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POLAROGRAPHY OF SUBSTITUTED IODONIUM SALTS

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INTRODUCTION

Polycovalent iodine compounds were discovered about 1890. Two men, working independently, are considered the pioneers in this field. They are Willgerodt and Victor Meyer. The literature of this period contains many contradictory statements and is in general somewhat confusing concerning these iodine compounds and their nature. For this reason it is difficult to cite the first report of an iodonium compound. Meyer and Wachter (1) in 1892 reported what was evidently an iodonium compound although it was not identified as such. It was two years later, in 1894, that an iodonium compound was reported and identified (2).

Early workers in their first reports of iodonium compounds discussed the obvious analogy between them and other "onium" compounds (2). It is to be noted, however, that in the case of iodine, the result though analogous is unique. The existence and isolation of covalent organic halides in which the halogen atom exerts a covalence greater than one appears to occur primarily with iodine. Sandin and Hay have recently reported (3) the isolation of stable solid diphenylenebromonium and diphenylenechloronium salts. The formation of di- and tri-covalent iodine compounds and their unusual reactions (4) have been interpreted upon the assumption that in the case of aryl iodides, the iodine atom is capable of holding temporarily ten electrons in its valence shell, but shows a strong tendency to revert to the normal octet. The structures of the stable derivatives involve only valence octets.

In a previous publication (5) the polarographic reductions of β-chlorovinylphenyliodonium and diphenyliodonium salts were reported. Mechanisms were proposed for these reductions consistent with the polarographic data obtained and the known properties of iodonium compounds. The presently reported study shows the influence of various substituent groups (chloro, methoxy, and methyl) on the polarographic reduction properties of β-chlorovinylphenyliodonium salts.

DISCUSSION

Pertinent facts in regard to the preparation of the intermediate substituted iodobenzene dichlorides are given in Table I. Similar data for the substituted iodonium salts investigated polarographically are in Table II. Half-wave potentials for the stepwise reductions of these iodonium salts are given in Table III.

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In the syntheses of the substituted iodobenzene dichlorides, a marked difference in the stabilities of the final products was noted. The methoxy substituted phenyliodonium dichlorides were very unstable especially in chloroform. No yield of the dichloride could be obtained in the case of the dichloride of *m*-iodoanisole. The reaction-product darkened during chlorination and no solid *m*-iodoanisole dichloride could be isolated. The mother-liquors from the preparation of the *o*- and *p*-iodoanisole dichlorides darkened within an hour on standing at room temperature and gave a distinct odor of hydrogen chloride. The *o*- and *p*-methoxy substituted derivatives were used immediately in preparing the corresponding iodonium salts. The methyl and chloro substituted iodobenzenes gave relatively stable dichlorides.

TABLE I

PREPARATION OF SUBSTITUTED IODOBENZENE DICHLORIDES

IODO-COMPOUND	CHLORINATION TIME, hrs.	YIELD, %
o-Iodotoluene	2¼	98.4
m-Iodotoluene	2¾	98.8
p-Iodotoluene	2	95.0
o-Chloroiodobenzene	3	84.0
m-Chloroiodobenzene	2¾	89.5
p-Chloroiodobenzene	3	64.3
o-Iodoanisole (1st run)	2¼	23.3
(2nd run)	3¼	48.8
m-Iodoanisole	3	0
p-Iodoanisole	2½	42.0

TABLE II

PREPARATION OF SUBSTITUTED β-CHLOROVINYLPHENYLIODONIUM CHLORIDES

IODONIUM SALT	REACTION TIME, hrs.	YIELD, %	M.P., °C.			
			$HgCl_2$ Double Salt from Ethanol		Monosalt from Water	
			Found	Reported	Found	Reported
o-Methyl-	3	30.6	99–100	98–99	201–202	202–203
m-Methyl-	4½	45.0	119–121		156–158	
p-Methyl-	6½	42.7	150–151	151–152	213–214	214–215
o-Chloro- (1st run)	9¾	7.7	100–103		143–147	
(2nd run)	2¼	9.8				
m-Chloro-	3	19.6	121–124		157–160	
p-Chloro-	3½	18.1	143–144	142–144	188–189	187–188
o-Methoxy- (1st run)	5	50.0	141–143		155–156	
(2nd run)	3¾	43.3				
p-Methoxy-	6¾	53.4	112–114		164–166	

Of all the iodonium salts prepared, the chloro substituted salts were obtained in the poorest yields and with the greatest difficulty. In these cases the reactions between the dichlorides and 1-chloro-2-mercuri-chloroethylene proceeded at extremely slow and impractical rates. It was found necessary to warm these mixtures at intervals to about 50°. This technique improved the yield to 18% instead of the previously reported (6) 6% for the *p*-chloro substituted iodonium salt. The *m*-methyl, *o*- and *m*-chloro, and *o*- and *p*-methoxy substituted iodonium salts have not been reported previously. Melting points and argentometric ionizable chloride analyses were used to identify the iodonium salts.

As observed previously (5) with unsubstituted β-chlorovinylphenyliodonium chloride, three main waves (I, III, and IV in Table III) were found in the stepwise reductions of the substituted salts when in water or water-alcohol solutions. Wave II, a secondary or "surface-limiting" wave, was found as before (5). In ethylene dichloride, solvent reduction interferes with the attainment of waves III and IV. These waves apparently are preceded by reduction of ethylene dichloride. Wave I is complicated by maxima, and it appears that in the case of ethylene dichloride the "surface-limiting" wave II is no longer obtained. It is seen (Table II) that in all three solvent systems studied the substituent groups exert little or no influence on the half-wave potential of wave I. Wave III showed little substitution influence. The one exception appears with the *o*-chloro substituted salt. In this case a considerably smaller half-wave potential was found. Wave IV is seen to agree substantially with the corresponding substituted iodobenzenes.

Slope analysis calculations (plot of $E_{d.e.}$ *vs.* log $I/I_d - I$) gave values approximately equal to 0.059 in all cases in 50% alcohol solutions for waves I and II and for wave I in water and ethylene dichloride. Larger slope values were found for the other waves in all solutions. These results are taken to indicate *one* electron reversible reductions in the cases cited and varying degrees of irreversibility in all the other instances. It is to be noted that the indicated pattern of reversibility for all the substituted salts parallels the behavior observed previously (5) with unsubstituted β-chlorovinylphenyliodonium chloride. In fact, a consideration of all the polarographic data obtained in this investigation seems to indicate that the various substituent groups do not materially change the previously proposed (5) stepwise reduction mechanism.

EXPERIMENTAL

Reagents. Iodobenzene, anisole, *o*-, *m*-, and *p*-iodotoluenes, *o*-, *m*-, and *p*-iodochlorobenzenes, and *o*-iodoanisole were Eastman Kodak Co. White Label grade and were used without further purification. Yellow Label grade Eastman Kodak Co. *m*-aminophenol and dimethyl sulfate were also used without purification. Reagent grade chloroform was dried over Drierite for 48 hours and distilled from fresh Drierite. Reagent grade ethylene dichloride was purified by simple distillation. Mercuric chloride, sodium hydroxide, and sodium dihydrogen phosphate were Baker's C.P. grade chemicals. The iodine used was Baker's U.S.P. resublimed grade. All other chemicals were ordinary Reagent grade and were used without any special purification.

Polarography. Previously reported polarographic investigations from this laboratory (5, 7) indicate the characteristics of the equipment and materials employed. Measurements were at 25.00 ±0.05° and at a drop-time equal to 3.00 sec. The aqueous and 50% alcohol *p*H 7 buffer solutions were as described earlier (5). The ethylene dichloride contained 0.01 *M* tetraethylammonium bromide as the supporting electrolyte. Maximum suppressors were not employed in obtaining the polarographic waves. Their use with many of the iodonium salts leads to erroneous (8) half-wave potentials.

Iodonium salts. The various iodonium salts were prepared by the previously outlined (5) method employed with the unsubstituted β-chlorovinylphenyliodonium chloride. *m*-Iodoanisole and *p*-iodonanisole, used in the syntheses and not available commercially, were prepared according to methods described by Votocek and Matejka (9) and Blicke and Smith (10). Essential data on the preparation of the various iodonium salts and the intermediate substituted iodobenzene dichlorides are given in Tables I and II.

TABLE III

HALF-WAVE POTENTIALS OF THE VARIOUS β-CHLOROVINYLPHENYLIODONIUM SALTS

SALTS	AQUEOUS *p*H 7[a]				50% ALC. *p*H 7[a]					ETHYLENE DI-CHLORIDE[b]
	Wave				Wave				Subst. Iodo-benzene	
	I	II	III	IV	I	II	III	IV		Wave I
o-Methyl	−0.09	[c]	−1.20	−1.60	−0.05	−0.28	−1.23	−1.69	−1.71	−0.08
m-Methyl	−0.09	[c]	−1.17	−1.58	−0.06	−0.25	−1.29	−1.76	−1.72	−0.09
p-Methyl	−0.03	[c]	−1.20	−1.59	−0.03	−0.37	−1.23	−1.73	−1.72	−0.08
o-Chloro	−0.05	[c]	−0.87	−1.18	−0.05	−0.22	−0.99	−1.40	−1.45	−0.06
m-Chloro	−0.05	[c]	−1.17	−1.42	−0.05	−0.22	−1.27	−1.58	−1.56	−0.08
p-Chloro	−0.04	[c]	−1.18	−1.49	−0.05	−0.21	−1.26	−1.62	−1.59	−0.06
o-Methoxy	−0.06	[c]	−1.13	−1.43	−0.05	−0.22	−1.30	−1.62	−1.55	−0.08
p-Methoxy	−0.09	−0.32	−1.23	−1.56	−0.05	−0.21	−1.31	−1.72	−1.66	−0.08
Unsubst.	−0.07	−0.22	−1.15	−1.56	−0.07	−0.21	−1.26	−1.67	−1.68	−0.07

[a] $E_{1/2}$'s are *vs.* S.C.E. for iodonium salt concs. equal to 0.001 *M*.

[b] $E_{1/2}$'s are *vs.* mercury pool for iodonium salt concs. equal to 0.0005 *M*.

[c] Surface-limiting wave not clearly defined.

Argentometric halide determinations. Ionizable chloride analyses were performed on the five newly reported iodonium salts by accepted argentometric procedure. The following results were obtained:

IODONIUM CHLORIDE	IONIZABLE CHLORIDE, %	
	Theor.	Found
m-Methyl-	11.3	11.4
o-Chloro-	10.6	10.5
m-Chloro-	10.6	10.6
o-Methoxy-	10.7	10.8
p-Methoxy-	10.7	10.8

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SUMMARY

The preparation of an isomeric series of chloro, methoxy, and methyl substituted β-chlorovinylphenyliodonium chlorides and the various intermediate substituted iodobenzene dichlorides is reported. Five of the iodonium salts have not been reported previously. A technique is described for increasing the yields of those chloro substituted salts which have been difficult to prepare.

The influence of the various substituents on the polarographic properties of the salts is noted in relation to the previously proposed stepwise reduction mechanism of iodonium salts.

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