[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS, THE PENNSYLVANIA STATE COLLEGE]

Polarographic Behavior of Organic Compounds. XII. Relative Ease of Carbon–Halogen Bond Fission in the Iodobenzoic Acids, Phthalic Anhydrides and Phthalates

BY PHILIP J. ELVING AND CLIFFORD L. HILTON

RECEIVED NOVEMBER 20, 1951

Benzoic acid and phthalic anhydride give no polarographic waves in the *p*H range of 5.4 to 11.5. In ammonium chloride–ammonium hydroxide buffer stepwise removal of halogen atoms was observed for polyiodophthalic anhydrides. Tetraiodophthalic anhydride yields four waves, triiodophthalic anhydride three waves, each of the four diiodophthalic anhydrides two waves, and 4-iodophthalic anhydride one wave. The reduction in each case corresponds with the fission of one carbon–halogen bond and the replacement of the halogen by hydrogen. In all other buffers, 3,6-diiodophthalic anhydride gives but one wave and triiodophthalic anhydride two waves; one wave in each case is apparently due to a loss of two halogen atoms. All other diiodo derivatives show two waves regardless of buffer or *p*H. The correlation of reduction potential and position in the molecule has been indicated for the iodo derivatives of benzoic and phthalic acids.

The present investigation was directed toward the determination of the effect of position on the ring upon the ease of carbon–halogen bond fission for various iodo derivatives of benzoic and phthalic acids.

Benzoic acid was reported[1] to be reducible at −1.87 v. *vs.* S.C.E. (saturated calomel electrode) in tetrabutylammonium iodide and 50% dioxane. In the present work, using only aqueous media, no reduction of benzoic was observed either in buffered solutions (*p*H 0.6 to 11.5) or in unbuffered 0.5 *M* LiCl solution. Furman and Bricker,[2] who investigated phthalic acid over the *p*H range of 1 to 8, reported that below *p*H 1.0 the phthalic acid wave merges with the hydrogen wave, from *p*H 1 to 2 one wave due to phthalate is obtained just before the hydrogen wave, and above *p*H 2.0 no waves are obtained unless multivalent cations are present. The present study of phthalic anhydride (*p*H 0.6 to 11.5) leads to similar conclusions; only in KCl–HCl buffer at *p*H 1.7 could any reduction be obtained, where two rather indistinct waves were found. Accordingly, it appeared likely that any reduction which did occur with the iodobenzoic acids and phthalic anhydrides and acids would represent loss of the halogen atom and replacement by a hydrogen atom.

Two more or less distinct waves were reported for each of the iodobenzoic acids in 66% ethanol and 0.01 *M* tetraethylammonium bromide, and in buffered solution[3]; single waves were found[4] in 20% 2-propanol containing 1% tetramethylammonium bromide and 2.65% sodium carbonate (*p*H 11.3). Diiodobenzoic acid derivatives gave two waves in the latter medium.[4]

The stepwise removal of halogen atoms from polyhalogenated compounds has been reported for the chlorinated methanes[5] and halogenated acetic acids.[6,7] It was felt that a polarographic study of the polyiodobenzoic and phthalic acid derivatives would provide data indicating the relative reactivities of halogen atoms in the various positions on the aromatic ring.

Although the present work deals largely with the iodobenzoic acids and diiodophthalic anhydrides, several runs were made with 3,4,6-triiodo- and 3,4,5,6-tetraiodophthalic anhydrides. Stepwise reduction representing fission of carbon–halogen bonds is also found in these aromatic compounds (Table VII). Of the four waves given by tetraiodophthalic anhydride, the most negative one coincides with the third wave of triiodophthalic anhydride; the second wave of diiodophthalic anhydride, and the only wave for monoiodophthalic anhydride. The third wave of the tetraiodophthalic anhydride corresponds with the second wave of the triiodophthalic anhydride. The noncoincidence of the second wave of tetraiodophthalic anhydride with the first wave of triiodophthalic anhydride is probably due to errors in measurement of the first wave of the latter compound at very low concentrations.

The first wave of the diiodo derivatives depends on the position of the iodine atoms on the aromatic ring. Iodine atoms meta to the carbonyl group seem to be more easily reduced than those in the ortho position. Also, when two iodine atoms are ortho to each other, the first is more easily removed than when they are meta. The meta configuration, in turn, is more readily attacked than the para. The small difference in potential between that for the fission of a carbon–iodine bond in the 3-position and that for one in the 4-position is understandable in terms of the equivalency of the two positions on the basis of analogous effects on ortho and para locations. A group in the 3-position is ortho and para to the two carboxyl groups while one in the 4-position is para and meta.

Although the iodine–carbon–carboxyl arrangements are not identical, the greater stability of an iodine–carbon bond in an aromatic molecule is seen by comparing the $E_{1/2}$ for *o*-iodobenzoic acid at *p*H 8.8 and 11.5 (−1.45 and −1.58 v.) with that of iodoacetic acid at the same *p*H values (−0.50 and −0.59 v.).

Experimental

Chemicals.—Eastman Kodak Co. white label grade *o*-, *m*- and *p*-iodobenzoic acids were used without further purification. The benzoic acid was a National Bureau of Standards sample, 99.98% pure. The *o*-phthalic anhydride was resublimed just before using. The iodinated phthalic anhydrides and the monosodium salts of the iodinated phthalic acids were prepared and purified during the course of another investigation carried out in these laboratories. Nitrogen used for degassing was deoxygenated and equil-

---

(1) S. Wawzonek, H. A. Laitinen and S. J. Kwiatkowski, THIS JOURNAL, **66**, 887 (1944).

(2) N. H. Furman and C. E. Bricker, *ibid.*, **64**, 660 (1942).

(3) E. Gergely and T. Iredale, *J. Chem. Soc.*, 13 (1951).

(4) E. T. Borrows, B. A. Hems and J. E. Page, *ibid.*, S204 (1949).

(5) I. M. Kolthoff, T. S. Lee, D. Stocesova and E. P. Parry, *Anal. Chem.*, **22**, 521 (1950).

(6) P. J. Elving and C. S. Tang, THIS JOURNAL, **72**, 3244 (1950).

(7) P. J. Elving, I. Rosenthal and M. K. Kramer, *ibid.*, **73**, 1717 (1951).

ibrated by bubbling through an alkaline pyrogallol solution, sulfuric acid, water and a portion of the test solution. The buffer solutions utilized are described in Table I.

TABLE I

COMPOSITION OF BUFFER SOLUTIONS

Buffer	*p*H	Composition
1	0.6, 1.1, 1.7	0.5 *M* KCl with added HCl
2	4.2, 5.4, 5.7	0.5 *M* NaOAc with added HOAc
3	8.2, 8.8	0.5 *M* NH_4Cl with added NH_4OH
4	9.2	0.024 *M* $Na_2B_4O_7$, 0.455 *M* KCl, added NaOH
	9.9	0.048 *M* $Na_2B_4O_7$, 0.355 *M* KCl, added NaOH
5	10.7, 11.5	0.1 *M* Na_2HPO_4 with added NaOH

Apparatus.—The polarographic curves were obtained with a Sargent Model XXI Polarograph. A Beckman model G *p*H meter was used. Capillaries used for the dropping mercury electrodes were prepared from Corning marine barometer tubing; *m* values for the capillaries used were 1.26, 1.16 and 1.00 mg./sec. at open circuit in distilled water. All potential measurements were checked with a potentiometer and are *versus* the S.C.E. at 25.0°. The temperature of the saturated calomel electrode and the sample cell was kept constant by means of a constant temperature bath which supplied circulating water for the water-jacketed H-cell used.[8] The saturated calomel electrode was connected to the sample cell by means of a potassium chloride–agar–fritted glass disk salt bridge.

Procedure.—Because of solubility difficulties, most of the test solutions were prepared by adding the compound directly to the buffer solution. In the case of the more soluble compounds, stock solutions were sometimes prepared. The test solutions were degassed for 15 minutes and then electrolyzed at a constant head of mercury (57 cm.). The nitrogen atmosphere was maintained throughout the electrolysis. The ionic strength of the test solution was 0.5 *M*.

Discussion

Benzoic Acid.—No reduction of benzoic acid was accomplished.

Iodobenzoic Acids.—The polarographic data are given in Table II. In all cases, diffusion coefficients have been estimated from the molar volumes of the compounds and the viscosity coefficients for the solutions, and have been used to approximate *n* values from the Ilkovic equation; *n* was found to be two. No reduction was obtained in the acid region except for *m*-iodobenzoic acid in acetate buffer at *p*H 5.7. Insufficient observations were made to state definitely the effect of *p*H on the half-wave potential, $E_{1/2}$. In general, the *p*H-independence of $E_{1/2}$ that is characteristic of acids on the alkaline branch of the S-shaped *p*H–$E_{1/2}$ curve[7,9] was apparent. The nature of the buffer system seems to be the important factor in this respect. Possibly interaction or complex formation may explain the greater difference in $E_{1/2}$ when going from one buffer to another in a given *p*H range than when changing *p*H within the same buffer system.

***o*-Phthalic Anhydride.**—Two waves were obtained in KCl–HCl buffer at *p*H 1.7; $E_{1/2}$ was −1.10 v. for the first wave and −1.20 v. for the second.

Iodophthalic Anhydrides and Sodium Phthalates.—The polarographic data are given in Tables III to VI. The data obtained at *p*H 8.8 are summarized in Table VII in order to emphasize the nature of the waves. The location of the carbon–halogen bond severed in producing each wave has been tentatively assigned.

TABLE II

THE IODOBENZOIC ACIDS

Buffer	*p*H	Acid concn., m*M*	$E_{1/2}$, v.	i_d, μa.	I^a
		o-Iodobenzoic acid			
1 or 2	0.6–4.2		No reduction observed		
2	5.3	0.310	Wave masked by buffer		
3	8.2	.208	−1.43	0.9	2.6
3	8.8	.307	−1.41	2.0	4.7
4	9.9	.278	−1.51	1.3	3.3
5	10.6	.274	−1.61	1.6	4.4
5	11.5	.250	−1.60	1.4	4.1
		p-Iodobenzoic acid			
2	5.4	0.339	Wave masked by buffer		
3	8.2	.173	−1.46	0.92	3.9
3	8.8	.283	−1.44	1.5	3.9
4	9.9	.246	−1.51	1.05	3.0
5	10.6	.282	−1.58	1.4	3.7
5	11.5	.274	−1.56	1.3	3.6
		m-Iodobenzoic acid			
1 or 2	1.1–4.6		No reduction observed		
2	5.7	0.282	−1.52	1.04	2.6
3	8.2	.193	−1.47	0.71	2.5
3	8.8	.282	−1.46	1.4	3.7
4	9.2	.250	−1.51	1.3	3.8
4	9.9	.282	−1.51	1.5	3.9
5	10.7	.267	−1.59	1.2	3.4
5	11.5	.267	−1.57	1.1	3.1

[a] $I = i_d/cm^{2/3}t^{1/6}$.

TABLE III

4-IODOPHTHALIC SPECIES

Buffer	*p*H	Added species	Concn., m*M*	$E_{1/2}$, v.	i_d, μa.	I^a
1	1.7	Na salt	. . .	−1.10	0.84	. . .
2	5.4	Anhydride	0.233	−1.48	1.4	4.5
2	5.4	Na salt	. . .	−1.03	0.36	. . .
3	8.2	Anhydride	.236	−1.34	0.75	2.3
3	8.8	Anhydride	.346	−1.35	1.7	3.6
4	9.9	Anhydride	.300	−1.50	1.3	3.2
4	9.9	Na salt	. . .	−1.48	6.4	. . .
5	10.7	Anhydride	.329	−1.57	1.4	3.1
5	11.5	Anhydride	.354	−1.56	1.8	3.6
5	11.5	Na salt	. . .	−1.55	2.8	. . .

[a] Footnote *a*, Table II.

There is little difference between the $E_{1/2}$ of the monosodium salt and that of the anhydride for a given compound in acetate buffer. Except for the 4-iodo and the 3,6-diiodo derivatives, the shift is only about 0.03 v. These two compounds, however, show a difference of about 0.4 v. Only the sodium salt of 3,4-diiodophthalic acid was studied in the NH_4Cl–NH_4OH buffer. In this case, there was a shift of about −0.1 v. for each wave both at *p*H 8.22 and 8.82. In borate and phosphate buffers only insignificant shifts were noticed regardless of the compound under study. Differences in $E^{1/2}$ between the anhydride and the corresponding sodium salt are ascribable to the slowness of hydrolysis of the anhydride under the experimental conditions.

---

(8) J. C. Komyathy, F. Malloy and P. J. Elving, *Anal. Chem.*, **24**, 431 (1952).

(9) P. J. Elving, J. C. Komyathy, R. E. Van Atta, C. S. Tang and I. Rosenthal, *ibid.*, **23**, 1218 (1951).

TABLE IV

THE DIIODOPHTHALIC ANHYDRIDES AND THE CORRESPONDING ACIDS AND SODIUM SALTS

Buffer	pH	Added species	Concn., mM	Wave I $E_{1/2}$, v.	Wave I i_d, µa.	I^a	Wave II $E_{1/2}$, v.	Wave II i_d, µa.	I^a
				3,4-Diiodophthalic species					
1	1.7	Na salt	0.130	−0.69	0.52	2.8	One wave only		
2	5.4	Anhydride	.107	− .84	0.44	2.9	Second wave masked by buffer		
2	5.4	Na salt	.130	− .82	0.51	2.5	Second wave masked by buffer		
3	8.2	Anhydride	.227	− .76	1.05	3.2	−1.34	1.09	3.5
3	8.2	Na salt	.130	− .87	0.56	3.0	−1.42	0.38	2.2
3	8.8	Anhydride	.227	− .75	1.02	3.1	−1.33	1.02	3.2
3	8.8	Na salt	.130	− .88	0.54	2.9	−1.43	0.36	2.9
4	9.9	Anhydride	.203	− .93	0.70	2.4	−1.47	.40	1.4
4	9.9	Na salt	...	− .96	1.20	...	−1.48	.68	...
5	10.7	Anhydride	.100	−1.03	0.37	2.6	−1.59	.23	1.7
5	10.7	Na salt	.130	−1.02	0.56	3.1	−1.58	.32	1.8
5	11.5	Anhydride	.232	−1.00	1.2	3.5	−1.56	.65	3.6
5	11.5	Na salt	.130	−1.01	0.72	3.9	−1.56	.38	2.0
				3,6-Diiodophthalic species					
1	1.7	Na salt	...	−0.72	0.41	...	One wave only		
2	5.4	Anhydride	0.192	−1.41	0.72	2.5	One wave only		
2	5.4	Na salt	...	−1.03	4.3	...	One wave only		
3	8.2	Anhydride	.227	−0.94	0.22	...	−1.37	0.25	...
3	8.8	Anhydride	.118	−0.94	.54	3.1	−1.33	0.72	4.4
4	9.9	Anhydride	.215	−1.45	.94	3.1	One wave only		
4	9.9	Na salt	...	−1.47	.64	...	One wave only		
5	10.7	Anhydride	.250	−1.56	1.5	4.5	One wave only		
5	11.5	Anhydride	.238	−1.58	1.8	5.6	One wave only		
5	11.5	Na salt	...	−1.53	2.0	...	One wave only		
				4,5-Diiodophthalic species					
3	8.2	Anhydride	0.227	−0.94	0.22	...	−1.37	0.25	...
3	8.8	Anhydride	.195	− .88	.39	1.4	−1.32	.44	1.6
4	9.9	Anhydride	.233	− .97	.94	2.8	−1.49	.67	2.3
4	9.9	Na salt	...	− .95	1.20	...	−1.48	.80	...
5	10.7	Anhydride	.100	− .97	0.38	2.7	−1.54	.28	2.1
5	11.5	Anhydride	.257	−1.00	1.23	3.3	−1.55	.96	2.7
				3,5-Diiodophthalic species					
1	1.7	Na salt	...	−0.90	0.60	...	One wave only		
2	5.4	Anhydride	0.222	−1.08	1.3	4.1	One wave only		
2	5.4	Na salt	...	−1.04	0.57	...	One wave only		
3	8.2	Anhydride	.115	−0.89	.38	2.3	−1.34	0.40	2.5
3	8.8	Anhydride	.114	−0.88	.30	1.8	−1.22	1.2	7.5
4	9.9	Anhydride	.235	−1.15	1.02	3.0	−1.49	1.01	3.1
4	9.9	Na salt	...	−1.15	0.44	...	−1.49	0.50	...
5	10.6	Anhydride	.200	−1.26	.62	2.2	−1.60	0.66	2.4
5	11.5	Anhydride	.228	−1.24	.94	2.9	−1.56	0.98	3.1
5	11.5	Na salt	...	−1.21	.30	...	−1.55	0.30	...

[a] Footnote a, Table II.

TABLE V

3,4,6-TRIIODOPHTHALIC ACID

Buffer		3	4	5
pH		8.8	9.9	11.5
Concn., mM		0.062	0.200	0.194
Wave I	$E_{1/2}$, v.	−0.61	−0.85	−0.87
	i_d, µa.	0.17	0.68	0.60
	I^a	.....	2.2	2.1
Wave II	$E_{1/2}$, v.	−0.94	−1.43	−1.53
	i_d, µa.	0.21	1.8	1.5
	I^a	.....	6.3	5.7
Wave III	$E_{1/2}$, v.	−1.33	Two waves only	
	i_d, µa.	0.30	Two waves only	
	I^a	.....	Two waves only	

[a] Footnote a, Table II.

Calculation of n values by the Ilkovic equation indicates that a two-electron process is involved for the first wave in most cases. The second, third and fourth waves, if present, are not so well defined as the first. Consequently, there is more apparent deviation from the n value of two; the manner of approximating diffusion coefficients from molecular volumes is not too satisfactory. In the case of 3,6-diiodophthalic anhydride, only one wave is obtained in acetate, borate and phosphate buffers. The height of the wave is approximately twice the height of the ordinary two-electron process, indicating either that two halogen atoms are removed simultaneously or that they are removed at a small potential difference. In the case of 3,4,6-triiodo-

TABLE VI

3,4,5,6-TETRAIODOPHTHALIC ANHYDRIDE

Buffer		3	4
*p*H		8.8	9.9
Concn., m*M*		0.178	0.195
Wave I	$E_{1/2}$, v.	−0.41	First one or two waves ill-defined
	i_d, μa.	0.42	
	I^a	1.6	
Wave II	$E_{1/2}$, v.	−0.67	First one or two waves ill-defined
	i_d, μa.	0.49	
	I^a	1.94	
Wave III	$E_{1/2}$, v.	−0.95	−0.89
	i_d, μa.	0.57	0.62
	I^a	2.1	2.2
Wave IV	$E_{1/2}$, v.	−1.34	−1.44
	i_d, μa.	0.63	0.98
	I^a	2.5	3.5

phthalic anhydride in borate and phosphate buffers, two waves were obtained, the more negative of which corresponds with the wave for 3,6-diiodophthalic anhydride. The 3,4,5,6-tetraiodophthalic anhydride in borate buffer gave an ill-defined first wave, which may or may not be two waves. The first well-defined wave corresponded with the first wave of the triiodo derivative, and the second well-defined wave corresponded with the second wave of the triiodo derivative in position but not in height. The *n* value (Ilkovic equation) for this wave was 2.5 rather than the value of 4.0 as in the case of the triiodo derivative.

In NH_4Cl–NH_4OH solution, the number of waves corresponds with the number of iodine atoms present.

Although it is assumed that at *p*H values other than 8.2 and 8.8, the reduction of the 3,6-diiodophthalic acid to phthalic acid takes place in a single step or two steps whose half-wave potentials are close together, another possibility exists. The alternative explanation is that in the buffers other than ammonia–ammonium chloride, the acid interacts with the buffer resulting in a shift of the wave to more negative potentials. As a result, all that is seen is the first wave, the second appearing beyond the buffer decomposition point. The diffusion currents which would normally decide between the two alternatives are not measurable accurately enough in this case. However the sum of the i_d constants for the two separate waves at *p*H 8.8 is 7.5, giving an average value for each two-electron step of 3.8. This indicates a two-electron step for the wave at *p*H 5.4 and 10.7, with the value at *p*H 11.5 being indecisive although the i_d constant is nearer that for a two-electron process than a four-electron process.

Additional support for the presence of complexation is that $E_{1/2}$ for the single 3,6-diiodophthalic acid wave found in acetate, phosphate and borate buffers is more negative than that of the more negative of the two waves found in the ammonia–ammonium chloride buffer. If the single wave resulted purely from a merging of two waves, $E_{1/2}$ for the combined wave would be intermediate in value.

TABLE VII

TENTATIVE ASSIGNMENT OF FISSION STEPS TO SPECIFIC CARBON–HALOGEN BONDS[a]

Phthalate species	Iodine positions relative to Carboxyl groups	Iodine positions relative to Each other	Wave D $E_{1/2}$, v.	Wave D Bond rupture	Wave C $E_{1/2}$, v.	Wave C Bond rupture	Wave B $E_{1/2}$, v.	Wave B Bond rupture	Wave A $E_{1/2}$, v.	Wave A Bond rupture
3,4,5,6-Tetraiodo	*o,m,o′,m′*		−0.41	5 in 5-4-6-3	−0.67	4 in 4-6-3	−0.95	6 in 6-3	−1.34	3
3,4,6-Triiodo	*o,m,o′*				− .61	4 in 4-6-3	− .94	6 in 6-3	−1.33	3
3,4-Diiodo	*o,m*	*o*					− .75	4 in 4-3	−1.33	3
3,5-Diiodo	*o,m′*	*m*					− .88	5 in 5-3	−1.32	3
3,6-Diiodo	*o,o′*	*p*					− .94	6 in 6-3	−1.33	3
4,5-Diiodo	*m,m′*	*o*					− .88	5 in 5-4	−1.32	4
4-Iodo	*m*								−1.35	4

[a] Data taken at *p*H 8.8.

Naturally, since complexation is always present in solution, it might be assumed that the reverse situation prevails, *i.e.*, the ammonia buffers interact with the organic compound to form a species more readily reducible than those existing in other buffers.

Solubility difficulties in the case of the iodophthalic anhydrides prevented working in aqueous solutions below *p*H 5.4. Even a 50% dioxane–water system did not prove satisfactory.

Values of *n* calculated from the slope of the current–potential wave varied from 0.4 to 1.9, with a majority of the values in alkaline solution being around 0.7; the reductions involved are apparently all irreversible.

Acknowledgment.—The authors wish to thank the Atomic Energy Commission which supported the work described in this paper.

STATE COLLEGE, PENNSYLVANIA