting current decrease observed in the present work.

(a) In the reduction wave of iodine (Fig. 2), the limiting current decreases at sufficiently negative potentials to the level of the iodine to triiodide ion reduction. In other words it appears that the electrode reaction can still take place where the reacting species are neutral molecules. On the other hand, the reduction wave of triiodide ion (Fig. 3) decreases nearly to zero beyond approximately −1.0 v. Analogous current decreases were found in studies of the bromine system and interhalogen species.[18]

(b) The normal reduction waves were observed for the cationic species, hydrogen ion and iron-(III) tris-1,10-phenanthroline ($E_{1/2}$ = −0.42 and −0.76 v., respectively).

(c) Nikolaeva and Grossmann[17] had noted that increasing the concentration of extraneous electrolyte eventually removed the minima they had observed. In acetonitrile, increasing the concentration of tetraethylammonium perchlorate from 0.1 to 1.0 molar had no effect on the current decrease behavior of an iodine current-voltage curve.

Observations (a) and (b) do substantiate the suggestion that repulsion of anions from the negatively-charged electrode surface does occur and is responsible for the limiting current decrease. However, the problem is more complex. It was pointed out in a preceding section that the oxide film on the platinum electrode was discharged at potentials more negative than −0.9 v. *The coincidence of this potential, where the electrode surface is transformed from oxidized to reduced condition,*

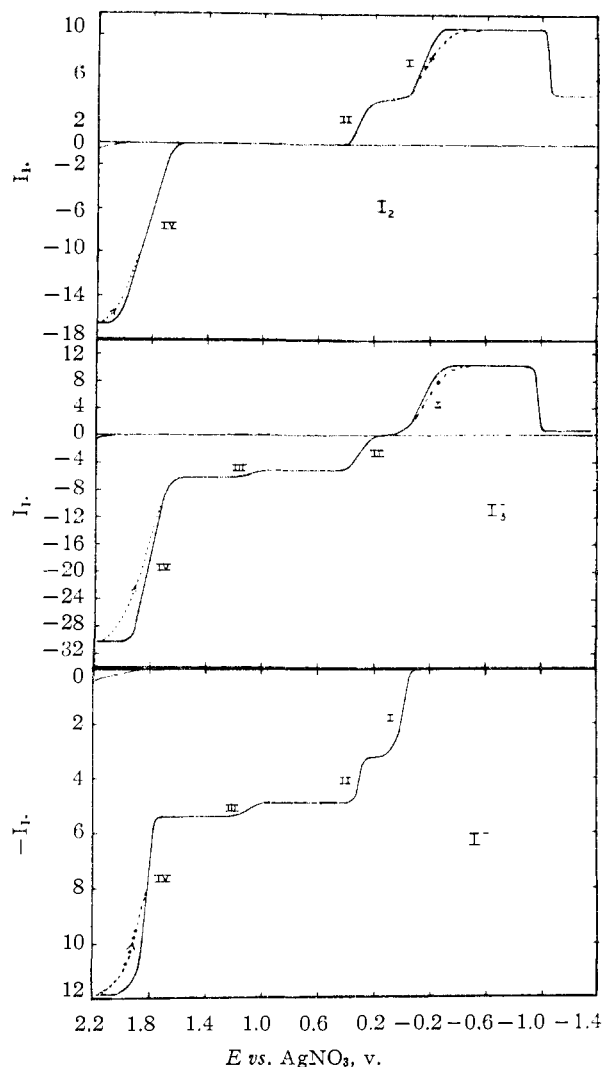(18) A. I. Popov and D. H. Geske, to be published.

Fig. 3.—Voltammetry of iodine species: top, iodine; middle, tetramethylammonium triiodide; bottom, sodium iodide. Current constant, μa. liter/mmole vs. potential of RPE, volts vs. Ag, AgNO$_3$ electrode.

with the beginning of the current decrease suggests that the two are interrelated. This suggestion was verified by the data presented in Fig. 2 for the cathodic portion of the current–voltage curve of a 1.15 mM iodine solution. Curve 1 was obtained on the forward trace with a preanodized electrode. When a retrace was attempted (the electrode presumably being in "reduced" condition), the dashed line was obtained. It should be noted that wave II is somewhat displaced to negative potentials and wave I seems to be entirely missing. The same trace (dashed line) was obtained when a reverse trace was made from −1.6 v. to more positive values (even with the electrode preanodized). This work indicates that wave II, the reduction of iodine to triiodide ion, has a higher overvoltage on a reduced electrode, and that wave I, the reduction of triiodide ion to iodide ion, apparently does not take place on a reduced platinum surface.

It is evident that the occurrence of the limiting current decrease is inextricably related to the con-

Table I

Voltammetric Data, Iodine System[a]

(0.1 M lithium perchlorate supporting electrolyte)

		NaI	Me$_4$NI$_3$	I$_2$	I(py)$_2$ClO$_4$
Wave I					
	$E_{1/2}$	-0.01^b	$-0.18^{e,f}$	-0.16^f	
	I_1, molar	-3.27 ± 0.05	9.52 ± 0.22	6.56 ± 0.25	
	I_1, normal	-3.27	3.17	3.28	
Wave II					
	$E_{1/2}$	0.31	0.32^e	0.32^g	
	I_1, molar	-1.64 ± 0.05	-5.08 ± 0.25	4.22 ± 0.08	
	I_1, normal	-1.64	-1.69	2.11	
Wave I + II					
	I_1, molar	4.91	14.90	10.78	
	I_1, normal	4.91	4.87	5.39	
Wave III					
	$E_{1/2}$	1.05	1.08	..	
	I_1, molar	-0.71 ± 0.07	-1.11 ± 0.1	..	
	I_1, normal	-0.71	-0.37	..	
Wave IV					
	$E_{1/2}$	1.82^c	1.80^c	1.79^c	
	I_1, molar	-6.3^d	-24.6^d	-16.6^d	
	I_1, normal	-6.3	-8.2	-8.3	
$\left\|\dfrac{\text{Wave I}}{\text{Wave II}}\right\|$		1.99	1.82	1.55	
Wave A	$E_{1/2}$				0.22
	I_1				1.22 ± 0.07
Wave B	$E_{1/2}$				0.11
	I_1				0.73 ± 0.1
Peak C	$E_{1/2}$				-0.95^h
	I_p				5.0^h

[a] $E_{1/2}$ values in volts vs. Ag, AgNO$_3$ electrode; I_1 values in μa. liter/millimole (milliequivalent). Anodic waves are given a negative sign. Uncertainty values are given in terms of average deviation. [b] $E_{1/2}$ at 10^{-3} M, see Fig. 11 for variation of $E_{1/2}$ with iodide ion concentration. [c] Reverse trace. [d] Current constant at 10^{-3} M, current–concentration relationship non-linear, see Fig. 4. [e] $E_{1/2}$ at 10^{-3} M, see Fig. 11 for variation of $E_{1/2}$ with triiodide ion concentration. [f] Forward trace. [g] $E_{1/2}$ at 10^{-3} M, see Fig. 11 for variation of $E_{1/2}$ with iodine concentration. [h] Apparent $E_{1/2}$, discrete wave not observed, rather a current peak.

dition of the electrode surface. The consistent observation of the current decrease when *anions* are diffusing to (or reacting at) the electrode strongly suggests that the postulation of anion repulsion is valid. However, it is not possible to eliminate from consideration the suggestion that a specific electrode effect may be in force which allows one particular reaction to occur and not another.

The limiting current decrease also occurs with a rotating gold electrode. The reduction wave of bromine using a gold indicator electrode showed an abrupt current decrease beginning *ca.* -0.8 v. The current decreased to the level of the bromine to tribromide ion reduction.

Because of the effect of electrode pretreatment on the voltammetric data, the RPE electrode was generally preanodized at 2.4 v. for one minute in the test solution before the voltammetric trace was made (except in the studies of effect of heterocyclic amines on iodide ion oxidation where the electrode was merely pretreated in nitric acid).

Hysteresis Effects.—Disagreement between the current–voltage curve obtained on the forward trace and that obtained on the reverse trace (*i e.*, a dependence upon direction of polarization) will be termed a hysteresis effect. Two types of hysteresis effects were encountered in this work; both are il-

lustrated in the top portion of Fig. 3. When a reverse trace with a preanodized electrode was made starting at -0.6 v., the current–voltage curve shown by the dotted line was obtained. Wave I of the iodine reduction was displaced to more negative potentials, while wave II coincides with the forward trace. Similar cases were encountered in the reverse traces of essentially all cathodic waves. It is not unlikely that these hysteresis effects are due to a variation in the condition of the electrode surface caused by the proximity of the starting potential to the potential at which the current decrease occurred.

The second type of hysteresis effect is shown in wave IV of the iodine current–voltage curve, as in the top portion of Fig. 3. A forward trace from 2.3 v. showed the wave displaced to positive potentials by comparison with the wave obtained on the reverse trace. This phenomenon occurred in every case where wave IV occurred in the iodine system. No explanation can be advanced.

Iodide Ion Voltammetry.—Voltammetric data for sodium iodide are summarized in Table I and Fig. 3.[19] As postulated by Kolthoff and Coetzee,[6] wave I represents the oxidation of iodide ion to

(19) For convenience of comparison, currents in Fig. 3 are expressed in terms of the current constant, I_1, μa liter/millimole.

triiodide ion and wave II corresponds to the oxidation of triiodide ion to iodine.

$$\text{wave I } 6I^- - 4e^- \longrightarrow 2I_3^- \qquad (1)$$

$$\text{wave II } 2I_3^- - 2e^- \longrightarrow 3I_2 \qquad (2)$$
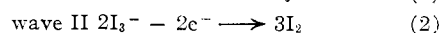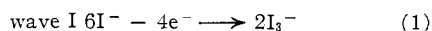
It will be noted that the value for the current constant for wave I, -3.27 ± 0.05 μa. liter/mmole, is almost exactly twice the value of the current constant for wave II, -1.64 ± 0.05 μa. liter/mmole, which is in agreement with the stoichiometry of the reactions written above.

It is surprising to note the occurrence of two oxidation waves beyond the molecular iodine state. Current constants for waves I, II and IV as a function of concentration are shown graphically in Fig. 4. It is seen that the current constant for wave IV is *not* independent of concentration as is the case with the constant for the other three waves.[20]
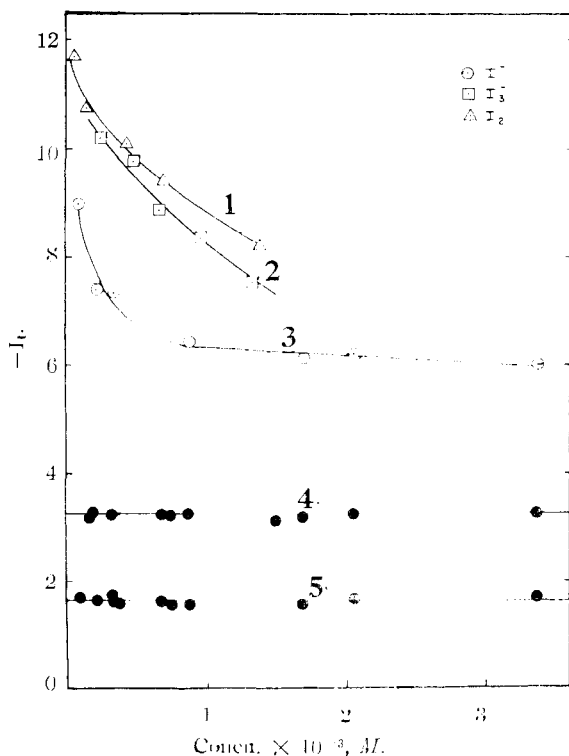

Fig. 4.—Limiting current constants, μa. liter/mmole (millicquivalent) *vs.* concentration, molar: (1) wave IV, iodine (equivalent constant); (2) wave IV, tetramethylammonium triiodide (equivalent constant); (3) wave IV, sodium iodide; (4) wave I, sodium iodide; (5) wave II, sodium iodide.

A study of the dependence of limiting current on rate of rotation gave α-values (from $I_1 = KR^\alpha$) 0.55, 0.60 and 0.55 for waves I, II and IV, respectively. All the waves have essentially the same temperature coefficient, approximately 1%. deg.$^{-1}$.

Kolthoff and Coetzee[6] report half-wave potentials of 0.3 and 0.6 v. (*versus* aqueous saturated calomel) for waves I and II, respectively, for a 5 $\times 10^{-4}$ M solution of sodium iodide. When these half-wave potentials are recalculated to the silver, silver nitrate (acetonitrile) scale, values of 0.0 and

(20) Values for the current constant for wave IV given in Fig. 3 are those observed for a one millimolar solution.

0.3 v. are obtained in agreement with the data reported here.

Triiodide Ion Voltammetry.—The voltammetry of tetramethylammonium triiodide is shown in Fig. 3. Numerical data are given in Table I. Wave I corresponds to the reduction of triiodide to iodide ion while wave II is identical with equation 2. Although it would be expected from the stoichiometry of these reactions that the ratio of wave I to wave II would be 2.00, it is seen from the data of Table I that the ratio has a value of 1.87. The variation of the current constant for wave IV to higher values at low concentration is shown in Fig. 4.

Iodine Voltammetry.—It previously has been pointed out[21] that iodine in acetonitrile shows an increase in conductance with time and does not follow Beer's law in the ultraviolet region of the spectrum. Apparently triiodide ion is slowly being formed, as evidenced by the increased absorption at 290 and 360 mμ, the absorption peaks of known triiodide ion compounds. In the present work, the voltammetric studies were made on freshly prepared solutions. A typical solution, 0.41 mM, showed only 0.9% of total iodine present as triiodide ion immediately after preparation, compared with 1.33% present three days later. Since the absorption due to iodine is not known in the ultraviolet region, the calculated triiodide ion concentration is the maximum amount of triiodide ion that could have been present.

Data on the voltammetry of iodine are given in Fig. 3 and Table I. Reduction waves I and II represent the reverse of the electrode reactions given in equations 1 and 2. It is seen that the ratio of current constants of wave I and wave II is 1.55, appreciably lower than the value of 2.00 expected from the stoichiometry of the above reactions.

The variation of the current constant of wave IV with concentration is shown in Fig. 4. It is significant that wave III *does not* occur in the current-voltage curve of iodine. A study of the dependence of current on rate of rotation gave α-values of 0.51, 0.59 and 0.54 for waves I, II and IV, respectively. The α-values for the current after the limiting current decrease was 0.51.

Voltammetry of Equimolar Mixtures of I_3^- and I_2 (I_5^-), and I_3^- and I^-.—Recently[22] it has been shown that the pentaiodide ion is quite highly dissociated in acetonitrile. It has been estimated that the dissociation constant for the pentaiodide ion (into iodine and triiodide ion) is approximately 2×10^{-3}. Thus a 4×10^{-4} M pentaiodide ion solution would be approximately 86% dissociated. It is obvious that for voltammetric studies, a dilute acetonitrile solution of pentaiodide ion may be regarded as an equimolar mixture of iodine and triiodide ion. The top portion of Fig. 5 gives the current-voltage curve for a 0.387 mM solution of tetramethylammonium pentaiodide; the lower portion is the current-voltage curve for a solution 0.45 mM in both sodium iodide and tetramethylammonium triiodide.

(21) A. I. Popov and N. E. Skelly, THIS JOURNAL, 77, 3722 (1955).

(22) A. I. Popov, R. H. Rygg and N. E. Skelly, *ibid.*, 78, 5740 (1956).

Table II

MILLICOULOMETRIC STUDIES

Run	Potential, v.	Waves	Iodide concn. $\times 10^3$, M	Q, μfara-days	Soln., ml.	Triiodide concn. $\times 10^4$, M	I_3^-, μmoles	n, fara-days/mole
A	0.91	I, II	0.85	0.397	20	1.05	0.21	0.95
B	1.41	I-III	0.85	0.465	20	1.19	.238	0.98
C	2.11	I-IV	1.15	1.696	23	2.74	.630	..
D	2.51	...	0.0	0.388	20			
E	2.21	IV	1.43^a	1.40	20	-1.54^b	-0.306^b	

^{a} Iodine solution. ^{b} Triiodide ion concentration decreased upon electrolysis. ^{c} Each triiodide ion is equivalent to consumption of two iodide ions. Values of molar absorbance indices of triiodide ion in acetonitrile, 48,800 at 290 mμ and 25,500 at 360 mμ are those reported by A. I. Popov and R. F. Swensen, This Journal, **77**, 324 (1955).

It should be noted that the limiting current decrease at ca. -0.9 v. as observed for both of these cases is in agreement with a postulation of anion repulsion, i.e., with pentaiodide ion the current decreased only to the level of the iodine to triiodide ion reduction, whereas with the triiodide ion–iodide ion mixtures, the current decreased essentially to zero.
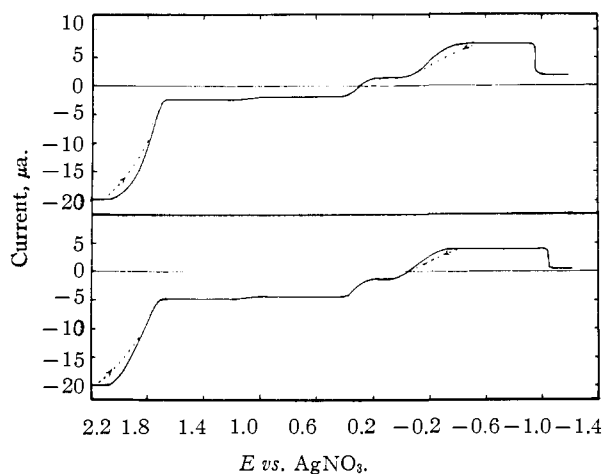
Fig. 5.—Voltammetry of tetramethylammonium pentaiodide and a sodium iodide–tetramethylammonium triiodide mixture; top, 0.387 mM tetramethylammonium pentaiodide; bottom, 0.45 mM sodium iodide plus 0.45 mM tetramethylammonium triiodide. Current, μa. vs. potential of RPE, volts vs. Ag, AgNO$_3$ electrode.

Millicoulometric Studies; Prolonged Electrolyses.—In a further attempt to determine the nature of waves III and IV, a number of millicoulometric studies were made. The crucial point in these particular long-term electrolyses is the fact that the product of the electrode reaction (eventually evidenced as triiodide ion with excess iodide ion present) can be detected spectrophotometrically in very small concentration because of the high molar absorbance indices of triiodide ion and also because the iodide ion does not absorb in the same wave length region.

Results of the millicoulometric studies are summarized in Table II. Prolonged electrolysis (0.39 μfaradays) of the supporting electrolyte solution at 2.5 v. with no depolarizer present gave a solution which did not oxidize iodide ion. The total electricity consumed by the residual current in runs C and D was estimated at 0.05 and 0.07 μfaraday, respectively.

Effect of Heterocyclic Amines on Voltammetry of the Iodine System.—It is known that the monovalent iodine cation is stabilized by coördination with heterocyclic amines.[9] Kolthoff and Jordan[5] found that iodide ion in a 0.1 M aqueous pyridine solution gave only a single two-electron wave. They considered this to be evidence for oxidation of iodide ion to dipyridine iodine (I), [I(py)$_2$]$^+$.

It was found that the iodine cation also was stabilized in acetonitrile by heterocyclic amines. Figure 6 shows the effect on the current-voltage
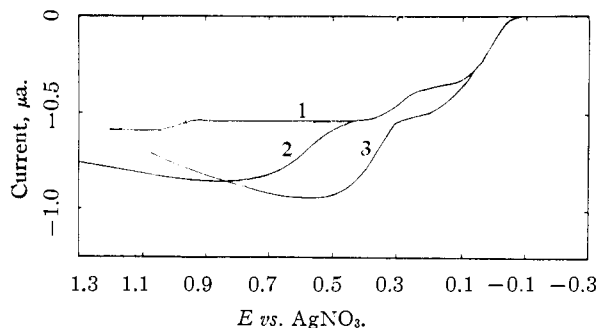
Fig. 6.—Effect of pyridine on oxidation of iodide ion: (1) 0.098 mM sodium iodide; (2) 0.098 mM sodium iodide, 2.5 $\times$ 10^{-3} M pyridine; (3) 0.098 mM sodium iodide, 3.0 M pyridine. Current, μa. vs. potential of RPE volts vs. Ag, AgNO$_3$ electrode. Reverse trace.

curve of sodium iodide on increasing the pyridine concentration. Table III summarizes the data for the oxidation of iodide ion in the presence of various heterocyclic amines. It was found that in general increasing the amine concentration increased the height of the positive iodine wave. Table III lists the current ratio $i_+/i_{I,II}$ where i_+ is the current due to the oxidation of iodine to positive iodine and $i_{I,II}$ is the current due to oxidation of iodide ion to iodine. This ratio was tabulated in order to minimize experimental deviations from one trace to another and also to allow a reasonable comparison between different concentrations of iodide ion. In Fig. 7 these current ratios are plotted as a function of amine concentration. For a particular amine concentration, the positive iodine wave was directly proportional to the iodide ion concentration.

It is seen from Fig. 6 that at highly positive potentials the anodic current begins to decrease toward zero for those solutions which contained pyridine. This apparently was caused by formation of an interfering film on the electrode. Polarization from negative to positive potentials was used

TABLE III

EFFECT OF HETEROCYCLIC AMINES ON OXIDATION OF THE IODIDE ION

Amine	Amine concn., M	Wave I $E_{1/2}$, v.	$-i$, μa.	Wave II $E_{1/2}$, v.	$-i$, μa.	I$^+$ wave $E_{1/2}$, v.	$-i$, μa.	$\frac{i_+}{i_{I,II}}$
Pyridine[a]	0.0	−0.02	0.324	0.25	0.162			
	.0025	− .02	.318	.27	.153	0.58	0.27	0.57
	.005	− .02	.314	.25	.152	.56	.29₆	.63
	.025	.0	.324	.28	.152	.53	.39	.82
	.05	− .01	.324	.26	.152	.53	.40	.84
	.10[b]	.0	.65[b]	.25	.315[b]	.54	.85	.88
	.25	.01	.304	.19	.15	.38	.39	.85
	1.00	Waves I and II merge, $E_{1/2}$ = 0.04 v.; i = −0.42₈ μa.				.41	.41	.95
	3.00	Waves I and II merge, $E_{1/2}$ = 0.00 v.; i = −0.46₆ μa.				.36	.42₈	.92
2-Picoline[c]	0.002	0.02	0.343	0.29	0.176	0.57	0.21₆	0.42
	.01	.02	.328	.24	.170	.53	.33₈	.68
	.05	.02	.308	.22	.206	.49	.372	.73
	.1	.05	.264	.21	.226	.46	.372	.76
	.2	.02	.324	Single wave, $E_{1/2}$ = 0.37 v.; i = 0.559 μa.				.7[d]
2,6-Lutidine[c]	0.001	−0.02	0.353	0.29	0.176	0.55	0.14₇	0.28
					Single wave			
	.009	− .02	.352		0.41 v.	0.335 μa.		.30[e]
	.1	.04	.353		.46	.372		.37[e]
	.2	.02	.353		.42	.41₁		.44[e]
	.5	.02	.314		.41	.40		.46[e]
4,4'-Bipyridine[c]	0.002	0.02	0.343	0.27	0.167	0.63	0.22₅	0.44
	.004	.04	.353	.30	.157	.64	.27₄	.54
	.01	.03	.353	.33	.176	.64	.314	.59
	.1	.04	.33	Single wave, 0.5 v.; 0.50 μa.				.68[f]
1,10-Phenanthroline[c]	0.1	0.02	0.343	0.30	0.166	0.72	0.07	0.14
2,2-Bipyridine[c]	.02	.02	.352	.31	.176	.67	.078	.15
	.1	.03	.362	.33	.167	.63	.076	.15
2,2',2''-Tripyridine[c]	.01	.03	.372	.33	.176	.67	.07	.13

[a] 9.84 × 10⁻⁵ M sodium iodide except where otherwise indicated. All data obtained on reverse trace; electrode was acid treated between runs. [b] Sodium iodide solution, 2.05 × 10⁻⁴ M. [c] Sodium iodide solution, 1.08 × 10⁻⁴. [d] Since waves are run together, definition of currents is somewhat arbitrary and value for current ratio is only approximate. [e] For purposes of calculation of ratio, the current due to wave II is assumed to be the same as was found with 0.001 M picoline present. [f] Approximate value, i_{II} estimated.

TABLE IV

EFFECT OF PYRIDINE ON VOLTAMMETRY OF TETRAMETHYLAMMONIUM TRIIODIDE, 1.3 × 10⁻⁴ M

Pyridine concn.	Wave I $E_{1/2}$, v.	i, μa.	Wave II $E_{1/2}$, v.	$-i$, μa.	I$^+$ wave $E_{1/2}$, v.	$-i$, μa.	$\frac{i_1}{i_{II}}$	$\frac{i_+}{i_{I,II}}$	$\frac{i_+}{i_{II}}$
0.0	−0.16	1.15	0.30	0.63			1.82		
.002	− .19	1.05	.30	.54₄	0.74	0.21₃	1.93	0.13	0.39
.004	− .17	1.10	.30	.56₉	.71	.33₈	1.93	.20	.59
.02	− .16	1.11	.30	.61₈	.65	.42₆	1.80	.25	.69
.05	− .14	1.10	.26	.63	.61	.59₅	1.75	.34	.94
.1	− .12	0.96	.25	.64₆	.62	.62₅	1.49	.39	.97
.5	− .16	1.03	.20	.67₆	.53	.66₁	1.52	.39	.98
1.0	− .14	1.01	.17	.70	.51	.70	1.45	.41	1.00
3.0	− .20	0.78	.09	.73	.46	.76₅	1.06	.49	1.04

to obtain the data given in Table III. A satisfactory *forward* trace could be obtained only if the trace was started at a potential no more positive than the potential corresponding to the beginning of the limiting current plateau for the I$^+$ wave. The suggestion of formation of an electrode film was verified by attempting a reverse retrace of the current–voltage curve immediately after the first trace. The current was greatly lowered throughout. Only when the electrode was cleaned in hot nitric acid could the original curve be reproduced. A 2 mM pyridine solution showed the same resid-

ual current as the supporting electrolyte, so no gross oxidation of pyridine could have taken place. The exact composition of the interfering film is not known, but it probably is the product of the destructive oxidation of pyridine, perhaps involving the $[I(py)_2]^+$ species. Rogers and Lord[23] encountered a similar situation in the oxidation of phenylenediamines on platinum and gold electrodes. They state that insoluble oxidation and/or polymerization products apparently formed on the electrode. An electrode would give a well-defined

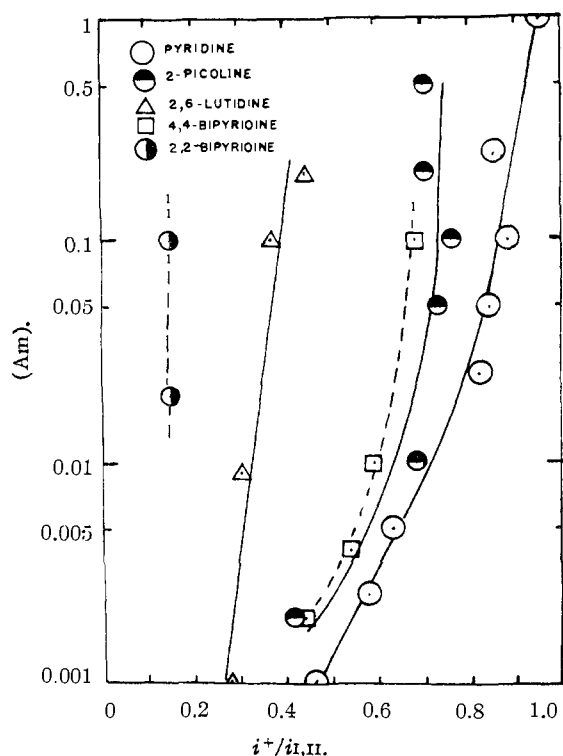(23) L. B. Rogers and S. S. Lord, Jr., *Anal. Chem.*, **26**, 284 (1954).

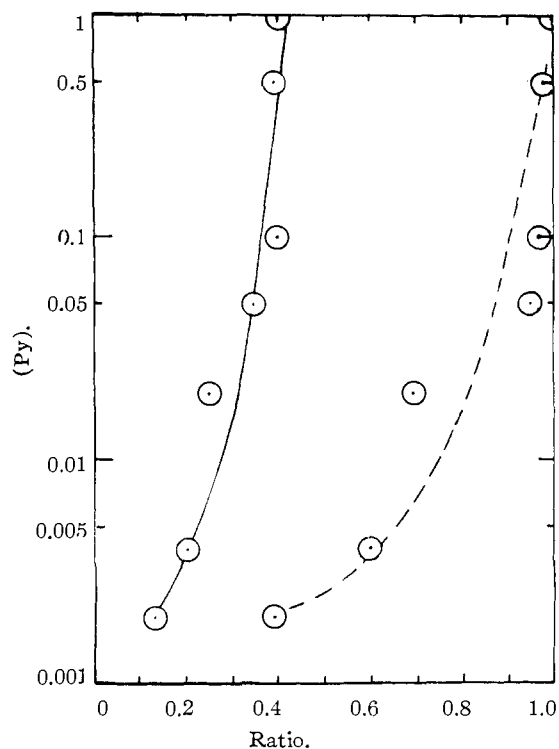Fig. 7.—Amine molarity (logarithmic scale) *vs.* current ratio.

Fig. 8.—Triiodide ion in presence of pyridine. Pyridine molarity (logarithmic scale) *vs.* current ratios.

wave the first time it was used, but subsequent polarograms became successively poorer.

The current decrease caused by this film formation prevents making an accurate statement on the behavior of wave IV upon addition of pyridine.

The presence of pyridine also influences the voltammetric behavior of triiodide ion. Data are given in Table IV and in Fig. 8.

It was of interest to investigate the voltammetric behavior of iodine (particularly the oxidation behavior) in the presence of pyridine. The problem is complicated, however, by the fact that acetonitrile solutions of iodine to which pyridine is added, rapidly form appreciable amounts of triiodide ion. The amount of triiodide ion increases with time. Thus in a freshly prepared 0.137 mM iodine solution, 0.05 M in pyridine, approximately 27% of the total amount of iodine was present as triiodide ion; 24 hr. later, the amount of triiodide ion was 50% of total iodine.

Despite this inherent complexity of the sample solution, a voltammetric study was made. The current–voltage curve of a freshly prepared 0.137 mM iodine solution 0.05 M in pyridine showed only a small anodic current in the potential region 0.4 to 1.5 v.

Voltammetry of Dipyridine Iodine (I) Perchlorate.—The reduction behavior of dipyridine iodine (I) perchlorate is shown in Fig. 9. The data in Table I are the average values for four determinations. The current increase labeled "C" cannot properly be described as a wave. The "peak" appearance is caused by the current decrease previously described. The current "constant" for the peak shows considerable variation,

probably as a result of small variations in the beginning of the current decrease.

A limited conductivity study was made of dipyridine iodine (I) perchlorate in acetonitrile. It was found that the compound is a strong electrolyte with a limiting equivalent conductance of approximately 180. Walden and Birr[24] found a
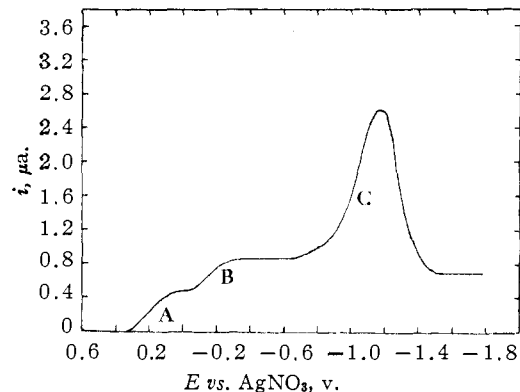

Fig. 9.—Voltammetry of dipyridine iodine (I) perchlorate, 0.416 mM, 0.1 M lithium perchlorate. Current, μa. *vs.* potential of RPE, volts *vs.* Ag, AgNO$_3$ electrode. Forward trace, anodized electrode.

limiting ionic conductance of 104.5 for the perchlorate ion in acetonitrile. Thus the limiting ionic conductance of the dipyridine iodine (I) ion is approximately 75.

Another positive iodine compound, diphenyliodonium perchlorate, showed no reduction waves at a rotating platinum electrode.

(24) P. Walden and E. J. Birr, *Z. physik. Chem.*, **144**, 269 (1929).

Effect of Chloride Ion on the Oxidation of the Iodide Ion.—Kolthoff and Jordan[5] found that iodide ion in aqueous solution 0.1 M in hydrochloric acid and 1 M in potassium chloride was oxidized to iodine monochloride. Figure 10 shows in curve 2 the effect of chloride ion on a 0.098 mM tetraethylammonium iodide solution. The arrows mark the height waves I and II would have had in the absence of chloride ion. It is seen that there is considerable current beyond that due to the oxidation of iodide ion to iodine. It is presumed that the reaction

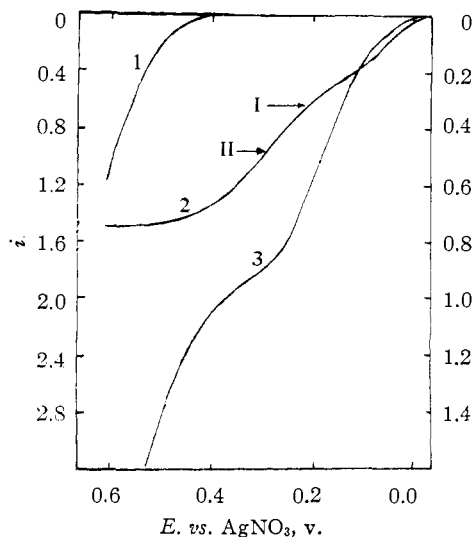$$^1/_2I_2 + Cl^- - e^- \longrightarrow ICl$$
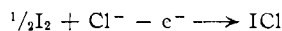
occurs to some extent.

Fig. 10.—Effect of chloride ion on iodide ion oxidation. (1) Residual current, 0.1 M tetrabutylammonium chloride (Bu$_4$NCl), left abscissa; (2) 0.098 mM tetraethylammonium iodide (Et$_4$NI), 0.01 M Bu$_4$NCl, 0.1 M lithium perchlorate, right abscissa; (3) 0.218 mM Et$_4$NI, 0.1 M Bu$_4$NCl, left abscissa. Current, μa. $vs.$ potential of RPE, volts $vs.$ Ag, AgNO$_3$ electrode; reverse trace.

Where 0.1 M tetrabutylammonium chloride was used as the supporting electrolyte, curve 3 was obtained. There is no well-defined wave, only an inflection point. The current at the inflection point is approximately twice that which would be expected for the oxidation of iodide ion to iodine in perchlorate ion supporting electrolyte.

Discussion

Waves I and II, Iodine System.—The electrode reactions which occur at wave I and II are unambiguously defined by the voltammetric data reported in the foregoing sections. They are

wave I $6I^- - 4e^- \longrightarrow 2I_3^-$

wave II $2I_3^- - 2e^- \longrightarrow 3I_2$
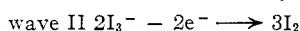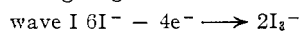
The result of the millicoulometric study, $n = 0.95$ faraday/mole, is in satisfactory agreement with the above statements, $i.e.$, a one-electron change for the over-all reaction on a molar basis.

It is interesting to note that Kolthoff and Jordan[5] found only a single wave for the over-all oxidation of iodide ion to iodine in $aqueous$ 0.1 M perchloric acid solutions; as already has been shown,

oxidation of iodide ion to iodine in acetonitrile involves a two-step wave. This difference in voltammetric behavior would seem to be quite largely due to the greater stability of triiodide ion in acetonitrile as compared with water. Katzin and Gebert[25] found a dissociation constant for the dissociation of triiodide ion into iodide ion and iodine of 1.01 $\times$ 10^{-3} in aqueous 0.1 M perchloric acid at 27.2°. The dissociation constant in acetonitrile[26] is 1 $\times$ 10^{-7} at 25°.

It was of interest to derive the equation of the polarographic wave for the electrode reactions corresponding to waves I and II. Previous workers[5] have pointed out that for the reduction reaction

$$I_2 + 2e^- \longrightarrow 2I^-$$
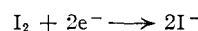
the reversible wave is given by the equation

$$E = \text{const.} + 0.03 \log \frac{i^2}{(i_d - i)}$$

It may be shown that for the electro-reduction corresponding to wave I, $(I_3^- + 2e^- \rightarrow 3 I^-)$, that

$$E = K - 0.03 \log \frac{i^3}{(i_1 - i)} \qquad (3)$$

while for the electroöxidation

$$E = K + 0.03 \log \frac{i}{(i_1 - i)^3} \qquad (4)$$

Evaluation of the half-wave potential from these equations gives

$$E_{1/2} = K' - 0.06 \log C \qquad (5)$$

where C is the concentration of the electroactive material.

It is expected that this wave equation would be applicable to wave I in the iodide ion oxidation and in the triiodide ion reduction. A plot of E $vs.$ log $i/(i_1 - i)^3$ for wave I in the oxidation of iodide ion gave a straight line with a slope of 38 mv. compared with the slope of 30 mv. predicted from equation 3. A plot of E $vs.$ log $i^3/(i_1 - i)$ for wave I of the triiodide ion reduction gave a slope of −50 mv. instead of the predicted −30 mv.

The variation of half-wave potential of wave I of the iodide ion oxidation is shown in plate A of Fig. 11. Though there is considerable scatter from a linear relationship, it can be seen that there is at least a tendency toward more negative potentials at higher concentrations of iodide ion. The solid line has a slope of −30 mv. A similar plot is given in plate B for wave I of the triiodide ion reduction. The slope of the solid line is −70 mv. It is seen that equation 5 predicts a slope of −60 mv. for a plot of $E_{1/2}$ $vs.$ log C.

Using a procedure analogous to that used to derive equation 4, the equation for a wave corresponding to wave II, $(2I_3^- - 2e^- \rightarrow 3I_2)$ is obtained

$$E = k + 0.03 \log \frac{(-i)^3}{(i_1 - i)^2} \qquad (6)$$

while for the corresponding reduction

$$E = k - 0.03 \log \frac{i^2}{(i_1 - i)^3} \qquad (7)$$

Evaluation of the half-wave potential gives

$$E_{1/2} = k' + 0.03 \log C \qquad (8)$$

(25) L. I. Katzin and E. Gebert, This Journal, **76**, 2049 (1954).

(26) N. E. Skelly, Ph.D. Thesis, State University of Iowa, 1955.

A plot of E vs. $\log (-i)^3/(i_1 - i)^2$ for wave II of the triiodide current–voltage curve gave a straight line with a slope of 31 mv.; a plot of E vs. $\log i^2/(i_1 - i)^3$ for wave II in the iodine reduction gave a straight line with a slope of -34 mv.

Plates C and D in Fig. 11 show the variation of half-wave potential with depolarizer concentration. Data in plate C for wave II of the triiodide ion oxidation at least show a tendency for a shift of half-wave potential to more positive values at higher concentrations. The solid line indicated has a slope of 44 mv. A similar plot for wave II of the iodine current–voltage curve (plate D) more closely approximates a linear relationship. The solid line has a slope of 55 mv.

Discussion of the results of the voltammetric studies of the iodine system in terms of equations 3–8 does give a basis for the concentration dependence of the half-wave potentials. Because of the reality of the influence of electrode surface condition, it does not seem that a completely valid evaluation of the "reversibility" of the electrode reaction can be made from the logarithmic analyses of the waves, which show some deviation from the predicted slope values. It is seen from the voltammetric data for iodide–triiodide ion and iodine–triiodide mixtures (Fig. 5) that there is *no inflection* at the zero current point for either wave I or wave II. On the basis of this observation, the conclusion is reached that electrode reactions corresponding to waves I and II are "reversible." The apparent deviations from reversible behavior are considered to be due to electrode surface effects.

From the same data (Fig. 5) it is possible to estimate the formal electrode potential for these half-reactions. Since both oxidized and reduced forms are present in solution in equal concentration, the zero current potential can be related to the formal electrode potential.

For the half-reaction

$$I_3^- + 2e^- \longrightarrow 3I^-$$

$$E = E^0 - 0.03 \log \frac{(C_{I^-})^3}{(C_{I_3^-})}$$

For the equimolar mixtures, $C_{I^-} = C_{I_3^-} = 4.5 \times 10^{-4}$ M, $E_{i=0} = -0.07$ v., thus $E^0 = -0.27$ v. vs. Ag, AgNO₃ electrode. An analogous calculation for the half-reaction

$$3I_2 + 2e^- \longrightarrow 2I_3^-$$
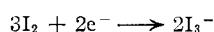
gives a value of 0.39 v. Strehlow[27] calculated the standard electrode potential for the iodine–iodide half-cell in acetonitrile from solubility measurements of sodium iodide. The reduction potential was calculated to be -0.1_6 v. vs. Ag, AgNO₃ electrode, a value intermediate to the formal potentials (in 0.1 M lithium perchlorate supporting electrolyte) given above.

Current constants are listed in Table I on both a molar and normal (termed "equivalent" constants)

(27) H. Strehlow, Z. Elektrochem., **56**, 827 (1952).

basis for purposes of comparison. From previous conductivity work,[22] the limiting equivalent conductances of tetramethylammonium iodide and triiodide are 195.7 and 191.5. Taking the limiting ionic conductance for the tetramethylammonium
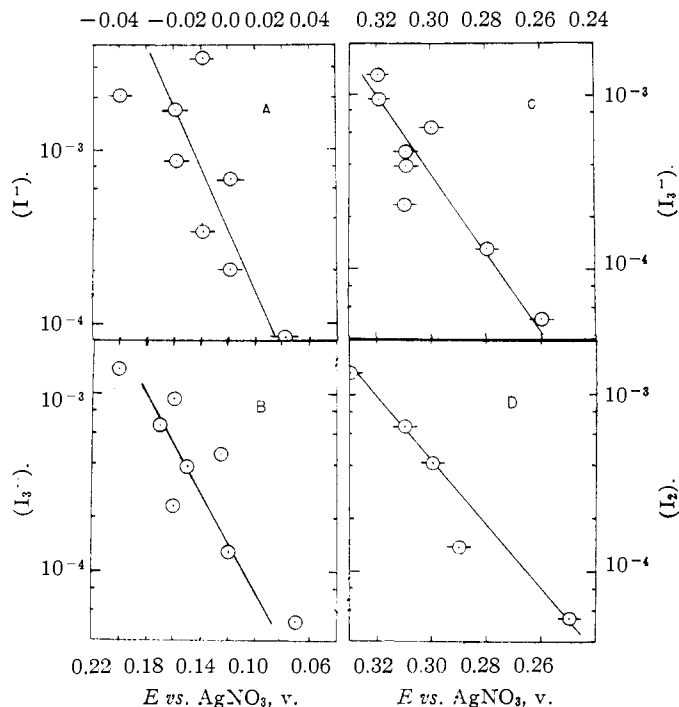

Fig. 11.—Variation of half-wave potential with concentration. Wave I: plate A, iodide ion oxidation; plate B, triiodide ion reduction. Wave II: plate C, triiodide ion oxidation; plate D, iodine reduction. Concentration of depolarizer (logarithmic scale) vs. half-wave potential, volts, vs. Ag, AgNO₃ electrode.

ion in acetonitrile as 92.9,[25] the limiting ionic conductances of iodide and triiodide ions are 102.8 and 98.6, respectively. It is seen that the sum of the equivalent current constants is essentially the same for iodide ion as for triiodide ion, as would be expected on the basis of their similar diffusion coefficients.

The diffusion coefficient of iodine in acetonitrile is not known. Consequently no effective comment can be made on the fact that the equivalent current constant for iodine is larger than the constant for both iodide and the triiodide ion.

The decrease of the ratio of the current constants of waves I and II in the series iodide ion, triiodide ion, iodine is indeed puzzling. From examination of the individual equivalent current constants it appears that it is the increase of the current constant for wave II (in the same series) that is responsible for the decrease of the ratio, particularly for iodine. No reason can be advanced to explain this situation.

Waves III and IV. Iodine System.—Waves III and IV observed in the voltammetric studies of the iodine system must represent oxidation of iodine to some positive valence state. It seems reasonable to disregard the oxygen-containing positive iodide ions as possible reaction products because of the non-oxygenated nature of the solvent and because it was

found that addition of 0.5% water had no effect on the oxidation of iodide ion. A number of positive iodine compounds of valences one and three are known.[9,28,29]

The current constant for wave III is grossly smaller than would be expected for the usual one-electron reaction. It is concluded that abnormal effects must be in force. The fact that the temperature coefficient for wave III is not grossly different from the temperature coefficient for waves I and II (which are assumed to be diffusion-controlled) strongly suggests that wave III is not a "kinetic" wave. It is seen in Table II that the millicoulometric data do not clearly distinguish a difference between the sum of reaction for waves I and II and the sum of waves I, II and III. The n values, 0.9_5 and 0.9_8 faradays/mole, respectively, coincide within experimental error with the expected value of 1.00 for the sum of waves I and II.

Perhaps the most significant experimental observation with regard to wave III is the fact that it does not occur in the current–voltage curve of molecular iodine, but it is found in the oxidation of triiodide and iodide ions. These observations suggest that wave III occurs only when nascent iodine is produced at the electrode surface.

It appears from the study of the effect of pyridine on iodine species that nascent iodine is also necessary for oxidation of iodine to the pyridine-stabilized monovalent cation (*vide infra*). The similarity of this case with the behavior of wave III is further intensified when it is noted that very low concentrations of pyridine, 5×10^{-4} M, apparently shift wave III in the iodide ion oxidation to more negative potentials (indicating a stabilization of the reaction product). However, the conclusion cannot be drawn from these data that the two waves necessarily represent the same electrode reaction.

It is not possible to determine unambiguously the nature of the electrode reaction at wave III; the best postulate seems to be that oxidation proceeds to the monovalent iodine cation by a mechanism that requires nascent iodine.

Wave IV occurs as an oxidation wave in the current–voltage curves of iodine, iodide ion and triiodide ion in acetonitrile. The fact that the current constants are dependent upon concentration (Fig. 4) suggests that the over-all electrode reaction is of a complex nature, perhaps involving more than one primary reaction; apparently at low concentration one of the primary electrode reactions makes a larger contribution to the total current than would be expected from a linear current–concentration relationship.

The possibility exists that the electrode cannot be considered totally inert. If electrode dissolution or interaction contributes to the total observed current at wave IV it is at least possible that the over-all current constant would not be independent of concentration, *i.e.*, the limiting current would not necessarily be strictly proportional to concentration.

(28) Gmelin's "Handbuch der Anorganischen Chemie," 8th Ed., Verlag Chemie, Berlin, 1933, System No. 8, p. 454 ff.

(29) J. Kleinberg. "Unfamiliar Oxidation States and Their Stabilization," University of Kansas Press, Lawrence, Kansas, 1950, p. 37 ff.

The similarity of α-values, which characterize the rate of rotation dependence for waves I, II and IV, indicates that oxide formation does not make an appreciable contribution to the current at wave IV. Under the criteria stated by previous workers[30] the α-value for wave IV also indicates that wave IV does not involve kinetic currents.

The magnitude of the current constant for wave IV may be altered by an electrode "interaction." The fact that at higher iodide ion concentration the current constant approaches a limiting value of -6 μa. liter/mmole, in comparison with a current constant of -4.91 μa. liter/mmole for the oxidation of iodide ion to iodine, gives some indication that the ultimate electrode reaction is oxidation of iodine to the monovalent state.

A further consideration of the millicoulometric data for electrolysis of iodide ion at 2.11 v. (Table II, run C) is given in Table V.

TABLE V
MILLICOULOMETRIC STUDY OF ELECTRODE REACTION, WAVE IV

I_3^-, μ moles	Electrode reaction	Electricity, μ faradays
...	Residual current	0.05
0.303	Waves I, II, III	0.60_6^a
0.327	Wave IV	1.04
0.63_0	Total observed	1.69_6

^{a} Estimated from height of limiting current for waves I, II and III.

The detection of positive iodine species produced electrolytically is based on their eventual reaction with iodide ions to form triiodide ions. Thus in the above listing, from the quantity of electricity consumed by reaction IV, 1.04 μfaradays, one would expect to find 1.04 μmoles of triiodide ion *if* the product of the electrode reaction were the I^+ species and *if* all of the I^+ underwent the oxidation reaction with iodide ions. The experimentally observed amount of triiodide ion was 0.327 μmole, considerably less than the expected 1.04 μmoles. It is possible that the product of the electrode reaction at wave IV (presumably I^+) not only reacts with iodide ion but also undergoes a side reaction, perhaps with the solvent.

In the case of the reaction corresponding to wave IV, *it is impossible to state unambiguously the exact nature of the electrode reaction.* The following seems to be a sound postulate: wave IV represents a complex electrode reaction involving the oxidation of iodine to at least monovalent positive iodine. Accompanying electrode interaction possibly causes the non-linear relation between limiting current and concentration and the high value for the current constant for wave IV.

Effect of Pyridine on Oxidation of Iodine Species.—The occurrence of a third wave in the current–voltage curve of iodide ion in the presence of pyridine is rather conclusive evidence for oxidation of iodine to the monovalent cation. The product of the electrode reaction is assumed to be dipyridine iodide (I), but the monopyridine iodine (I) ion is also known.[9]

(30) S. S. Lord, Jr., and L. B. Rogers, *Anal. Chem.*, **26**, 284 (1954).

The plot of current ratio vs. pyridine concentration for the iodide ion oxidation, as given in Fig. 7, approaches a value of one as would be expected for equivalent one-electron reactions as

$$I^- - e^- \longrightarrow \tfrac{1}{2}I_2$$
$$\tfrac{1}{2}I_2 + 2py - e^- \longrightarrow [I(py)_2]^+$$
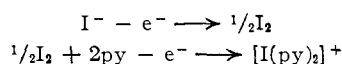
The presence of pyridine, even up to 3 M concentration, had substantially no effect on the magnitude of waves I and II. The half-wave potential of wave II was shifted to more negative potentials with increasing pyridine concentrations. This fact apparently is responsible for the merging of waves I and II at high pyridine concentrations.

The derivation of a relationship between pyridine concentration and the half-wave potential of the positive iodine wave is rather difficult since it involves treatment of a consecutive wave. It is sufficient to note that a shift of the half-wave potential for the positive iodine wave (for both iodide ion oxidation, Table III, and triiodide ion oxidation, Table IV) to more negative potentials with increasing pyridine concentration was observed.

The effect of pyridine on the oxidation of triiodide ion was generally analogous to the electro-oxidation of iodide ion in the presence of pyridine. However, it is seen in Fig. 8 that the plot of current ratio, $i_+/i_{I,II}$ vs. pyridine concentration, does not aproach a value of one, as was the case for iodide ion. The limiting value ca. 0.4 is grossly less than the value of 0.95 found with the iodide ion. This indicates that relatively less iodine is being oxidized to the monovalent state with triiodide ion than with iodide ion. The conclusion drawn from the plot of current ratio, i_+/i_{II}, vs. pyridine concentration (Fig. 8) where i_{II} is the oxidation current of triiodide ion, is that only as much iodine is oxidized to the plus one state as is produced electrolytically by oxidation of triiodide ion, where the oxidation is considered to proceed through dissociation of triiodide ion into iodine and iodide ion. These observations suggest that nascent iodine is a prerequisite of oxidation to the monovalent state. A further test of this statement would be offered by investigation of the voltammetry of iodine in the presence of pyridine. As was indicated earlier, the complex nature of acetonitrile solutions of iodine and pyridine (increasing triiodide ion concentration) prevents a totally rigorous voltammetric study. However, the absence of any gross oxidation current in the iodine–pyridine current–voltage curve in the potential region 0.4 to 1.5 v. offers support for the contention that nascent iodine is necessary for the oxidation of iodine to the monovalent cation in the presence of pyridine.

A possible reaction scheme might be

$$I^- - e^- \longrightarrow I^* + 2py - e^- \xrightarrow{k} I(py)_2^+$$
$$\downarrow I^* \qquad\qquad\qquad (9)$$
$$I_2$$
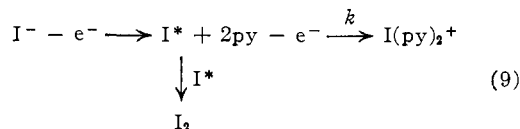
where I* is atomic iodine at the electrode surface. This scheme would qualitatively account for the dependence of the magnitude of the positive iodine wave on pyridine concentration, i.e., at high pyridine concentrations, the probability for the oxida-

tion of iodine "atom" may be increased in comparison with its probability for recombination with another iodine atom to give an iodine molecule (which is inert to further oxidation).

The postulation of atomic iodine on the electrode is based on the work of Vetter[31] who found that the reaction

$$I + e^- \longrightarrow I^-$$
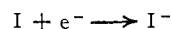
was the potential-determining step in the establishment of the iodine–iodide oxidation–reduction potential on a platinum electrode.

Effect of Other Heterocyclic Amines on Iodide Ion Oxidation.—It is seen from Fig. 7 that there is a distinct difference in the extent to which oxidation of iodide ion to the monovalent cation occurs in the presence of various amines. The fact that the current ratios decrease in the order pyridine > 2-picoline >> 2,6-lutidine, strongly suggests that steric factors are of importance in the electrode reaction. This assertion is further supported by the observed current ratios for the polynuclear amines. Thus 4,4'-bipyridine stabilizes the iodine cation almost as effectively as 2-picoline, whereas the formation of the iodine cation occurs to a very small extent in the presence of 2,2'-bipyridine. The 2,2'-bipyridine molecule may presumably exist in solution in either the cis or trans configuration. Fielding and LeFèvre[32] found by dipole measurements that the 2,2'-bipyridine molecule exists in the trans configuration in benzene solutions. In either configuration, cis or trans, 2,2'-bipyridine would show more steric hindrance to reaction with iodine species than would the 4,4'-isomer. It should be acknowledged that the apparent stability of the 4,4'-bipyridine iodine (I) complex may be due in part to a tendency toward polymerization.[33]

Brown, et al.,[34] have pointed out that base strength must be considered a function of the steric requirements of the acid. The order of base strength toward hydrogen ion is pyridine > 2-picoline > 2,6-lutidine. There is an inversion to the reverse order with an acid such as trimethylboron. Thus it is difficult to separate clearly basicity effects from steric considerations.

If the assumption is made that the electrode reaction scheme is analogous to equation 9, it seems qualitatively correct to suggest that the steric characteristics of the amine affect the rate constant, k, which in turn influences the observed current. Such an approach would agree with a low current ratio in the case of iodide ion oxidation in lutidine solutions. The pronounced decrease in observed current might then be attributed to the "blocking" effect of the two methyl groups in a reaction between the amine and the iodine atom. This would be particularly true if it were required that two amines coördinate with the iodine.

The true base strength might be expected to determine the stability of the iodine amine complex. This stability would in turn influence the half-wave

(31) K. J. Vetter, Z. Elektrochem., 55, 121 (1951); Z. physik. Chem., 199, 22, 285 (1952).

(32) P. E. Fielding and R. J. W. LeFèvre, J. Chem. Soc., 1811 (1951).

(33) F. B. Stute, Ph.D. Thesis, State University of Iowa, 1957, p. 109.

(34) H. C. Brown, D. Gintis and L. Domash, THIS JOURNAL, 78, 5387 (1956).

potential of the positive iodine wave. Perusal of the half-wave potentials in Tables III and IV does not show any clear pattern. It is concluded that the half-wave potential is not grossly affected by the base strength of the amine with the series pyridine, 2-picoline, 2,6-lutidine. Rather the voltammetric behavior is influenced to a greater extent by the configuration of the amine.

Voltammetry of Dipyridine Iodine (I) Perchlorate.—It is difficult to interpret the observed voltammetric behavior of dipyridine iodine (I) perchlorate because the limiting currents are substantially smaller than would be expected. From the current constant for the over-all reaction, $I^- - e^- \rightarrow \frac{1}{2} I_2$, -4.91 μa. liter/mmole, one would estimate an over-all current constant of 9 to 10 μa. liter/mmole for the reaction[35]

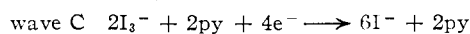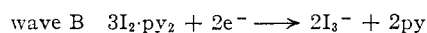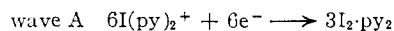$$[I(py)_2]^+ + 2e^- \longrightarrow I^- + 2\,py$$
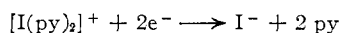
The current constant for wave A is only 1.22 μa. liter/mmole. This low current constant can only be partly accounted for by a decreased diffusion coefficient. Cases of similar abnormally small current constants were found in the interhalogen and

(35) The dependence of limiting current observed at a RPE on the diffusion coefficient ranges from 0.5 to 1.0 ($i_1 = kD^{0.5-1.0}$). From the limiting ionic conductances of the dipyridine iodine (I) ion and the iodide ion, 75 and 102.8, respectively, it is evident that even a direct proportionality between limiting current and diffusion coefficient gives a ratio of only 0.74 between the current constant for the iodide ion to iodine oxidation and the reduction of dipyridine iodine (I) to iodine.

mixed polyhalide ion reduction.[19] No satisfactory explanation has been found.

The following electrode reactions are tentatively proposed to explain the current–voltage curve observed for dipyridine iodine (I) perchlorate.

wave A $\quad 6I(py)_2^+ + 6e^- \longrightarrow 3I_2\cdot py_2$

wave B $\quad 3I_2\cdot py_2 + 2e^- \longrightarrow 2I_3^- + 2py$

wave C $\quad 2I_3^- + 2py + 4e^- \longrightarrow 6I^- + 2py$

In view of the abnormally low current constant of wave A, the current constant for wave B, 0.7 μa. liter/mmole, seems qualitatively satisfactory for the reduction of iodine to triiodide ion (the observed current constant for the reduction of iodine to triiodide ion is 2.11 μa. liter/mmole).

It has not been possible to establish definitely the nature of the electrode reactions taking place in the electrochemical reduction of dipyridine iodine (I). The electrode reaction tentatively suggested for wave A probably involves an appreciable overvoltage because its half-wave potential is even slightly more negative than that for the reduction of iodine to triiodide ion. It would seem reasonable to suppose that it would require less energy to reduce an electronegative group like $[I(py)_2]^+$ than to reduce molecular iodine. This irreversibility is also found in the electrode reactions postulated for wave B and peak C.

IOWA CITY, IOWA

The Heat of Formation of Boric Oxide[1]

BY BERNARD H. ECKSTEIN[2] AND ERVIN R. VAN ARTSDALEN[2]

The heat of formation of amorphous B_2O_3 is 304.6 kcal./mole as determined by burning crystalline boron in oxygen without the use of any organic initiator. This agrees well with the value of 302 kcal./mole found by Prosen using the decomposition of diborane as the experimental route.

Introduction

This paper describes the determination of the heat of formation of largely amorphous boric oxide by the direct union of elementary crystalline boron and oxygen without the use of any organic initiator. The heat of formation is defined as the enthalpy change for this reaction

$$2B(\text{cryst}) + 3/2\,O_2(g) = B_2O_3(\text{amorph})$$
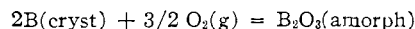
The earlier determinations of this heat of formation are summarized in Table I. Note the wide divergence in the results obtained whenever organic initiators were used. The agreement between the 304.6 kcal./mole found in this study, using the most direct method of determining heats of formation, and the very careful work by Prosen, *et al.*,

(1) The work here reported was carried out at the Department of Chemistry, Cornell University, during 1948 and 1949. It forms part of a Ph.D. thesis submitted to Cornell in February, 1953, by B. H. Eckstein.

(2) Research Laboratories, National Carbon Company, Division of Union Carbide Corporation, P. O. Box 6116, Cleveland 1, Ohio.

makes it seem very likely that the heat of formation of B_2O_3 is indeed *ca.* 302 kcal./mole.

Description of Apparatus

The actual combustions were carried out in a double valve type, self-sealing Parr Oxygen Bomb of 330-ml. capacity, made of Illium steel. This bomb was immersed in about 2600 g. of distilled water, weighed to 0.1 g., in a calorimeter consisting of three concentric cylindrical cans, all chrome plated and highly polished. There were an outer and an inner can and an interspersed aluminum radiation guard. All three elements were fastened at the top to a "Lucite"[12] ring. The bomb in the inner can was completely submerged but did not touch bottom, so that water could circulate freely about the bomb. The cover for the assembly consisted of a chrome-plated brass disc as the lower face, a monel metal plate as the upper face and a one inch block of "Lucite" as insulating material in between. The cover was pierced to permit access for the various leads to the bomb, the resistance thermometer, and a platinum resistance thermometer for calibration purposes. The pump type stirrer consisted of a shaft with four four-bladed propellers. The stirrer shaft was made in two sections joined by a section of "Lucite" to minimize heat losses. The pump housing served as support for a four-lead copper resistance thermometer. Because the calorimeter was completely submerged in a constant temperature bath a superstructure