the chloromethyl group lies between the larger benzoyl group and bromine.

The disparity between the quantities of ortho and para isomers found in the chloromethylation of toluene as reported by H. C. Brown⁹ and this work may result because the former's reaction was carried out in glacial acetic acid. Rather good agreement with Shacklett and Smith¹⁰ has been obtained by us. Rapp and Kornev¹¹ recently reported nearly equal amounts of ortho and para chloromethyl toluenes arising from the chloromethylation reaction.

EXPERIMENTAL

A Perkin-Elmer Model 21 Infrared Spectrometer was used for the qualitative and quantitative examination of the alkyltoluenes. The gas-liquid chromatographic work was performed on a Perkin-Elmer Fractometer 154B equipped with a 1/4-in. \times 10-foot silicone oil (Dow Corning 550) column and thermal conductivity cells. In addition, a Barber-Coleman capillary column chromatograph was employed with a 100-foot Ucon 2000 capillary column and an ionization gauge detector. The packed column instrument effectively separated the ortho and para isomers but failed to resolve the *meta* from the *para*. Of many columns examined, only 7,8-benzoquinoline was somewhat effective for the separation of the isomeric xylenes. The capillary column coupled with ionization gauge nicely resolved all of the isomers (Figs. 1, 2). The chromatographic assays were obtained by the normalization technique and practically no area correction factors were necessary when using the Perkin-Elmer instrument. The infrared analytical wave lengths selected were as follows:

Alkyltoluene	ortho	meta	para	
Methyl Ethyl, <i>i</i> -propyl, <i>t</i> -butyl	13.46 µ 13.18- 13.25	13.02μ 12.74- 12.76	12.55μ 12.25- 12.27	

Known mixtures bracketing the values obtained by gasliquid chromatography were prepared and standard curves drawn. *i*-Octane solutions were used for determining the major components and neat spectra recorded for the minor constituents.

The alkylbenzenes used as starting materials were of commercial quality and ranged between 95 and 98% pure. The chloromethylation reaction was carried out according to the method of Shacklett and Smith¹⁰ and yielded products with analyses (alkaline hydrolysis) of over 99%. A.P.I. alkyltoluenes were used for the infrared standard curves.

The chloromethyl derivatives were transformed into the analogous alkyltoluenes by shaking 30 ml. of 50% ethanolic solution with 0.3 g. of 10% palladium-barium sulfate catalyst for 1 hr. at 50 p.s.i. hydrogen in a Parr hydrogenation apparatus. About 90% of the theoretical amount of hydrogen was absorbed. In all instances between 5 and 8% (determined by GLC) of unchanged chloromethylated material was found in the reduced product. A second reduction was carried out after filtering, driving off the hydrochloric acid and adding fresh catalyst. This sufficed to eliminate the unchanged residue. There was no difference in the isomer ratios of the alkyltoluenes when the first and second reductions were compared, indicating that the isomers of a particular alkyl chloromethyl benzene were hydrogenolyzed at the same rate. The analyses were carried out subsequent to filtering of the solutions, neutralizing with sodium carbonate and stripping off the alcohol.

Acknowledgment. The author expresses his appreciation to Professor H. C. Brown of Purdue University for some helpful comments concerning this investigation.

We are indebted to Dr. M. J. Schlatter of the California Research Corp. for supplying purified samples of the isomeric *i*-propyltoluenes.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING, CASE INSTITUTE OF TECHNOLOGY]

Solvent and Catalytic Effects in the Reaction of Ferric Chloride with Aromatic Compounds¹

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A large number of metal halides were investigated for their influence as solvents or catalysts upon the reaction of anhydrous ferric chloride with simple aromatic compounds. Yield and isomer distribution of products, and rate of the various reactions which occur were affected by certain of the metal halides. The significance of the results is discussed.

It has been reported² that compounds of the Friedel-Crafts catalyst type, present either in small amounts or as solvents, decrease the temperature at which reaction occurs ("initiation temperature") and alter the isomer distribution in the chlo-

 Paper V in the series, "Reactions of Metal Halldes with Organic Compounds"; an abstract of a portion of the Ph.D: thesis of C. Wu, Case Institute of Technology, 1960.
P. Kovacic and N. O. Brace, J. Am. Chem. Soc., 76, 5491 (1954). rination of chlorobenzene by ferric chloride. Moreover, nitrobenzene, a solvent which would be expected to coordinate strongly with ferric chloride, retarded the reaction. These effects were interpreted as evidence for a polar mechanism. Catalytic influences in the ferric chloride-benzene system are treated elsewhere.³

Our intention in the present work was to make

⁽³⁾ P. Kevacic and C. Wu, forthcoming publication.

a more thorough investigation of solvent and catalytic effects in the reaction of ferric chloride with simple aromatic compounds.

RESULTS

Halobenzenes. The reaction of chlorobenzene with ferric chloride was studied principally. The catalysts examined included aluminum chloride, cupric chloride and bromide, cuprous chloride, mercuric chloride, zinc chloride, titanium tetrachloride, and antimony pentachloride (Table I). Addition of these substances resulted invariably in a lowering of the "initiation temperature." A number of them (mercuric chloride, zinc chloride, aluminum chloride) were found to have little or no effect on the isomer distribution of the product, whereas the copper halides increased the amount of ortho substitution. In some cases (aluminum chloride, titanium tetrachloride, antimony pentachloride), there were indications of the operation of temperature effects, *i.e.*, decreased ortho substitution at lower temperatures. Less than 1% of the meta isomer was obtained in all cases.

Some of the metal chlorides, such as titanium tetrachloride, antimony trichloride, stannic chloride, and arsenic trichloride, when used as diluent, were found to lower the initiation temperature and promote the reaction remarkably. The initiation temperatures were 50°, 92°, 116°, and 120°, respectively. In titanium tetrachloride, dichlorobenzene was obtained in 85% yield at 132° in fifteen minutes, and 74% at 100° in 1.8 hours. In contrast, no detectable reaction occurred at 120° in the absence of the solvent, a temperature of at least 125-130° being required. Reaction failed to take place at 132° in the presence of large amounts of pyridine or nitrobenzene, but dichlorobenzene was formed in low yield in nitrobenzene at higher temperatures (168-180°). In titanium tetrachloride (Matheson Coleman and Bell) and antimony trichloride, there was increased ortho substitution. It is interesting that in titanium tetrachloride from the Baker Chemical Co. decreased ortho substitution was observed (Table I).

In earlier work,² interaction of bromobenzene and ferric chloride was apparent at 126° yielding 93% of chlorobromobenzene (o/m/p = 13/<1/87). In the presence of large amounts of titanium tetrachloride, reaction began at 55° and gave a 79% yield (o/m/p = 23/<1/77). No reaction was observed previously between fluorobenzene and ferric chloride at the reflux temperature (85°), and only traces of chlorofluorobenzene were obtained on heating the reaction mixture at 100° for four hours in a pressure vessel.² In titanium tetrachloride solvent, however, a 7% yield was realized at 47–97° in two hours.

Alkylbenzenes. While some metal chlorides (titanium tetrachloride, antimony trichloride, cupric chloride) used in small amounts or as solvent, were

TABLE I FERRIC CHLORIDE AND CHLOROBENZENE^a

		Time,	Dichl	%	
Solvent	Temp.	hr.	Yield	orthob	para
None	131-132	2.0	69	11	89
TiCl₄°	129 - 132	0.25	85	21	79
TiCl4 ^d	128 - 132	0.25	77	5	95
TiCl₄°	100	1.8	74	24	76
SbCl ₃	128 - 132	1.0	71	21	79
$AsCl_3$	118 - 122	3.0	63	12	88
SnCL	118 - 120	2.0	57	7	93
C₅H₅N	130-132	2.0	0		• •
$C_6H_5NO_2$	130-132	2.0	0		
C6H5NO2e, f	168 - 180	1.5	9	15	85
Catalyst					
AlCl ₃	130-134	1.0	60	11	89
AlCl ₃	130 - 134	2.0	72	11	89
AlCl ₃ ^{f,g}	119 - 134	2.0	83	7	93
TiCl.º	78 - 132	1.8	82	6	94
SbCls ^{1,h}	112 - 138	1.25	88	9	91
HgCl ₂	117-134	2.5	72	11	89
$\overline{CuCl_2}$	115 - 126	1.1	84	18	82
CuCl ₂ ⁱ	105 - 122	1.8	83	18	82
Cu_2Cl_2	118 - 120	1.1	78	16	84 ^j
$CuBr_2$	122 - 128	1.1	86	18	82 ^j
ZnCl ₂	90-138	1.7	64	10	90 ¹

^a Chlorobenzene (1 mole), ferric chloride (0.5 mole), andsolvent (1 mole) or catalyst (0.02 mole). ^b Less than 1% of *meta* isomer by infrared analysis. ^c Matheson Coleman and Bell. ^d Baker Chemical Co. ^e Chlorobenzene (0.6 mole), ferric chloride (1.0 mole), and nitrobenzene (250 g.). ^f Ref. (2). ^e Chlorobenzene (2 moles), ferric chloride (1 mole), and aluminum chloride (0.02 mole). ^h 0.05 mole. ⁱ 0.15 mole. ^j Determined by the m.p.-f.p. method; see Experimental.

found to influence orientation in the chlorination of chlorobenzene, these same adjuncts did not exert any appreciable effect on isomer distribution in the toluene reaction (Table II). Titanium tetrachloride solvent and aluminum chloride catalyst were effective in favoring chlorination at the expense of polymerization. However, in titanium tetrachloride temperatures above 100° were necessary to maintain the reaction at a rapid rate. Antimony trichloride and nitrobenzene both retarded the chlorination, allowing facile polymerization.

The reaction of *p*-chlorotoluene with ferric chloride took place with vigor at 104°, yielding among the products 9% of dichlorotoluene and a large quantity of red tar.^{2,4} In titanium tetra-chloride as solvent, the reaction proceeded quite smoothly at the same temperature with an increased yield (38%) of dichlorotoluene and negligible amounts of tar.

An energetic reaction of *m*-xylene with ferric chloride occurred at 17° , yielding 23% of chloro*m*-xylene in addition to 2,2',4,4'-tetramethylbiphenyl and polymer (Table III). Aluminum chloride in catalytic amounts acted in favor of nuclear chlorination. In small quantities titanium tetrachloride exerted little influence, but when used as a solvent favored chlorination at the expense of poly-

⁽⁴⁾ P. Kovacic, C. Wu, and R. W. Stewart, J. Am. Chem. Soc., 82, 1917 (1960).

FERRIC CHLORIDE AND IOLUENE"								
Solvent or			Time.		Chlorotoluene, %		Polymer,	
Catalyst,	Moles	Temp.	hr.	Yield	ortho	meta	para	g.
None		110	0.5	27	15	1	84.	10
None ^b	• • •	45-68	4	40	13	1	87	6.5
TiCl	1	110	2	61	15	1	84	0
SbCl ₃	1	110	1	3	14	1	85	12
C.H.NO.	1	110	1	3	15	1	84	12
CuCl ₂	0.01	60-64	1	19	13	1	87	10
AlCl.	0.09	40-60	3	62	11	i	89	
AICL	0.02	37-70	3	88	đ			0.5
BF.	0.02	31-104	2	52	đ			6.5

TAELE II Ferric Chloride and Toluene^a

^a Ferric chloride (0.5 mole) and toluene (1 mole). ^b Extrapolated from a double scale run. ^c Ferric chloride (1 mole) and toluene (3.5 moles). Ref. (2). ^d Not determined. ^e Experiment by F. J. Donat.

	TABLE	ш	
FERRIC	CHLORIDE ^a	AND	<i>m</i> -Xylene

C _s H10, Mole	Solvent or Catalyst	Moles	Temp.	Time, hr.	C ₈ H ₉ Cl, %	High boiler, g.	Polymer, ^b g.
2	None		17-26	1.0	23	8¢	16 ^d
2	$None^{e}$		17 - 82	5.5	33	2	16
2	AlCl3	0.02	47-71	3.5	77	$\overline{2}$	3
2	TiCl	0.02	2490	5.0	37	2	18
0.5	TiCl ₄	1.3	40-98	4.5	50	107	1

^a 1 mole. ^b Residue from steam distillation of the reaction mixture. ^c 2,2',4,4'-Tetramethylbiphenyl.^s ^d Residue from fractional distillation. ^e Ref.^s. ^f 4,6-Dichloro-*m*-xylene, b.p. 221° (743 mm.), m.p. 70-70.5°, leaflets from ethanol; lit.⁷ b.p. 223-224°, m.p. 68.5°.

merization. In this same medium some of the chloro- $\P\P$ Chlorobenzene and toluene are completely *m*-xylene initially formed was converted to the miscible with the metal chlorides used as solvents, but ferric chloride is at most only slightly soluble

DISCUSSION

In accord with previous findings.^{2,6} catalytic amounts of aluminum chloride facilitated nuclear chlorination by ferric chloride, while decreasing the extent of polymerization. Other metal halides also possessed the ability, in common with aluminum chloride, to lower the initiation temperature. A somewhat related phenomenon has been observed⁸ in the Friedel-Crafts reaction wherein one metal halide can increase the activity of another. Several plausible explanations may be offered to account for the pronounced catalytic action of aluminum chloride. Studies of the ArH-AlX₃-HX system⁹ have established that a polar complex is formed, which may provide a favorable medium for ionic reactions—a category which apparently² includes chlorination by ferric chloride. Alternatively, reaction may be favored by the existence of complexes of the type $Cl_2FeCl \rightarrow AlCl_3$. However, the low meta isomer content does not indicate any large increase in "activity"9 of the attacking species on addition of aluminum chloride.

miscible with the metal chlorides used as solvents, but ferric chloride is at most only slightly soluble in these organic and inorganic media. Whether ferric chloride is more soluble in the aromaticmetal chloride solution is not known. In general, the metal chloride solvents promoted the chlorination of chlorobenzene by ferric chloride and in some cases altered the isomer distribution of the product. With toluene, titanium tetrachloride favored chlorination whereas antimony trichloride favored polymerization. In both cases the isomer distribution of the chlorotoluene remained unchanged, as was also the case for cupric chloride catalyst. These results suggest that the halogen atom on the aromatic nucleus may play a vital role in the altered isomer distribution produced by adjunct metal chlorides. The increased o/p ratio from chloro- and bromobenzene in titanium tetrachloride (Matheson Coleman and Bell), from chlorobenzene in antimony trichloride, and from chlorobenzene in the presence of copper chloride catalysts may result from formation of a complex in which ortho substitution is facilitated. The wide dis-



⁽⁹⁾ K. L. Nelson and H. C. Brown, in *The Chemistry of Petroleum Hydrocarbons*, Reinhold Publishing Corp., New York, N. Y., 1955, Vol. 3, p. 465.

⁽⁵⁾ P. Kovacic and C. Wu, forthcoming publication.

⁽⁶⁾ R. W. Stewart, M.S. thesis, Case Institute of Technology, 1957.

⁽⁷⁾ E. Koch, Ber., 23, 2318 (1890).

⁽⁸⁾ C. C. Price, Org. Reactions, III, 1 (1946).

crepancy in results with titanium tetrachloride from different sources may possibly be due to differences in trace impurities present.

Several experiments were concerned with the rearrangement of aromatic chlorides by a Friedel-Crafts catalyst. Our results, together with the findings of Mattano,¹⁰ show that rearrangement of o-dichlorobenzene by aluminum chloride leads to appreciable amounts of the *meta* isomer. It is significant that under the conditions used for chlorination by ferric chloride the proportion of *meta* isomer in the dichlorobenzene product is extremely low (about 1%).

Although the isomer distribution from the ferric chloride-antimony trichloride-chlorobenzene system resembles fairly closely that² from antimony pentachloride-chlorobenzene, the analogy does not hold in the case of ferric chloride-antimony trichloride-toluene and antimony pentachloride-toluene.

We have shown³ that co-catalysts play an important role in the formation of polymer from benzene-ferric chloride. Since added titanium tetrachloride very pronouncedly inhibited benzene polymerization, its effect was attributed³ to destruction of traces of co-catalyst. The ability of titanium tetrachloride to reduce polymer formation from alkylbenzenes may be similarly interpreted.

Nitrobenzene and pyridine markedly retarded or completely inhibited nuclear chlorination, presumably because of their ability to coordinate strongly with ferric chloride. This type of complex formation should decrease the Lewis acid strength of ferric chloride and therefore interfere with the electrophilic chlorination reaction⁴ effected by this reagent. On the other hand, nitrobenzene did not inhibit the formation of polymer in the toluene reaction. The alkyl side-chain is very likely involved in the polymerization reaction, although our studies with benzene suggest that a nuclear polymerization might also occur. The reaction of ferric chloride with alkane is known¹¹ to proceed in the presence of nitrobenzene. These results lead us to believe that ferric chloride is involved in quite different ways in the chlorination and polymerization processes.

At the present stage many aspects of the action of catalysts and solvents in this heterogeneous system are little understood.

EXPERIMENTAL

Materials. High purity, commercial materials were used. Unless otherwise specified, the source of titanium tetrachloride was Matheson Coleman and Bell. General procedure. The general procedure described in a previous report⁴ was used with slight adaptations. Usually the aromatic compound (1 mole) was mixed with ferric chloride (0.5 mole), and the solvent¹² (1 mole) or catalyst (0.02 mole) was then added at room temperature. The reaction mixture was heated with stirring to the initiation temperature, the temperature at which hydrogen chloride was first detected. For the constant temperature reactions (in Table II and the titanium tetrachloride solvent experiments in Table I), the aromatic compound and the solvent were heated to the desired temperature, and then ferric chloride was quickly added. In the aluminum chloride catalyst experiments at 130–134° in Table I, the reaction mixture was quickly heated to the indicated temperatures.

Ferric chloride and bromobenzene in titanium tetrachloride. A mixture of bromobenzene, ferric chloride, and titanium tetrachloride was heated to 120° during 1 hr. with vigorous stirring. Hydrogen chloride was first detected at 55°. After an additional hour at $120-128^{\circ}$, the reaction mixture was poured onto ice and worked up in the usual manner. Bromochlorobenzene (38 g., 79%; o/m/p = 23/< 1/87) was collected at 96-97° (33 mm.).

Ferric chloride and fluorobenzene in titanium tetrachloride. The reaction mixture was heated at $47-97^{\circ}$ for 2 hr. The evolution of hydrogen chloride was slow. A 7% yield of chlorofluorobenzene (b.p. $129-130^{\circ}$) was obtained.

Ferric chloride and p-chlorotoluene in titanium tetrachloride. p-Chlorotoluene was added from a dropping funnel to a mixture of ferric chloride and titanium tetrachloride at 104°. After 1.5 hr. at 104–108°, the reaction mixture was steam distilled. Fractionation of the dried distillate yielded dichlorotoluene (14 g., 36%), b.p. 190–196°. Infrared analysis showed it to consist of 2,4- and 3,4-dichlorotoluene with the former predominating. The residue from fractionation was 1 g. of oil whose infrared spectrum resembled that⁴ of (p-chlorobenzyl)-4-chlorotoluene. There was no tarry material.

Isomerization studies. A mixture of chlorobenzene (0.5 mole), o-dichlorobenzene (0.5 mole), and aluminum chloride (1 mole) was stirred at $130-133^\circ$ for 3 hr., with dry hydrogen chloride being introduced beneath the surface of the reaction mixture. After work-up, infrared examination of the dichlorobenzene fraction revealed the presence of meta and para bands with the former being more intense.

In a similar manner, a mixture of toluene, o-chlorotoluene, and aluminum chloride was treated with hydrogen chloride at 60-63° for 3 hr. The infrared spectrum of the reaction product exhibited pronounced *meta* bands.

Analytical procedure.⁴ The isomer distributions were determined by the infrared method. The wave lengths (μ) used for the determination of dichlorobenzene were 13.38 (o), 12.78 (m) and 12.23 (p); those for chlorotoluene were 13.38 (o), 12.78 (m) and 12.43 (p). In some cases, the isomer distributions of dichlorobenzene were determined by the melting-freezing point method of Holleman and van der Linden.¹³ These results were found to deviate from the infrared analyses by no more than $\pm 1\%$ for the *p*-isomer. For the determination of chlorobromobenzene, the meltingfreezing point method¹³ was used.

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⁽¹⁰⁾ L. A. Mattano, U. S. Patent 2,727,075 (1955); Chem. Abstr., 50, 9444 (1956).

⁽¹¹⁾ P. Kovacic and H. C. Volz, J. Am. Chem. Soc., 81, 3261 (1959).

⁽¹²⁾ Denotes a liquid adjunct present in molar quantities, which may also act as a catalyst.

⁽¹³⁾ A. F. Holleman and T. van der Linden, Rec. trav. chim., 30, 305 (1911).