25. *The Kinetics of Aromatic Halogen Substitution. Part IV. The 1-Halogenonaphthalenes and Related Compounds.*

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Naphthalene, its 1-halogeno-derivatives, and certain other compounds, in the concentration region M/5—M/20 in acetic acid, are brominated by a mechanism resulting in reaction orders of up to 4. Alterations in the conditions have effects similar to those found for the third-order brominations in more dilute solution, but the high orders appear to be more persistent in the former case. Both brominations and chlorinations are acid-catalysed. Rate comparisons are recorded for the chlorination of PhF, PhCl, PhBr, and of 1-fluoro-, -chloro-, and -bromo-naphthalene; and for the bromination under various conditions of naphthalene and its 1-halogeno-derivatives (R′X), the reactivities of which, per replaceable hydrogen atom, are in the order R′F > R′H > R′I > R′Cl > R′Br. The kinetics of bromination are consistent with the participation of a mechanism involving Br_4 molecules. The rate ratios can be interpreted in terms of the electron-withdrawing inductive effect and the electron-donating mesomeric effect; the presence of a polarisability effect contributing to the rate differences in the order I > Br > Cl > F provides a reasonable explanation of the differences between the results for bromination and those recorded by other workers for nitration.

(a) *Kinetics of Bromine Substitution.*—In Part I (*J.*, 1943, 276), bromine substitution of relatively rapidly reacting substances (such as anisole, mesitylene, acetanilide) in dilute (*ca.* M/40) acetic acid solution was shown to proceed by third-order kinetics. Two possible mechanisms were proposed :

$$AH + Br_2 \rightleftarrows AHBr_2; \quad AHBr_2 + Br_2 \longrightarrow ABr + HBr + Br_2 \quad . \quad . \quad . \quad (a)$$

$$Br_2 + Br_2 \rightleftarrows Br_4; \quad AH + Br_4 \longrightarrow ABr + HBr + Br_2 \quad . \quad . \quad . \quad . \quad (b)$$

At high temperatures, great dilutions, or in aqueous acetic acid, the incursion of a bimolecular mechanism caused the kinetics to change towards second order.

More slowly reacting compounds examined in the concentration region M/10 were found to give kinetic orders greater than 3. This at first surprising result was shown not to be associated with disturbances due to the formation of HBr_3, which is less active than Br_2 in substitution, but may catalyse the substitution process. Such high orders considerably restrict the range of dilution over which the reaction can be accurately followed; but it was shown that, as for the third-order substitutions, the kinetic order was reduced by dilution or by high temperature.

Reaction orders approximating to $n = 4{\cdot}0$ have now been established for *o*- and *m*-xylene (in acetic acid containing 1% of water, M/5—M/10); and for naphthalene and its 1-halogen-derivatives (in acetic acid, M/5—M/10). Similarly, *N*-methylacetanilide gave in acetic acid $n = 3{\cdot}6$ (M/5—M/10); $n = 3{\cdot}3$ (M/10—M/20). The high reaction orders do not, therefore, appear to be peculiar to a particular type of compound, but are general, and are consistent with the participation in the reaction of associated bromine molecules, Br_4. There is no evidence, other than kinetic, as far as we are aware, for the existence of Br_4 in acetic acid solution, but a very small concentration might account for the observations, as the polar form $Br^{\oplus}Br_3^{\ominus}$ should be an active electrophilic reagent. The lowering of the reaction order on dilution is due to the gradual dominance of the concomitant third-order reaction; if only the fourth-order and the second-order reactions were present, the rate would fall off more rapidly as the concentration was decreased. Similarly, the results of Part I established the existence of a distinct third-order mechanism in the bromination of acetanilide and other compounds.

The contribution of the aromatic compound to the high reaction order is scarcely greater than one, as shown by the following results (in acetic acid at 25°) : naphthalene + bromine, reactants M/5, k_2 (l. g.-mol.$^{-1}$ min.$^{-1}$, $x = 10\%$ reaction) 0·116; M/10, 0·029; naphthalene M/5, bromine M/10, 0·029. Similarly for 1-bromonaphthalene, reactants at the same concentrations, $k_2 = 0{\cdot}0025$, 0·00062, 0·00066, respectively. Bromine substitution, like electrophilic bromine addition, therefore, proceeds by a composite mechanism, the full rate expression being :

$$-d[Br_2]/dt = k_4[A][Br_2]^3 + k_3[A][Br_2]^2 + k_2[A][Br_2]$$

(cf. Swedlund and Robertson, *J.*, 1947, 630).

In acetic acid containing 1% of water, the rate of bromination of naphthalene and of *m*-xylene is increased by a factor of *ca.* 1·5, with no detectable change in reaction order. Further dilution with water reduces the order; thus for 1-chloronaphthalene in acetic acid containing 17% of water, the rate is increased some 40 times as compared with the rate in pure acetic acid, and the order (M/5—M/10) is reduced to 3·6. The high reaction order persists in methyl alcohol (in which solvent, bromine addition to stilbene is bimolecular, as shown by Bartlett and Tarbell, *J. Amer. Chem. Soc.*, 1936, **58**, 466). In this solvent at 25°, the rate of reaction between bromine and naphthalene is only slightly greater than the corresponding rate in acetic acid, and the order *n* (M/5—M/10) was found to be 3·6. In acetic acid containing carbon tetrachloride, the rate, as expected, is considerably reduced. Under drastic conditions in aqueous acetic acid the second-order mechanism may be established, as was observed for 1-chloronaphthalene in acetic acid containing 49% of water at 52° (*n*, M/80—M/160, 2·0).

Acids are catalysts for substitution in acetic acid. Thus for naphthalene at 25°, bromine substitution is catalysed ten-fold by M/2-perchloric acid, and the kinetic order is reduced to 3·6 (M/5—M/10). In strongly aqueous acetic acid, however, catalysis by acids is relatively slight. It would appear, therefore, that acid catalysis is due to proton transfer to one of the intermediates in the reaction, this transfer being more easily effected by $H_2OAc^{\oplus}$ than by $H_3O^{\oplus}$ (cf. acid catalysis of addition to αβ-unsaturated aldehydes, *J.*, 1945, 888). We assume that this proton transfer assists in the removal of hydrogen bromide to complete the substitution process.

The exact nature of the intermediates concerned in the reaction cannot be decided with certainty. In particular, it is not clear whether Br_4 is a participant in the third-order reaction, though the arguments of Part I in favour of the alternative process are in no way conclusive. A reasonable possibility, consistent with the experimental facts, is as follows :

$AH + Br_2 \longrightarrow ABr + HBr$ . . . . second order

$AH + Br_2 \rightleftharpoons AHBr_2$; $AHBr_2 + Br_2 \longrightarrow ABr + HBr + Br_2$ . . . . third order

$Br_2 + Br_2 \rightleftharpoons Br_4$; $AH + Br_4 \longrightarrow AHBr_2 + Br_2$;
$AHBr_2 + Br_2 \longrightarrow ABr + HBr + Br_2$ . . . . fourth order.

The envisaged intermediates are associations of molecules formally neutral but polarised and presumably stabilised by solvation. They are not to be regarded as " transition states "; the manner in which they contribute to the observed kinetics is believed to imply that they represent true chemical entities present in the reacting system in small but finite concentrations, possibly not stationary during the course of the reaction.

(b) *The Effect of Halogen Substituents on the Rate of Substitution.*—In order to discuss with assurance the effect of substituent groups on the rate of substitution, it is desirable to examine rate differences under conditions which isolate a single simple mechanism. Chlorination in acetic acid fulfils this condition, being a bimolecular reaction, as established by Bradfield, Jones, and their co-workers (cf. *Trans. Faraday Soc.*, 1941, **37**, 726) for phenol ethers and anilides; and by the present authors even under conditions favourable to fourth-order bromine substitution (chloronaphthalene, chlorine, in acetic acid at 25°, M/5—M/40, $n = 2{\cdot}1$). In acetic acid containing 20% of water at 24°, the following rates were obtained for the chlorination of the phenyl halides, RX, the rate for benzene being interpolated from a comparison of benzene and chlorobenzene in acetic acid containing 1% of water :

X =	H.	F.	Cl.	Br.
k_2 (l. g.-mol.$^{-1}$ min.$^{-1}$)	0·010	0·012	0·0011	0·00079
Relative rates	100	120	11	7·9

Iodo-compounds cannot be included in comparisons of rates of chlorination, since iodo-dichlorides are formed. The rates of bromination of the phenyl halides in acetic acid recorded by Lauer and Oda (*Ber.*, 1936, **69**, 978) must be regarded as fictitious; these authors neglected to correct for errors due to volatility and to impurities, and their results are many times the true rates, which we find too slow to measure. The 1-halogenonaphthalenes (R′X), however, brominate at measurable rates in acetic acid, and thus permit the inclusion of the iodo-derivative. Since substitution, at least for the initial stages of the reaction, is predominantly in the 4-position (cf. Schumann, Gueffray, and Winkelmuller, *Annalen*, 1931, **487**, 270; Hirtz, *Ber.*, 1896, **29**, 1404), ambiguities arising from variation in the ortho/para ratio are avoided. Because a high reaction order was found under the conditions of the rate measurements, three series were examined, to establish that the major rate differences were independent of the reaction order. Table I, which includes the rates of chlorination, shows that the change in experimental conditions does not affect the relative rates in such a way as to obscure the relationship between the reactivities of the compounds examined, *viz.*, $R'H \sim R'F \gg R'I > R'Cl > R'Br$. The reactivity per replaceable hydrogen atom (*i.e.*, corrected for the statistical factor arising from the fact that naphthalene has four equivalent positions available for substitution) is in the order $R'F > R'H > R'I > R'Cl > R'Br$.

TABLE I.

Relative rates of halogenation of the 1-*halogenonaphthalenes*, R′X, *in* HOAc.

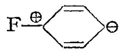
X =	H.	F.	Cl.	Br.	I.
Cl_2, M/40, 25° ($n = 2$)	100	100	6·0	5·0	—
Br_2, M/5—M/10, 25° ($n = 4$)	100	92	3·2	2·1	5·5
Br_2, M/5—M/10, 25°, $HClO_4$ M/2 ($n = 3{\cdot}5$)	100	88	2·8	1·9	3·8
Br_2, M/10—M/20, 52°, $HClO_4$ M/2 ($n = 3{\cdot}1$)	100	99	3·6	2·8	6·9

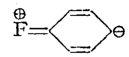
The bromination rates are more widely spaced than the chlorination rates, as was also found for the alkylbenzenes (Part II, *J.*, 1943, 279). This difference may depend on a difference in mechanism between the two reactions; whereas the rates of chlorination depend only on a velocity constant ($-\,d[Cl_2]/dt = k[A][Cl_2]$), the bromination rates depend also on an equilibrium ($-\,d[Br_2]/dt = Kk[A][Br_2]^n$, for third- or fourth-order kinetics). If K and k alter in the same sense with change in the substituent X, the bromination series will be more widely spaced than the chlorination series. The few available results in the field of halogen addition reveal a similar trend.

The influence of ring-substituted halogen on reactions and equilibria has been the subject of much discussion and controversy. Watson (" Modern Theories of Organic Chemistry ", Oxford University Press, 1937, p. 76) summarises much of the evidence, which may conveniently be considered under three headings :

(i) *Physical data.* The dipole moments of the halogenobenzenes indicate an overall electron withdrawal from the aromatic nucleus, and are in the irregular order $Cl \sim Br > F > I$. In conjunction with the dipole moments of the alkyl halides, these values, according to Sutton (*Proc. Roy. Soc.*, 1931, **133**, *A*, 668) and Groves and Sugden (*J.*, 1937, 1992) lead to the conclusion that the halogens possess (in addition to the electron-withdrawing inductive effect, the accepted order of which is $F > Cl > Br > I$) a capacity for electron release to the aromatic nucleus which decreases in the order $F > Cl > Br > I$. Hugill, Coop, and Sutton (*Trans. Faraday Soc.*, 1938, **34**, 1518) have discussed bond-length data in relation to the above results. Extending their values by inclusion of the fluoro-compound (from the work of Finbak and Hassel, *Chem. Abstr.*, 1942,

36, 6408) we find bond shortenings (% of the normal bond-length) in the monohalogenobenzenes of 7·1% (C–F); 4·0% (C–Cl); 1·6% (C–Br); 3·8% (C–I). The contribution of the double-bonded form will follow the same irregular order, which does not agree completely with that deduced from the corresponding dipole moments. This small discrepancy being neglected, however, the relatively large shortening of the C–F bond length in fluorobenzene suggests that it is unnecessary to assume resonance forms such as (I), postulated by Bennett and his co-workers (*J.*, 1935, 1827) in order to explain the observed electron release. The experimental results are

(I.) 

 (II.)

on the whole consistent with the assumption that the mesomeric effect of the halogens in aromatic combination results from contribution of double-bonded structures (II). Similarly, Pauling (" The Nature of the Chemical Bond ", Cornell University Press, 1945, p. 236) deduces from interatomic distances in the polyhalogenomethanes that " chlorine has about half the power to form double bonds that fluorine has ".

(ii) *Equilibria.* The dissociation constants of the halogen-substituted acetic acids show that halogen substituents possess an inductive effect resulting in electron withdrawal in the order F > Cl > Br > I. Similar values for the *p*-halogeno-substituted phenols and phenylacetic acids confirm the conclusion from dipole-moment data that in such compounds the halogens also may release electrons mesomerically, in the order F > Cl > Br > I, which conclusion was reached independently by Bennett (*J.*, 1933, 1112), and by Bettman, Branch, and Yaabroff (*J. Amer. Chem. Soc.*, 1934, **56**, 1865). It is important to realise that the relative contribution of the inductive and mesomeric effects will differ according to the system considered. We find, therefore, as was clearly illustrated by Dippy and Lewis (*J.*, 1936, 644), that the order in which the halogen-substituted compounds fall will differ in different series. The data of Table II, taken from Watson (*op. cit.*), exemplify this point.

TABLE II.

The effects of halogen substituents on acid strengths.

Substituent (X).	H.	F.	Cl.	Br.	I.
Dissociation constant of $X{\cdot}CH_2{\cdot}CO_2H$ ($\times 10^5$)	1·8	217	155	138	75
Dissociation constant of m-$X{\cdot}C_6H_4{\cdot}OH$ ($\times 10^{11}$)	3·2	15	49	44	39
Dissociation constant of p-$X{\cdot}C_6H_4{\cdot}CH_2{\cdot}CO_2H$ ($\times 10^5$)	4·9	5·7	6·4	6·5	6·6
Dissociation constant of p-$X{\cdot}C_6H_4{\cdot}OH$ ($\times 10^{11}$)	3·2	2·6	13	16	22

Dissociation constants of acids are increased by electron withdrawal. In the halogen-substituted acetic acids, as would be expected, the inductive effect controls the observed order. In the *m*-substituted phenols, a small contribution from the mesomeric effect, thought to be relayed inductively to the *m*-position, results in an irregular series. In the *p*-substituted phenylacetic acids and phenols, the mesomeric effect controls the order, and in the latter series, in which the ionizing group is conjugated with the halogen, the overall effect of fluorine as a substituent is that of electron release.

(iii) *Reaction rates.* Equilibria are determined only by the energy contents of the equilibrium states, and thus only permanent electron displacements are concerned in establishing the positions of such equilibria. The above results make it clear, however, that as far as the effects of substituent halogens on reacting systems are concerned, a wide variety of phenomena could be interpreted in terms only of the two opposing permanent displacements, which interact in such a complex fashion as to obscure the magnitude of the contribution of possible time-variable effects. As shown by the equilibria quoted in Table II, the order of electron release from halogen substituents may vary regularly in either direction, or may pass through a minimum; and the overall effect, for fluorine at least, is not necessarily that of electron withdrawal, but may be that of electron donation if the system is powerfully electron demanding. It is not surprising, therefore, that ambiguities may sometimes arise in the interpretation of reaction rates in series such as are shown in Table III. Reactions 1 and 2 (Watson, *op. cit.*) are facilitated by electron withdrawal, and exemplify the dominance of the inductive effect. Reaction 3, from the work of Bennett and Jones (*J.*, 1935, 1815), is apparently a unimolecular solvolysis facilitated by electron donation. In this series, fluorine as a substituent facilitates, and the other halogens retard the reaction. The effects here parallel those shown in the acid strengths of the *p*-halogeno-substituted phenols. Reactions 4 (Baker, *J.*, 1936, 1448; *Trans. Faraday Soc.*, 1941, **37**, 632) and 5 and 6 (Ingold and co-workers, *J.*, 1938, 918, 929) have been regarded as providing evidence for the differential contribution of a polarizability effect to the rates, and are discussed below. Series 7 is the mean of the three bromination series given above, and (cf. series 5 and 6) is corrected for the statistical factor arising from the fact that naphthalene has four equivalent positions of attack.

Table III.

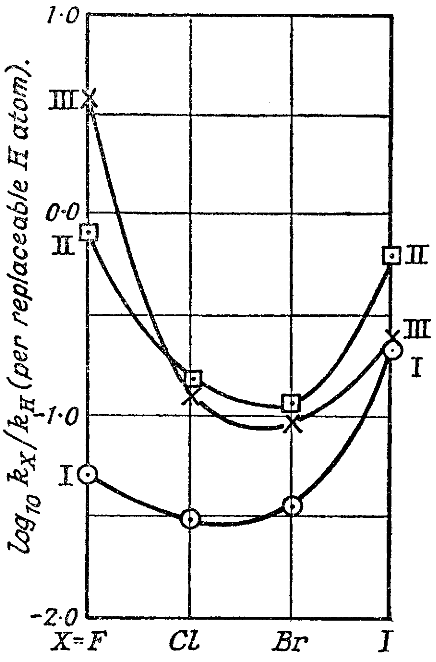
*Effects of halogen substituents on reaction rates.**

Substituent (X).	H.	F.	Cl.	Br.	I.
(1) p-X·C_6H_4·CH_2Cl + KI in acetone	1·0	1·5	3·2	2·4	2·3
(2) Alkaline hydrolysis of p-X·C_6H_4·CO_2Et	1·0	1·9	4·3	4·9	5·1
(3) p-X·C_6H_4·CH_2Cl + H_2O in 50% acetone	1·0	1·6	0·57	0·50	0·46
(4) p-X·C_6H_4·CH_2Br + C_5H_5N in acetone	1·0	1·2	1·0	1·1	1·2
(5) o-Nitration of PhX	1·0	0·05	0·030	0·034	0·2
(6) p-Nitration of PhX	1·0	0·79	0·14	0·11	0·6
(7) 4-Bromination of 1-X·$C_{10}H_7$	1·0	3·7	0·13	0·09	0·22

* Relative to the unsubstituted compound.

The relatively high velocity of bromination of fluoronaphthalene (supported by related data on fluorobenzene) provides perhaps the most convincing evidence for the operation of a polarisability factor. Dipole-moment data show that these compounds are permanently polarised in the direction of electron withdrawal from the aromatic ring; yet reactivity towards halogenation is (per replaceable hydrogen atom) increased considerably by the presence of a fluorine substituent. We have, therefore, some experimental, together with considerable theoretical reasons for assuming the existence of a polarisability factor contributing to the observed rate differences between halogen-substituted compounds. In Fig. are plotted for the electrophilic substitutions of Table III (reactions 5, 6, and 7) the values of $\log_{10}$ ($k_{\text{Hal.}}/k_{\text{H}}$), the subscripts referring to the substituent, and the rates being per replaceable hydrogen atom.

Relative rates of substitution of aromatic halides.

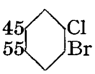


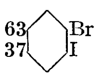
I, o-*Nitration of* PhX.
II, p-*Nitration of* PhX.
III, *Bromination of* 1-$C_{10}H_7X$.

The nature of the difference between curves 1 and 2 (representing o- and p-nitration respectively of the phenyl halides) may be explained as follows (cf. Lapworth and Robinson, *Mem. Proc. Manchester Lit. Phil. Soc.*, 1927, **72**, 43). Since the deactivating influence of the inductive effect is expected to decrease with distance from the controlling dipole, it must be relatively highly effective for o-substitution. The mesomeric effect, on the other hand, for reasons of symmetry (cf. *Trans. Faraday Soc.*, 1941, **37**, 745) will be relayed more powerfully to the p- than to the o-position. Accordingly, o- as compared with p-nitration is powerfully deactivated. This deactivation, as shown by the decreasing divergence of curves 1 and 2 (see fig.), is least for iodobenzene and greatest for fluorobenzene, thus decreasing with the inductive effect of the substituent, despite the probability that steric hindrance of substitution would oppose this tendency.

In comparing curves 2 (p-nitration) and 3 (4-bromination) we neglect differences shown in Table I dependent on the order of the reaction. These are small, and would not invalidate our conclusions. We are also forced to neglect possible differences between the phenyl and the naphthyl series, as ortho/para ratios are not available under the conditions of kinetic measurement, and the critical value for the iodo-compound is not accessible. The virtual identity of the dipole moments of each pair of compounds (PhF, $C_{10}H_7F$, etc.) is, however, an indication that one of the controlling factors, namely, the permanent polarisation of the molecule, is similar in the two series. With the above reservations, the observed differences can be interpreted in terms of the differences between the attacking reagents. The permanent polarisation of the aromatic compound (roughly measured by the dipole moment, Cl $\sim$ Br $>$ F $>$ I) is expected to result in a more powerful repulsion of the $NO_2^{\oplus}$ ion (which is the effective nitrating agent) than of the formally neutral bromine molecule. From the figure it is clear, however, that nitration as compared with bromination is deactivated only for the fluoro-compound. For the other three compounds, nitration is activated, very slightly for the chloro-, rather more for the bromo-, and considerably for the iodo-derivative. If the above interpretation of the deactivation of the fluoro-compound is accepted, therefore, we require an effect resulting in activation of nitration as compared with bromination, and decreasing in the order I > Br > Cl > F. This is the order postulated by Baker and by Ingold for the electromeric effect. We interpret the experimental observations as signifying that a positive ion ($NO_2^{\oplus}$), as compared with a formally neutral molecule (Br_2 or Br_4), evokes the polarisability effect more powerfully, since its disturbing electrostatic field is greater. One might venture to predict that nitration involving attack by a molecular nitrating agent (*e.g.*, the N_2O_5 molecule) would result in a rate series for nitration approximating more closely to that observed for bromination. The importance of the overall permanent deactivation of the aromatic compound, as shown by the dipole moments and by the fact that nitration is deactivated relative to the unsubstituted compound for all the halogen-substituted benzenes, accounts for the partial success of the calculations of Ri and Eyring (*J. Chem. Physics*, 1940, **8**, 433), who assumed that the relative rates of nitration at different positions in the benzene ring are determined only by the distribution of electrostatic charges on the carbon atoms at which substitution is occurring.

The theoretically expected order in which halogen substituents would provide an electromeric electron release is not agreed. Bennett *et al.* (*loc. cit.*) assumed that it would follow the order of the mesomeric effect F > Cl > Br > I, but that the operation of a polarisability factor in the order I > Br > Cl > F sufficed to account for the fact that the substitution of *o*-chlorofluorobenzene is predominently *para* to the fluorine atom, whereas *o*-bromoiodobenzene is substituted to a greater extent *para* to iodine (Ingold and Vass, *J.*, 1928, 417; Holleman, *Rec. Trav. chim.*, 1915, **34**, 204). Bird and Ingold, on the other hand (*J.*, 1938, 918), assumed that an electromeric polarisability in the order I > Br > Cl > F contributed to the rate differences in the nitration of the halogenobenzenes, since they regarded this reaction as highly suitable for the observation of such electron displacements. The irregular series quoted above from the work of Baker (Table III, reaction 4), was thought by the latter author to suggest the operation of an electromeric effect in the same order. In the latter case it is interesting that all the halogens appear to be electron donating, though the differences are small and the polar character of the reaction is theoretically uncertain.





Our experimental results appear to be explained most readily on the assumption that we are observing a polarisability effect, the order of which is I > Br > Cl > F. If this is accepted, and if also it is agreed that in the system under consideration we can neglect inductomeric as compared with electromeric polarisability, then it must be concluded that Bennett's order for the electromeric effect, which has recently been supported by Remick (" Electronic Interpretations of Organic Chemistry ", John Wiley and Sons, N.Y., 1943), is incorrect. An alternative possibility is that we have observed the effect of inductomeric polarisability of the C–Halogen bond. Such a disturbance, partially reversing the permanent inductive polarisation, should vary with the halogen in the manner found, and should, comparing as reagents the $NO_2^{\oplus}$ ion and the Br_2 molecule, be considerably more powerfully evoked by the electrostatic field of the positive ion. Insofar as we have considered only differences between nitration and bromination, we cannot on this basis make any deductions concerning the total polarisability effect. The latter might still be in the order F > Cl > Br > I, and particularly is this possible for halogenation, for which reaction we theoretically expect inductomeric disturbances to be relatively small, and, for which, experiment shows an unexpectedly great reactivity for the fluoro-substituted compound.

EXPERIMENTAL.

The technique, both for bromination and for chlorination, has been given in Parts I and II (*loc. cit.*), where are described some of the compounds used in this work, together with certain of the results used in the present discussion. Methyl alcohol was Baker's " Analysed ", and reacted inappreciably with bromine under the conditions of the kinetic measurements. The following additional compounds were examined : 1-fluoronaphthalene, E.K., redistilled, b. p. 90—91° (*ca.* 15 mm.); 1 -chloronaphthalene, E.K., redistilled, b. p. 152—153° (*ca.* 30 mm.), $n_D^{20°}$ 1·634; 1-bromonaphthalene, E.K., redistilled, b. p. 60—63° (*ca.* 0·1 mm.), $n_D^{20°}$ 1·658; 1-iodonaphthalene, E.K., redistilled, b. p. 156° (*ca.* 15 mm.); fluorobenzene, prepared from benzenediazonium borofluoride, b. p. 85° 760 mm.), $d_{15°}^{15°}$ 1·031;

chlorobenzene, B.D.H., redistilled, b. p. 132° (756 mm.); bromobenzene, B.D.H., redistilled, b. p. 155° (760 mm.); *N*-methylacetanilide, recrystallised, m. p. 103°.

Solutions of perchloric acid in acetic acid were prepared as described elsewhere (*J.*, 1945, 888). The following results are for the bromination of the 1-halogenonaphthalenes, $C_{10}H_7X$, as times (min.) for $x = 10\%$ absorption of bromine in acetic acid :

X =	H.	F.	Cl.	Br.	I.
Reactants M/5, 25°	4·6	5·5	139	222	91
Reactants M/10, 25°	37·0	37·3	1170	1800	620
Reactants M/5, M/2-$HClO_4$, 25°	0·4	0·5	14·0	22·0	10·0
Reactants M/10, M/2-$HClO_4$, 25°	2·3	2·4	81	122	63
Reactants M/10, M/2-$HClO_4$, 52°	1·0	1·0	28	36	14
Reactants M/20, M/2-$HClO_4$, 52°	4·3	4·4	120	148	64

The following are similar values for other bromine substitutions, in acetic acid at 25°, except where otherwise stated.

Naphthalene at 24°; M/5, 4·8; M/10, 38·6; M/5, Br_2 M/10, 18·5. In acetic acid containing 1% water, at 24° : M/5, 3·0; M/10, 24·1. In acetic acid containing 50% CCl_4, M/5, 55. In methyl alcohol, M/5, 3·4; M/10, 18·1.

1-Chloronaphthalene, in acetic acid containing 17% water, M/5, 3·5 : M/10, 21·5 (+ 0·169M-$HClO_4$, 19); M/20, 110. In acetic acid containing 49% water, at 52°, $x = 20$, M/80, 8·1; M/160, 16·0.

1-Bromonaphthalene M/5, Br_2 M/10, 815.

For chlorinations, the following times were obtained (minutes, $x = 20\%$ reaction, reactants each M/40 in acetic acid at 25°, except where otherwise stated) : naphthalene, 2·4; 1-fluoronaphthalene, 2·5; 1-chloronaphthalene, 45 (M/5, 4·6); 1-bromonaphthalene, 54. The k_2 values given for the halogenobenzenes are the mean of three or more concordant measurements, with aromatic compound M/5, Cl_2 M/20.

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