Nine of these fifteen combinations can be checked against our data. We have already shown how the combination we consider most probable, 1 + 2, satisfies the data. None of the remaining eight mechanisms that we can handle is, however, consistent with our data. As an example, we consider the case of 2 + 3, which is the mechanism found to be operative in the aminolysis of α-naphthyl acetate.[1b] Here, by operations entirely analogous to those whereby equations 22 and 25 were derived, we find

$$[\mathrm{RNH_2}]_0{}^{1/2}\, k_3{}^0 = \frac{k_2K_{\mathrm{am}}}{K_{\mathrm{b}}{}^{1/2}[\mathrm{R'OH}]^{1/2}} + \frac{k_3K_{\mathrm{b}}{}^{1/2}[\mathrm{R'OH}]^{1/2}}{[\mathrm{RNH_2}]_0} \quad (31)$$

$$[\mathrm{RNH_3}^+]k_3{}^0 = k_2K_{\mathrm{am}} + \frac{k_3[\mathrm{RNH_3}^+]^2}{[\mathrm{RNH_3}]_0} \quad (32)$$

When the data of Tables VI and VII are fed into these equations, the appropriate plot for (31) is found not to be linear, thereby showing that these data do not fit mechanism 2 + 3. In like manner, we eliminate the seven combinations 2 + 4, 2 + 5, 2 + 6, 2 + 3 + 4, 2 + 3 + 5, 2 + 4 + 5, and 2 + 5 + 6. We are thus left with six possible mechanisms that we cannot either accept or reject on the basis of our present treatment of our data: 1 + 2 + 3, 1 + 2 + 4, 1 + 2 + 5, 1 + 2 + 6, 2 + 3 + 6 and 2 + 4 + 6. Three of these combinations contain the term 3 or 5, corresponding to acid catalysis, and we must then conclude that if there is an acid catalysis term in the rate equation, it will appear in one of these combinations.

The foregoing analysis has thus disclosed no simple mechanism other than 1 + 2 which satisfactorily accounts for our results, and consequently has furnished no positive evidence for acid catalysis in the reaction under study. It has, however, led to a list of six other mechanisms which our treatment does not test, and thus has shown that our present assignment of mechanism, even though most reasonable chemically, nevertheless may not be uniquely demanded by the experimental results.

The formal similarity among ammonolysis, aminolysis, and hydrolysis has been remarked upon by several previous authors.[1b,3,20] Hydrolysis, however, has been considered either as separately base catalyzed or separately acid catalyzed,[21] and it has not been experimentally demonstrated that both processes may be operative in the same reaction. Such a demonstration should be possible when both base and acid are present at approximately the same concentrations as, for example, in neutral aqueous solution, and when the susceptibility of the ester to acid hydrolysis is of the same order of magnitude as its susceptibility to base catalysis. Rates of hydrolysis under such conditions are generally low and often complicated by changes in mechanism to alkyl–oxygen fission.[21] A more ideal situation exists in aminolysis, however, since $\mathrm{RNH^-}$ has undoubtedly much greater nucleophilic reactivity toward carbonyl carbon than $\mathrm{OH^-}$ and thus rapid rates may be realized without added catalysts. Since it is generally the case that in hydrolysis the acceleration afforded by a given level of base is greater than that resulting from the same concentration of acid, it is not unexpected that in aminolysis the reaction of $\mathrm{RNH^-}$ may far overshadow the effect of $\mathrm{RNH_3^+}$ upon the ester. Thus it is possible that only in those instances in which base catalysis is relatively ineffective, as is probably the case with α-naphthyl acetate, would a term involving $\mathrm{RNH_3^+}$ be large enough to detect. This would mean that our results are by no means in contradiction with those of Hawkins[1b] but represent a more restricted, but probably more common, aspect of the mechanism of aminolysis.

Acknowledgment.—We are indebted to Dr. S. Gratch, Dr. L. P. Hammett, and Dr. C. Huggett for many stimulating discussions during the course of this work.

[20] C. K. Ingold, "Structure and Mechanism in Organic Chemistry" Cornell University Press, Ithaca, N. Y., 1953, pp. 782–784.

[21] Reference 20, p. 752, *et seq.*

PHILADELPHIA, PA.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF CALIFORNIA AT DAVIS]

The Kinetics of the Zinc Chloride-catalyzed Bromination of Polymethylbenzenes in Acetic Acid Solution

BY L. J. ANDREWS AND R. M. KEEFER

RECEIVED MARCH 26, 1956

Partial rate factors for substitution at positions *ortho*, *meta* and *para* to a methyl substituent on the benzene ring have been determined through an investigation of the kinetics of the zinc chloride-catalyzed bromination of a series of methylbenzenes in acetic acid solution. Evidence has been obtained that not only the *ortho* partial rate factors but also the *meta* and *para* factors are subject to steric influences of ring methyl substituents. The bromination reactions are first order with respect to halogen, to aromatic hydrocarbon and to catalyst. The reactions are inhibited by $\mathrm{HZnCl_2Br}$ which accumulates in the medium as the reaction proceeds. This substance has no catalytic activity but can react with a reaction intermediate to regenerate the starting materials. Ethyl-, isopropyl- and *t*-butylbenzene are only slightly less reactive than toluene, but *p*-di-*t*-butyl- and *sym*-tri-*t*-butylbenzene brominate very slowly.

Partial rate factors for nuclear halogenation of the benzene ring at positions *ortho*, *meta* or *para* to methyl substituents have been calculated.[1] These calculations were based on the known isomer distribution of products resulting from the chlorination of toluene in the presence of antimony pentachloride and iodine[2] and on values reported for the relative rates of chlorination of benzene and toluene in 80% acetic acid.[3] These partial rate factors

---

[1] F. E. Condon, THIS JOURNAL, **70**, 1963 (1948).

[2] E. Wertyporoch, *Ann.*, **493**, 153 (1932).

[3] P. B. D. de la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943).

have been used to estimate the relative halogenation rates for a series of polymethylbenzenes. The predicted reactivities are in reasonably good agreement with experimental values obtained through studies of chlorination or in some cases bromination, of the alkylbenzenes in pure acetic acid.[3] Since the relative rates of electrophilic substitution at various positions in substituted benzenes are sensitive to changes in the electrophilic reagent and to the introduction of catalysts,[4] it is surprising that the halogenation data, which were collected under such diverse experimental conditions, may be correlated with any success.

A re-evaluation of partial rate factors for halogenation at various positions in toluene has, therefore, been made through study of the rates of the zinc chloride-catalyzed reaction of bromine with a series of polyalkylbenzenes in acetic acid. The comparisons are restricted to reactions which are identical in mechanism.[5]

Experimental

Materials.—The procedures used in preparing pure acetic acid, the aromatic hydrocarbons and the anhydrous salts (zinc chloride and sodium bromide) have been described previously.[5-7] A reagent grade of bromine was used without further purification.

Hydrogen bromide was generated by dropping bromine into a solution of phenol and acetic anhydride. The evolved gas was passed through a two foot coil condenser and trapped in pure acetic acid. The resultant stock solution was analyzed gravimetrically for hydrogen bromide content.

Rate Runs.—The same spectrophotometric method which was used previously[7] to study the kinetics of bromination of mesitylene in acetic acid was employed in this investigation. The changes in bromine concentrations of the reaction mixtures were followed by measuring the changes in the optical densities of the solutions at 450 mμ (using pure acetic acid as a blank) as a function of time. The molecular extinction coefficient of bromine in acetic acid at this wave length, 124, is not appreciably affected by zinc chloride or hydrogen bromide in the medium at concentrations comparable to those used in the rate runs. In calculating rate constants for runs at the higher zinc chloride concentrations, small corrections for contribution of the salt to the measured optical densities were made.

The Effects of Hydrogen Bromide and Zinc Chloride on the Spectrum of Bromine in Acetic Acid.—As has been found for solutions of bromide ion and bromine in 90% acetic acid,[5] solutions of bromine and hydrogen bromide in pure acetic acid show marked ultraviolet absorption which is presumed to be characteristic of tribromide ion or HBr_3. A few measurements of the ultraviolet spectra of a series of solutions of bromine (about 5×10^{-3} M), which varied in hydrogen bromide concentration from 0.035–0.014 M, were made in an attempt to estimate the equilibrium constant K for this interaction at 25.4° ($K = (HBr_3)/(Br_2)(HBr)$). In more concentrated hydrogen bromide solutions a relatively rapid reaction to form bromine (presumably by air oxidation) interfered with the absorption measurements. The method was essentially that described for the evaluation of the equilibrium constant for tribromide ion formation in 90% acetic acid.[8] The value of K was found to be of the general order of magnitude of 100. This figure is less than that reported much earlier[8] but approximates the value found for the reaction to form tribromide ion in 90% acetic acid.[5]

In the presence of excess zinc chloride, however, the pronounced ultraviolet absorption of solutions of bromine and hydrogen bromide in acetic acid disappears. It appears that the zinc chloride must combine selectively with hydrogen bromide so that the latter is no longer free to interact with bromine. These facts are illustrated in Table I which lists the extinction coefficients at several wave lengths of solutions of bromine, of bromine and hydrogen bromide, and of bromine, hydrogen bromide and zinc chloride in acetic acid. Reagent concentrations of solutions described in this table are comparable to those used in the rate runs.

Zinc chloride in concentrations up to 0.5 M produces no significant changes in the visible absorption spectrum of bromine in dilute solution in acetic acid. The presence of zinc chloride at this high concentration does produce some enhancement of the intensity of ultraviolet absorption of bromine in the region below 350 mμ, but the effects are minor compared to those produced by hydrogen bromide.

The Product of the Zinc Chloride-catalyzed Bromination of Mesitylene.—To establish the position of substitution (side chain or ring) in the kinetic experiments the product of this reaction was isolated using experimental conditions comparable to those employed in the rate runs. To a solution of 10 g. (0.084 mole) of mesitylene and 11.4 g. (0.084 mole) of dry zinc chloride in 1 l. of acetic acid was added 4 ml. (0.084 mole) of bromine in eight equal portions. Each addition was delayed until the color of the previous addend had disappeared from the solution.

The resultant solution was concentrated to one-fourth its original volume under reduced pressure. The concentrate was diluted with 1 l. of water, and the heavy oil which separated was removed by extraction with carbon disulfide. The extract was washed with dilute alkali, dried and distilled. From the distillation 11.4 g. (68% yield) of 2-bromomesitylene was recovered; b.p. 78–80° (2 mm.). The product gave no precipitate when boiled with alcoholic silver nitrate solution.

Results

The Rate Law.—The results of preliminary studies of the zinc chloride-catalyzed bromination of mesitylene in acetic acid suggested that the reaction is essentially first order with respect to hydrocarbon and to halogen at any given catalyst concentration.[7] Accordingly the rate data recorded for the reactions of the various alkylbenzenes at fixed concentrations of zinc chloride have been interpreted by equation 1.

TABLE I

THE SPECTRA OF SOLUTIONS OF BROMINE IN ACETIC ACID[a]

	$(Br_2)_T = 9.3 \times 10^{-4}$ M	$(Br_2)_T = 5.5 \times 10^{-4}$ M (HBr) = 0.014 M	$(Br_2)_T = 9.5 \times 10^{-4}$ M (HBr) = 0.035 M $(ZnCl_2)$ = 0.05 M
λ, mμ	ϵ	ϵ	ϵ
340	40	1220	58
350	65	813	77
360	96	595	110
370	128	508	142
390	173	458	185
410	174	334	179
430	149	203	154
450	124	126	124

[a] The listed values of ϵ are based on total bromine concentrations.

$$R = \frac{-d(Br_2)}{dt} = k(ArH)(Br_2) \qquad (1)$$

It was found in analyzing the results of runs on toluene at varying initial concentrations of the reagents that values of k drifted downward during the course of the runs. In runs in which only the initial bromine concentrations were varied the instantaneous rates measured at equal values of (Br_2) diminished with increasing initial halogen content of

---

(4) H. C. Brown and C. W. McGary, Jr., THIS JOURNAL, **77**, 2300, 2306, 2310 (1955).

(5) R. M. Keefer and L. J. Andrews, *ibid.*, **78**, 3657 (1956).

(6) N. Ogimachi, L. J. Andrews and R. M. Keefer, *ibid.*, **77**, 4202 (1955).

(7) R. M. Keefer, A. Ottenberg and L. J. Andrews, *ibid.*, **78**, 255 (1956).

(8) W. J. Jones, *J. Chem. Soc.*, **99**, 392 (1911).

the medium. These facts can be explained on the assumption that bromination is inhibited by hydrogen bromide which forms during the course of the reaction.

This inhibition cannot result from the trapping out of bromine as unreactive HBr_3. Spectrophotometric studies (see Experimental section) show that in the presence of excess zinc chloride, hydrogen bromide does not interact with bromine in acetic acid. Rather, the hydrogen bromide appears to interact with the salt, probably to form the acid $HZnCl_2Br$.

The hydrogen bromide effect on the reaction rate can be explained satisfactorily in terms of the mechanism suggested in equations[9] 2 and 3. If it is assumed

$$\mathrm{ArH} + \mathrm{Br_2} + \mathrm{ZnCl_2{\cdot}HOAc} \underset{k_2}{\overset{k_1}{\rightleftarrows}} \mathrm{ArHBr^{+}OAc^{-}} + \mathrm{H^{+}ZnCl_2Br^{-}} \quad (2)$$

$$\mathrm{ArHBr^{+}OAc^{-}} \xrightarrow{k_3} \mathrm{ArBr} + \mathrm{HOAc} \quad (3)$$

sumed that a steady-state concentration of $ArHBr^+OAc^-$ is maintained during the course of the runs, it follows from equations 1–3 that

$$\frac{1}{k} = \frac{(\mathrm{ArH})(\mathrm{Br_2})}{R} = \frac{1}{k_a} + \frac{(\mathrm{HZnCl_2Br})}{k_b} \quad (4)$$

where $k_a = k_1\,(\mathrm{ZnCl_2{\cdot}HOAc})$ and $k_b = k_1k_3\,(\mathrm{ZnCl_2{\cdot}HOAc})/k_2$.

The kinetic data for the bromination of toluene at several different zinc chloride concentrations have been shown, as illustrated in Fig. 1, to conform to equation 4. Plots of values of $1/k$ against the corresponding hydrogen bromide concentrations are linear. It has been assumed in making these plots that the concentration of $HZnCl_2Br$ in the reaction mixtures is equal to the concentration of hydrogen bromide (as produced by the bromination reaction). The values of R, required to calculate $1/k$, were determined from the slopes of plots of bromine concentration *versus* time for each of the runs.

The data for runs in 0.25 *M* zinc chloride solution at several different initial concentrations of toluene and bromine are all nicely accommodated by a single line in Fig. 1. Values of k_a for toluene (the reciprocals of the ordinate intercepts—Fig. 1) vary three- to fourfold with a twofold change in zinc chloride concentration. This large change probably results from a salt effect, peculiar to runs at relatively high zinc chloride concentrations, which is superimposed on a reaction which is first order in zinc chloride.

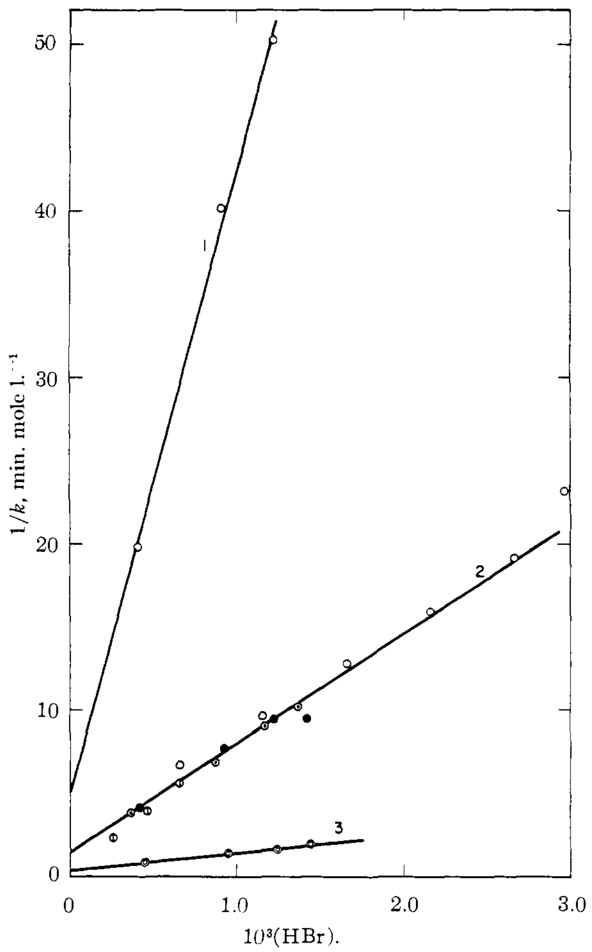

Fig. 1.—The effect of hydrogen bromide on the rate of bromination of toluene in the presence of a zinc chloride catalyst at 25.4°. The initial molar concentrations of bromine, toluene and zinc chloride are, respectively, (1) 1.86×10^{-3}, 0.0943, 0.500; (2) 0.90×10^{-5} to 3.60×10^{-3}, 0.0476 to 0.0943, 0.250; (3) 1.86×10^{-3}, 0.0943, 0.125. In line 2 the various types of circles differentiate runs at different initial bromine concentrations.

Mesitylene is a sufficiently reactive hydrocarbon so that its bromination rate could conveniently be studied using low (10^{-2}–10^{-3} *M*) concentrations of zinc chloride. Under these conditions k_a values appear to vary directly with the *free* zinc chloride concentration of the medium. In runs on this hydrocarbon in which the initial zinc chloride and bromine concentrations were about 0.03 and 2×10^{-3} *M*, respectively, values of k remained relatively constant throughout the reactions. In other words the reverse reaction of equation 2 is unimportant for this hydrocarbon. In runs on mesitylene in which the initial concentrations of the salt and the halogen were of the order of magnitude of 10^{-3} *M*, k values again diminished during the reaction. Presumably this decrease occurred because appreciable quantities of the catalyst were converted to $HZnCl_2Br$ (which is not a bromination catalyst) as hydrogen bromide accumulated in the medium. However, these reactions continued at an appreciable rate even when the hydrogen bromide concentration of the medium exceeded that of the salt. Therefore, the assumption that the interaction of the hydrogen halide and the salt is quantitative is not sufficiently precise for the interpretation of runs at high zinc chloride dilution

---

(9) The exact formulas for the various reactants and intermediates in equations 2 and 3 are uncertain. The idea that a reactive intermediate is formed from a molecule each of bromine, hydrocarbon and zinc chloride by a process which is reversible may be expressed in several alternate ways. An improbable termolecular collision may be avoided in equation 2 by showing zinc chloride or the aromatic hydrocarbon in coördination with bromine. In this case the definitions of k_a and k_b (see equation 4) must be modified to include the equilibrium constant for the coördination reaction. Zinc chloride has been written in solvated form, since in this fashion the rate inhibition by $HZnCl_2Br$ is explained without making the unlikely assumption that free ions are formed as reaction intermediates; *cf.* S. Bruckenstein and I. M. Kolthoff, THIS JOURNAL, **78**, 1 (1956).

(10^{-2}–10^{-3} *M*). In analyzing data from runs in which zinc chloride concentrations ranged between 0.03 and 10^{-3} *M* an equilibrium constant of 500 for formation of $HZnCl_2Br$ (equation 5) was used to

$$K = (HZnCl_2Br)/(ZnCl_2)(HBr) \qquad (5)$$

calculate the concentration of free zinc chloride $(ZnCl_2)_f$ at various stages of the runs. Values of $k/(ZnCl_2)_f$ thus obtained remained relatively constant throughout individual runs and were independent of the initial zinc chloride concentrations of the reaction mixtures. Two of these runs are interpreted in this way in Table II.[10]

The kinetic data for all of the aromatic hydrocarbons which were investigated at zinc chloride concentrations of 0.0312 *M* or higher were treated satisfactorily by equations 1–4 as described in detail for the runs with toluene. The k_a and k_b/k_a values calculated for these hydrocarbons are listed in Table III.

TABLE II

THE BROMINATION OF MESITYLENE IN DILUTE SOLUTIONS OF ZINC CHLORIDE IN ACETIC ACID (25.4°)[a,b]

Run 1
$(ArH)_i = 0.0225$ *M*
$(Br_2)_i = 2.16 \times 10^{-3}$ *M*
$(ZnCl_2)_i = 0.03125$ *M*

Run 2
$(ArH)_i = 0.184$ *M*
$(Br_2)_i = 1.85 \times 10^{-3}$ *M*
$(ZnCl_2)_i = 1.00 \times 10^{-3}$ *M*

$(HBr)_T \times 10^3$, mole/l.	$(ZnCl_2)_f \times 10^3$, mole/l.	$k/(ZnCl_2)_f$, mole^{-2} l.^{2} sec.$^{-1}$	$(HBr)_T \times 10^3$, mole/l.	$(ZnCl_2)_f \times 10^3$, mole/l.	$k/(ZnCl_2)_f$, mole^{-2} l.^{2} sec.$^{-1}$
0.96	30.3	15.5	0.36	0.89	14.8
1.16	30.1	15.8	0.86	.76	15.5
1.36	30.0	16.1	1.16	.70	14.4
1.56	29.8	16.4	1.36	.65	14.2
1.76	29.6	15.5			

[a] The reported values of $(HBr)_T$ include both free hydrogen bromide and $HZnCl_2Br$. [b] Other runs at initial zinc chloride concentrations of 3.125×10^{-3} *M*, 6.25×10^{-3} *M* and 1.25×10^{-3} *M* gave values of $k/(ZnCl_2)_f$ which averaged about 14.0.

The slopes of the plots of $1/k$ *versus* hydrogen bromide concentration were measured to obtain $1/k_b$. The k_b/k_a values are of no immediate theoretical use, since they represent ratios of the constants k_3 and k_2 for the reactions of the intermediate $ArHBr^+$ OAc^- to form, respectively, the aromatic bromide and the starting materials. They are included to demonstrate that the influence of the back reaction (with rate constant k_2) on the total reaction rate becomes less important as the hydrocarbon becomes more reactive.

TABLE III

RATE CONSTANTS FOR THE ZINC CHLORIDE CATALYZED BROMINATIONS AT 25.4°

Aromatic	Molar concn. ArH	Molar concn. $ZnCl_2$	10^2 k_a, mole^{-1} l. sec.$^{-1}$	10^3 k_b/k_a, mole^{-1} l.
Benzene	0.095	0.500	0.022	0.50
Toluene	.094	.500	4.2	.38
	.094, 0.047	.250	1.38	.18
	.094	.125	0.35	.13
o-Xylene	.097	.500	21.4	.47
	.097	.250	11.8	.14
m-Xylene	.094	.125	10.2	1.05
	.094	.0625	3.02	1.01
	.094	.0312	0.64	1.91
p-Xylene	.096	.500	10.3	1.20
	.096, 0.043	.250	4.7	0.29
	.096	.125	1.43	.17
Pseudocumene	.093	.125	18.7	1.68
	.093	.0625	5.95	1.71
Mesitylene	.023	.0312	55.5	7.15
	.045	.0125	17.2	13.9
Durene	.075	.0625	24.2	0.70
	.075, 0.038	.0312	6.7	.80
Isodurene	.074	.0312	123	5.9
Pentamethylbenzene	.011	.0312	235	8.2
Ethylbenzene	.094	.500	3.5	0.46
	.094, 0.044	.250	1.38	.14
	.094	.125	0.32	.10
Isopropylbenzene	.094	.500	2.04	.47
	.094, 0.047	.250	0.83	.15
	.094	.125	0.208	.10
t-Butylbenzene	.095	.500	2.84	.31
	.095	.250	0.67	.18
p-Di-*t*-butylbenzene	.080	.500	1.97	.46
sym-Tri-*t*-butylbenzene	.066	.500	0.17	.56
sym-Triethylbenzene	.023	.0312	19.4	4.7
	.045	.0125	6.3	5.8

The Partial Rate Factors.—Because of the wide variation in reactivity of the methylbenzenes, it was not feasible to compare their bromination rates at some fixed catalyst concentration. This is unfortunate since the reactions do not show any simple order with respect to zinc chloride over the range of salt concentrations at which measurements can be made easily (see Table III). In the procedure finally chosen for comparing rate data the k_a values of *p*-xylene were taken as points of reference. Insofar as data were available at the same zinc chloride concentrations, the ratios k_a(ArH)/k_a(*p*-xylene) were calculated for each hydrocarbon (ArH). For the more reactive hydrocarbons rate measurements were made only at 0.03125 *M* zinc chloride, and for *p*-xylene no runs were made at less than 0.125 *M* zinc chloride. These figures, however, represent the extremes of the range of zinc chloride concentrations over which runs with *m*-xylene were made. For the more reactive hydrocarbons values of $k_{a(ArH)}/k_{a(p\text{-xylene})}$ were calculated from ratios of $k_{a(ArH)}/k_{a(m\text{-xylene})}$ at 0.03125 *M* zinc chloride and of $k_{a(m\text{-xylene})}/k_{a(p\text{-xylene})}$ at 0.125 *M* zinc chloride using the assumption that the ratios are independent of the salt concentration at which they are measured. This assumption is undoubtedly not exactly correct. The ratios $k_{a(\text{ethylbenzene})}/k_{a(p\text{-xylene})}$ are, for example, 0.34, 0.30 and 0.22, respectively, at zinc chloride concentrations of 0.50, 0.25 and 0.125 *M*, and the ratios $k_{a(o\text{-xylene})}/k_{a(p\text{-xylene})}$ at 0.50 and 0.250 *M* salt concentration are 2.1 and 2.5. The resultant values of $k_{a(ArH)}/k_{a(p\text{-xylene})}$ obtained in this way constitute measures of the k_1 values of the various hydrocarbons relative to that of *p*-xylene. The relative rates of bro-

---

[10] In the preliminary studies of the zinc chloride-catalyzed bromination of mesitylene, the hydrogen bromide effect on the rates of reaction at low concentrations of zinc chloride was not detected.[7] Rather the drop in *k* values during the course of the individual runs was attributed to a small contribution of a second order reaction in bromine to the over-all rate. However, the activation energy reported earlier for the reaction which is first order in bromine and in zinc chloride is correct, since it was calculated from the ratio of instantaneous rates at two different temperatures of reaction mixtures which were identical in composition.

mination of the various methylbenzenes, which were determined experimentally, are summarized in Column I of Table IV in terms of values of $k_{a(ArH)}/k_{a(benzene)}$.

The relative k_a values for the three isomeric xylenes have been used, as described elsewhere,[4] to estimate the rates of bromination at positions *ortho*, *meta* and *para* to a methyl group relative to that at one position in benzene. This calculation involves the solution of three simultaneous equations which have two sets of solutions. One improbable solution indicates higher substitution rate at *meta* than at *ortho* and *para* positions. The other solution indicates partial rate factors, o_f, m_f and p_f, of 50, 14.5 and 180, respectively. These values were used to calculate the theoretical rates of bromination of the polymethylbenzenes which appear in column II of Table IV. A second set of partial rate factors was calculated from the relative k_a values for mesitylene, durene and pentamethylbenzene ($o'_f = 87, m'_f = 3.5, p'_f = 79$). The theoretical bromination rates which appear in column III, Table II, were calculated using these values.

TABLE IV

THE RELATIVE k_a VALUES FOR THE AROMATIC HYDROCARBONS (25.4°)[a]

Aromatic	$k_{a(ArH)}/k_a$ (benzene) I	II	III
Benzene	1	....	....
Toluene	148	52	43
o-Xylene	1,100	1,110	194
m-Xylene	3,400	3,450	3,550
p-Xylene	480	480	200
Pseudocumene	6,400	29,600	8,600
Mesitylene	300,000	225,000	300,000
Durene	31,000	175,000	31,000
Isodurene	650,000	2,200,000	700,000
Pentamethylbenzene	1,240,000	16,000,000	1,220,000

[a] Column I reports experimental values. Columns II and III report calculated values derived, respectively, from o_f = 50, m_f = 14.5 and p_f = 180 and from o'_f = 87, m'_f = 3.5 and p'_f = 79.

The agreement between experimental and calculated relative rates for the series of polymethylbenzenes is generally better if the comparison is based on the partial rate factors derived from the kinetic data for the more highly alkylated benzenes rather than on those for the xylenes. The major difference between the two sets of partial rate factors lies in the magnitudes of the values for positions *meta* and *para* to methyl groups. Those derived from the data for mesitylene, durene and pentamethylbenzene are considerably less than those based on the rates of reaction of the xylenes. The *ortho* partial rate factors are less sensitive to their origins. It is noteworthy that in the more highly alkylated benzenes there are, in general, few if any positions open for substitution which are not adjacent to at least one ring carbon which carries a methyl substituent. It is probable that substitution at such a position is subject to steric hindrance which partially nullifies the favorable electronic effects of methyl groups which are *meta* and *para* as well as of those which are *ortho* to this position. Unlike the *meta* and *para* partial rate factors the *ortho* partial rate factors for any methylbenzene are subject to these steric effects. It is not surprising, therefore, that calculated values of o_f and o'_f are in closer agreement than are m_f and m'_f and p_f and p'_f.[11]

To correlate the relative rates of mercuration of the methylbenzenes it has been necessary to assume that o_f for a position flanked by two methyl groups is less than that for a position adjacent to only one methyl substituted ring carbon.[4] No such flanking effects are apparent in the results of the present work on the methylbenzenes, although such effects undoubtedly are of major importance in controlling the reactivity of the poly-*t*-butylbenzenes. These compounds, as would be expected,[12] brominate very slowly (see Table III). Like ethylbenzene and isopropylbenzene, *t*-butylbenzene brominates at a rate which is only slightly less than that of toluene. Indeed it is somewhat more reactive than ethylbenzene, a fact which suggests that the *t*-butyl group may actually activate *meta* and *para* positions more than do the less branched alkyl groups. This activating effect is, of course, counteracted sterically when ring carbons adjacent to these *meta* and *para* positions also carry *t*-butyl substituents.

In bromination of the methylbenzenes in the presence of zinc chloride activation at positions *meta* to methyl groups, relative to that at *ortho* and *para* positions, is greater than that reported for halogenations in the absence of a catalyst.[1] This fact would seem to support the prediction that a catalyst which serves to enhance the electrophilic activity of an aromatic substituting agent should facilitate reaction at *meta* positions.[13] However, for reasons outlined in the Introduction, some caution should be exercised in using the older halogenation data for more than qualitative speculation.

Acknowledgment.—The authors are indebted to the National Science Foundation for a grant in support of this research.

DAVIS, CALIFORNIA

---

(11) Even the values of m_f and p_f calculated from the xylene rate data are not entirely free of steric influences of methyl groups. It is probably for this reason that these partial rate factors lead to a predicted k_a value for toluene which is considerably lower than that observed experimentally.

(12) P. D. Bartlett, M. Roha and R. M. Stiles, THIS JOURNAL, **76**, 2349 (1954).

(13) H. C. Brown and K. L. Nelson, *ibid.*, **75**, 6292 (1953).