463. *Aromatic Reactivity. Part XVI.*[1] *Detritiation of Halogenobenzenes.*

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We have measured the rates of detritiation of monotritio-benzene and -halogenobenzenes in trifluoroacetic acid containing either aqueous sulphuric acid or aqueous perchloric acid, and have obtained accurate rate factors for detritiation *ortho* and *para* to the halogens, along with rough values for the reaction *meta* to the halogens. Fluorine activates the *para*-position, and the other halogens deactivate this position in the order Cl < I < Br. The halogens deactivate the *ortho*- more than the *para*-position, and deactivate the *ortho*-position in the order F < I < Cl < Br; fluorine, however, deactivates the *ortho*- less than bromine does the *para*-position. The halogens deactivate the *meta*- much more than the *ortho*- and *para*-positions, iodine apparently being the least effective in this deactivation.

The substituent effects are compared with those in other electrophilic aromatic substitutions.

WE have measured the rates of detritiation of monotritiated halogenobenzenes and monotritiated benzene in trifluoroacetic acid containing either aqueous sulphuric acid (at 25·0°) or aqueous perchloric acid (at 55°). The results are given in the Table as first-order rate constants, k_{ex}, and as rates, f, relative to those for [$^3H_1$]benzene. In the case of the medium containing sulphuric acid, the value of k_{ex} is obtained by subtracting from the observed rate of tritium-loss, $k_{obs.}$, the rate of sulphonation $k_{sulph.}$ either measured or estimated (see refs. 2 and 3).

The results represent the first determinations of partial rate factors for the *ortho*- and *para*-positions of halogenobenzenes in hydrogen exchange. The main features of the

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[1] Part XV, Eaborn and Taylor, *J.*, 1961, 1012.
[2] Eaborn and Taylor, *J.*, 1960, 3301.
[3] Eaborn and Taylor, *J.*, 1961, 247.

Detritiation of $X{\cdot}C_6H_4{\cdot}{}^3H$.[a]

	$CF_3{\cdot}CO_2H–H_2O–H_2SO_4$ (25·0°) (83·40)–(1·98)–(14·62)[b]				$CF_3{\cdot}CO_2H–H_2O–HClO_4$ (55·0°) (96·77)–(0·82)–(2·41)[b]		$CF_3{\cdot}CO_2H–H_2O–HClO_4$ (55·0°) (89·50)–(4·55)–(5·95)[b]	
X	$10^7k_{obs.}$	$10^7k_{sulph.}$	10^7k_{ex}	f	10^7k_{ex}	f	10^7k_{ex}	f
H	560	63	497	1	3025	1	12,800	1
p-F	882	22[c]	860	1·73	5420	1·79	—	—
p-Cl	65·5	2·5	63	0·127	487	0·161	—	—
p-Br	38·5	2·5[d]	36	0·072	298	0·098	1090	0·085
p-I	45·5	2·5[d]	43	0·0865	339	0·112	—	—
o-F	—	—	—	—	412	0·136	1610	0·126
o-Cl	—	—	—	—	107	0·035	465	0·036
o-Br	—	—	—	—	83	0·027	350	0·027
o-I	—	—	—	—	129	0·043	525	0·041
m-F	—	—	—	—	—	—	(25)	~0·002
m-Cl	3·42	2·46	1·0	0·002	—	—	(16)[e]	~0·001
m-Br	—	—	—	—	—	—	(16)[e]	~0·001
m-I	—	—	—	—	—	—	(42)[e]	~0·003

[a] Rate constants in sec.$^{-1}$. [b] Mole-percentages in parentheses. [c] It is assumed that fluorobenzene is sulphonated about 9 times as fast as chlorobenzene; the ratio is *ca.* 5 in nitration and *ca.* 11 in molecular chlorination. [d] Iodo- and bromo-benzene are assumed to be sulphonated at about the same rate as chlorobenzene. [e] Rough figures only, see text.

results, including comparisons with data for other electrophilic aromatic substitutions, are as follows:

(i) The spread of rates is dependent upon the medium in the manner previously noted with other aromatic compounds.[1-3] A plot of log f in one medium against log f in either of the other media is a straight line.

(ii) Fluorine clearly activates the *para*-position in detritiation, as it does in molecular bromination and chlorination,[4] the $+T$ effect outweighing the $-I$ effect. In nitration,[5] proto-,[6,7] mercuri-,[8] and bromo-desilylation,[9] and in proto-degermylation,[10] and -destannylation,[11] fluorine deactivates the *para*-position. The activation in detritiation is consistent with the observation that the demand on the electromeric effect of substituents is large in this reaction.[1] (Because a *p*-Bu^t group activates more than a *p*-Me group in detritiation in media of the type used in the present work, we previously suggested that demand on $+E$ effects of substituents might not be large, in spite of large values of f_p^{Me} which would normally be associated with a strong call on polarizability effects.[3] Results from detritiation of [$^3H_1$]biphenyls and [$^3H_1$]naphthalenes,[1] and now of *p*-[$^3H_1$]fluorobenzene, show clearly that the demand on $+E$ effects *is* large. The difficulty of explaining the activation order *p*-Bu^t > *p*-Me in terms of electrical effects of substituents only is thus even greater than we had indicated.[3])

Additional results for the *p*-F atom, not shown in the Table, are that it activates 2·18 times in 76·29 wt.-% aqueous sulphuric acid, in which *p*-Me activates 240 times,[2] 1·7 times in $CF_3{\cdot}CO_2H$ (92·04)–H_2O (5·45)–$HClO_4$ (2·51) in which *p*-Me activates 313 times,[3] and 2·4 times in $CF_3{\cdot}CO_2H$ (85·08)–H_2O (6·42)–H_2SO_4 (8·50) in which *p*-Me activates 540 times. It seems that the value of f for *p*-F does not necesarily rise with f for *p*-Me.

(iii) The deactivation order *p*-Cl < *p*-I < *p*-Br applies in detritiation, as in molecular bromination (of 3-halogeno-1,2,4,5-tetramethylbenzenes) in nitromethane.[12] In nitration, *p*-I is several times less deactivating than *p*-Cl and *p*-Br substituents,[13] and this has been

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[4] de la Mare and Ridd, " Aromatic Substitution, Nitration and Halogenation," Butterworths Scientific Publ., London, 1959, pp. 138—139.

[5] Bird and Ingold, *J.*, 1938, 918.

[6] Eaborn, *J.*, 1956, 4858.

[7] Deans and Eaborn, *J.*, 1959, 2299.

[8] Eaborn and Webster, unpublished work.

[9] Eaborn and Webster, *J.*, 1957, 4449; 1960, 179.

[10] Eaborn and Pande, *J.*, 1961, 297.

[11] Eaborn and Waters, *J.*, 1961, 542.

[12] Illuminati and Marino, *J. Amer. Chem. Soc.*, 1956, **78**, 4975.

[13] Roberts, Sanford, Sixma, Cerfontain, and Zagt, *J. Amer. Chem. Soc.*, 1954, **76**, 4525.

attributed either to a small demand on electromeric effects,[14] or to a large demand on inductomeric effects made by a positively charged reagent.[15,16] However, the demand on electromeric effects is probably even smaller in proto-desilylation and -degermylation, in which *p*-I deactivates more than *p*-Cl, and moreover, in these reactions, as in detritiation, a positively charged reagent is involved. The deactivation order *p*-I $<$ *p*-Cl $<$ *p*-Br applies in molecular bromination (of 1-halogenonaphthalenes [16]) and possibly in molecular chlorination; [17] these are reactions with a large electron-demand, and the *p*-chloro-atom, with its larger $+E$ effect, might have been expected to deactivate less than the *p*-iodo-atom.

(iv) Deactivation by *ortho*-substituents is in the order F $<$ I $<$ Cl $<$ Br. The reduction in rate on moving the halogen from the *para*- to the *ortho*-position decreases in the order F $>$ Cl $>$ Br $>$ I, which is consistent with increased importance of the $-I$ effect at the *ortho*-position. It is noteworthy that the importance of the $+T$ effect for the *o*-fluoro-substituent is still sufficient to make this atom less deactivating than a *p*-Br substituent.

In nitration by acetyl nitrate in nitromethane, deactivation by *ortho*-halogens is reported to be in the order I $<$ F $<$ Br $<$ Cl, with iodine several times less deactivating than fluorine.[13]

(v) A plot of log f for detritiation of $X{\cdot}C_6H_4{\cdot}{}^3H$ compounds in $CF_3{\cdot}CO_2H(96{\cdot}77)$–$H_2O(0{\cdot}82)$–$HClO_4(2{\cdot}41)$ against log k_{rel} for hydrolysis of $X{\cdot}C_6H_4{\cdot}CMe_2Cl$ compounds in 90% aqueous acetone at 25° [18] (k_{rel} is the rate relative to that of the compound with X = H) is a good straight line for X = H, *p*-Cl, *p*-Br, and *p*-I, but the point for X = *p*-F falls slightly away from this line (see Figure). The approximate points for the *meta*-halogens (see below) lie close to this line. (It follows that except for the deviation by the *p*-F substituent, the effects of the *para*- and *meta*-halogens can be related to the σ^+ constants [19] of the substituents.)

A similar relation applies for the *ortho*-halogens, but the appropriate line lies well away from that for the *meta*- and *para*-substituents (see Figure). Since steric effects of *ortho*-substituents appear to be very small in detritiation,[20] the existence of this relation at first sight implies that steric effects are also negligible for solvolysis of the *o*-$X{\cdot}C_6H_4{\cdot}CMe_2Cl$ compounds. However, even in absence of steric effects this linear free-energy relation would not be expected, because the extra carbon atom between the substituent and the reaction site in the solvolysis should result in a different balance of $-I$ and $+T$ effects. If, as is usual, the greater deactivation by *ortho*- than by *para*-halogen is attributed mainly to the stronger operation of $-I$ effects to the *ortho*-position, then deactivation by *ortho*-relative to that by *meta*- or *para*-halogens would be expected to be greater in detritiation than in the solvolysis, but the contrary is the case. (Except for fluorine, the halogens deactivate in the hydrolysis more from the *ortho*- than from the *meta*-position.) The low reactivity of the *o*-halogeno-compounds in the hydrolysis has been attributed in part to a steric effect,[18] and it is possible that a chance combination of polar and steric effects results in the linear free-energy relation we have obtained.

The rates of detritiation of *m*-$X{\cdot}C_6H_4{\cdot}{}^3H$ compounds could be measured only very roughly because of side-reactions. These are more serious for the *meta*- than for the *ortho*- and *para*-compounds because the detritiation is slower and because the exchange is taking place at the least reactive aromatic position. In the medium containing sulphuric acid, sulphonation was serious, but an approximate value of f was obtained for the *m*-Cl compound. The nature of the interference by side reactions in the medium containing perchloric acid is described in the Experimental section; we did not identify these reactions

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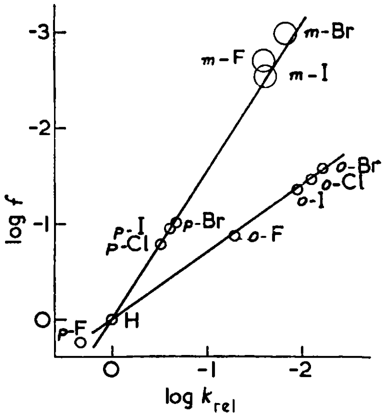
[14] Kohnstam, *J.*, 1960, 2066.
[15] Ref. 4, p. 240.
[16] de la Mare and Robertson, *J.*, 1948, 100.
[17] de la Mare, *J.*, 1954, 4450.
[18] Brown, Okamoto, and Ham, *J. Amer. Chem. Soc.*, 1957, **79**, 1906.
[19] Brown and Okamoto, *J. Amer. Chem. Soc.*, 1957, **79**, 1913.
[20] Baker and Eaborn, unpublished work.

but we believe that electrophilic substitution of the aromatic compound was involved (possibly in addition to decomposition of the medium) since it was most serious with fluorobenzene, normally the most reactive halogenobenzene towards such substitution. It seemed to be least serious for iodobenzene, and the value of *f* for *m*-I (see Table) is probably more accurate than those for other *meta*-halogens. The values of *f* for the *meta*-substituents could be in error by ±100%, but there is reasonable agreement between the values for *m*-Cl measured in two media. A safe conclusion is that *meta*- deactivate markedly more than *ortho*- and *para*-halogen, as in other electrophilic aromatic substitutions. It also seems likely that *m*-I deactivates less than the other *meta*-halogens, as in molecular bromination (of halogeno-tri- and -tetra-alkylbenzenes) in nitromethane.[12]



Plot of log f for detritiation of $X\cdot C_6H_4\cdot {}^3H$ *compounds in* $CF_3\cdot CO_2H$ (96·77)–H_2O (0·82)–$HClO_4$ (2·41) *at* 55° *against* log k_{rel} *for hydrolysis of* $X\cdot C_6H_4\cdot CMe_2Cl$ *compounds in* 90% *acetone at* 25°.

EXPERIMENTAL

General.—A precision-made Vigreux column of low hold-up and equivalent to 18 theoretical plates was used in fractionations.

Stated activities of tritiated aromatic compounds were calculated by assuming maximum use of tritiated water in hydrolysis of Grignard or organolithium reagents, and may be up to five times too large.[2,3]

Measurements of tritium activity were by Eaborn, Taylor, and Matsukawa's method,[21] (with some improvements which will be described later), in which a galvanometer deflection, proportional to the activity, is recorded.

[p-$^3H_1$]*Halogenobenzenes.*—These compounds, of activity *ca.* 4—5 mc/g., were prepared from tritiated water (50—100 mc/g.) and the monomagnesium derivative from *p*-bromofluoro-, *p*-bromochloro-, *p*-dibromo-, or *p*-di-iodo-benzene. In the last case a 1 : 3·5 ether–benzene mixture was used in preparing the Grignard reagent. In this preparation, as in that from *p*-dibromobenzene, [^3H]benzene was also obtained, indicating that some dimagnesium derivatives had been formed. The properties and yields of the *p*-$^3H\cdot C_6H_4\cdot X$ compounds were as follows: (X =) F, b. p. 85·2°/760 mm., n_D^{20} 1·4658, 70%; Cl, b. p. 132·1°/754 mm., n_D^{20} 1·5245, 75%; Br, b. p. 157·2°/760 mm., n_D^{20} 1·5601, 45%; I, b. p. 188°/760 mm., n_D^{20} 1·6141, 66%.

[m-$^3H_1$]*Halogenobenzenes.*—These were prepared in analogous fashion from *m*-bromofluoro-, *m*-bromochloro-, *m*-bromoiodo-, and *m*-di-iodo-benzene. No benzene was used in the preparation of the Grignard reagent from the last compound. [$^3H_1$]Benzene was formed in large amount (75%) in the preparation starting from *m*-di-iodobenzene, and in small amount in that from *m*-bromoiodobenzene. Properties and yields of the *m*-$^3H\cdot C_6H_4\cdot X$ compounds were as follows: (X =) F, b. p. 84—84·5°/750 mm., 58%; Cl, b. p. 132°/750 mm., n_D^{20} 1·5244, 77%; Br, b. p. 156°/760 mm., 53%; I, b. p. 187—188°/760 mm., 11%.

[o-$^3H_1$]*Fluorobenzene.*—Preparation of this compound *via* the Grignard reagent from *o*-bromofluorobenzene was unsatisfactory. The product appeared from rate studies to be

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[21] Eaborn, Matsukawa, and Taylor, *Rev. Sci. Instr.*, 1957, **28**, 725.

contaminated with [$^3H_1$]benzene, and, in agreement with this, the material of b. p. 156°, presumed to be mainly unchanged starting material was strongly active and almost certainly contained [$^3H_1$]bromobenzene (b. p. 156°). It thus seems that both the fluorine and bromine enter into the Grignard reaction.

The desired compound was satisfactorily obtained from an organolithium reagent. n-Butyllithium, from butyl bromide (0·08 mole) in ether, was added to a cooled solution of *o*-bromofluorobenzene (0·07 mole) in ether at such a rate that the temperature of the mixture remained below −70°. When addition was complete, tritiated water (0·7 g. of 100 mc/g. activity) was added, followed by an excess of normal water. The usual working-up and fractionation gave [o-$^3H_1$]fluorobenzene (2·0 g., 30%), b. p. 85°, and unchanged *o*-bromofluorobenzene (3·5 g.).

[o-$^3H_1$]*Chlorobenzene*.—The Grignard reagent from *o*-bromochlorobenzene (0·10 mole) and magnesium (0·11 mole) in ether (70 ml.) was treated with tritiated water (1·0 g. of 100 mc/g. activity) followed by an excess of normal water. The usual working-up and fractionation gave [*o*-$^3H_1$]chlorobenzene (5·5 g., 50%), b. p. 131·5—132° (of *ca.* 6 mc/g. activity).

[o-$^3H_1$]*Bromo- and* [o-$^3H_1$]*Iodo-benzene*.—A Grignard reagent was prepared from *o*-bromoiodobenzene (35 g., 0·083 mole) and magnesium (2·02 g., 0·083 mole) in ether (70 ml.), and quickly hydrolysed with tritiated water (2·5 g. of 100 mc/g. activity) followed by an excess of normal water, the mixture being kept below room temperature throughout. After the usual working-up, and addition of 2 ml. each of bromo- and iodo-benzene, fractionation gave benzene (2·0 g.), [*o*-$^3H_1$]bromobenzene (4·2 g.), b. p. 155—156°, and [*o*-$^3H_1$]iodobenzene (4·7 g.), b. p. 187—188°. The calculated activities of the halogenobenzenes were *ca.* 4 mc/g.

Reaction Media.—The trifluoroacetic acid–sulphuric acid medium was prepared by mixing 163·26 g. of 100·0% trifluoroacetic acid and 25·22 g. of 99·7% sulphuric acid, corresponding with a molar-percentage composition of $CF_3{\cdot}CO_2H$ (83·40)–H_2O (1·98)–H_2SO_4 (14·62).

The trifluoroacetic acid–perchloric acid media were made up by weight as follows: (i) 212·29 g. of 100·0% trifluoroacetic acid, 7·112 g. of 72·02 wt.-% aqueous perchloric acid, and 19·56 g. of trifluoroacetic anhydride, corresponding with a molar-percentage composition of $CF_3{\cdot}CO_2H$ (96·772)–H_2O (0·822)–$HClO_4$ (2·406); (ii) 143·74 g. of 100·0% trifluoroacetic acid, 14·39 g. of 72·02 wt.-% perchloric acid, and 30·47 g. of trifluoroacetic anhydride, corresponding with a molar-percentage composition of $CF_3{\cdot}CO_2H$ (89·50)–H_2O (4·55)–$HClO_4$ (5·95).

Rate Measurements.—For detritiation, the general techniques were as previously described, sealed tubes being used for samples in the runs.[1-3] Usually about 0·02—0·07 g. of [$^3H_1$]-halogenobenzene was dissolved in about 7·5 g. of the acid medium. In calculating "equilibrium" deflections at the end of the exchange it was assumed that two aromatic positions were available for tritium in *para*- (one *para* and roughly half of each *ortho*-position), three in *ortho*-, and five in *meta*-halogenobenzenes.

The following sample run refers to [*o*-$^3H_1$]fluorobenzene, 0·0575 g. of which was dissolved in 7·3287 g. of $CF_3{\cdot}CO_2H$ (96·77)–H_2O (0·82)–$HClO_4$ (2·41). Five samples of equal volume were transferred to sealed tubes; a residue of 0·0972 g. of mixture remained, which meant that each sample contained 0·0113 g. of [*o*-$^3H_1$]fluorobenzene. Separate experiments showed that this amount in a 10 ml. extract would give rise to a deflection of 390 mm. at zero time, and thus to 10·5 mm. (D_∞) at equilibrium. In the Table are shown the time of removal of a sample (after the arbitrary zero of the first sample), the deflection, $D_{\text{obs.}}$, per 4·365 g. of extract, the deflection D_t calculated for 10·0 ml. of extract, along with the first-order rate-constant, k_{ex}, calculated from the formula $k_{\text{ex}}t = 2{\cdot}303 \log [(D_0 - D_\infty)/(D_t - D_\infty)]$.

Time (hr.)	0	0·75	2·45	4·90	7·05
$D_{\text{obs.}}$ (mm.)	185·6	167·2	131·8	91·2	68·1
D_t	373·7	336	265·5	184	137
10^7k_{ex} (sec.$^{-1}$)	—	402	400	419	416

A value of 10^7k_{ex} of 410 sec.$^{-1}$ was derived graphically. In a second experiment a value of 414 sec.$^{-1}$ was obtained.

With [*m*-$^3H_1$]halogenobenzenes accurate measurement of rate constants was prevented by side reactions, which revealed themselves as follows: (i) The reaction mixture progressively darkened. (ii) A scintillation quencher was produced during the reaction, and survived the extraction and decolorization. [This was demonstrated for fluorobenzene by keeping a solution of untritiated fluorobenzene in $CF_3{\cdot}CO_2H$ (89·50)–H_2O (4·55)–$HClO_4$ (5·95) at 55° for 90 hr. and then carrying out the normal extraction and decolorization. When a known weight of the extract was added to a standard solution of tritiated toluene and liquid scintillator in toluene, the deflection obtained (143 mm.) was lower than that (158 mm.) obtained when the standard solution was diluted with the same weight of toluene containing an appropriate amount of fluorobenzene.] (iii) The initial rate of tritium-loss increased as the initial concentration of [*m*-$^3H_1$]halogenobenzene was lowered, presumably because a side-reaction was removing an increasing proportion of the halogenobenzene. This effect was marked with fluorobenzene and small with bromo- and iodo-benzene. (iv) First-order rate constants fell during a run at normal concentrations of [*m*-$^3H_1$]halogenobenzene, but even with [*m*-$^3H_1$]fluorobenzene this was not as large an effect as might have been expected from observations described under (iii). It seems likely that a fall-off in the rate of loss of tritium was to some extent obscured by the production of a quencher, which would lead to low tritium counts and hence to an apparent increase in the rate of tritium-loss as reaction proceeded.

The effects described under (iii) and (iv) were small for [*m*-$^3H_1$]bromo- and [*m*-$^3H_1$]iodo-, somewhat more marked with [*m*-$^3H_1$]chloro-, and large with [*m*-$^3H_1$]fluoro-benzene. For [*m*-$^3H_1$]iodobenzene the variation in rate-constant from the mean during a run was less than ±10%, while the mean rate-constant did not vary by more than 10% over several runs at different initial concentrations, and the value of k_{ex} for this compound is probably accurate to within ±20%. For [*m*-$^3H_1$]fluorobenzene the value of k_{ex} could be in error by ±100%.

The rates of sulphonation of benzene and *m*-chlorobenzene were measured by spectrophotometric analysis as previously described.[3]

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