57. *Alkaline Halogenation. Part I. The Chlorination of Sodium Benzoate.*

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THE literature contans several references to the action of chlorine and hypochlorites on solutions of sodium benzoate, but records only one quantitative investigation. Lossen (D.R.-P. 146174; Friedländer's "Fortschritte," 1902, **7**, 115) describes processes which "give the three chlorobenzoic acids side by side, and especially the ortho, the meta being in small quantity." The theoretical significance of this reversal of the orientation in benzoic acid substitution has not escaped notice, and it has generally been recognised as the converse of the example of aromatic amines, which when free are attacked in the *o,p*-positions and when in the form of salts in the *m*-position. In both series the reversal in the direction exercised by the group is associated with the appearance of an electrical charge, a positive charge of the substituted ammonium kation and a negative charge in the benzoic anion.

Although a relation between the acquired charges and the observed orientation is evident, yet the precise nature of the influence exerted by the ionic group is by no means clear; *e.g.*, it has been suggested that the *m*-directing influence of the carboxyl group in benzoic acid becomes a typical *o,p*-influence on ionisation (cf. Ingold, Ingold, and Shaw, J., 1927, 817). Further, Flürscheim and Holmes (J., 1926, 1564), interpreting Lossen's results, state that ". . . the nuclear atoms are affected in the order *o*- > *p*- > *m*- on account of the direct neutralisation of residual affinity between *p*-atoms, which results in the direct transmission of the polar effect from the substituted atom to the *p*-atom . . ." It is hardly necessary, however, to discuss these theories in detail, because further investigation has shown that the COO′ group does not produce a typically *o,p*-directive effect. The products of the chlorination of sodium benzoate have now been analysed, and correspond to *o*-substitution 47, *m*- 33, and *p*- 20%. This order of activation (*o*- > *m*- > *p*-) is difficult to reconcile with the view that there is a direct neutralisation between atoms in the *p*-positions to each other. As the total *o*- + *p*- is greater than the *m*-chlorination, it might be suggested that two activations by the *ordinary* types are involved, (*a*) an *o,p*-activation and (*b*) a *m*-activation, giving also perhaps 20% of *o*-derivative; but in view of the extreme slowness of the *ordinary* *m*-substitution process, this explanation, in the author's opinion, is unsatisfactory. The evidence points to activation in all positions by the negative charge, the effect decreasing with distance from the charge, and in no case is the mechanism postulated similar to that which obtains in the substitution of benzoic acid itself. Although it is not justifiable to draw too close an analogy with the orientation in the ammonium kation ($PhNR_1R_2R_3^{\cdot}$), the fact that the predominant *m*-substitution in the kation is accompanied by *p*- rather than by *o*-substitution (Ing and Robinson, J., 1926, 1660) lends support to the view that a distance factor is involved.

The problem of the mechanism of chlorination by hypochlorite solutions as well as studies of hypobromite and hypoiodite reactions will be dealt with in other parts of this series.

EXPERIMENTAL.

Chlorination.—The many experiments performed may be divided into four groups :

(i) (Lossen's procedure). A solution of hypochlorite was prepared by passing chlorine (71 g.) into an ice-cold solution (4500 c.c.) of sodium hydroxide (80 g.). Benzoic acid (f. p. 121°; 122 g.) was added, and the mixture shaken, any undissolved solid being removed by filtration. The clear solution containing benzoate and hypochlorous acid in equimolar proportion was kept at 35—40° until all the latter had disappeared (18—24 hours) and was then cooled. The precipitate of solid acids (A) was filtered off and dried (20—27 g., but containing inorganic matter). On account of its bulk the filtrate was worked up in two parts. Each was acidified with concentrated hydrochloric acid (120 c.c.) and extracted three times with ether (total volume of ether 1100 c.c.). After drying (sodium sulphate) and evaporation, the extract yielded 112—125 g. of solid acids (B) (dried for 3 days at 30°). Eight experiments gave 183 g. of A (m. p. 195—200°) and 927 g. of B (m. p. 84—95°, equiv., 137—139).

(ii) After the same proportions of material as in (i) had reacted, a further 0·5 g.-mol. of hypochlorous acid (from chlorine, 35·5 g.; sodium hydroxide, 40 g., in ice-water, 500 c.c.; followed by concentrated hydrochloric acid, 43 c.c., in ice-water, 50 c.c.) was added, and the mixture left at 40° until no hypochlorite was present (2—4 days). The mixed product (A + B fractions) had equiv. 150, so that here, as in procedure (i), only about half the expected amount of chlorine was introduced : fraction A (precipitated acids *), 24 g., m. p. 210—220°, equiv. 153·2; fraction B (extracted), 121 g., m. p. 100—106°, equiv. 149·5.

(iii) After the reaction had finished as in (ii), $\frac{1}{3}$ g.-mol. of hypochlorous acid was added, and the mixture left for 24 hours at 35—40°; a sample of the solution then gave acids of m. p. 110°, equiv. 154; later, when these values were 112° and 156·6 (Calc. for $C_6H_4Cl\cdot CO_2H$, 156·5), the reaction mixture was cooled and filtered, and the B acids extracted.

(iv) When (i) was modified so that sufficient sodium hydroxide (120 g.) was used to convert both benzoic and hypochlorous acids into their sodium salts, much hypochlorite remained unchanged after 4 days at 39° (compare Ayling, J., 1929, 254). 1 Equiv. of hydrochloric acid was then added, and the mixture left for 40 hours longer. The A fraction had m. p. 180—210°, and the B fraction m. p. 83—93°, equiv. 137.

Preliminary Examination of the Chlorination Products.—The high m. p.'s showed that all the A fractions were largely *p*-chlorobenzoic acid. Extraction with benzene or ether in a Soxhlet apparatus freed the solid from inorganic matter (originating from the glass of the flasks). Procedure (i) gave a B fraction mainly of unchanged benzoic acid (equiv. 137—139). By procedure (iii) a B fraction had been obtained with m. p. 112°, equiv. 156·6. This might have been almost entirely monochlorobenzoic acids, but analysis by an approximate cryoscopic method showed that this mixture contained *o*-chloro-, 50; *m*-chloro-, 24; *p*-chloro-, 3; and benzoic acid 2%, the remaining 21% probably being dichlorobenzoic acids. Obviously the chlorination had gone too far for an accurate determination of the monochlorination products. By procedure (ii) a total of 92 g. of A fractions (m. p. 210°) and 472 g. of B fractions (m. p. 100—107°; equiv. 149, corresponding to 78 mols. % of monochlorobenzoic acids) were prepared. Esterification of 300 g. of B and fractional distillation of the esters (as described below for the main analysis) showed that B contained 10—15% of dichlorobenzoic acids. Obviously it would be unsatisfactory to chlorinate more than half the benzoic acid, and procedure (i) was adopted for the preparation of the mixture to be analysed.

Isolation of the Chlorobenzoic Acids.—The products obtained by procedure (ii) were used :

p-*Chlorobenzoic acid.* 5·5 G. of the acid precipitate (A, m. p. 210°), recrystallised from benzene (125 c.c.), gave 2·3 g. of m. p. 225°, and after two further crystallisations from benzene, 1·5 g. of m. p. 237—238°, equiv. 156·3 (Calc. : 156·5). A mixture with *p*-chlorobenzoic acid of m. p. 239° (corr.) melted at 239°.

m-*Chlorobenzoic acid.* (a) The mother-liquors after removal of the *p*-chloro-acid (above) were evaporated, and deposited a solid of m. p. 133—136°, raised by recrystallisation from benzene to 146—148°, equiv. 155. The m. p. was depressed to 110° and raised to 150—152°

* Freed from inorganic matter.

by admixture with *o*- and *m*-chlorobenzoic acid (m. p. 154°) respectively. (b) The B mixed acids (20 g.) from procedure (ii) were dissolved in sufficient 10% sodium hydroxide solution, and an excess of calcium chloride solution added. The precipitated calcium salts yielded 6·7 g. of an acid, m. p. 119°, equiv. 150. Recrystallised four times from benzene, this mixture gave 1·5 g. of m. p. 153°, equiv. 156·5; mixed with pure *m*-chlorobenzoic acid, it melted at 153—154°.

o-*Chlorobenzoic acid.* To hasten the purification, a new method of eliminating most of the benzoic acid was employed, based on the following experiment. If a mixture of sodium benzoate and *o*-chlorobenzoate (from 2 g. of the acid in each case) in 50 c.c. of water is mixed with a cold solution of copper sulphate (slight excess) and the total volume kept at about 100 c.c., the precipitate yields impure benzoic acid (1·65 g., m. p. 110—118°); from the filtrate, hydrochloric acid precipitates 1·75 g. of *o*-chlorobenzoic acid, m. p. 134—137°.

The filtrate from the calcium salts (above, isolation of *m*-chlorobenzoic acid) on acidification yielded 12·6 g. of solid, m. p. 115—121°, equiv. 153. This solid (9·2 g.) was dissolved in sufficient sodium hydroxide solution, the volume made up to 200 c.c., and copper sulphate solution (100 c.c. containing 5 g. of crystals) added at 10°. From the filtrate, hydrochloric acid precipitated 5·4 g., m. p. 128—130° (perhaps 85% *o*-); recrystallised from benzene (30 c.c.), it gave 3·1 g., m. p. 137—138°, and again recrystallised, 2·4 g., m. p. 141°, equiv. 156·3. A mixture with pure *o*-chlorobenzoic acid (m. p. 142°) melted at 142°.

Method of Analysis.—As it was impossible to convert all the benzoic acid into monochlorobenzoic acids without considerable dichlorination, the problem became that of estimating the relative amounts of each monochlorobenzoic acid in a mixture [from procedure (i)] of all three with much benzoic acid and traces of dichloro-acids. The products naturally separated into two fractions owing to the sparing solubility of the *p*-chlorobenzoic acid; this separation was retained, because mixing would have produced a mixture with a percentage of *p*-chlorobenzoic acid inconvenient for thermal analysis. The two fractions, therefore, were esterified separately with the minimum of loss and each fractionally distilled through a long column (cf. Hope and Riley, J., **1922**, **121**, 2510). The aim was to eliminate methyl benzoate and dichlorobenzoates as much as possible, and also to group the fractions so that the analysis would depend mainly on the accurate analysis of 3 or 4 large fractions, approximations being sufficient for the smaller ones. No attempt was made to separate the individual monochloro-esters. Hydrolysis gave quantitative yields of the acids. Van der Linden (*J. Chim. physique*, 1910, **12**, 465) has shown that the binary systems of benzoic acid with the monochloro-acids (Holleman and Bornwater, *Rec. trav. chim.*, 1912, **31**, 231) can be used for the analysis of ternary mixtures. Part of the system *o*-chloro–*m*-chloro-benzoic acid (see below) was found unsuitable for analysis because of complications from compound formation; but by addition of either isomeride in known amount the composition was brought into more suitable regions.

Esterification. The crude acid A [150 g. out of the 183 g. by procedure (i)] was esterified with methyl alcohol and sulphuric acid (20 hours). By recovering and esterifying the unchanged acid, 153 g. (above 90% yield) of ester (b. p. 108—122°/19 mm.) were obtained. Similarly the acid B (850 g. out of the 927 g.) was esterified in lots of about 200 g. with all precautions to avoid loss, giving 857 g. (92% yield) of distilled ester.

Fractionation. The ester from A was distilled (25 mm.) twice through a 60-cm. column of glass rings, yielding A_1, 43 g., b. p. 85—120·5° (mainly methyl benzoate), and A_2, 105 g., b. p. 120·5—127·2°.

The ester from B (857 g.) was distilled five times through the column, finally yielding the fractions :

	Temp.	Press., mm.	Wt., g.	Cl, %.*		Temp.	Press., mm.	Wt., g.	Cl, %.*
B_1	93·5— 95·5°	25	230	—	B_4	123·5—129°	25	353	20·4
B_2	95·5— 98·0	,,	109·5	0·4	B_5	129—141	16	35	—
B_3	98·0—123·5	,,	73	11·5	B_6	141—143	,,	11	—
							Total	812 g.	

* By fusion with sodium peroxide.

Analysis of the Fractions.—Hydrolysis. A mixture of ester (A_1, 19·8 g.), ethyl alcohol (3 c.c.), and aqueous sodium hydroxide (35 c.c. of 20%) was boiled until the smell of ester had disappeared (10 hours; 0·5—2 hours with other fractions), then acidified in presence of ether (250 c.c.) and again extracted with ether (70 c.c.); the extracts were mixed, washed once with water, and carefully evaporated, yielding 17·7 g. (dried at 40°), m. p. 173·5°.

From the m. p., the acid would contain 32·5 mols. % of *p*-chlorobenzoic acid if it were regarded as a mixture of benzoic and *p*-chlorobenzoic acids; or to 35% *p*- if a mixture of *p*-

and *m*-chlorobenzoic acids. Titration with alkali gave equiv. 138, or 54 mols. % of benzoic acid. In order to determine the other constituent, it was necessary to eliminate the *p*-acid. 5·0 G. of A_1 were refluxed with benzene (40 c.c.) and then left for 2 hours at room temperature, giving a residue (1·6 g.), m. p. 231° (90% *p*-), and on evaporation 3·3 g. of an acid $A_1\alpha$, m. p. 102°, mainly benzoic acid. Addition of 0·80 g. of *m*-chlorobenzoic acid to 0·80 g. of $A_1\alpha$ gave a mixture, m. p. 124·6° (60·5% *m*-), corresponding to 17·5 mols. % *m*- in $A_1\alpha$ and to 12 mols. % *m*- in A_1. Thus the m. p. shows *p*- = 34%; equiv., 138 shows benzoic acid 54%; and extraction shows *m*-chloro-acid 12%; total 100%.

Analysis of A_2. After hydrolysis of the ester, the liquid was diluted and acidified. The solid acids precipitated were collected, washed with water, and left to dry, the filtrate and washings yielding no more acid on ether extraction. After removal of inorganic matter by extraction with ether (Soxhlet), the acid melted at 209·5° in a sealed tube (corr.); yield, quantitative. 5·0 G. of the A_2 acids, extracted twice with benzene (50 c.c. each time), gave 2·95 g. of residue, m. p. 238° (pure *p*-chloro-), and 1·9 g. of soluble acids shown to be a mixture of *o*-chloro- (15%), *m*-chloro- (64%), and benzoic acid (18%). Thus for A_2, the m. p. 209·5° indicates 64 mols. % of *p*-chloro-, extraction indicates 26% of *m*-chloro-, 6% *o*-chloro-, and 7% benzoic acid (the equiv. 154·2 indicates 6% of benzoic acid), total 102·5%.

B_1 contained only traces of chlorine and was almost pure methyl benzoate.

B_2 (Cl, 0·4%) contained only 2 g. of chlorobenzoic acid in the total of 109 g. and was neglected.

B_3 on hydrolysis gave a quantitative yield of acids, m. p. 92·3°, equiv. 140·2 (47·5 mols. % of benzoic acid). 1·0 G. of B_3 acids mixed with 1·0 g. of benzoic acid gave a mixture melting at 102·6° (71% benzoic acid). Therefore B_3 contains 48·5 mols. % of benzoic acid. Determination of *m*-chlorobenzoic acid: 0·8 g. B_3 acid + 0·8 g. *m*-chloro- had m. p. 127·8° (65% *m*-), whence 25 mols. % *m*- in B_3; 0·8 g. B_3 acids + 1·1 g. *m*- had m. p. 132·6° (71% *m*-), whence 26% *m*- in B_3. Determination of *o*-chlorobenzoic acid: 0·8 g. B_3 acids mixed with 0·8, 1·0, and 1·2 g. of *o*-chloro-acid had m. p. 113·0°, 116·7°, and 119·5° respectively, whence the proportions of *o*-chloro-acid in the mixtures were 63, 67·5, and 70·5%, and those in the original B_3 were 22, 22·5, and 22 mols. %. Estimation of *p*-chlorobenzoic acid: 1·6 g. of B_3 acids + 0·4 g. of *p*- had m. p. 114·5° (23·5% *p*- from benzoic–*p*-chlorobenzoic curve), whence *ca.* 3·5% *p*- in B_3. Thus B_3 contains 48% of benzoic acid, 22% of *o*-, 25·5% of *m*-, and 3·5% of *p*-chlorobenzoic acids.

B_4 was hydrolysed completely in 20 minutes to a mixture of acids, m. p. 110·2°, equiv. (mean) 155·7, *i.e.*, 2·5% of benzoic acid. Determination of *o*-chloro-acid: 1·0 g. of B_4 acids mixed with 1·0 and 1·5 g. of *o*-chloro-acid had m. p. 127·6° and 130·6° respectively, whence *o*- = 79 and 84% in mixture, or 58 and 60 (mean, 59) mols. % of *o*-acid in B_4. Determination of *m*-chloro-acid: 1·0 g. of B_4 acids mixed with 0·5 and 0·766 g. of *m*-acid had m. p. 121·0° and 127·0° respectively, whence *m*-acid in mixture = 56, 62·5%, and in B_4 = 34, 34 mols. %. By gradual addition of *m*- to 2·578 g. of B_4 acids, the eutectic composition was reached (48% *m*-) with 0·46 g. *m*-, whence B_4 contains 38% *m*-. Determination of *p*-chloro-acid: the eutectic m. p. of B_4 acids was 108·5°. A mixture (synthetic) containing 57% *o*-, 41% *m*-chloro-acids, and 2·5% benzoic acid has eutectic temp. 109·9°. It being assumed that the further depression in B_4 is due to *p*-chlorobenzoic acid, B_4 will contain 3% of *p*- (see p. 218). Thus B_4 contains 59% *o*-, 35% *m*-, 3% *p*-chloro-acids, and 2% benzoic acid.

B_5 gave a mixture of acids, m. p. 126·5°, equiv. 170 (61% of monochloro-acids). The m. p. was depressed by *m*- and *p*- and raised by *o*-chlorobenzoic acid. A mixture of B_5 (1·5 g.) and *o*-acid (0·3 g.) had m. p. 129·6°. The monochloro-acid present is thus mainly *o*-, but consistent results could not be obtained by thermal analysis. In this relatively unimportant fraction (7% of the total monochloro-esters) a content of 60% *o*- is assumed.

B_6 was hydrolysed to acids of m. p. 120—122°, equiv. 184 (Calc. for $C_6H_3Cl_2{\cdot}CO_2H$: 191). This small fraction (1% of the total) was thus mainly a mixture of dichloro-acids (compare Hope and Riley, *loc. cit.*, and J., 1923, 123, 2470) and was not further investigated.

In order to calculate the composition of the original chlorination product, an adjustment must be made between the weights of the A and the B fraction. Of the A fraction (183 g. total), 150 g. were esterified (159 g. ester) and distillation yielded 148 g. of $A_1 + A_2$: factor 1·40. Similarly, the use of 850 g. (out of the 927 g.) of B giving 857 g. of ester and finally 812 g. of fractionally distilled product requires a factor 1·25. In col. 3 of Table I the weights have been corrected by means of these factors.

There are obviously many sources of error in this estimation: the unavoidable dichlorination probably reduces the proportion of *m*- and *p*-chlorobenzoic acids; esterification and fractionation both involve losses, but these are likely to eliminate benzoic and dichlorobenzoic acids rather than the monochloro-acids; finally the methods of thermal analysis employed are only approximate. When full allowance is made for these errors, however, there can be no doubt that under the conditions of the experiments the rate of substitution is in the order *o*- > *m*- > *p*-.

TABLE I.

Fraction.	Wt., g.	Wt., g., corr.	Composition, mols. %. *o*-.	*m*-.	*p*-.	$Ph{\cdot}CO_2H$.	Wt., g., in fraction. *o*-.	*m*-.	*p*-.
A_1	43	60		12	33	54		7	20·5
A_2	105	147	6	26	64	6·5	9	38	94
B_1	230					100			
B_2	109·5					99·6			
B_3	73	91	22	25·5	3·5	48	20	23	3·5
B_4	353	441	59	35	3	2	260	154	13
B_5	35	44	60				26		
B_6	16	20	mostly dichloro						
						Total	315	222	131

The relative proportions are thus :

o-, 47·2; *m*-, 33·2; *p*-, 19·7.

The System o- *and* m-*Chlorobenzoic Acid.*—The acids used were Kahlbaum's products crystallised from benzene to constant m. p. Holleman and Bornwater (*loc. cit.*) found the f. p.'s of mixtures indefinite, and recorded the maximum temperatures of crystal growth. It was more convenient here to determine the clearing points of the slowly heated mixtures, the values obtained being 0·1—0·2° above those of the crystal growth. Mixtures containing between 65 and 43% of *o*-chlorobenzoic acid give evidence of compound formation (not recorded previously), rapid heating of the cooled mixture giving clearing points for the compound, and slow heating (which allows time for decomposition) giving the equilibrium temperature between pure *o*-chlorobenzoic acid and the liquid phase. For this very unstable compound (perhaps 3 mols. of *o*-chloro- to 1 mol. of *m*-chloro-benzoic acid) the transition temperature could not be determined but appeared to lie between 112 and 114°. The eutectic temperature (obs. 110·65°, and from curve 110·7°, 52—53% of *o*-) is in agreement with that given by Hope and Riley (110·6° at 53% *o*-). In their second paper (*loc. cit.*), Hope and Riley prove the existence of compounds of 2 : 5-dichlorobenzoic acid with *m*-chloro- and with 2 : 3-dichloro-benzoic acid.

The data are in Table II.

TABLE II.

Mixtures of o- *and* m-*Chlorobenzoic Acid.*

(A = *o*-chloro-acid.)

A, mols. %.	M.p.*	A, mols. %.	M.p.*	A, mols. %.	M.p.*	Eutectic.	A, mols. %.	M.p.*	Eutectic.
100	141°	66·5	119·5°	61·2	113·5°	—	51·3	113·2°	110·7
89·2	134·1	64·8	118·2	56·9	112·2	110·9°	49·4	115·3	110·6
85·0	131·6	63·4	117·2	54·5	111·6	110·7	47·7	117·0	—
78·3	127·4	62·5	116·5, 113·9	52·9	111·1	110·6	37·1	127·2	—
68·6	120·6	62·0	113·7						
68·0	120·35								

* Actually, clearing point (see above).

Mixtures of Benzoic Acid and m-*Chlorobenzoic Acid.*—The following points confirm those of Holleman and Bornwater (*loc. cit.*).

Benzoic acid, % by wt.	100	78·2	72·0	64·9	57·8	49·3
M. p.	121·9°	108·4°	103·65°	96·4° *	104·1°	114·0°

* Eutectic 96·0°.

Ternary Mixtures.—Addition of benzoic acid to the eutectic mixture of *o*- and *m*-chlorobenzoic acids (*o*- 52%, *m*- 48%) :

Benzoic acid, % by wt.	0·0	2·0	4·3	7·4
Eutectic temp.	110·65°	110·05°	109·1°	107·8°

A mixture of benzoic acid (70%), *o*-chloro-acid (15%), and *m*-chloro-acid (15%) had m. p. 101·7°, which is exactly the m. p. of benzoic acid (70%) plus *m*-chloro-acid (30%).

Quaternary Mixture.—Addition of benzoic and *p*-chlorobenzoic acids to the eutectic mixture of *o*- and *m*-chlorobenzoic acids :

Benzoic acid, %.	*p*-Chloro-acid, %.	M. p.
2	2	108·8°
2	4	107·4

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