Numerous attempts were made to observe the third wave of fluorenone reported by Ashworth[2] as appearing in dilute solutions of alkali hydroxides. Runs were made in solutions as dilute as 0.0001 M in sodium hydroxide, up to 0.001 M in fluorenone, as low as 7.5% in ethanol, and with different degrees of damping, but in no case were we able to obtain a third wave. The half-wave potential of the second wave was shifted to more negative values as the concentration of alkali was reduced. For example in 30% ethanol the values for the two waves were -1.08 and -1.32 v. in 0.1 M NaOH; in 0.005 M NaOH the values were -1.09 and -1.47 v. the values were -1.09 and -1.47 v. The potential of this second wave was also shifted to more positive values by the addition of small amounts of a neutral salt, such as potassium chloride. Ashworth,[2] while pointing out that the third wave observed with fluorenone corresponded to the second wave of benzophenone, listed values of shifts of half-wave potentials of the second wave of fluorenone with change in alkali concentration or concentration of neutral salt.

The over-all behavior of these four ketones as regards double wave formation in basic solution is qualitatively that which one would expect from the tendencies of the groups attached to the carbonyl to increase the stability of a metal ketyl intermediate. Fluorene shows the greatest tendency to form double waves, followed by benzanthrone, benzophenone and α-benzoylnaphthalene. The 9-fluoryl group is least effective in promoting free radical stability, followed by the benzanthryl, phenyl and α-naphthyl groups. It is also true that the same tendency holds in acid solutions, with the possible exception of benzanthrone, which could not be studied in solutions of low alcohol content. In acid solution, however, the dimerization of a free radical is presumably not reversible[7] and leads to the production of a pinacol. The explanation used for basic media would not then be applicable unless one assumes that solution conditions about the mercury drop are considerably different from those existing in usual organic preparative procedures. The fact that the second wave of benzanthrone in basic solution splits more readily than that of fluorenone may be the result of the second step proceeding partly through a free radical intermediate and partly through the metal ketyl.[2] If the dimerization of the metal ketyl alone is influenced by the concentration of alkali, this splitting of the second wave is plausible.

Acknowledgment.—The authors wish to express their appreciation to the University Center in Georgia and the Emory University Research Committee for contribution of funds which aided in obtaining the new Electro-Chemograph.

[7] Ref. 6, p. 612.

EMORY UNIVERSITY, GEORGIA

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF PORTLAND]

Polarographic Reduction of Iodonium Salts

BY EUGENE L. COLICHMAN AND HECTOR P. MAFFEI

RECEIVED DECEMBER 10, 1951

The polarographic reduction at the dropping mercury cathode of both symmetrically and unsymmetrically substituted iodonium salts is noted and reported. The mercury electrode is apparently involved in the reaction. A mechanism for the three step reduction is proposed in agreement with the experimentally found and derived polarographic data. The effect of buffering, acidity, solvent and concentration are reported in connection with the mechanism and analytical scheme for determining iodonium salts quantitatively.

Reported polarographic studies on positive halogen compounds are scarce and rather incomplete. Heller and Jenkins[1] studied the behavior of hypochlorite and N-chloroamines at the dropping mercury electrode. Their brief report shows an irreversible two electron reduction at +0.08 to −0.13 volt *vs.* S.C.E.

The presently reported investigation deals with the polarographic characteristics of a special series of positive iodine compounds, namely, iodonium salts. The study is restricted to this one member of the halogen family since only in the case of iodine are these dicovalent halogen "onium" compounds stable enough to be isolated from solution. There is good evidence, however, for the existence in solution of bromonium[2,3] and even chloronium[4] ions.

The previous work, on the mechanisms of basic[5] and thermal[6] decompositions of iodonium salts, is pertinent to the present polarographic reduction. Sandin and Brown's results[5] suggest that the decomposition of iodonium salts follows a free radical mechanism which is enhanced in the presence of some metals, for example mercury. Lucas, Kennedy and Wilmot[6] show that the decomposition under thermal conditions proceeds by scission of a C–I bond through an ionic mechanism. Medlin[7] has shown conclusively, by X-ray data, that the iodine–iodine bond in diphenyliodonium iodide is an ionic, not a covalent bond. Furthermore, the

[1] K. Heller and E. N. Jenkins, *Nature*, **158**, 706 (1946).

[2] I. Roberts and G. E. Kimball, THIS JOURNAL, **59**, 947 (1937), interpreted P. D. Bartlett's and D. S. Tarbell's earlier kinetic studies in terms of a postulated intermediate bromonium ion.

[3] The extensive work of S. Winstein, H. J. Lucas and their coworkers proves conclusively that bromonium ions are real intermediates. See G. W. Wheland, "Theory of Resonance," John Wiley and Sons, Inc., New York, N. Y., 1944, p. 242, and A. E. Remick, "Electronic Interpretations of Organic Chemistry," John Wiley and Sons, Inc., New York, N. Y., 2nd Ed., 1949, p. 337, for a review of the subject.

[4] H. J. Lucas and C. W. Gould, THIS JOURNAL, **63**, 2541 (1941).

[5] R. B. Sandin and R. K. Brown, *ibid.*, **69**, 2253 (1947).

[6] H. J. Lucas, E. R. Kennedy and C. A. Wilmot, *ibid.*, **58**, 157 (1936).

[7] W. V. Medlin, *ibid.*, **57**, 1026 (1935).

thermal decomposition studies of Lucas and co-workers[6] and Juliusburger, Topley and Weiss' radioactive iodine work[8] indicate that the covalent iodine and the anionic iodine atoms do not interchange during either thermal decomposition or aqueous reactions.

Diphenyliodonium iodide and perchlorate and unsymmetrically substituted β-chlorovinylphenyliodonium chloride were studied in the present polarographic investigation in order to ascertain if iodine exchange and/or disproportionation occur(s) during the reduction in the presence of mercury. These considerations are important in connection with the over-all mechanism of reduction of iodonium salts.

Experimental

Apparatus.—The apparatus, accessories and conditions were the same as described previously[9] except that a Lingane and Laitinen H-Cell,[10] with a saturated calomel anode, was used. An additional side arm was added to the cell to allow the "oxygen-free" nitrogen gas to pass over the solution during electrolysis. Measurements were at 25 ± 0.01°. A drop time of 3.00 sec. was employed with all the experimental data cited. The "m" value for the capillary was 2.00 mg. per second in both the aqueous and 50% alcohol buffers. The capillary constant, $m^{2/3}t^{1/6}$, was found to be an average value of 1.907 mg.$^{2/3}$ sec.$^{-1/2}$ (open circuit) in both solvent systems at 25° (h = 64 cm.).

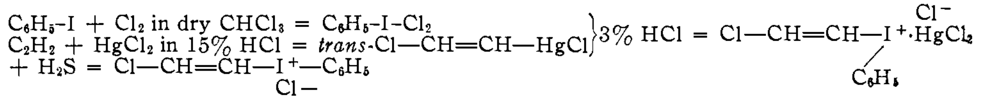
Reagents.—The iodobenzene was Eastman Kodak Co. White Label grade. Commercial tank acetylene was used. The inorganic chemicals such as mercuric chloride, potassium biphthalate and potassium dihydrogenphosphate were J. T. Baker C.P. grade. The sodium hydroxide was J. T. Baker C.P. special, low in chloride and iron. Sodium perchlorate was G. F. Smith Chemical Co. Reagent grade. The other chemicals such as hydrochloric acid were C.P. or Reagent grade.

Buffer Solutions.—The buffer solutions used in the polarographic investigation were made as given in Table I.

TABLE I

Buffer	Potassium dihydrogen phosphate, M	Sodium hydroxide, M	Potassium biphthalate, M	Hydrochloric acid, M	Potassium chloride, M
Aq. pH 7	0.05	0.03			
50% alc. pH 7	.05	.006			
50% alc. pH 6		.024	0.05		
50% alc. pH 5		.0004	.05		
50% alc. pH 4			.05	0.012	
50% alc. pH 3			.05	.037	
50% alc. pH 2				.011	0.05

Preparation of Iodonium Salts.—β-Chlorovinylphenyliodonium chloride was prepared by the exchange reaction described by Brainina and Freidlina,[11] according to the scheme



$$\left.\begin{array}{l} C_6H_5\text{-}I + Cl_2 \text{ in dry } CHCl_3 = C_6H_5\text{-}I\text{-}Cl_2 \\ C_2H_2 + HgCl_2 \text{ in } 15\%\ HCl = \textit{trans}\text{-}Cl{-}CH{=}CH{-}HgCl \end{array}\right\} 3\%\ HCl = Cl{-}CH{=}CH{-}\overset{Cl^-}{I^+}\cdot HgCl_2\ (C_6H_5)$$

$$+ H_2S = Cl{-}CH{=}CH{-}\underset{Cl-}{I^+}{-}C_6H_5$$

It was purified for polarographic use by recrystallization from 70% alcohol; melting point reported,[11] 224–226°, found 224°; picrate reported,[11] 167°, found 166°. Diphenyliodonium iodide was prepared by the Lucas and Kennedy method[12] from synthesized iodosobenzene[13] and iodoxybenzene.[14] Purification by recrystallizations from aqueous alcohol yielded a product melting at 173–174°, reported value[12] 172–175°. Diphenyliodonium perchlorate was formed by metathesis from the corresponding iodide. The iodide was dissolved in a sufficient quantity of boiling 50% alcohol saturated with a large excess of sodium perchlorate. The precipitated iodonium perchlorate was recrystallized from aqueous alcohol, melting point found 165°, reported[15] 165°.

Results

Half-wave potentials, slope analyses and diffusion current-concentration ratios for the stepwise reduction of iodonium salts are given in Tables II and III. Typical recorded polarograms are shown in Figs. 1–3. It is seen that iodonium salts, when either symmetrically or unsymmetrically substituted, are reduced according to processes involving three steps. With either iodonium salt, it appears that wave II is due to an "excessive" or "kinetic" diffusion current.[16] Evidence for the fact that wave II is a "spurious" wave is shown by the enhanced diffusion current found for the combined waves I and II. The diffusion current increases as the drop time is increased not in accordance with the Ilkovič equation. In the case of the unsymmetrically substituted β-chlorovinylphenyliodonium salt, it is seen that disproportionation, during reduction, could account for the split wave III and the "apparent" one electron wave IV. Half-wave potential data show that wave IV, with either type iodonium salt, is due to reduction of iodobenzene which requires two electrons per mole.[17] The "apparent" one electron wave IV in this case is in agreement with the effect of disproportionation in causing the concentration of iodobenzene to be half of the concentration expected on the basis of the precursor iodonium salt. These derived data (Tables II and III) and polarograms (Figs. 1–3) offer evidence for the proposed mechanism of the stepwise reduction of iodonium salts which is given in the Discussion Section.

As shown (Fig. 1 and Tables II and III), buffered pH 7 and unbuffered neutral aqueous solutions give the same polarographic results for the complete stepwise reduction of iodonium salts. Waves I and II are not altered by pH change. Waves III and IV show the influence of acidity. The $E_{1/2}$ value of wave III changes about +0.055 volt per pH unit decrease *per mole of iodonium salt*, in agreement with the participation of one mole of hydrogen ion per mole of R–Hg•, the proposed product at this stage in the reduction (see mechanism discussed below). Buffer solutions above pH 7 were not

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[8] F. Juliusburger, B. Topley and J. Weiss, *J. Chem. Soc.*, 1295 (1935).

[9] E. L. Colichman, THIS JOURNAL, **74**, 722 (1952).

[10] J. J. Lingane and H. A. Laitinen, *Anal. Chem.*, **11**, 504 (1939).

[11] E. M. Brainina and R. K. Freidlina, *Bull. acad. sci. U. R. S. S., Classe sci. chim.*, 623 (1947).

[12] H. J. Lucas and E. R. Kennedy, *Org. Syntheses*, **22**, 52 (1942).

[13] H. J. Lucas, E. R. Kennedy and M. W. Formo, *ibid.*, **22**, 70 (1942).

[14] H. J. Lucas and E. R. Kennedy, *ibid.*, **22**, 72 (1942).

[15] E. R. Kline and C. A. Kraus, THIS JOURNAL, **69**, 814 (1947).

[16] Otto H. Muller, "The Polarographic Method of Analysis," Chemical Education Publishing Co., Easton, Pa., 2nd edition, 1951, p. 74.

[17] See footnote (c) in Table III.

TABLE II

HALF WAVE POTENTIALS (VOLTS) AND SLOPE ANALYSES OF IODONIUM SALTS AT 0.001 M IN AQUEOUS AND 50% ALCOHOL SOLUTIONS

Salt	Supporting electrolyte	Wave I Slope	Wave I $-E_{1/2}$	Wave II Slope	Wave II $-E_{1/2}$	Wave III Slope	Wave III $-E_{1/2}$	Wave IV Slope	Wave IV $-E_{1/2}$
Iodobenzene	50% alc. buffer pH 7							0.088	1.68
Phenylchlorovinyl-	0.05 M KCl aqueous	0.059	0.07	0.120	0.23	[a] [a]	1.12 1.21	0.091	1.57
	Aq. buffer pH 7	.061	.07	.121	.22	[a] [a]	1.12 1.21	.093	1.56
	50% alc. buffer pH 7	.058	.07	.063	.21	0.110 .120	1.20 1.31	.093	1.67
	50% alc. buffer pH 5	.062	.06	.060	.21	.105 .109	1.14 1.25	No wave	
	50% alc. buffer pH 2	.057	.07	.058	.22	No wave		No wave	
Diphenyl-	50% alc. buffer pH 7	.061	.07	.125	.30	0.112	1.22	0.090	1.67
	50% alc. buffer pH 5	.058	.07	.114	.30	.114	1.11	No wave	
	50% alc. buffer pH 2	.060	.07	.130	.31	.020	0.87	No wave	

[a] No linear relationship for plot of E vs. log $I/I_d - I$.

TABLE III

DIFFUSION CURRENT–CONCENTRATION RATIOS[a] AND APPARENT NUMBER OF ELECTRONS INVOLVED DURING THE STEPWISE REDUCTION OF THE IODONIUM SALTS

Salt	Supporting electrolyte	Wave I i_d/C_t	Wave I i_d/C_s	Wave I n	Wave II i_d/C_t	Wave II i_d/C_s	Wave II n	Wave III[b] i_d/C_t	Wave III[b] i_d/C_s	Wave III[b] n	Wave IV i_d/C_t	Wave IV i_d/C_s	Wave IV n
Iodobenzene	50% alc. buffer pH 7										800	800	2.0[c]
Phenylchlorovinyl-	0.05 M KCl aqueous	480	480	1.0[d]	500	500	1.04[e]	260	520	1.08[e] 1.0[f]	460	920	2.0[c,f]
	Aq. buffer pH 7	520	520	1.03[d]	480	480	0.92[e]	280	560	1.08[e] 1.0[f]	460	920	2.0[c,f]
	50% alc. buffer pH 7	300	300	0.98[d]	320	320	1.03[d]	185	370	1.16[g] 1.0[f]	425	850	2.0[c] 2.12[h]
Diphenyl-	50% alc. buffer pH 7	340	340	1.04[d]	330	330	0.94[e]	360	360	1.03[e] 1.0[f]	780	780	2.0[c] 1.95[h]

[a] Diffusion current i_d is in mm., calculated at full galvanometer sensitivity. C_t is original concentration of iodonium salt. C_s is the concentration of the species responsible for the wave under consideration (in accordance with the proposed mechanism). Concentration unit used is millimoles per liter. Galv. calib. factor 0.0048 microamp./mm. [b] Values given are average for both parts one and two of wave III in the case of phenylchlorovinyliodonium chloride. [c] M. V. Stackelberg and W. Stracke, *Z. Elektrochem.*, **53**, 118 (1949), showed n to be two for the iodobenzene polarographic reduction in either 75% dioxane or 90% butanol with tetraethylammonium bromide as a supporting electrolyte. [d] Value based on slope analyses (see Table II) showing reversible reaction, that is, slope/0.059. [e] Obtained by ratio of i_d/C_s to same for reversible one electron wave I. [f] Obtained by process of elimination based on over-all total reduction and mechanism. [g] Obtained by ratio of i_d/C_s to same for reversible one electron wave II. [h] Obtained by ratio of i_d/C_s to i_d/C of iodobenzene under same conditions.

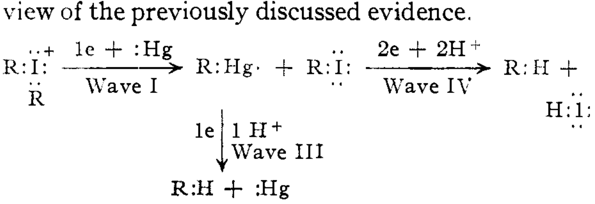
employed due to the instability of iodonium salts in basic solutions.[5]

In the case of β-chlorovinylphenyliodonium chloride, it was found that $-E_{1/2}$ varies directly in proportion to log C for all waves except I which does not vary with concentration in the region investigated (0.010–0.0005 M). The variation of waves III and IV is given approximately by the equation: $(E_{1/2})_{C_2} = (E_{1/2})_{C_1} - 0.16 \log (C_2/C_1)$. Reference values of $(E_{1/2})_{0.001\,M}$ are given in Table II. A similar concentration study was not made with the diphenyliodonium salts due to their insolubility at concentrations above 0.001 M.

Both diphenyliodonium iodide and perchlorate gave identical polarographic results showing that the covalent iodine and the anionic iodine do not interchange during the reduction. It thus seems that neither polarographic, thermal,[6] nor aqueous exchange reactions[8] favors interchange of the two different iodine species during decomposition of iodonium salts.

Discussion

Mechanism of Reduction of Diphenyliodonium Salts.—In agreement with the polarographic results and derived data given in Tables II and III, the following mechanism is proposed to account for the total four electron reduction, $(C_6H_5)_2I^+ + 3H^+ + 4e^- = 2C_6H_6 + HI$. Wave II is regarded as a "surface-limiting" or "extraneous" wave in view of the previously discussed evidence.



$$\underset{R}{R{:}\ddot{\underset{..}{I}}{:}^{+}} \xrightarrow[\text{Wave I}]{1e\,+\,:Hg} R{:}Hg\cdot + R{:}\ddot{\underset{..}{I}}{:} \xrightarrow[\text{Wave IV}]{2e\,+\,2H^+} R{:}H + H{:}\ddot{\underset{..}{I}}{:}$$

$$R{:}Hg\cdot \xrightarrow[\text{Wave III}]{1e \mid 1H^+} R{:}H + {:}Hg$$

The following is cited as evidence for the proposed mechanism: (1) Benesch and Benesch reported[18] the two-step reduction of phenylmercuric

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(18) R. Benesch and R. E. Benesch, THIS JOURNAL, **73**, 3391 (1951).

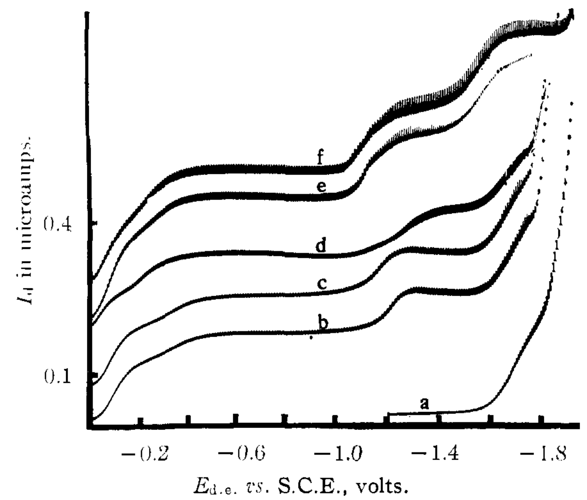


Fig. 1.—0.001 *M* concentrations at galvanometer shunt ratio *f* 1/20: (a) iodobenzene in 50% alcohol buffer *p*H 7; (b) diphenyliodonium perchlorate in 50% alcohol buffer *p*H 7; (c) diphenyliodonium iodide in 50% alcohol buffer *p*H 7; (d) β-chlorovinylphenyliodonium chloride in 50% alcohol buffer *p*H 7; (e) β-chlorovinylphenyliodonium chloride in aqueous *p*H 7 buffer; (f) β-chlorovinylphenyliodonium chloride in aq. 0.05 *M* potassium chloride.

halides. The $E_{1/2}$ of the first step ($C_6H_5HgX + 1e = C_6H_5Hg\bullet + X^-$, in acid or neutral solutions) was found to be independent of concentration and equal to about −0.1 volt *vs.* S.C.E. The present results (wave I) yield a value of −0.07 volt and show (see Figs. 1 and 2) the same "surface-limiting" wave as is evidenced in Benesch and Benesch's polarograms (their Fig. 1). (2) General agreement of the present $E_{1/2}$ results on wave III (see Table II) with Benesch and Benesch's results for the second step[19] in their reduction of phenyl mercuric salts offers additional evidence for the over-all validity of the mechanism proposed here in terms of the free radical $C_6H_5Hg\bullet$ as an intermediate. (3) That each mole of diphenyliodonium salt produces a mole of iodobenzene on reduction is demonstrated by comparing polarogram *a* with *b* or *c* in Fig. 1.

It is seen (Table I) that when the acidity is raised to *p*H 2, wave III occurs at a considerably lower voltage and according to slope analyses corresponds to a *reversible* three electron step. Possibly at high acidities phenylmercury free radicals and iodobenzene are complexed into a single free radical molecule which is then reduced in one single *reversible* three electron step to two molecules of benzene, one molecule of hydriodic acid, and one atom of mercury. It is, of course, quite possible that the "apparent" number of electrons as calculated from slope analysis data does not in actuality correspond to the right number of electrons.

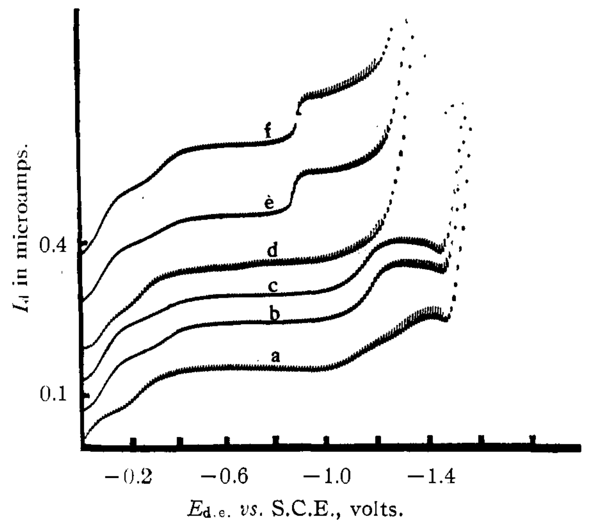


Fig. 2.—0.001 *M* concentrations in 50% alcohol at galvanometer shunt ratio *f* 1/20: (a)-(c) buffer *p*H 5; (d)-(f) buffer *p*H 2; (a) and (d) β-chlorovinylphenyliodonium chloride; (b) and (e) diphenyliodonium perchlorate; (c) and (f) diphenyliodonium iodide.

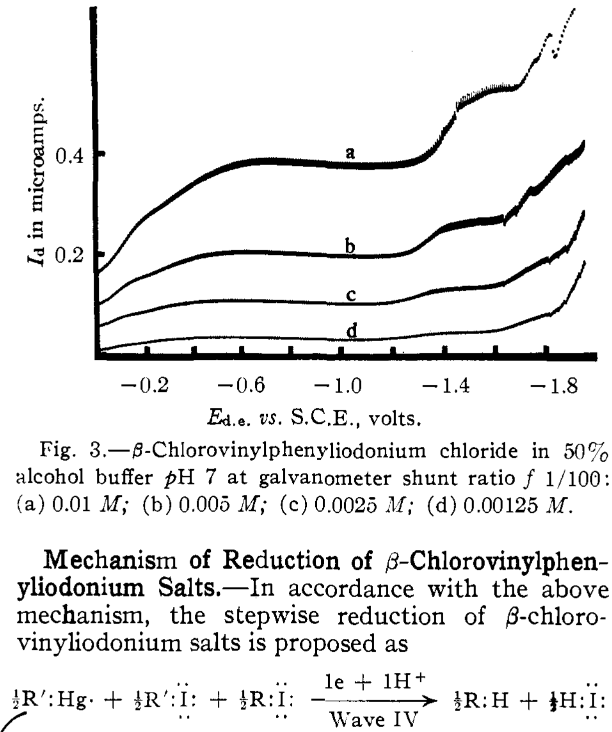
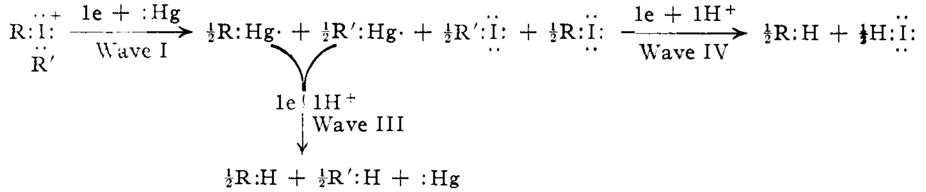


Fig. 3.—β-Chlorovinylphenyliodonium chloride in 50% alcohol buffer *p*H 7 at galvanometer shunt ratio *f* 1/100: (a) 0.01 *M*; (b) 0.005 *M*; (c) 0.0025 *M*; (d) 0.00125 *M*.

Mechanism of Reduction of β-Chlorovinylphenyliodonium Salts.—In accordance with the above mechanism, the stepwise reduction of β-chlorovinyliodonium salts is proposed as



$$\underset{R'}{R\!:\!\overset{..+}{I}\!:} \xrightarrow[\text{Wave I}]{1e\,+\,:Hg} \tfrac{1}{2}R\!:\!Hg\cdot + \tfrac{1}{2}R'\!:\!Hg\cdot + \tfrac{1}{2}R'\!:\!\ddot{I}\!: + \tfrac{1}{2}R\!:\!\ddot{I}\!: \xrightarrow[\text{Wave IV}]{1e\,+\,1H^+} \tfrac{1}{2}R\!:\!H + \tfrac{1}{2}H\!:\!\ddot{I}\!:$$

$$\downarrow\ 1e\ 1H^+\ \text{Wave III}$$

$$\tfrac{1}{2}R\!:\!H + \tfrac{1}{2}R'\!:\!H + :Hg$$

Wave III, split into approximately equal heights, may be accounted for by a disproportionation into equimolar amounts of $C_6H_5Hg\bullet$ and $ClCH{=}CHHg\bullet$ and their subsequent reductions. The "apparent" one electron step for wave IV (if based on i_d/C_t) might be due to non-reducible[20] ClCH—CHI in

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(19) Benesch and Benesch, ref. 18, give −1.20 v. as the upper limit for their second wave. By extrapolation from the data given in their Fig. 1, a value of −1.24 v. was estimated for a concentration of 1×10^{-3} *M*. It is thus seen that the present results (wave III) are in excellent agreement.

(20) The results given by ref. 17 lend support to the prediction of a high and perhaps unrealizable reduction potential for vinyl halides. For example, vinyl chloride is not reducible and vinyl bromide reduces at −2.47 v.

aqueous solutions, and thus only half as many equivalents of C_6H_5I would be available for reduction as a result of the proposed disproportionation.

It is seen (Fig. 2) that at higher acidity β-chlorovinylphenyliodonium chloride is not completely reduced. Instead, the solvent decomposition (hydrogen wave) merely precedes and prevents formation of waves III and IV.

Quantitative Analysis of Iodonium Salts.—Diffusion currents of all the reduction waves were found to be proportional to concentration when tested between 5×10^{-4} *M* and 1×10^{-2} *M* in 50% alcohol as a solvent. The solubility of the diphenyliodonium salts limits the analytical determinations to concentrations in the region of 0.001 *M*. Acidities in the region *p*H 6–7 are recommended since higher acidities do not allow full development of all waves, and basic solutions decompose iodonium salts. Maxima in any of the waves are not particularly large or troublesome, see Fig. 3. These maxima are completely absent at iodonium salt concentrations around 0.001 *M*. At higher concentrations, the maxima are easily eliminated by the addition of small quantities of gelatin or long chain quaternary ammonium salts as suppressors. Gelatin is recommended since concentrations slightly in excess of the "Maximum Suppression Point" (M.S.P.)[9,21] do not alter the polarographic results. The use of, for example, lauryltrimethylammonium bromide introduces complications. The minimum concentration of quaternary ammonium salt necessary to eliminate the maximum in wave III (its M.S.P. value[21]) shifts the $E_{1/2}$ value of wave IV to an erroneous smaller negative voltage. Apparently, the RHg• free radicals, postulated in the reduction, result in another example of substantivity causing an anomalous[9,21] maxima suppression behavior.

Acknowledgment.—The support of this investigation by the Research Corporation is acknowledged with appreciation.

(21) E. L. Colichman, THIS JOURNAL, **72**, 4036 (1950).

PORTLAND, OREGON

[CONTRIBUTION FROM THE EDWARD DAVIES LABORATORIES, THE UNIVERSITY COLLEGE OF WALES, ABERYSTWYTH]

The Iodine–Iodide Interaction

BY MANSEL DAVIES AND EMRYS GWYNNE

RECEIVED JUNE 8, 1951

The well-known equilibria in dilute aqueous iodide–iodine solutions have been re-examined systematically at a number of temperatures by the partition technique. The increase in heat content (ΔH_3) associated with the formation of the triiodide ion is found to be markedly temperature dependent. The next detectable step in polyiodide formation is the occurrence of $2I_3^- \rightleftarrows I_6^=$. The structure and binding in the triiodide ion are discussed on the basis of an electrostatic model.

The equilibrium $I^- + I_2 \rightleftarrows I_3^-$ has been one of the most frequently studied of ion–molecule interactions. The well-known distribution method was systematically applied to its study at 25° by Jakowkin[1]; his results and those of many later workers serve to show that the process is not confined to the triiodide stage. Most of the numerous determinations of the equilibrium constant (K_3) for the triiodide formation have been made at 25° and few explicit evaluations of the corresponding increase in heat content (ΔH_3) have been reported; in fact Dawson's[2a] and Jones and Kaplan's[2b] papers are exceptional in quoting K_3 values at two temperatures.[3] Although these authors did not calculate ΔH_3, this has been done by Moelwyn-Hughes.[4] On the practical side, the purpose of the present work was to make a systematic determination of ΔH_3 and also an examination of what further equilibria play a significant role in dilute solutions. For comparison with the former, a calculation of the expected net interaction energy arising principally from an ion-induced dipole term has been made.

Experimental

Distribution measurements between aqueous and carbon tetrachloride phases at 25.00 ± 0.02, 38.38 ± 0.03, 49.65 ± 0.05, 63.05 ± 0.05° form the basis of the results presented. A. R. chemicals, appropriately dried when used as volumetric standards, were used throughout the work, together with calibrated weights and carefully standardized volumetric apparatus. In view of the numerous previous studies of this system, between which marked discrepancies are often found (see later), the experimental errors in our methods were evaluated at each stage. Equilibrium was established in an all-glass cell of the form sketched by Brown and Bury[5] and samples of the layers were displaced by air pressure with precautions against loss of volatile iodine. Such samples for analysis were weighed and concentrations converted to volume units largely on the basis of recorded densities[6] and, for aqueous $KI + I_2$ solutions at temperatures other than 25°, from our own determinations of a few points over the ranges involved. Frequently standardized thiosulfate was used for the I_2 estimations. The aqueous phase was throughout made 0.0010 *M* in H_2SO_4; this concentration of acid sufficing to ensure that the hydrolysis of I_2 to HIO is negligible.[7] It is worth mentioning that the presence of the acid led to significantly better reproducibility in the distribution ratio (K_1) for iodine itself between the two solvents. In each run with the potassium iodide solutions dilution was continued until the total titratable iodine reached the lower limit for accurate determination: accepting a maxi-

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[1] A. A. Jakowkin, *Z. physik. Chem.*, **20**, 19 (1896).

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