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Aromatic Substitution. XVII.[1] Ferric Chloride and Aluminum Chloride Catalyzed Chlorination of Benzene, Alkylbenzenes, and Halobenzenes

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The ferric and aluminum chloride catalyzed chlorination of benzene and alkylbenzenes in nitromethane and excess aromatic solution at 25° was investigated. Relative reactivities and isomer distributions were determined in competitive experiments by gas–liquid chromatography and infrared spectroscopy. Low to intermediate substrate selectivities but at the same time high positional selectivity were obtained, giving *m*-isomers in amounts of less than 3%. The relative reactivities show better agreement with π-complex than with σ-complex stabilities of the same substrates. The chlorinations are somewhat more substrate selective than related brominations. Chlorination of benzene-d_6 shows a small secondary, reverse kinetic isotope effect. The mechanism of the investigated chlorinations is discussed.

The present status of the electrophilic chlorination of benzene and alkylbenzenes has been recently reviewed.[2] The kinetics and mechanism of electrophilic aromatic chlorinations, using either molecular chlorine or sources of "positive" chlorine in aqueous or organic solvent systems (ethylene dichloride, diethyl ether, acetic acid, acetonitrile, nitromethane, trifluoroacetic acid, etc.) has been investigated by Andrews and Keefer, Berliner, Brown, De la Mare, Mason, Robertson, Stock, and others.[3a–l]

Lebedev and his co-workers investigated the effect of different acidic halide catalysts ($AlCl_3$, $FeCl_3$, $ZrCl_4$, $SnCl_4$, and I_2) on the relative reactivities of toluene and benzene,[4] using excess aromatics as solvent. The $k_{toluene}:k_{benzene}$ relative rates obtained in competitive experiments showed low substrate selectivity in the case of $AlCl_3$ (3.5) and $FeCl_3$ (6.4), but could have been influenced by the heterogeneous nature of the reaction mixtures (see subsequent discussion in present work).

The rates of chlorination of benzene and alkylbenzenes with molecular chlorine in acetic acid solution, according to data of Brown and Stock,[5] are shown in Table I.

TABLE I

CHLORINATION OF BENZENE AND ALKYLBENZENES WITH MOLECULAR CHLORINE IN ACETIC ACID SOLUTION AT 25°[3d,4]

	$k_{Ar}:k_{benzene}$	*ortho*, %	*meta*, %	*para*, %
Benzene	1.0			
Toluene	344	59.8	0.5	39.7
t-Butylbenzene	110	21.8	2.1	76.1
o-Xylene	2,100			
m-Xylene	18,500	23, 2-chloro-*m*-xylene		
p-Xylene	2,080	77, 4-chloro-*m*-xylene		
Mesitylene	15,600,000 (calcd.)			

The effect of solvents as nitromethane, nitrobenzene, acetonitrile, acetic anhydride, and chlorobenzene on rates of chlorination of toluene (as well as benzene and other alkylbenzenes) with molecular chlorine was recently demonstrated by Stock and Himoe.[6]

All these chlorinations show high substrate selectivity. For example, from data of Stock the relative reactivity of toluene over benzene in molecular chlorination in nitromethane solution at 25° can be calculated to be $k_{toluene}:k_{benzene} = 2445$.

The activated state for electrophilic chlorination of aromatics is generally presumed to be an aggregate of molecules of the aromatic compound, the halogen, and an additional compound.[3a] The primary function of this additional substance is to assist rupture of the bond between the two atoms of the chlorine molecule. In a medium of low polarity, such as carbon tetrachloride, the halogen itself or hydrogen halide may serve as the third member of the aggregate. When alternatively a polar medium is used, the solvent itself may serve as a third component of the activated complex.

Robertson, De la Mare, and Swedlund[7] have discussed implications of the rate data for the mechanism of electrophilic chlorination. They suggested that chlorine reacts directly in molecular form, the rate-determining step being the formation of an intermediate with the aromatics ($ArH{\cdot}Cl_2$).

The final proton elimination is extremely rapid.

In all chlorinations with molecular chlorine the effective chlorinating agent is only slightly polarized and therefore only a weak electrophile. In order to obtain satisfactory comparison of electrophilic chlorination with other electrophilic aromatic substitutions, as nitration or alkylation, it is desirable to choose a reagent which indeed does react as a positive entity. In this way differences resulting from polar influences of the media can be minimized. It was suggested by De la Mare and co-workers that chlorination using acidified hypochlorous acid could fulfill this condition,[8] since under these circumstances the effective reagent can be shown to be either the chloronium ion Cl^+ or the corresponding hydrated form $ClOH_2^+$.[9]

The acid-catalyzed chlorination of toluene by hypochlorous acid in water was found by De la Mare and co-workers[31] to be 60 times faster than that of benzene and gives 74.6% *o*-, 2.2% *m*-, and 23.2% *p*-chlorotoluene.

Few quantitative studies of the electrophilic chlorination reactions of halobenzenes have been reported. The chlorination in 80% acetic acid was investigated by De la Mare and Robertson,[10] which provided the

(1) Part XVI: *J. Am. Chem. Soc.*, **86**, 1046 (1964).

(2) P. B. D. De la Mare and J. H. Ridd, "Aromatic Substitution," Academic Press, Inc., New York, N. Y., 1959.

(3) For pertinent discussions see: (a) L. J. Andrews and R. M. Keefer, *J. Am. Chem. Soc.*, **81**, 1063 (1959); (b) S. F. Mason, *J. Chem. Soc.*, 1233 (1959); (c) P. W. Robertson, *ibid.*, 1267 (1954); (d) L. M. Stock and H. C. Brown, *J. Am. Chem. Soc.*, **81**, 5615 (1959); (e) R. M. Keefer, A. Ottenberg, and L. J. Andrews, *ibid.*, **78**, 255 (1956); (f) E. Berliner and M. C. Beckett, *ibid.*, **79**, 1452 (1957); (g) R. M. Keefer and L. J. Andrews, *ibid.*, **82**, 4547 (1960); (h) P. B. D. De la Mare and P. W. Robertson, *J. Chem. Soc.*, 279 (1943); (i) E. Berliner and F. J. Bondhus, *J. Am. Chem. Soc.*, **68**, 2355 (1946); **70**, 854 (1948); (j) P. W. Robertson, P. B. D. De la Mare, and B. E. Swedlund, *J. Chem. Soc.*, 782 (1953), (k) P. B. D. De la Mare and J. T. Harvey, *ibid.*, 36 (1956); 131 (1957); (l) P. B. D. De la Mare, J. T. Harvey, M. Hasson, and S. Varma, *ibid.*, 2756 (1958).

(4) N. N. Lebedev, I. I. Baltadzhi, and V. Kozlov, *Zh. Vsesoyuz. Khim. Obschchestva im. D.I. Mendeleeva*, **5**, 236 (1960); *Chem. Abstr.*, **54**, 18048 (1960).

(5) H. C. Brown and L. M. Stock, *J. Am. Chem. Soc.*, **79**, 5175 (1957).

(6) L. M. Stock and A. Himoe, *ibid.*, **83**, 1937, 4605 (1961).

(7) P. W. Robertson, P. B. D. De la Mare, and B. E. Swedlund, *J. Chem. Soc.*, 782 (1953).

(8) P. B. D. De la Mare in "Progress in Stereochemistry," Vol. 2, Klyne and De la Mare, Ed., Butterworth, London, 1958, p. 65.

(9) (a) E. A. Shilov and N. P. Kaniev, *Compt. rend. Acad. Sci. U.S.S.R.*, **24**, 890 (1939); (b) A. E. Derbyshire and W. A. Waters, *J. Chem. Soc.*, 73 (1951); (c) P. B. D. De la Mare, E. D. Hughes, and C. A. Vernon, *Research* (London), **3**, 192 (1950).

(10) P. B. D. De la Mare and P. W. Robertson, *J. Chem. Soc.*, 100 (1948).

relative chlorination rates of benzene and halobenzenes; benzene, 1.0; fluorobenzene, 1.2; chlorobenzene, 0.11; and bromobenzene, 0.08.

The isomer distributions of the chlorohalobenzenes formed were not given, although in later work De la Mare mentioned that the composition of fluorochlorobenzenes was 10% *ortho* and 90% *para*.[11]

One of us investigated previously[12] the electrophilic chlorination of fluorobenzene and found the isomer distribution: 16% *ortho* and 84% *para* (analysis based on ultraviolet spectra). The relative rates observed were (benzene, 1.0): fluorobenzene, 1.30; chlorobenzene, 0.31; bromobenzene, 0.15.[13]

Stock and Baker[14] published recently their observations relating the noncatalytic chlorination of halobenzenes in aqueous acetic acid. In acetic acid containing 20.8 *M* water at 1.70 *M* hydrogen chloride (about 60% acetic acid by volume) at 25° they obtained the relative rates: benzene, 1.0; fluorobenzene, 0.74; chlorobenzene, 0.10; and bromobenzene, 0.07. No *m*-isomers were found to be formed in any of the chlorinations.

Results and Discussion

Electrophilic chlorination of aromatics with molecular chlorine even in polar solvents can be considered only to involve a weak electrophilic substitution agent and therefore shows high substrate selectivity. The only kinetic investigation of an electrophilic aromatic chlorination involving a strong electrophile, believed to be Cl^+ or its hydrated form $ClOH_2^+$, was carried out by De la Mare in aqueous medium.[31] Consequently this system could correspond very much to an aqueous mixed acid nitration system, which in previous investigations was found to show substantially higher substrate selectivity than the corresponding anhydrous systems involving substantial concentrations of the effective electrophile (NO_2^+).[15]

It was felt useful in continuation of related work on bromination[16] to extend our investigation to the chlorination of benzene, alkylbenzenes, and halobenzenes in nonaqueous solution in the presence of strong Lewis acid catalysts.

(a) **Alkylbenzenes.**—The aluminum and ferric chloride-catalyzed competitive chlorinations of benzene and alkylbenzenes were investigated at 25° in either nitromethane solutions, or with the soluble $AlCl_3 \cdot CH_3NO_2$ catalyst in excess aromatics as solvent. Because in the case of chlorination of aromatics no σ-complex formation with the product is observed, it was possible to use homogeneous aromatic solutions of ferric chloride without added solvent. Data obtained are summarized in Tables II, III, and IV.

Owing to the higher reactivities of *m*-xylene and mesitylene, relative rates in these cases were determined from competitive experiments with toluene and *p*-xylene, respectively.

No evidence of the formation of di- or higher chlorinated products was observed in any of the investigated chlorinations in the limitations of the used analytical methods (based on gas–liquid chromatographic analyses, mass spectroscopic, and infrared investigations of the systems). There was also no indication of any side-chain or ring addition chlorination.

(11) P. B. D. De la Mare, *J. Chem. Soc.*, 4450 (1954).

(12) G. Olah, A. Pavlath, and G. Varsanyi, *ibid.*, 1823 (1957).

(13) G. Olah, A. Pavlath, S. Kuhn, and G. Varsanyi in "Elektronentheorie der homeopolaren Bindung," Akademie Verlag, Berlin, 1956, pp. 79–97.

(14) L. M. Stock and F. W. Baker, *J. Am. Chem. Soc.*, **84**, 1661 (1962).

(15) G. A. Olah, S. J. Kuhn, S. H. Flood, and J. C. Evans, *ibid.*, **84**, 3687 (1962).

(16) G. A. Olah, S. J. Kuhn, S. H. Flood, and B. A. Hardie, **86**, 1039 (1964).

TABLE II

$FeCl_3$ CATALYZED CHLORINATION OF BENZENE AND ALKYLBENZENES IN NITROMETHANE AT 25°

Aromatic	$k_{Ar}:k_{benzene}$	Chloroalkylbenzenes, % *ortho*	*meta*	*para*
Benzene	1.0			
Toluene	13.5	67.8	2.3	29.9
Ethylbenzene	11.9	55.9	2.5	41.5
o-Xylene	38.0	56.1, 4-chloro-*o*-xylene; 3-chloro-*o*-xylene		43.9,
m-Xylene	110.0	71.5, 4-chloro-*m*-xylene;		28.5,
p-Xylene	43.9	2-chloro-*m*-xylene		
Mesitylene	(632)[a]			

[a] Value probably influenced by fast, noncatalytic chlorination in solvent.

TABLE III

$AlCl_3 \cdot CH_3NO_2$ CATALYZED CHLORINATION OF BENZENE AND ALKYLBENZENES IN EXCESS AROMATIC SOLUTIONS AT 25°

Aromatic	$k_{Ar}:k_{benzene}$	Chloroalkylbenzenes, % *ortho*	*meta*	*para*
Benzene	1.0			
Toluene	18.3	63.2	2.0	34.8
Ethylbenzene	17.4			
o-Xylene	69.6	56.1, 4-chloro-*o*-xylene; 3-chloro-*o*-xylene		43.9,
m-Xylene	201.3	23.0, 2-chloro-*m*-xylene;		77,
p-Xylene	73.2	4-chloro-*m*-xylene		
Mesitylene	(1875)[a]			

[a] Value probably influenced by fast, noncatalytic chlorination.

TABLE IV

$FeCl_3$ CATALYZED CHLORINATION OF BENZENE AND ALKYLBENZENES IN EXCESS AROMATICS AT 25°

Aromatic	$k_{Ar}:k_{benzene}$	Chloroalkylbenzenes, % *ortho*	*meta*	*para*
Benzene	1.0			
Toluene	14.8	63.0	2.2	34.8
Ethylbenzene	13.0	55.3	2.6	42.1
o-Xylene	62.4	58.9, 4-chloro-*o*-xylene; 3-chloro-*o*-xylene		41.1,
m-Xylene	177.3	25.1, 2-chloro-*o*-xylene;		74.9
p-Xylene	74.0	4-chloro-*m*-xylene		
Mesitylene	(920)[a]			

[a] Value probably influenced by fast, noncatalytic chlorination.

As molecular chlorine in nitromethane solution is capable of effecting chlorination by a high selectivity, but low activity reaction, the observed higher substrate selectivities, at least in the case of the highly reactive *m*-xylene and mesitylene, could be partially effected by the noncatalytic or solvent-promoted chlorination. However, with exception of very reactive aromatics, this reaction is substantially slower than the Lewis acid-catalyzed chlorinations.

To obtain information on the nitromethane-promoted noncatalytic chlorination of *m*-xylene and mesitylene, we extended Stock and Himoe's previous investigations of the nitromethane promoted chlorination of benzene and toluene to these hydrocarbons. Chlorinations were carried out at 25° and in the dark, using the competitive method of relative rate determination to establish relative reactivities. Data obtained are summarized in Table V.

The high reactivities of *m*-xylene and mesitylene support the suggestion that with these reactive aromatics the solvent effect in catalytic chlorinations can be more significant than with less reactive hydrocarbons.

In order to minimize solvent-promoted chlorination and to achieve a high conversion based on chlorine introduced, it was necessary in the $FeCl_3$ catalyzed reactions in nitromethane solution to use a 1:1 catalyst: chlorine mole ratio (similarly to the previously in-

TABLE V

RELATIVE RATES OF SOLVENT-PROMOTED CHLORINATION OF BENZENE AND ALKYLBENZENES IN NITROMETHANE SOLUTION AT 25°

Aromatic	$k_{Ar}:k_{benzene}$	Ref.
Benzene	1.0	
Toluene	2,445	6
p-Xylene	14,200	6
m-Xylene	247,000[a]	Present work
Mesitylene	~5,000,000[b]	Present work

[a] From competition of *m*-xylene–toluene. [b] From competition of mesitylene–*m*-xylene.

vestigated related brominations[16]). In chlorinations using only excess of aromatics as solvent a much lower catalyst concentration was sufficient to achieve similar results.

All the chlorination systems investigated were strictly homogeneous. It is necessary to stress the importance of the homogeneity of the reaction systems because it was found that if even the smallest amount of unsolved catalyst was left in the systems (which consequently always were carefully filtered from even traces of solid acidic halides) the substrate selectivities and also isomer distributions showed irreproducible changes, indicating that at least to a certain degree the reactions (including secondary isomerizations) were taking place on the solid catalyst surface.

Competitive chlorination of toluene and benzene in the presence of acidic halide catalysts when the reaction mixture was not entirely homogeneous (due to unsolved catalyst, $FeCl_3$) gave generally low $k_T:k_B$ values ($FeCl_3$ 4.9, $GaCl_3$ 7.5). These values are similar to those reported by Lebedev and co-workers[4] but cannot, in our opinion, be considered significant, because in heterogeneous systems many factors can influence the relative rate values (and isomer distributions).

Competitive chlorinations of all alkylbenzenes were carried out against benzene, with the exception of *m*-xylene and mesitylene, which were run against toluene as reference substance (the substantially higher alkylbenzene:benzene ratios would otherwise in these systems cause significant errors) and recalculated from the knowledge of the toluene–benzene rate against benzene.

The competitive method of rate determination, suited otherwise to follow fast reactions (such as the present chlorination), can be applied only if the reactivities are dependent on the aromatic substrates.

In order to establish whether the present system indeed involves competition and does not proceed through statistical distribution, concentration variation of toluene and benzene was investigated in a fairly wide range in competitive chlorination experiments at 25°. If the reactions involve competition between substrate molecules, then the relative rates should change according to concentration ratios (taking for granted that the reactions are first order in aromatics). However, if the fast reactions are only statistically regulated, then the relative rates should be directly proportional only to the concentrations (with some possible variation due to mixing or diffusion differences due to imperfectness to achieve theoretical mixing of reagents before reaction). Table VI shows the data obtained from the concentration variation of toluene and benzene, the ratio varying from 9:1 to 1:9, a range considered sufficient to evaluate the system.

From the data of Table VI the conclusion can be drawn that the chlorinations are indeed first order in the aromatic substrates, and thus competitive rate determination can be used to establish the relative reactivities of benzene and alkylbenzenes for the

TABLE VI

FIRST-ORDER DEPENDENCE IN AROMATICS OF THE $FeCl_3$ CATALYZED CHLORINATION OF TOLUENE AND BENZENE IN NITROMETHANE SOLUTION AT 25°

Ratio of toluene:benzene		Obsd. rel. rate	$k_T:k_B$
1	9	1.3	11.7
1	5	2.1	10.5
1	3	3.9	11.7
1	1	12.5	12.5
3	1	38.7	12.9
5	1	67.0	13.4
9	1	129.0	14.3
		Average	12.4

halogenation reaction, even if limitations to the absolute accuracy of the method must be considered.

If the relative reactivities of benzene and alkylbenzenes are compared with the relative stabilities of known π-complexes of the same substrates, fair agreement is observed although the chlorinations show higher substrate selectivity than the previously investigated brominations. On the other hand, no close correlation seems to exist with HF + BF_3 complex stabilities (σ-complexes).

It is consequently suggested that chlorination systems involving a strong electrophile (incipient, if not necessarily free chloronium ion) in organic solvents (nitromethane or excess aromatics) show substrate reactivities of benzene and alkylbenzenes corresponding to π- and *not* σ-complex stabilities. These chlorinations therefore show significant differences from previously investigated molecular or "positive chlorine" chlorinations, carried out in aqueous acetic acid or dioxane solutions. In the latter solutions either a considerably more solvated, and therefore less electrophilic and more selective, halogenating agent is present, producing chlorinations more through a σ-complex type activated state or, more plausible, the chloronium species as such is perhaps not present, except in the form of a weaker precursor, which then interacts with the aromatics in a highly selective reaction.

The isomer distributions observed in this investigation suggest that they represent the nonisomerized isomer distributions obtained in kinetically controlled substitutions. The low amount of *m*-isomers produced substantiate this view, in accordance with previous investigations on the Friedel–Crafts isomerization of halotoluenes.[17]

Kinetic Isotope Effect.—In order to determine whether electrophilic aromatic chlorination of deuterated aromatics in these nonaqueous systems shows a kinetic isotope effect, the previously described competitive method of kinetic isotope effect determination was used.[18] Competitive chlorination of benzene and benzene-d_6 with Cl_2 + $FeCl_3$ in nitromethane solution could not be used, because mass-spectroscopic investigations have shown extensively hydrogen–deuterium exchange. Anhydrous $AgClO_4$ and Cl_2 in nitromethane produced only slight hydrogen exchange and could therefore be used for the determination of the kinetic isotope effect. At 25° a small secondary, reverse isotope effect, $k_H:k_D = 0.87 \pm 0.05$, was observed. The reasons for small secondary isotope effects in electrophilic aromatic substitutions have been discussed previously.[18,19] It is of some interest to note that the secondary kinetic isotope effect in these chlorination

(17) G. A. Olah and M. W. Meyer, *J. Org. Chem.*, **27**, 3464 (1962).

(18) G. A. Olah, S. J. Kuhn, and S. H. Flood, *J. Am. Chem. Soc.*, **83**, 4571 (1961).

(19) G. A. Olah, S. J. Kuhn, and S. H. Flood, *ibid.*, **84**, 1688 (1962).

is larger and its direction opposite to that observed in related brominations.

(b) **Halobenzenes.**—The ferric and aluminum chloride catalyzed competitive chlorination of benzene and halobenzenes in nitromethane and excess aromatic solutions, respectively, was carried out under conditions identical with those used for the chlorination of alkylbenzenes. Tables VII and VIII summarize data of the competitive chlorination of benzene and halobenzenes, together with the corresponding isomer distributions. (Analyses were carried out with gas–liquid chromatography, as described in the Experimental part.)

TABLE VII

COMPETITIVE CHLORINATION OF BENZENE AND HALOBENZENES WITH Cl_2 + $FeCl_3$ IN NITROMETHANE SOLUTION AT 25°

Aromatic	$k_{halobenzene}$: $k_{benzene}$	Chlorohalobenzene, % *ortho*	*meta*	*para*
Benzene	1.0			
Fluoro-	0.29	25.5	2.0	72.5
Chloro-	.17	42.5	3.1	54.4
Bromo-	.15	44.6	3.2	52.2

TABLE VIII

COMPETITIVE CHLORINATION OF BENZENE AND HALOBENZENES WITH Cl_2 + $AlCl_3 \cdot CH_3NO_2$ IN EXCESS AROMATIC SOLUTION AT 25°

Aromatic	$k_{halobenzene}$: $k_{benzene}$	Chlorohalobenzene, % *ortho*	*meta*	*para*
Benzene	1.0			
Fluoro-	0.34	24.9	2.4	72.7
Chloro-	.19	41.4	3.6	55.0
Bromo-	.15	43.7	3.0	53.3

The competitive method of relative rate determination could be again used conveniently, since the variation in concentration of benzene and chlorobenzene in competitive experiments at 25° showed first-order dependence of relative rates on aromatic substrates (Table IX).

TABLE IX

FIRST-ORDER DEPENDENCE OF THE Cl_2 + $FeCl_3 \cdot CH_3NO_2$ CHLORINATIONS IN AROMATICS

Ratio of fluorobenzene	benzene	Obsd. rel. rate	$k_F : k_B$
5	1	1.55	0.31
2	1	0.58	.29
1	1	.29	.29
1	2	.15	.30
1	5	.06	.30
		Average	0.30

The observed relative reactivities of halobenzene and benzene show good agreement with relative stabilities of complexes of halobenzenes with Ag^+, Br_2, I_2, ICl, SO_2, picric acid, tetracyanoethylene, HCl, and HF, which are considered to be π-complex-forming agents.

No data are available on σ-complex-forming ability of halobenzenes (HF + BF_3). It seems that under conditions where the alkylbenzenes give stable benzenonium ions, no similar complex formation takes place with halobenzenes.

The stabilities of the π-complexes do not vary greatly with the nature of the halogen substituents. Thus the relative reactivities observed in chlorinations in the present work show only small differences of the same order of magnitude for benzene and halobenzenes. (The halobenzenes take part with their π-sextet as donor entities in the rate-determining π-complex-forming step.) This order of reactivity of the aromatic substrates is different from that in reactions where relative stabilities of intermediate σ-complexes in individual positions are involved. These frequently show relative reactivities orders of magnitude different from that of an individual benzene position. It is suggested that the isomer distributions observed in these investigations represent the nonisomerized, kinetically controlled distributions.

The small amount of *m*-isomers produced substantiates this view, in accordance with investigations of the Friedel–Crafts isomerizations of dihalobenzenes.[20]

The greater the reactivity of an electrophilic substituting agent, generally the smaller its selectivity. This means low substrate selectivity with different aromatics, but not necessarily also a simultaneous change of the isomer distribution toward the statistical value (40% *ortho*, 40% *meta*, and 20% *para*) demonstrated by an increase in the concentration of the *m*-isomer.

The present competitive chlorinations showing low substrate selectivity of the halobenzenes gave at the same time isomer distributions of the monochloro products containing only a small amount (2–3%) of the *m*-isomers.

The electron distribution of the halobenzenes gives an explanation for the directing effect in chlorinations. The $-I > +T$ effect of the halogen substituents results in the region of the *o*-positions generally in some degree of compensation of the two opposed effects. As the inductive effect diminishes with distance, in the *p*-position the conjugative effect becomes predominant. This is best shown by comparing the *ortho*:*para* ratios of chlorohalobenzenes obtained in chlorination of halobenzenes (Table X), which gives a sequence opposed to the expected based on steric *ortho* effects, considering the radii of the halogen atoms.

TABLE X

COMPARISON OF ISOMER RATIOS IN CHLORINATION OF HALOBENZENES

Halobenzene	*ortho*:*para* ratio $FeCl_3$ catalyst	$AlCl_3$ catalyst
Fluoro-	0.35	0.34
Chloro-	.78	.75
Bromo-	.85	.82

The over-all effect can be further increased through polarization by the strong electrophilic reagent. The higher *o*-isomer values obtained in present chlorinations of halobenzenes, as compared with previous data for electrophilic chlorinations with molecular chlorine, can be explained by steric differences (the incipient Cl^+ ion being a smaller entity than Cl_2, both possibly solvated).

Conclusions

Electrophilic aromatic chlorinations using anhydrous conditions and a strong electrophile (which must apply to the system Cl_2 + $FeCl_3$ or Cl_2 + $AlCl_3 \cdot CH_3NO_2$), give low to intermediate substrate but high positional selectivity with benzene and alkylbenzenes. The amount of *m*-isomer formed is less than 3% in the chlorination of toluene and ethylbenzene. No 5-chloro-1,3-dimethylbenzene is formed in the similar chlorination of *m*-xylene. It is therefore suggested that this system represents a further example of electrophilic aromatic substitution of alkylbenzenes with strong electrophiles, showing low to intermediate substrate, but high positional selectivity in accordance with a mechanism involving an oriented π-complex type activated state in the rate-determining step.

When results of the present chlorination are compared with previously investigated related bromina-

(20) G. A. Olah, W. S. Tolgyesi, and R. E. A. Dear, *J. Org. Chem.*, **27**, 3449 (1962).

tions it is seen that chlorination shows higher substrate selectivity than bromination, whereas positional selectivities in both cases are comparably high. This observation substantiates previous suggestions that the bromonium ion, actual or incipient, is a stronger electrophile than the chloronium ion, actual or incipient. Bromination thus shows close similarity with nitration, benzylation, and isopropylation (all affected by strong electrophiles), whereas chlorination shows more resemblance to *t*-butylation, sulfonation, and acylations, (affected by weaker electrophiles).

Experimental

The purity of benzene, alkylbenzenes, and halobenzenes was the same as used in previous investigations. Anhydrous ferric chloride and aluminum chloride (purified, sublimed Fisher reagent) and chlorine (99.9%, The Dow Chemical Co.) were used without further purification.

Nitromethane was purified as described by Winstein and Smith.[21]

Competitive $FeCl_3$ Catalyzed Chlorination of Benzene and Alkylbenzenes in Nitromethane Solutions.—Benzene (0.25 mole), 0.25 mole of alkylbenzene, and 20 g. (0.13 mole) of $FeCl_3$ were dissolved in 50 g. of nitromethane. The reaction flask, fitted with thermometer, reflux condenser, and gas inlet tube, was placed into a constant temperature bath at 25 ± 0.1° and 0.05 mole of chlorine was introduced into the vigorously stirred mixture (generally in the course of 10 min.). The temperature of the mixture was kept at 25 ± 0.5° during the reaction. After the introduction of chlorine the reaction mixture was stirred for an additional 5 min., then washed with 200 ml. of 5% HCl–water solution, subsequently with 100 ml. of water, dried over $CaCl_2$, and analyzed by gas–liquid chromatography.

Competitive $AlCl_3 \cdot CH_3NO_2$ Catalyzed Chlorination of Benzene and Alkylbenzenes in Excess Aromatics.—$AlCl_3$ (0.05 mole) and 0.05 mole of CH_3NO_2 were dissolved in a mixture of 0.25 mole of benzene and 0.25 mole of alkylbenzene. The reaction flask was then placed into a constant temperature bath at 25 ± 0.1° and 0.05 mole of chlorine gas was introduced in 15 min., while the temperature of the rapidly stirred reaction mixture was kept at 25 ± 0.5°. After the addition of the chlorine was completed, the mixture was stirred for an additional 5 min., then washed with 200 ml. of ice–water, then with 200 ml. of water, dried over $CaCl_2$, and analyzed by gas–liquid chromatography.

Competitive $FeCl_3$ Catalyzed Chlorination of Benzene and Alkylbenzenes in Excess Aromatics.—$FeCl_3$ (1 g.) was added into a mixture of 0.25 mole of benzene and 0.25 mole of alkylbenzene. The mixture was stirred for 5 min., then the undissolved $FeCl_3$ was filtered off. The reaction flask was placed into a constant temperature bath at 25 ± 0.1° and 0.05 mole of chlorine gas was introduced in a 15-min. period while the temperature of the rapidly stirred mixture was kept at 25 ± 0.5°. After the addition of the chlorine, the reaction mixture was stirred for 5 min., then washed twice with 200 ml. of water, dried over $CaCl_2$, and analyzed by gas–liquid chromatography.

Competitive Noncatalytic Chlorination of Alkylbenzenes in Nitromethane Solution.—The competing alkylbenzenes, 0.25 mole each, were dissolved in 40 g. of nitromethane. The reaction flask was wrapped with aluminum foil, fitted with a thermometer, and placed in a constant temperature bath at 25°. Chlorine, 0.05 *M*, was dissolved in 40 g. of nitromethane and the chlorine solution was added dropwise to the vigorously stirred mixture of aromatics (generally in the course of about 10 min.). The temperature of the mixture was kept at 25 ± 1° during the reaction. After the addition of the chlorine solution, the reaction mixture was stirred for an additional 10 min., then washed twice with water, dried over $CaCl_2$, and analyzed by gas–liquid chromatography. Data obtained are summarized in Table V.

Competitive Chlorinations of Benzene and Halobenzenes with $FeCl_3$ Catalyst in Nitromethane Solution.—Competitive chlorinations were carried out by dissolving 0.125 mole (20 g.) of anhydrous ferric chloride in 50 g. of nitromethane and adding to this solution 0.25 mole each of benzene and the competing halobenzene. The reaction mixture was placed in a three-necked flask, equipped with a thermometer, reflux condenser, and gas inlet tube and kept in a constant temperature bath at 25 ± 0.1°.

Chlorine (0.05 mole, 3 g.) was then introduced into the stirred solution while keeping the temperature at 25 ± 0.5°. The reaction mixture was stirred for another 10 min. after the introduction of chlorine was completed. It was then washed with water, three times with a 100-ml. portion of 5% NaOH solution, and again with water. After drying over $CaCl_2$ the solutions were analyzed by gas–liquid chromatography.

(21) Method used in Department of Chemistry, University of California, Los Angeles, Calif.; see ref. 16.

As direct competition between benzene and chlorobenzene cannot be analyzed with the method used (chlorobenzene being also one of the products), the relative reactivity of chlorobenzene was established from competitive chlorination of chlorobenzene with bromobenzene.

In order to avoid difficulties in separation of chlorobenzene from chlorofluorobenzenes instead of the direct competition of fluorobenzene with benzene, the competition of chlorobenzene with fluorobenzene and bromobenzene with fluorobenzene were determined.

Competitive Chlorination of Benzene and Halobenzenes with $CH_3NO_2 \cdot AlCl_3$ Catalyst in Solution of Excess Aromatics.—$CH_3NO_2 \cdot AlCl_3$ (0.05 mole) was dissolved in a mixture of 0.25 mole of benzene and 0.25 mole of halobenzene. Thereafter 0.05 mole of Cl_2 gas was introduced during a period of 15 min. while the temperature of the rapidly stirred mixture was kept at 25 ± 0.5°. After the introduction of the chlorine, the reaction mixture was stirred for an additional 5 min., then washed, dried over $CaCl_2$, and analyzed by gas–liquid chromatography.

Determination of Kinetic Isotope Effect.—Benzene (0.1 mole), 0.1 mole of benzene-d_6, and 0.02 mole of $AgClO_4$ were dissolved in 50 g. of nitromethane. Chlorine (0.02 mole) was then introduced into the vigorously stirred solution. The temperature was kept at 25 ± 0.5° during the reaction. After the introduction of chlorine was completed the mixture was stirred for another 5 min. AgCl was then removed by filtration; the organic layer was washed twice with 50 ml. of water, dried over $CaCl_2$, and analyzed by mass spectroscopy.

Analyses of Reaction Mixtures.—All analyses were carried out by gas–liquid chromatography, carried out on a Perkin–Elmer Model 154-C vapor fractometer equipped with an electronic printing integrator. A 4-m. by 0.25 in. stainless steel column packed with polypropylene glycol (UCON LB 550-X) supported on diatomaceous earth was used. The column temperature was 150° for most analyses. Approximately 50 ml. of hydrogen per minute was used as carrier gas. Sample sizes injected were between 50 and 100 μl.

Relative response data were determined by running known solutions of the various alkylchlorobenzenes with chlorobenzene in excess benzene, in the approximate proportions as occurred in the reaction mixtures. Characteristic retentions of chloroalkylbenzenes and chlorohalobenzenes are given in Table XI.

TABLE XI

RETENTION TIMES OF CHLOROBENZENE, CHLOROALKYLBENZENES, AND CHLOROHALOBENZENES ON PACKED COLUMN AT 150°

Compound	Retention time, min.
Chlorobenzene	8
Chlorotoluenes	12
o-Chloroethylbenzene	17
p-Chloroethylbenzene	19
Chloro-*o*-xylenes	25
Chloro-*m*-xylenes	23
Chloro-*p*-xylene	19
Chloromesitylene	33
o-Chlorofluorobenzene	9
m-Chlorofluorobenzene	7
p-Chlorofluorobenzene	8
o-Chlorobromobenzene	16
m-Chlorobromobenzene	13
p-Chlorobromobenzene	14
o-Dichlorobenzene	22
m-Dichlorobenzene	17
p-Dichlorobenzene	19

The isomers of chloro-*m*- and -*o*-xylene did not separate on the packed column and were analyzed on a 150-ft. Golay capillary column, with a Perkin–Elmer Model 154-D vapor fractometer equipped with hydrogen flame ionization detector. The column was coated with polypropylene glycol. The general column conditions were: temperature 110°, helium carrier gas pressure 13 p.s.i.g., with characteristic retention times for a column given in Table XII.

TABLE XII

RETENTION TIMES OF CHLOROXYLENES ON CAPILLARY COLUMN AT 100°

Xylene	Retention time, min.
3-Chloro-*o*-	18.1
4-Chloro-*o*-	19
2-Chloro-*o*-	15.5
4-Chloro-*o*-	16

The isomeric chlorotoluenes and chloroethylbenzenes were not separated sufficiently well even on capillary columns, although it was possible to separate well the *o*-isomers from the combined *meta* + *para* isomers. In these cases the isomers were analyzed by infrared spectroscopy.

Analyses were carried out by the standard baseline technique, with suitable corrections made for the interference of any isomer on the others by use of an electronic computer.

It was found advantageous for the infrared analyses to separate the combined chlorotoluene or chloroethylbenzene fractions by preparative scale gas chromatography, thus eliminating solvent and other aromatic interferences. The following analytical wave lengths were used for the analyses (μ): *o*-chlorotoluene, 13.40; *m*-chlorotoluene, 12.96; *p*-chlorotoluene, 12.42; *o*-chloroethylbenzene, 13.37; *m*-chloroethylbenzene, 12.90; *p*-chloroethylbenzene, 12.18.

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Aromatic Substitution. XVIII.[1] Friedel–Crafts *t*-Butylation of Benzene and Methylbenzenes with *t*-Butyl Bromide and Isobutylene

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Friedel–Crafts *t*-butylation of benzene and methylbenzene with *t*-butyl bromide and isobutylene was investigated in nitromethane solution with various acidic halide and proton acid catalysts. Relative rates and isomer distributions were determined by gas–liquid chromatography. *t*-Butylation of toluene and benzene under nonisomerizing conditions shows intermediate substrate selectivity ($k_{toluene}:k_{benzene}$ = 14–16). The isomer distribution of the *t*-butyltoluenes formed was found to be 5.7–7% *m*- and 94.3–93% *p*-isomer. No *t*-butylation *ortho* to a methyl group was observed in homogeneous butylations of methylbenzenes in nitromethane solution with either *t*-butyl bromide or isobutylene. *t*-Butylation of *m*-xylene gave only 5-*t*-butyl-1,3-dimethylbenzene, with a reaction rate only one-twentieth of that of the butylation of *o*-xylene. A small secondary isotope effect was observed in the *t*-butylation of benzene-d_6. The mechanism of the reactions is discussed.

Introduction

Orientations in Friedel–Crafts alkylations have frequently been considered to be anomalous,[2-4] and it has been difficult to explain directive effects in alkylation of aromatics. Temperature, solvent, nature, and amount of catalyst seemed to have a large effect on the orientation of the products formed.

To explain the relatively high proportions of *m*-isomers in Friedel–Crafts alkylation of toluene and other alkylbenzenes under nonisomerizing conditions, Brown suggested that this is a consequence of a high reactivity and resulting low selectivity aromatic electrophilic substitution reactions.[3]

Brown reported low selectivity in the *t*-butylation of toluene and benzene in aluminum and gallium bromide catalyzed reactions with *t*-butyl bromide in excess aromatics as solvent.[5] The relative reactivity of toluene and benzene was found $k_T:k_B$ = 1.61, whereas the isomer distribution of *t*-butyltoluenes was reported as 32.1% *m*- and 67.9% *p*-isomer, with no *o*-*t*-butyltoluene formed.

In view of Schlatter's data,[6] which indicated in a number of *t*-butylations of toluene with isobutylene or *t*-butyl alcohol the isomer distribution as 7% *m*- and 93% *p*-isomer, the values for the *t*-C_4H_9Br butylation were acknowledged as being due to partial isomerization.[5,7,8] Schlatter's lowest *m*-isomer containing isomer distribution with *t*-butyl chloride butylation was 15% *m*- and 85% *p*-isomer. No consideration was give to the possible effect of intermolecular isomerization (disproportionation) on the observed relative reactivity values.

Allen and Yats[8] recently reviewed the present status of concurrent alkylation and isomerization of alkylbenzenes with alkyl halides, olefins, and alcohols. They concluded, on the basis of Schlatter's results, that all *t*-butylations of toluene could have been obtained by alkylations producing isomeric mixtures containing 7% *m*- and 93% *p*-*t*-butyltoluene and subsequent or concurrent isomerization of the mixtures. However, they carried out no butylations of their own to substantiate this suggestion and no rate data were available to allow conclusions relating the effect of disproportionation to relative rates.

Allen[9] concluded from his observations, that in the alkylations of toluene the particular catalysts and alkylating agents used influence the extent of isomerization that accompanies the alkylation. He found in the cases he studied that the ratio of *p*- to *m*-substitution was constant within experimental error. In the case of *t*-butylation steric hindrance prevents the formation of *o*-isomer.

Results and Discussion

Brown's *t*-butylation work was carried out using only an excess of aromatic as solvent. Under these conditions formation of σ-complexes (preferentially with the more basic alkylation products) is to be expected

$$ArH + GaX_3 + HX \rightleftharpoons ArH_2^+GaX_4^- \text{ or}$$
$$ArH + Ga_2X_6 + HX \rightleftharpoons ArH_2^+Ga_2X_7^-$$

The formation of these complexes also promotes secondary isomerization. In the case of *t*-butyltoluenes secondary or concurrent isomerization involving predominantly intermolecular migration of the *t*-butyl group was suggested.[9] Therefore, if isomerization takes place, not only is the isomer distribution affected, but the relative toluene–benzene butylation rates may also be affected. Disproportionation could easily lower the relative rate, as *t*-butyltoluenes are more basic and consequently more sensitive to intermolecular isomerization then *t*-butylbenzene.

To prove this point we carried out an investigation of the effect of Lewis acid halide catalysts on the isomeric *t*-butyltoluenes (neat and also in nitromethane and benzene solution). Details of this investigation

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