

75. *The Kinetics of Aromatic Halogenation. Part II. The Chlorination of Hydrocarbons.*

By P. B. D. DE LA MARE and P. W. ROBERTSON.

The rates of chlorination of benzene and naphthalene, and the heats of activation, have been measured in acetic acid solution. The relative rates of chlorination of the series RPh, where R = Me, Et, Pr^β, Bu^γ, are in the order 100, 84, 51, 32, showing the operation of alkyl conjugation. The xylenes, mesitylene, and pentamethylbenzene were also examined: the halogenation rate of pentamethylbenzene is 4×10^9 that of benzene, per replaceable hydrogen atom.

THE chlorination of phenol ethers has been investigated by Bradfield, Jones, and co-workers (J., 1927, 986; 1928, 1006, 3073). These reactions are bimolecular, slightly catalysed by hydrogen chloride, and belong to the class of slow reactions, with *P* values clustering between 10^{-5} and 10^{-6} . Lauer and Oda (*Ber.*, 1936, 69, 1061) measured the chlorination rates of aromatic hydrocarbons, including benzene and naphthalene, and concluded (a) that although benzene reacts at a much slower rate than naphthalene, there is a lower *E* value for the reaction, (b) that hydrogen chloride retards the chlorination of benzene and has the reverse effect on that of naphthalene, and (c) that the action of hydrogen chloride is specific and due to formation of HCl₃. They

accordingly elaborated a theory considered to be in accord with their observations on the absorption spectra of these hydrocarbons. We are unable to confirm these results, and believe that Lauer and Oda failed to realise the importance in chlorination kinetics of errors due to volatility losses of chlorine. With a special technique to reduce that source of error, we, on the contrary, find (a) that benzene has a higher heat of activation than naphthalene, and both compounds give P values of the same order as the phenol ethers, (b) that hydrogen chloride accelerates both reactions, and (c) that the effect is not specific, for sulphuric acid is also a catalyst.

The mechanism by which acids in acetic acid solution accelerate the rate of chlorine substitution has not been elucidated. It would appear to be related to the breaking away of the hydrogen ion, for a similar catalysis (to a relatively smaller extent) is found for bromine substitution, but not for chlorine or bromine electrophilic addition to olefinic compounds. Lithium chloride is also a catalyst for both substitutions, and for electrophilic (but not nucleophilic) bromine addition (work to be published). It is known that lithium chloride behaves practically as a strong electrolyte in acetic acid, and its catalytic activity is regarded as a salt effect.

The investigation was extended to the alkylbenzenes, C_6H_5R , where $R = Me, Et, Pr^{\beta}, Bu^{\gamma}$. The suggestion that alkyl conjugation might operate by an electromeric effect, and consequently be detected by kinetic measurements, was made by Baker and Nathan (J., 1935, 1844). This theory was illustrated by reference to the action of pyridine on members of the series $p-R \cdot C_6H_4 \cdot CH_2Cl$, which showed the relative rates 60, 100, 90, 81, and 82 for $R = H, Me, Et, Pr^{\beta},$ and Bu^{γ} respectively. The relatively small difference in rate between the methyl derivative and the unsubstituted compound made this series unfavourable for the unambiguous detection of the effect under consideration. Hughes, Ingold, and Taher (J., 1930, 949) concluded that unimolecular nucleophilic substitution represented a favourable type of reaction, and measured the hydrolysis of the p -alkylbenzhydryl chlorides, $C_6H_4R \cdot CHPhCl$, in 90% aqueous acetone, finding the relative rates 3.4, 100, 75, 56, and 43 for the same series of substituents, respectively.

Aromatic halogenation is determined by tautomeric electron displacement to carbon atoms at which substitution takes place, followed by the anionisation of the negatively polarised halogen atom of the attacking molecule. In a dissociating solvent such as acetic acid the tendency for side-chain substitution is known to be slight. Such reactions may consequently be regarded as suitable for the comparison of the relative influence of different alkyls, and moreover, the large difference in rate between benzene and toluene, for nitration, indicated the possibility of a well-spaced series. This expectation was justified, as shown by the following relative rates at 24° : I, chlorination in acetic acid; II, bromination in 15% aqueous acetic acid:

	H.	Me.	Et.	Pr^{β} .	Bu^{γ} .
I	0.29 *	100	84	51	32
II	—	100	76	44	23

* Owing to the slowness of the benzene reaction this ratio is for 20% aqueous acetic acid at 24° ; a second value, in 1% aqueous acetic acid at 35° , is 0.28. The nitration ratio by the competition method is 4.2 (Ingold *et al.*, J., 1931, 1959).

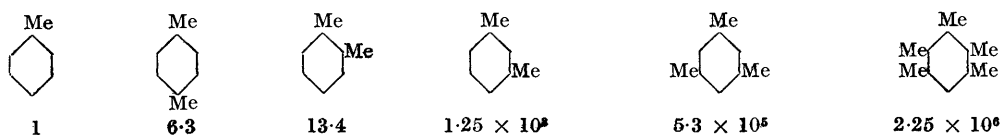
It is possible that the greater divergence in the bromination series may be due to a steric effect, as a result of which bromination is relatively hindered more than chlorination in the o -position. In the alkylbenzenes the extent of o -substitution (for nitration) decreases from Me ($\frac{1}{2}o : p = 0.80$) to Bu ($\frac{1}{2}o : p = 0.13$) (Ingold, Lapworth, Rothstein, and Ward, J., 1931, 1959; Craig, *J. Amer. Chem. Soc.*, 1930, 52, 195). This may be related to a variation in the symmetry factor in the mesomeric structures (Bradfield, *Trans. Faraday Soc.*, 1941, 746) or it may be a purely steric effect (Le Fèvre, J., 1938, 980). The values for halogenation are not known; it is clear, however, that the relative fall in rate for p -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 alkyl conjugation.

A comparison of the relative effects of methyl and *tert.*-butyl was also made in compounds of a different type (total rates of bromination for all available positions in acetic acid at 24.0°):



As in mesitylene, substitution may take place equally in all three free positions, but in 1 : 3-dimethyl-5-*tert.*-butylbenzene (owing to steric hindrance) almost exclusively in position *; the comparative rates for the one position become 100 : 39, showing again the greater activity of methyl than of *tert.*-butyl in promoting aromatic substitution.

A series of methylbenzenes has also been investigated, giving the following relative rates of halogenation in acetic acid solution:



The measurement of such great differences in rate between the extreme members of the series was realised by a comparison of the chlorination rates of the first three, and the bromination rates of the last four compounds. The accumulated effect of five methyl groups becomes very considerable. Pentamethylbenzene brominates at about the same rate as anisole, and, per replaceable hydrogen atom, its halogenation rate is 4×10^9 times that of benzene.

EXPERIMENTAL.

The compounds used had the following properties: benzene, b. p. $79.8^\circ/763$ mm.; naphthalene, m. p. 80.0° ; toluene, b. p. $110.2^\circ/755$ mm.; ethylbenzene, b. p. $135.5-136.5^\circ/755$ mm.; isopropylbenzene, b. p. $150.7-151.0^\circ/756$ mm.; *tert.*-butylbenzene, b. p. $165.8^\circ/758$ mm.; *o*-xylene, b. p. $142.2-142.5^\circ/750$ mm.; *m*-xylene, b. p. $138.5-139.0^\circ/760$ mm.; *p*-xylene, b. p. $136.2-136.4^\circ/744$ mm.; mesitylene, b. p. $165.0^\circ/760$ mm.; pentamethylbenzene, m. p. $53.0-53.5^\circ$; 1:3-dimethyl-5-*tert.*-butylbenzene, b. p. $201.5-202.3^\circ/752$ mm. For the last compound we are indebted to the kindness of Dr. D. V. Nightingale, University of Missouri; fractionation of the specimen yielded fractions with identical rates.

The chlorination technique devised to avoid volatility errors (J., 1939, 1509) has been modified. For the faster reactions, 5 ml. of chlorine solution and 5 ml. of compound solutions are mixed in a brown reaction bottle of only slightly more than 10 c.c. capacity. From this reaction mixture 1 ml. is removed for titration at *ca.* 20% absorption, and a second 1 ml. at *ca.* 40% absorption. A blank is carried out similarly with 5 ml. each of chlorine solution and solvent, 1 ml. portions being titrated when the main titrations are performed. The whole operation is repeated, samples being taken at *ca.* 30% and *ca.* 60% absorption, with corresponding blanks. The % absorptions are calculated, and a curve drawn through the points thus obtained.

Experimental details for *m*/80-naphthalene + *m*/80-chlorine in 1% aqueous acetic acid at 24.0° were:

Time (mins.)	5.15	10.35	8.26	18.64
Blank titre (ml.)	2.03	2.01	1.94	1.94
Reaction titre (ml.)	1.45	1.03	1.15	0.66
Absorption, %	28.4	47.9	41.3	67.0

The following are the bimolecular coefficients thus obtained, the k_2 values rising owing to autocatalysis (the corresponding values at *m*/40 are included for comparison):

Absorption, %	20	30	40	50
k_2 (<i>m</i> /80)	—	6.3	6.7	7.1
k_2 (<i>m</i> /40)	6.0	6.2	6.5	6.7

At 15.3° the values for this reaction were: *m*/40, $k_2(x=20) = 4.2$; *m*/80, $k_2 = 4.1$; E , 7,500 cal. Lauer and Oda gave no experimental details, but summarised: *m*/30, $k_2(15^\circ) = 3.00$; $(22.5^\circ) = 8.54$; E , 23,450 cal.

For the very slow reactions, one sample only (2 ml.) is removed from the 10 ml. in the reaction bottle, blanks (2 ml.) being run as before. For *m*/2-benzene + *m*/20-chlorine in 1% aqueous acetic acid at 34.2° , these results were obtained:

	Time (mins.).	Blank titre (ml.).	Reaction titre (ml.).	$k_2 \times 10^4$.
Expt. I	1610	3.99	3.30	2.38
Expt. II	1475	4.04	3.41	2.34
Expt. III	1512	4.08	3.43	2.31

Hence $k_2(34.2^\circ) = 2.34 \times 10^{-4}$, and as $k_2(24.0^\circ) = 0.89 \times 10^{-4}$, $E = 17,000$ cal. Lauer and Oda give for *m*/30-reactants: $k_2(18^\circ) = 10.5 \times 10^{-4}$, $k_2(30^\circ) = 25.1 \times 10^{-4}$, $E = 12,800$ cal. For the effect of hydrogen chloride (amount not specified) they give: $k_2(18^\circ) = 5.7 \times 10^{-4}$. We find for *m*/2-benzene + *m*/20-chlorine + 1.31*M*-hydrogen chloride, $k_2(24.0^\circ) = 4.0 \times 10^{-4}$, showing positive catalysis for benzene as for other compounds on chlorination in acetic acid.

The influence of catalysts is shown as the ratio of catalysed to uncatalysed reactions: *m*/40-naphthalene + *m*/40-chlorine + 0.88*M*-hydrogen chloride, 3.7; +0.51*M*-sulphuric acid, 4.9; +0.099*M*-sodium acetate, 1.4; *m*/10-toluene + *m*/40-chlorine + 0.062*M*-lithium chloride, 1.57.

The following is a summary of the experimental results for the alkylbenzenes at 24.0° , x being the absorption %, and t the time in mins.:

x .	<i>m</i> /10-PhR + <i>m</i> /40-Cl ₂ in acetic acid.				<i>m</i> /20-PhR + <i>m</i> /20-Br ₂ in 85% HOAc + 15% H ₂ O.			
	t (R = Me).	t (R = Et).	t (R = Pr ^{β}).	t (R = Bu ^{γ}).	t (R = Me).	t (R = Et).	t (R = Pr ^{β}).	t (R = Bu ^{γ}).
10	32.9	39.8	64	106	660	860	1540	2870
15	54.0	63.8	106	167	1130	1480	2570	4970

The values from which the relative rates of the methylbenzenes are calculated are from measurements in acetic acid (99.9%) at 24.0° ($x = 20$), times being in mins.: *m*/10-toluene + *m*/40-chlorine, 81.8; *p*-xylene (same concns.), 13.0; *o*-xylene (same concns.), 6.12; *m*/5-*o*-xylene + *m*/5-bromine, 283; *m*-xylene (same concns.), 3.02; *m*/40-*m*-xylene + *m*/40-bromine, 820; mesitylene (same concns.), 1.95; pentamethylbenzene (same concns.), 0.46.

The relative rates of benzene and toluene are derived from the values in 80% acetic acid + 20% water at 24.0° : *m*/20-benzene + *m*/40-chlorine, $t = 240$ mins.; toluene (same concns.), $t = 0.68$ min.