160. *The Kinetics of Aromatic Halogen Substitution. Part IX.* Relative Reactivities of Monosubstituted Benzenes.*

By P. W. ROBERTSON, P. B. D. DE LA MARE, and B. E. SWEDLUND.

The rates of halogenation are given of various monosubstituted benzenes, relative to that of benzene, the range being from dimethylaniline, 10^{18}, to nitrobenzene, $1{\cdot}8 \times 10^{-6}$, the more extreme values having been estimated indirectly. Included among the new rate measurements are those for diphenylmethane, phenol, diphenyl ether, phenyl benzoate, *N*-methylacetanilide, ethyl phenylacetate, *NN*-dimethyl-*m*-nitroaniline, *m*-nitroacetanilide, and ethyl *p*-toluate. The proportions of *para*-isomer formed in the bromination of toluene and of *tert.*-butylbenzene have been determined under the conditions of kinetic measurements, and the relative rates of *para*-bromination have thence been established for these two compounds as 100 : 31.

THIS paper concludes a series in which the rates of halogenation of numerous monosubstituted benzenes have been measured under conditions of controlled kinetics. The results, together with values for certain other compounds not previously examined, are presented as a Table. The large rate differences preclude the measurements for the same halogen in the same solvent, and it has been necessary to examine a rapidly reacting compound, such as phenol, at very low concentrations, with bromine, in anhydrous acetic acid; whereas the rate of chlorination of bromobenzene, a relatively unreactive compound, was measured at high concentration in aqueous acetic acid, the results being calculated as relative rates ($r = k_{\text{ArX}}/k_{\text{ArH}}$) by comparison with compounds of intermediate reactivity. Comparison of series of compounds, for which both chlorination and bromination velocities are known, and steric effects are either absent or constant in the series [*e.g.*, the halogenonaphthalenes (Part IV, *J.*, 1948, 100) and the phenol ethers (Bradfield and Jones, *Trans. Faraday Soc.*, 1941, **37**, 726)], shows that rates of bromination tend to be rather more widely spread than those of chlorination. This does not cause any ambiguity, since the rates in the Table lower than that for benzene are for chlorination, and those more rapid (with the exception of certain compounds reacting at about the same rate as benzene) are for bromination.

Phenol ($r = 10^8$) and bromobenzene ($r = 10^{-1}$) represent the extreme experimental limits for the practicable direct measurement of reaction velocities. Compounds outside these limits are included in the Table, but it should be noted that values in such cases have been assessed on the principle that substituents affect substitution at a given position independently (Bradfield and Jones, *loc. cit.*); *e.g.*, the value for the carbethoxy-sub-

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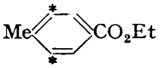
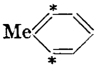
* Part VIII, *J.*, 1950, 812.

stituent was calculated by reference to the rate ratio of the compounds (I) and (II), for the positions marked, the known value (58%; cf. Wahl, Normand, and Vermeylen, *Bull. Soc. chim.*, 1922, **31**, 570; Wertyporoch, *Annalen*, 1932, **493**, 153) for the proportion of *ortho*-chlorination in (II) being used. This result, combined with the rate ratios found by Bradfield and Jones for the chlorination of phenol ethers *p*-MeO·C_6H_4X, gives the values quoted for substitution *meta*- to deactivating groups, such as COPh, CO_2H, and NO_2. Reversely, the effect of the highly activating dimethylamino-group was estimated by introducing also the deactivating nitro-group, and comparing the relative rates of halogenation of (III) and (IV), in which substitution takes place substantially in the positions indicated.[*]

The mechanisms of halogenation under the conditions of our measurements are, despite adverse criticisms of this point by Baker ("Hyperconjugation," Oxford Univ. Press, 1952, pp. 49—54), reasonably well established. The halogens themselves react directly, as molecules, the rate-determining process being the formation of an intermediate (*e.g.*, for chlorination, ArH,Cl_2); the final stage, involving the removal of the aromatic hydrogen atom as a proton, is extremely rapid. For chlorination, this is indicated by the specific catalytic power of chloride ions when *N*-chloroanilides (cf. Orton, Soper, and Williams, *J.*, 1928, 998) or hypochlorous acid (cf. de la Mare, Hughes, and Vernon, *Research*, 1950, **3**, 192) is used as a source of electrophilic chlorine. Similarly, Bradfield, Davies, and Long (*J.*, 1949, 1389) concluded that bromination by solutions of bromine in aqueous acetic acid involved bromine molecules as essential electrophilic reagent, rather than such other possible intermediates as bromine hydroxide, bromine acetate, or "positive bromine." These findings agree completely with our observations on the influence of electrolytes on the rates of chlorine and bromine substitution (cf. de la Mare and Robertson, *J.*, 1943, 279; Robertson, Dixon, Goodwin, McDonald, and Scaife, *J.*, 1949, 294).


(I)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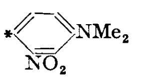
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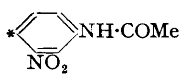
(IV)

The rate ratios in the Table are for a molecule of each compound, compared with a molecule of benzene, except for the symmetrical compounds PhN:NPh, Ph_2O, $COPh_2$, and CH_2Ph_2, in which the values have been divided by 2 to give the value per phenyl group.

Relative rates (r) *of halogen substitution of compounds* PhX (PhH = 1).

+ *T*, − *I* (*p*, *o*)		+ *T*, − *I* (*p*, *o*)		+ *T*, − *I* (*p*, *o*)	
NMe_2	5×10^{18}	OH	$1{\cdot}1 \times 10^{11}$	F	1·2
NH·COMe ...	$2{\cdot}1 \times 10^{8}$	OMe	$1{\cdot}2 \times 10^{9}$	Cl	0·11
NMe·COMe ...	$2{\cdot}4 \times 10^{5}$	OPh	$1{\cdot}4 \times 10^{7}$	Br	0·08
N:NPh	4·6	O·COPh	$2{\cdot}0 \times 10$	I	0·18
+ *T*, + *I* (*p*, *o*)		+ *T*, − *I* (*p*, *o*, *m*)		− *T*, − *I* (*m*)	
CH_3	$3{\cdot}4 \times 10^{2}$	CH_2Ph	$5{\cdot}1 \times 10$	COPh	$7{\cdot}6 \times 10^{-4}$
CH_2Me	$2{\cdot}9 \times 10^{2}$	$CH_2{\cdot}CO_2Et$ ...	2·3	CO_2Et	$5{\cdot}0 \times 10^{-4}$
$CHMe_2$	$1{\cdot}8 \times 10^{2}$	CH_2Cl	0·76	CO_2H	$2{\cdot}6 \times 10^{-4}$
CMe_3	$1{\cdot}1 \times 10^{2}$	$CH_2{\cdot}CN$	0·17	NO_2	$1{\cdot}8 \times 10^{-6}$

Discussion.—(a) *Amines and related compounds.* In these compounds, the inductive (−*I*) influence of the substituent, greater in the *ortho*- than in the *para*-position, and the relatively large bulk of the entering bromine atom, combine to reduce greatly, or, as for acetanilide, to inhibit, *ortho*-substitution. The relative rates in the Table, therefore, are essentially those for unimpeded *para*-substitution. A remarkably high power of electron-release

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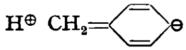
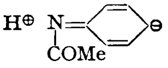
[*] From 4·6 g. of *NN*-dimethyl-*m*-nitroaniline there were obtained, on bromination in acetic acid containing sodium acetate, 4·9 g. (72%) of 4-bromo-*NN*-dimethyl-3-nitroaniline, m. p. 92—93°. Forster and Coulson (*J.*, 1922, **121**, 1995) record m. p. 94° for a specimen similarly prepared. A similar yield is to be expected in the chlorination of (IV) (cf. Chattaway, Orton, and Evans, *Ber.*, 1900, **33**, 3057; Wheeler, *Amer. Chem. J.*, 1895, **17**, 613) but we do not claim great accuracy for the very large value ($r = 5 \times 10^{18}$) thus derived for the activating effect, obtainable only in this indirect manner, of the dimethylamino-group; we are indebted to the Referees for suggesting clarification of this point.

is shown by the dimethylamino-group, which causes dimethylaniline to be more reactive than anisole by a factor of 10^9. Francis's finding (*J. Amer. Chem. Soc.*, 1925, **47**, 2340), that bromination by the competition method shows the opposite order of reactivity, does not contradict this result, since his experiments were carried out in aqueous solution in the presence of acids, and, under these conditions, the transformation of the amine into an unreactive salt must be considerable. In our experiments, in acetic acid solution, this difficulty has been avoided by the introduction of a nitro-substituent, which considerably weakens the basicity of the amine, and by the presence of sodium acetate, which reduces the proton-donating properties of the medium. On changing from acetanilide to *N*-methylacetanilide, the rate of bromination is decreased by a factor of 10^3. The same order of reactivity has also been observed for chlorination (Orton, Soper, and Williams, *loc. cit.*; Bradfield and Jones, *J.*, 1928, 3073), despite the fact that none of these halogenations appears to proceed *via* the *N*-halogeno-derivative (cf. also Hughes and Ingold, *Quart. Reviews*, 1952, **6**, 34). It is now recognised that the bonding electron-pairs of a group such as methyl can behave as though they can be released to an attached unsaturated system, by hyperconjugation, represented as in (V), the resulting effect on chemical reactivity being greater for the methyl than for the *tert.*-butyl group. We suggest that a similar structure such as (VI), important particularly in the transition state of substitution, accounts for the greater reactivity of acetanilide than of *N*-methylacetanilide in halogen substitutions. The presence of the electron-withdrawing acyl group may favour this process; it has been proposed similarly (Swindale, Swedlund, and Robertson, *J.*, 1950, 812) that the extent of hyperconjugation in the benzyl and allyl halides is increased by the electronegativity of the halogen atom.


(V)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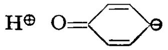

(VII)

Azobenzene is chlorinated in aqueous acetic acid only slightly more rapidly than benzene; the significance of the low power of electron-release of the N:NPh group is discussed by Robertson, Hitchings, and Will (*J.*, 1950, 808). In acetic acid solution in the presence of hydrogen chloride, the reaction follows a different course, there being a preliminary addition of hydrogen chloride.

(b) *Phenol and related compounds.* For the same reasons as given in the preceding section, the proportion of *ortho*-bromination for these compounds is relatively small, and the rates in the Table are a measure of electron-release to the *para*-position. In spite of the inductive effect of the alkyl group, anisole is seen to have a smaller reactivity than phenol. This difference is, however, not due to the participation of the highly reactive phenoxide ion; phenol is too weak an acid to be measurably ionised in acetic acid, and addition of sulphuric acid to the reaction mixture was found not to reduce the rate of bromination. The greater reactivity of phenol than of anisole may then also be attributed to hyperconjugation (VII). The very pronounced effect of an acyl group in reducing the reactivity is seen in this series, as also in the amines; phenyl benzoate is 3×10^6 times less reactive than anisole, the O·COPh group thus becoming less effective even than an alkyl group in promoting electrophilic substitution.

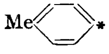
(c) *Halogenobenzenes.* *para*-Substitution predominates also in this series, although the proportions of isomers formed on chlorination are not accurately known. The values in the Table for fluoro-, chloro-, and bromo-benzene are for chlorination in aqueous acetic acid; the same sequence was observed (de la Mare and Robertson, *J.*, 1948, 100) for the chlorination and bromination of the 1-halogenonaphthalenes, in which substitution occurs, under polar conditions, substantially in the 4-position (cf. Zalkind and Faerman, *J. Russ. Phys. Chem. Soc.*, 1930, **62**, 1021); the value for iodobenzene is assessed by reference to the relative rates for bromination of 1-bromo- and 1-iodo-naphthalene.

The difference between halogenation and nitration is especially apparent in this series; *e.g.*, a fluoro-substituent activates the position *para*- to itself by a factor of 3 for halogenation, whereas for nitration in the same position, the rate is reduced to one-fifth. Such an effect is related, in our opinion, to the fact that the halogens react as neutral molecules, whereas in nitration the effective reagent is the nitronium ion, and thus the inductive effect of the substituent is of more dominating importance in substitution by the latter reagent. Another example of such a difference in behaviour is described in the following section.

(d) *Alkylbenzenes.* The considerable fall in reactivity in the series PhMe, PhEt, $PhPr^i$, $PhBu^t$, which for the extreme members of the series was 100 : 32 for chlorination and 100 : 23 for bromination in aqueous acetic acid, was discussed by de la Mare and Robertson (*J.*, 1943, 279). Considering the possibility that this sequence might be due to a steric effect, we concluded : " the relative fall in rate for *para*-substitution would be less than the fall in total rate, but would still remain considerable. Thus these experiments on the relative rates of halogenation of the alkylbenzenes can be regarded as further evidence of the operation of hyperconjugation."

Since that time, the relative rates of bromination of toluene and *tert.*-butylbenzene have been re-examined independently (*a*) by the competition method, with iodine as catalyst (Berliner and Bondhus, *J. Amer. Chem. Soc.*, 1946, **68**, 2355), and (*b*) by the kinetic method, with aqueous acetic acid containing sodium acetate as solvent (Berliner and Berliner, *ibid.*, 1949, **71**, 1195). These authors obtained results, *viz.*, method (*a*) 100 : 25, method (*b*) 100 : 18, differing only slightly from ours (100 : 23). They also rediscussed the relevant data concerning *o* : *p*-ratios in the bromination of these compounds, and assessed the most probable relative rates of *p*-substitution under their conditions as 100 : 27. Their theoretical interpretation was identical with ours.

Any remaining uncertainty with regard to the relative rates of *para*-bromination of toluene and *tert.*-butylbenzene has now been removed by measurement of the amounts of the *para*-derivative formed from these compounds on bromination in 12% aqueous acetic acid, *viz.*, toluene 69%, *tert.*-butylbenzene 92%. A measurement of the relative rates of bromination under these experimental conditions showed an overall rate ratio of 100 : 23. A combination of these values gives the relative rates for *para*-bromination in the positions marked in (VIII) and (IX). For comparison are given values previously recorded for mesitylene (X) and 5-*tert.*-butyl-*m*-xylene (XI) (Part II). The second pair of compounds react more rapidly than the first by a factor of about 10^5, but the rate ratios for comparable positions are substantially the same, as indeed they should be, by the principle that substituents affect independently the reactivities of related benzene derivatives. Although there is unimpeded *para*-substitution in the first two compounds, yet there is the possibility of steric hindrance by the two *o*-methyl groups in the second pair, but this must be the same for both compounds, and thus cannot affect the relative rates. The reagent under these conditions is molecular bromine, as has been shown by our kinetic measurements, and confirmed by Bradfield, Davies, and Long (*loc. cit.*). The doubts expressed by Baker (*op. cit.*) are thus resolved in favour of our interpretation quoted above.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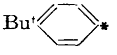
(VIII)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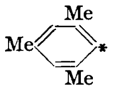
(IX)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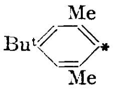
(X)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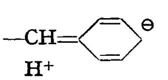
(XI)

† This value should be slightly reduced to allow for substitution *ortho* to the *tert.*-butyl group.

This ratio for *para*-bromination, 100 : 31, is different from the value obtained for nitration, 100 : 140, as reported by Cohn, Hughes, Jones, and Peeling (*Nature*, 1952, **169**, 291). In both reactions, the stage involving removal of a proton is not rate-determining. The first stage, therefore, determines the rate, the reagents being in the one reaction a neutral molecule (Br_2 or Br_4), and in the other a positive ion (NO_2^+). As the dipole moments, identical here with the mesomeric moments, of *tert.*-butylbenzene ($\mu = 0{\cdot}70$) and of toluene ($\mu = 0{\cdot}37$) appear to be determined chiefly by the inductive effects of the substituents, in the reactions with bromine some other factor than the inductive effect must be in operation to cause the rate sequence observed, *viz.*, toluene>*tert.*-butylbenzene. The result could be explained, for instance, by the postulate that hyperconjugation does not appreciably contribute to the mesomeric moment for toluene, but becomes of considerable importance in the excited transition state. In the nitration of toluene also, both effects must operate, but in nitration the permanent electrostatic forces appear to dominate; the influence of the inductive effect becomes relatively more important than hyperconjugation, and the rate order for the two compounds is reversed.

(e) *Compounds* CH_2PhX. In this series the $-I$ effect and the bulk of the group each tend to reduce the extent of *ortho*-substitution; at the same time the amounts of *meta*-isomer produced are not large, so that *para*-substitution predominates. Consequently the relative rates in the Table represent very nearly the order of electron-release for the groups CH_2X. These rates are distributed on either side of benzene, as the $+T$ effect, due to conjugation, is more or less offset by the $-I$ effect of X. The phenyl group, for example, weakly withdraws electrons, as is illustrated, *e.g.*, by the strength of the acid $CH_2Ph{\cdot}CO_2H$ ($K = 4{\cdot}9 \times 10^{-5}$) as compared with that of acetic acid ($K = 1{\cdot}8 \times 10^{-5}$), and by the relative rates of chlorination of the aryl ethers, o-$MeO{\cdot}C_6H_4X$ (100), $CH_2Ph{\cdot}O{\cdot}C_6H_4X$ (68) (Bradfield and Brynmor Jones, *loc. cit.*). This negative effect of the phenyl group may be regarded as due to a limited tautomeric displacement due to hyperconjugation (see inset) whereby a very weak permanent dipole is created. The relative rates of bromination of toluene and diphenylmethane, per phenyl group, are 100 : 15, the difference in reactivity becoming rather less when calculated for unimpeded *para*-substitution. The reactivity of diphenylmethane is, however, still some 50 times greater than that of benzene. Benzyl cyanide, on the other hand, containing the much more powerfully electron-withdrawing cyano-group, reacts 6 times less rapidly than benzene.



(f) *Compounds with* —I, —T *groups*.—These combined effects in a substituent X cause the compound PhX to be less reactive than benzene, and result in halogenation *meta* to the group X, without the rather large amount of *ortho*-derivative which often accompanies nitration of these compounds. Reference to the Table shows that the variability of effectiveness of these groups is considerably less than in the case of groups with $+T$ characteristics. As might be expected, there is a close correspondence between the reactivities of compounds p-$RO{\cdot}C_6H_4X$ in substitution, and of $PhCH{:}CHX$ in addition, when X is a group with $-I$, $-T$ effects (cf. de la Mare, *Quart. Reviews*, 1949, **3**, 126). In both these series there is the possibility that the rate of reaction may be somewhat modified by hydrogen-bonding of the substituent with the solvent, especially when the group X is of the type COR. The possibility of such an effect has not been investigated, but it is believed that, especially in aqueous acetic acid, the deactivating power of the group X is not thereby changed sufficiently to alter considerably the values quoted in the Table.

EXPERIMENTAL

The methods have been described in previous communications. Results are given as times (t, min.), for a definite percentage (x) of disappearance of halogen, or as values of k_2 (l. g.-mol.$^{-1}$ min.$^{-1}$) in acetic acid, at 25°, unless otherwise stated.

To eliminate the possibility of salt-formation with the solvent, or with the hydrogen bromide produced in the reaction, dimethyl-*m*-nitroaniline, m. p. 50·5°, was examined in the presence of excess of sodium acetate, lithium bromide being also added to reduce the rate to a measurable value, and was compared with anisole under the same conditions, with the following results: 0·00102M-m-$NMe_2{\cdot}C_6H_4{\cdot}NO_2$ + 0·00105M-Br_2 + 0·068M-NaOAc + 0·035M-LiBr, $x = 20$, $t = 0{\cdot}29$; $x = 50$, $t = 1{\cdot}12$, $k_2 = 850$; 0·0254M-anisole + 0·0100M-Br_2 + 0·068M-NaOAc + 0·035M-LiBr, $k_2 = 0{\cdot}95$. Hence dimethyl-*m*-nitroaniline reacts faster than anisole by a factor of 10^3, and benzene by a factor of 10^{12}; direct comparison cannot be made with *m*-nitroacetanilide. The latter compound, m. p. 152°, 0·100M, with 0·0714M-chlorine, gave $k_2 = 0{\cdot}0040$, which may be compared with the corresponding value for toluene, $k_2 = 0{\cdot}028$ (de la Mare and Robertson, *J.*, 1943, 279). The nitro-group, by comparison with acetanilide, has reduced the reactivity by a factor of $4{\cdot}3 \times 10^6$.

The following are other values not previously reported: 0·100M-phenyl benzoate + 0·0100M-Cl_2, $x = 10$, $t = 760$; 0·050M-*N*-methylacetanilide + 0·05M-Br_2, $x = 10$, $t = 181$; 0·0125M-diphenyl ether + 0·0125M-Br_2, $x = 10$, $t = 45$; 0·00100M-phenol + 0·00100M-Br_2, $x = 20$, $t = 0{\cdot}82$; $x = 50$, $t = 3{\cdot}30$, no alteration in rate of reaction being observed in the presence of 0·0074M-H_2SO_4. In acetic acid containing 20% of water the following values were obtained: 0·100M-diphenylmethane + 0·050M-Br_2 (35°), $x = 10$, $t = 292$; 0·200M-toluene + 0·050M-Br_2 (35°), $x = 10$, $t = 43$; 0·50M-ethyl phenylacetate + 0·050M-Cl_2, $x = 10$, $t = 6{\cdot}8$; 0·252M-ethyl *p*-toluate + 0·120M-Cl_2, $x = 20$, $t = 156$.

There now follows a description of the measurements of the amounts of *para*-bromination of toluene and *tert.*-butylbenzene in aqueous acetic acid.

(i) *Radioactive* p-*bromotoluene.* This was prepared from *p*-toluidine by the Sandmeyer method, 2 g. of radioactive ammonium bromide being introduced with the solution of cuprous bromide in hydrobromic acid. The crude *p*-bromotoluene was fractionally frozen several times; the final sample (B) had f. p. 25·8°, and was therefore, from van der Laan's f. p. data (*Rec. Trav. chim.*, 1907, **26**, 1), of purity 98%; an earlier fraction (sample A), f. p. 24·5°, was also kept for radioactive measurements.

(ii) *Bromination of toluene.* Toluene (46 g.) was allowed to react with 2 l. of 0·178M-bromine in acetic acid containing 12·5% of water. After *ca.* 1000 min., 0·0660M-Br_2 had reacted; 1·108 g. of radioactive *p*-bromotoluene, m. p. 25·8°, were added to the reaction mixture (1·95 l.), which was poured into excess of alkali and sodium formate. The organic product was extracted with ether, washed with water, dried, and fractionated, giving 16·4 g. (75%), b. p. 178—186°/760 mm., n_{D}^{25} 1·5507, f. p. 5·0° (Sample C). There was *ca.* 1 g. of residue of higher b. p. A portion of sample C was recrystallised three times from light petroleum at −80°, giving sample D, f. p. 25·6°, *i.e.*, of purity 97·5%.

(iii) *Radioactive measurements.* The above samples, A, B, C, and D, were appropriately diluted, and counted by the type of counter usual for liquid samples, and standard scaling and recording equipment. Each sample was counted twice. From the decay curves, which corresponded, within the statistical error, with those expected for ^{82}Br, $t_{\frac{1}{2}} = 36$ hours, values were interpolated to give counts for each sample at the same arbitrary time. The data are collected in the following Table.

Radioactive measurements for samples of p-*bromotoluene.*

Sample	F. p.	*p*-Bromotoluene, % (from f. p.)	Counts/min.	Relative dilution	Counts/min., corrected (*a*) for dilution	Counts/min., corrected (*b*) for dilution and f. p.
A	24·5°	95·5	912	100	912	955 ± 7
B	25·8	98·0	380	241·8	919	938 ± 9
C	5·0	64·0	750	5·571	41·8	65·3 ± 0·4
D	25·6	97·5	1072	5·817	62·3	63·9 ± 0·4

The disagreement between each of the two pairs of values is only slightly greater than would be expected on the basis of random fluctuations in the rate of counting, as indicated by the limits given in the last column. Any error resulting from the use of the freezing points to correct the results is clearly small. The results for the purest samples, B and D, being taken as giving the best estimate of the dilution, the weight of *p*-bromotoluene produced in the experiment is (1·108 × 938/63·9 − 1·108) = 15·15 g. The consumption of bromine corresponds with the formation of 22·0 g. of bromotoluenes, and hence there is formed in the reaction 69% of *p*-bromotoluene. The f. p. of the crude bromotoluenes isolated in 75% yield, corrected for the added radioactive *p*-bromotoluene, gives a value of 61%, indicating imperfect fractionation, which source of error is absent in the isotopic-dilution method.

(iv) *Bromination of* tert.*-butylbenzene.* *tert.*-Butylbenzene (67 g.; n_{D}^{25} 1·4904) was dissolved in 2 l. of a solution of bromine (0·094M) in acetic acid containing 12·5% of water. After 2 weeks, 0·047M-bromine had reacted, and the product was isolated as before. After removal by fractionation of the excess of *tert.*-butylbenzene and of an intermediate fraction (n_{D}^{25} 1·5128; 0·3 g.) there were obtained 14·2 g., b. p. 84—85°/4 mm., n_{D}^{25} 1·5302, f. p. 12·1°. *p*-Bromo-*tert.*-butylbenzene, purified to constant f. p. 15·7° by fractional freezing, has n_{D}^{25} 1·5309, and its f. p. is lowered to 12·1° by addition to 1·273 g. of 0·081 g. (8 g.-mols. %) of *o*-bromotoluene. Pure samples of *o*- or *m*-bromo-*tert.*-butylbenzene were not available, but the error arising from this source is almost certainly negligible. From the above data, it is estimated that *tert.*-butylbenzene gives 92% of *p*-bromination. We consider that this value is accurate to within 1—2 units %.

(v) *Relative rates of bromination of toluene and* tert.*-butylbenzene.* A redetermination of the relative rates of bromination of toluene and *tert.*-butylbenzene (each 0·25M) with bromine (0·133M) in acetic acid containing 12% of water at 25° gave a value of 100 : 23. This is identical with that recorded by de la Mare and Robertson (*loc. cit.*) for slightly different conditions, and very close to the value obtained for iodine-catalysed bromination by Berliner and Bondhus (*loc. cit.*), who used the competition method. We have also shown that the ratio of rates is independent, within experimental error, both of the concentration of bromine and of the aromatic substance, thus demonstrating that the order with respect to each reactant is the same. With due allowance for the proportions of isomers formed, and the relative velocities of the total reaction, the rates of *para*-bromination of toluene and *tert.*-butylbenzene are in the ratio 100 : 31.

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