562. *The Kinetics and Mechanisms of Aromatic Halogen Substitution. Part VII.* Some Experiments relating to the Halogenation of Toluene and* tert.*-Butylbenzene.*

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The acid-catalysed chlorination of toluene by hypochlorous acid in water is 60 times faster than that of benzene, and gives *o*- 74·6%, *m*- 2·2%, and *p*-chlorotoluene 23·2%. Chlorination of *tert.*-butylbenzene by molecular chlorine in 99% acetic acid is accompanied by 0·13% of chlorodebutylation. The proportion of *meta*-substitution in the bromination of toluene by molecular bromine in 87·5% acetic acid, as determined by the method of isotopic dilution, is 0·20%. With hypochlorous acid in 75% acetic acid, *tert.*-butylbenzene gives 42% of *p-tert.*-butylchlorobenzene. Comparison with results for other electrophilic reagents indicates that there is appreciable steric hindrance to the *ortho*-chlorination of *tert.*-butylbenzene by positive chlorine, and suggests that there may be a little steric hindrance to the *ortho*-bromination of toluene by positive bromine.

Bromination of toluene, by acidified hypobromous acid as the source of bromine, gives 70·3% of *ortho*-substitution.[1] Molecular bromine, on the other hand, gives predominantly *para*-substitution.[2,3] It is of interest to see whether a difference of this kind applies also to chlorination, and therefore the partial rate factors have been determined for the acid-catalysed chlorination of toluene in water. We had intended to extend this work to a study of the chlorination by molecular chlorine of toluene and *tert.*-butylbenzene; but data on these topics have now been presented by H. C. Brown and his co-workers [3,4] so herein are presented only such of our results as usefully extend their measurements.

Experimental

Most of the materials and general methods have been described in previous papers.[1,2,5] The chlorotoluenes were commercial specimens, carefully purified by fractional distillation, and had b. p. at 760 mm.: *o*-, 159°; *m*-, 161°; *p*-, 162°. *p-tert.*-Butylchlorobenzene, prepared from *p-tert.*-butylaniline by the Sandmeyer method and purified by fractional distillation and fractional freezing, had m. p. 23·7°. Other samples were prepared by fractional crystallisation from ethanol of specimens prepared by chlorination of *tert.*-butylbenzene.

Kinetics of Chlorination in Water.—The measurements were made in the presence of 0·01M-silver perchlorate, to repress the formation of free chlorine. Controls showed that the decomposition of hypochlorous acid could be neglected. The following example is typical of the rate-measurements all of which were made at 25°. From a solution containing 0·0088M-toluene, 0·0004M-hypochlorous acid, 0·01M-silver perchlorate, and 0·60M-perchloric acid, samples (25 ml.) were removed at intervals for titration with sodium thiosulphate. Results were:

Time (min.)	0·0	10·0	20·0	30·0	40·0	50·0	60·0	75·0
Titre (ml. of 0·004-N-$Na_2S_2O_3$)	5·00	4·55	4·15	3·80	3·50	3·25	3·00	2·50
k_2 (l. mole^{-1} min.$^{-1}$)	—	1·1	1·0	1·0	1·0	1·0	0·9	1·0

The following are mean values of k_2 (l. mole^{-1} min.$^{-1}$) for substantially similar concentrations of toluene, hypochlorous acid, and silver perchlorate at various acidities:

$HClO_4$ (M)	0·184	0·60	1·00	1·20	1·38
k_2 (l. mole^{-1} min.$^{-1}$)	0·28	1·0	1·4	1·8	2·5
k_2/H^+ (l.^{2} mole^{-2} min.$^{-1}$)	1·5	1·7	1·4	1·5	1·8

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* Part VI, *J.*, 1958, 1519.

[1] de la Mare and Harvey, *J.*, 1956, 36.

[2] Robertson, de la Mare, and Swedlund, *J.*, 1953, 782.

[3] Brown and Stock, *J. Amer. Chem. Soc.*, 1957, **79**, 1421.

[4] *Idem, ibid.*, p. 5175.

[5] de la Mare, Ketley, and Vernon, *J.*, 1954, 1290.

Corresponding values for benzene (0·22—0·37M) with hypochlorous acid (*ca.* 0·004M) are as follows (values of h_0 have been taken from Paul and Long's review [6]):

$HClO_4$ (M)	1·00	2·00	2·30	3·00	4·00	5·00
k_2 (l. mole^{-1} min.$^{-1}$)	0·025	0·11	0·18	0·60	1·8	3·9
k_2/H^+ (l.^{2} mole^{-2} min.$^{-1}$)	0·025	0·056	0·078	0·20	0·45	0·78
k_2/h_0 (l.^{2} mole^{-2} min.$^{-1}$)	0·015	0·018	0·023	0·035	0·034	0·023

Isomeric Proportions in the Chlorination of Toluene in Water.—The method of isotopic dilution was used. The tracer was introduced into the reaction mixture as hypochlorous acid, ($HO^{36}Cl$), and the mixed products were diluted with the appropriate inactive chlorotoluene. Final estimates of radioactivity were made after oxidation to the corresponding benzoic acid. Allowance was made for decomposition of hypochlorous acid by means of a control experiment. For the determination of *m*-chlorotoluene, the final measurement of radioactivity was made after adding, to the nearly pure *m*-chlorobenzoic acid, inactive *o*- and *p*-chlorobenzoic acid to act as hold-back carriers. The product was then again recrystallised until the m. p. was 157—158°, and the specific activity was unchanged on further recrystallisation. A solution (0·17M), in alkali, of the finally recovered acid had, after correction for background, an activity of 39 counts/min., quite high enough for satisfactory measurement. The values obtained were: *o*-, 74·4; *m*-, 2·2; and *p*-, 23·1%; the total (99·7%) accounts for all the reaction within experimental error.

Chlorodebutylation of tert.*-Butylbenzene in* 99% *Acetic Acid.*—*tert.*-Butylbenzene (0·1157M) and $^{36}Cl_2$ (0·0840M) were allowed to react to completion. To the product, which should have contained 2·803 g. of mixed *tert.*-butylchlorobenzenes, was added inactive chlorobenzene (11·99 g.). This was recovered by fractional distillation and nitrated. The resulting 1-chloro-2 : 4-dinitrobenzene was recrystallised till its activity was 26 counts/min. (1·0M). The chlorine solution converted into lithium chloride had an activity of 120 counts/min. (0·00092M). Hence not more than 0·13% of chlorobenzene was produced in the reaction by chlorodebutylation. To the residue of highly active *tert.*-butylchlorobenzenes was added more chlorobenzene, and the mixture was fractionated as before. The recovered chlorobenzene had negligible activity.

p*-Chlorination of* tert.*-Butylbenzene by Hypochlorous Acid in* 75% *Acetic Acid.*—The method of isotopic dilution was used, final measurements of radioactivity being made on *p-tert.*-butylchlorobenzene. There was formed 42% of *p-tert.*-butylchlorobenzene.

m*-Bromination of Toluene by Molecular Bromine in* 87·5% *Acetic Acid.*—Toluene (0·130M) and bromine (0·130M) in 87·5% acetic acid were allowed to react until 1·06 g. of bromotoluenes had been produced in 480 ml. of solution. Then were added sodium formate and 11·07 g. of inactive *m*-bromotoluene. The mixed bromotoluenes were recovered and oxidised; recrystallisation of the acidic product gave *m*-bromobenzoic acid (2 g.; m. p. 155°). This was further recrystallised to constant specific activity; treatment with *o*- and *p*-bromobenzoic acid as hold-back carriers did not further reduce the specific activity. The original hypobromous acid had an activity of 470 counts/min. (0·000445M). The diluted pure *m*-bromobenzoic acid had an activity, at the same time, of 62·3 counts/min. (0·302M). Hence 0·00217 g. (0·20%) of *m*-bromotoluene was produced in the reaction. This value is slightly smaller than those (0·24, 0·30%) obtained by Brown and Stock,[3] using the method of infrared analysis, for reaction in a slightly more aqueous solvent. The method of isotopic dilution, when applied to components present in such small proportions, is more likely to give high than low values, so it is considered that the present figure reliably estimates the amount of *m*-bromination under the conditions adopted.

DISCUSSION

Chlorodebutylation by Molecular Chlorine.—In Part III [7] it was shown that, for the reaction of *tert.*-butylbenzene with acidified hypobromous acid, bromodebutylation contributed to the reaction to the extent of about 1·9 moles %, the partial rate factor for this reaction being rather greater than that for attack by this reagent on a single position in benzene itself. For chlorination by molecular chlorine, proportionately less debutylation accompanies the reaction. Using the relative reactivities of benzene and *tert.*-butylbenzene recorded elsewhere [8] leads to a partial rate factor for chlorodebutylation of about

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[6] Paul and Long, *Chem. Rev.*, 1957, **87**, 1.

[7] de la Mare and Harvey, *J.*, 1957, 131.

[8] de la Mare and Robertson, *J.*, 1943, 279.

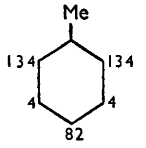
1; so the smaller proportion is mainly a reflection of the greater spread of reactivities conferred by substituents in chlorination by molecular chlorine than in bromination by positive bromine.

Chlorination of Toluene in Water.—The chlorination of toluene and of benzene by hypochlorous acid in water followed the kinetic form, $-d[ClOH]/dt = k[ArH][ClOH]f(H^+)$. In the region of acidity below about 1M-perchloric acid, the rate of reaction depends directly on the concentration of acid, and the rate-comparison used below represents an estimate, from the graphs of rate against concentration of acid, of the relative rates of reaction at 1·0M-perchloric acid.

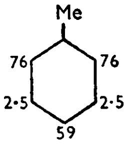
With higher concentrations of acid, the rate increases more rapidly, being approximately proportional, up to 5M-perchloric acid, to the value of Hammett's acidity function, h_0. This proportionality is shown by the ratios, given above, of k_1/h_0; such behaviour accords, as far as can be seen from their graphs, with that recorded by Derbyshire and Waters [9] for the acid-catalysed chlorination of sodium toluene-ω-sulphonate by hypochlorous acid. It is a result which is not unexpected for a reaction involving a pre-equilibrium proton-transfer, $ClOH + H^+ \rightleftharpoons ClOH_2^+$. The data are not such as to allow a test of the hypothesis [10] that the rate might follow the acidity function J_0, if, as would be required by the theory discussed elsewhere,[5] the above pre-equilibrium were followed by the formation of Cl^+ by the equilibrium: $ClOH_2^+ \rightleftharpoons Cl^+ + H_2O$. It seems probable that J_0 does not differ very considerably from H_0 in the experimental region under consideration.

The rate of reaction of sodium toluene-ω-sulphonate is, at any given acidity, one-third of that of benzene, the former reaction having been investigated at 21·5° and the latter at 25°. The kinetic form for the former reaction shows that it is a reaction of the negative ion, $Ph\cdot CH_2\cdot SO_3^-$; and the $\cdot CH_2\cdot SO_3^-$ grouping in this compound is known to be substantially *ortho-para*-directing, both for nitration [11] and for chlorination in water.[12] If, as in nitration, chlorination gives about 50% of the *para*-isomer, then, when allowance is made for the slightly lower temperature used in Derbyshire and Waters's measurements, the *para*-position in the toluene-ω-sulphonate ion can be estimated to be slightly activated relative to a single position in benzene, and of course deactivated relative to the *para*-position in toluene. The negative charge on the SO_3^- group is not, apparently, sufficient to overcome the electron-withdrawing inductive effect of the powerfully electronegative sulphur atom formally one atom nearer to the aromatic ring.

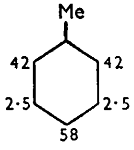
The experimentally determined proportions of isomers in the chlorination of toluene account for 99·7% (*i.e.*, all, within experimental error) of the uptake of hypochlorous acid; the normalised figures used in the calculation of partial rate factors are: *o*, 74·6; *m*, 2·2; *p*, 23·2%. These, and the relative rates of reaction of toluene and benzene in 1M-perchloric acid (60 : 1, from the graphs of rate against acidity) give the partial rate factors shown in the diagram and there compared with those for other aromatic replacements by positively charged reagents in hydroxylic solvents.[1, 13]



Cl^+



Br^+ (or $BrOH_2^+$)



NO_2^+

The $\frac{1}{2}m : p$-ratios in the three reactions (0·049, 0·042, and 0·042) are approximately constant. It seems reasonable, therefore, to attribute the corresponding decrease in

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[9] Derbyshire and Waters, *J.*, 1951, 73.

[10] Gold and Hawes, *J.*, 1951, 2102.

[11] Ingold, Ingold, and Shaw, *J.*, 1927, 828.

[12] D.R.-P. 146,946; cf. *Chem. Zentr.*, 1904, **75**, I, 66.

[13] Cohn, Hughes, Jones, and Peeling, *Nature*, 1952, **169**, 291.

$\frac{1}{2}$*o* : *p*-ratio (1·64, 1·28, 0·73) to increase in steric inhibition by the *o*-methyl group, in the order $Cl^+ < Br^+ < NO_2^+$, for introduction of these groups by a positively charged electrophilic entity. The order $Cl_2 < Br_2$ is well established for molecular halogenation, and is generally attributed to steric effects.[3,4,14]

This view receives some support when the proportions of *para*-substitution in toluene and *tert.*-butylbenzene are compared. Limitations of solubility have prevented us from examining *tert.*-butylbenzene in water; but it can be chlorinated with hypochlorous acid in aqueous acetic acid, in which solvent the reagent is a positive species.[15] The annexed Table shows the percentage of *para*-substitution under various conditions. Qualitatively, substitution is always relatively less easy *ortho* to a *tert.*-butyl group; this has, for the other reagents,[1,3,13] been attributed to steric hindrance, so it seems reasonable to use the same explanation for chlorination of *tert.*-butylbenzene by positive chlorine, and to believe that there may be a small residue of differential steric hindrance manifest in the comparison of bromination and chlorination of toluene by positive reagents.

Percentage of para-*substitution in some alkylbenzenes.*

Reagent	Solvent	% *para*-Substitution Toluene	 *tert.*-Butylbenzene	Ref.
Positive chlorine ...	H_2O	23	42 (solvent aq. HOAc)	This paper
Positive bromine ...	H_2O	27·4	53·2	1, 7
NO_2^+	aq. HOAc	40·0	79·5	13
Cl_2	HOAc	40	76	4, and H. C. Brown and L. M. Stock, personal communication
Br_2	aq. HOAc	67	92	1, 2, 3

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[14] Holleman, *Chem. Rev.*, 1925, **1**, 187.

[15] de la Mare, Ketley, and Vernon, *Research*, 1953, **6**, 12s.