NOTE.

Alkaline Halogenation. The Bromination of Sodium Benzoate. By P. L. HARRIS and J. C. SMITH.

OWING to the rapid decomposition of hypobromite solutions the bromination of sodium benzoate in aqueous solution gives varying results. In the corresponding chlorination, which is much more rapid, substitution occurs in the order $o > m > p$, an orientation attributed to the localised negative charge on the benzoate anion (Smith, J., 1934, 213). For bromination the ratios are probably nearer $o : m : p = 1$, but are not constant, since, when the reaction mixture becomes acid, the conditions are similar to those found by Stark (*Ber.*, 1910, **43**, 670) to favour bromination in the *m*-position. The use of two equivalents of alkali (giving the proportion $Ph{\cdot}CO_2Na$: NaOBr) almost completely stops bromination, and a similar weakness of the hypochlorite ion as a chlorinating agent compared with halogen was observed in preliminary experiments (compare Francis, *J. Amer. Chem. Soc.*, 1925, **47**, 2340; Bartlett and Vincent, *ibid.*, 1935, **57**, 1596).

Benzoic acid (61 g.) in a solution of sodium hypobromite (2000 c.c., from 40 g. of sodium hydroxide and 80 g. of bromine) began after 2 days at 35° to deposit a solid (mainly *p*-bromobenzoic acid) and after 7 days (free bromine having been present continuously) the mixture was cooled and filtered. The mixture of acids obtained from the filtrate (largely unchanged benzoic acid) was esterified, and by methods similar to those used for the chlorobenzoic acids the total bromination was estimated to yield *o*-bromobenzoic acid 6 g., *m*- 5 g., and *p*- 7 g. In a second bromination under similar conditions the products were *o*-bromobenzoic acid 4 g., *m*- 6 g., and *p*- 4 g.

Repetition of the bromination of an aqueous suspension of benzoic acid with hypobromous acid (Stark, *loc. cit.*) confirmed the statement that the product was mainly *m*-bromobenzoic acid. Two successive treatments with hypobromous acid gave a product (Found : *M*, 188. Calc. for $C_7H_5O_2Br$, 201), m. p. 128·2°; the m. p. was depressed by admixture with *o*-bromobenzoic acid (5%) or *p*- (2%), but raised with *m*- (5%). The crude acid, twice crystallised from water and once from benzene, melted at 152—154° alone or mixed with *m*-bromobenzoic acid.—THE DYSON PERRINS LABORATORY, OXFORD UNIVERSITY. [*Received, November* 19*th*, 1935.]