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Oxidation by Iron(III) Complexes. VIII. The Reactions of Iron(III) Chloride with Toluene and Substituted Toluenes[1)]

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The thermal and photochemical reactions of toluene with anhydrous iron(III) chloride in the solid state result in nuclear chlorination. In a homogeneous system, a side-chain reaction occurs under irradiation with light, although no product is obtained in the thermal reaction. The addition of water to the iron(III) chloride–toluene system in the range of the molar ratio of 1—5 changes the course of the photochemical reaction; in the water/iron(III) chloride molar ratios of 1—1.7, 3, and 4—5, the main products are the diphenylmethane-type compound, *o*- or *p*-chlorotoluene ($o>p$), and benzyl chloride respectively. Pyridine as a ligand acts to give benzyl chloride selectively. The Mössbauer data of the $FeCl_3/nH_2O$ solid show that the arrangement of the Cl^- ion around the Fe(III) ion changes upon the addition of water. The thermal and photochemical reactions of *p*-methoxytoluene with anhydrous iron(III) chloride give 2,2′-dimethoxy-4,4′-dimethylbiphenyl by oxidative aryl coupling. Water inhibits the aryl coupling reaction.

Previously we investigated the photo-oxidative cleavage of the carbon-carbon bond of 1,2-glycols[2)] and the carbon-carbon coupling of the active methylene group of alkyl aryl ketones in the presence of iron(III) chloride.[3)] As part of a series of studies of oxidation by iron(III) salts, we will here investigate the oxidation of toluenes by iron(III) chloride.

Anhydrous iron(III) chloride reacts with alkylbenzenes to bring about nuclear chlorination, the formation of diphenylmethane-type hydrocarbons, and polymerization.[4,5)] Furthermore, the reaction of toluene and iron(III) chloride-lithium chloride in acetic acid under ultraviolet irradiation gives benzyl chloride and iron(II) chloride.[6)] In this paper, we will describe the role of a ligand environment around the Fe(III) ion in controlling various competing reactions and the effect of the substituent at the *p*-position of toluene upon the reaction pathway. Some of the results of this investigation have been reported in a previous communication.[7)]

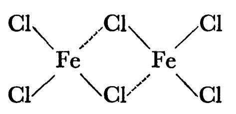
Results and Discussion

Reaction of Toluene with Iron(III) Chloride. *Thermal Reaction*: When a homogeneous solution of iron(III) chloride in toluene was heated at 70 °C, no product was detected by glc. In a heterogeneous system, however, the isomeric chlorotoluenes (I) (o: $(m+p)=13$: 87) were produced in a satisfactory yield, along with iron(II) chloride (Table 1). The isomer distribution reflects the electrophilic property of the chlorination species.

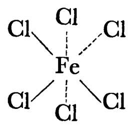
$$C_6H_5CH_3 \xrightarrow[\Delta]{(FeCl_3)_m} \underset{\text{I}}{ClC_6H_4CH_3}$$

Photo-reaction: The irradiation of a homogeneous solution of iron(III) chloride in toluene yielded 98% phenyltolylmethanes (II) with an isomer ratio of $o:p=46:54$, plus a small amount of bibenzyl. When the iron(III) chloride was dispersed in toluene, I was produced along with II. The isomer distribution coincided with that in the thermal reaction. Although the amount of I produced under irradiation with light increased with the increase in the amount of iron(III) chloride dispersed, the amount of II came to be nearly constant independently of the dispersion amount; it depended on that of the iron(III) chloride dissolved in the toluene, as is shown in Fig. 1. Thus, anhydrous iron(III) chloride in the solid state undergoes nuclear chlorination. Iron(III) chloride has been reported to exist as a dimer (III) in non-polar solvents.[8)] On the other hand, the iron(III) chloride in the solid state has a $FeCl_6$ octahedral structure (IV) as a structural unit, as will be described later. Thus, the structure of the iron(III) chloride in the reaction system affects the reaction course of either the nuclear chlorination or the side-chain reaction.

$$C_6H_5CH_3 \xrightarrow[h\nu]{FeCl_3} \underset{\text{II}}{C_6H_5CH_2C_6H_4CH_3}$$



III



IV

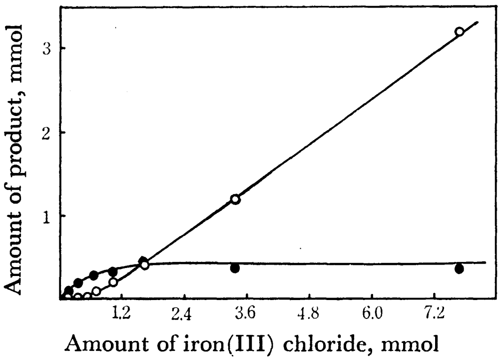


Fig. 1. The relationship between the amount of I (—○—) or II (—●—) produced and that of iron(III) chloride added in toluene (10 ml). (under irradiation with light).

Effect of Water. Water was added to an anhydrous iron(III) chloride–toluene system consisting of 1.4 mmol of iron(III) chloride in 10 ml of toluene (Table 1).

At the water/iron(III) chloride molar ratio (n) of 1.7, the thermal reaction gave I and II in low yields of 6 and 10% respectively (70 hr). At molar ratios higher than 3, no product was detected by glc. In the photoreaction, however, I, II, and benzyl chloride (V) were obtained in higher yields. Furthermore, the yields changed depending on the value of n (Table 1). At n=1—1.7, the reaction yielded II along with the small amount of I. This phenomenon was similar to the results of the thermal toluene–copper(II) bromide reaction.[9] However, the course of the reaction again altered in the direction of nuclear chlorination with the predominance of the o-position (o: (p+m)=67: 33) upon the further addition of water. In addition, V was obtained. The maximum selectivity for nuclear chlorination was observed at n=3. When n became larger than 3, the yields of I and II decreased and that of V increased. The maximum yield of V was observed at n=4—5. Thus, water significantly changes the course of the photochemical reaction of toluene with iron(III) chloride.

$$C_6H_5CH_3 \xrightarrow[h\nu]{FeCl_3/(4-5)H_2O} \underset{V}{C_6H_5CH_2Cl}$$

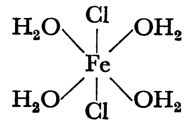
Table 1. The reaction of toluene with iron(III) chloride[a)]

Additive	Molar ratio Additive/ FeCl$_3$	Therm. or hν	Yield of product, %[b)]		
			I(o/p+m)	II(o/p)[e)]	V
None[c)]	0	70 °C	60(13/87)	0	0
None[d)]	0	hν	44(13/87)	51(46/54)	0
H_2O	1.7	70 °C	6	10	0
H_2O	1.7	hν	12(65/35)	52(46/54)	0
H_2O	3	70 °C	0	0	0
H_2O	3	hν	54(67/33)	10(48/52)	28
H_2O	4—5	hν	0	8	91
C_5H_5N	5	hν	0	0	100

a) Reaction time: 70 hr. Amount of FeCl$_3$: 1.4—1.6 mmol in 10 ml of toluene. b) The yields of I, II, and V were calculated from 2 × (number of moles of the products/ that of FeCl$_3$) × 100. c) Yield of FeCl$_2$: 77%. d) Yield of FeCl$_2$: 96%. e) The isomer distribution of phenyltolylmethanes which were prepared by the reaction of toluene with benzyl chloride in the presence of iron(III) chloride was o/p=43/57.

Effect of Pyridine. When the pyridine/iron(III) chloride molar ratio was higher than 1, the thermal reaction (70 °C, 70 hr) yielded I in a yield lower than 10% and the photochemical reaction gave (V) selectively; thus, the yield of V was 100% in the molar ratio of 5 (Table 1). II was not obtained at all in the thermal and photochemical reactions. This finding was similar to that in the case of water.

Mössbauer Data. The Mössbauer spectra were measured at room temperature for the iron(III) chloride solid containing water at n=1.7, 3, and 6. The results are compared in Table 2. All the samples are characterized by approximately the same isomer shift (0.38—0.44 mm/s). Thus, the electron density at the Fe nucleus appears to be about the same. However, the quadrupole splitting (Q.S.) changes with the amount of water. Anhydrous iron(III) chloride exhibits a single narrow resonance line, Q.S.=0. This means that the anhydrous salt has a FeCl$_6$ octahedra (IV) as a structural unit.[10] In FeCl$_3$/6H$_2$O, we found Q.S.= 0.83 mm/s, which was the same as was found by Nozik and Kaplan.[10] An X-ray diffraction study[11] shows that the structural unit in the crystal is the octahedral complex $Fe(H_2O)_4Cl_2$, with the Cl$^-$ ions being coaxial (VI). On the other hand, in FeCl$_3$/3H$_2$O we found Q.S.=0.36 mm/s. This indicates that the arrangement of the Cl$^-$ ion and H$_2$O surrounding the central Fe(III) ion differs from the case of FeCl$_3$/6H$_2$O. The FeCl$_3$/1.7H$_2$O solid exhibits a broad resonance line, thus indicating that the arrangement of the Cl$^-$ ions is disturbed by water.



VI

Table 2. Mössbauer data of the FeCl$_3$/nH$_2$O solid

FeCl$_3$/nH$_2$O	Isomer shift mm/s	Q.S. mm/s
FeCl$_3$	0.44	0
FeCl$_3$/1.7H$_2$O	0.44	—
FeCl$_3$/3H$_2$O	0.38	0.36
FeCl$_3$/6H$_2$O	0.45	0.83

Reaction Pathway. When the FeCl$_3$/nH$_2$O solid is irradiated with light, the Cl· ion is oxidized by the excited Fe(III) ion, thus leading to the formation of Cl·(VII). The reactivity of the Cl· thus formed is affected by the ligand environment around the Fe(III) ion and affords either nuclear chlorination or hydrogen abstraction from the methyl group leading to the benzyl radical. That is, the iron(III) chloride solid (n=0) with the structure of Fe–Cl···Fe undergoes nuclear chlorination. When the iron(III) chloride solid contains water, the reaction proceeds *via* the formation of the benzyl radical, followed by the Friedel-Crafts reaction giving II in the case of n=1—1.7, or by ligand-transfer oxidation[12] giving V in the case of n=4—5. In the case of n=3, however, the reaction pathway is uncertain. The formation of I (o>p) may mean that the ligand-transfer oxidation of the benzyl radical occurs at the o- or p-position. However, the reason why the reaction pathway changes with the arrangement of the Cl$^-$ ion and water around the Fe(III) ion is not yet clear.

$$(FeCl_3\text{-}nH_2O)_m \xrightarrow{h\nu} \underset{VII}{(Cl\cdot FeCl_2\text{-}nH_2O)(FeCl_3\text{-}nH_2O)_{m-1}}$$

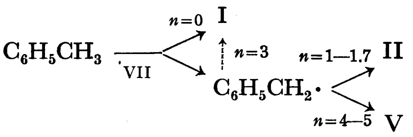
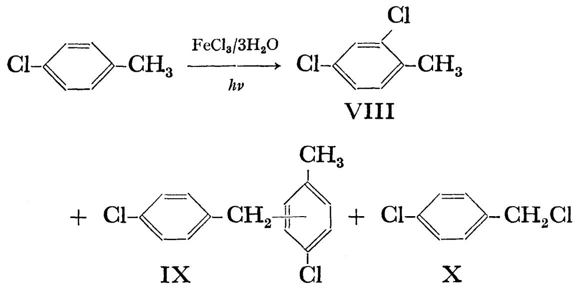


Table 3. The reactions of the substituted toluenes with iron(III) chloride[a]

p-Substituent	Additive	*n*	Therm. or *hν*	Yield of product,[b] %					Polymer mg
				N-Cl	S-Cl	-CH$_2$-	N-N	FeCl$_2$	
Cl	None	0	70 °C	23	0	6	0	52	7
Cl[c]	None	0	*hν*	7	0	28	0	70	71
Cl	H$_2$O	3	*hν*	18	11	7	0	—	—
CH$_3$O	None	0	70 °C	—	—	13	19	88	110
CH$_3$O	None	0	*hν*	—	—	21	41	64	81
CH$_3$O	H$_2$O	3	*hν*	—	—	35	0	53	40

a) Amount ofFeCl$_3$: 1.4—1.7 mmol in 10 ml of toluene. Reaction time: 40 hr for *p*-chlorotoluene and 20 hr for *p*-methoxytoluene. b) N-Cl, S-Cl, -CH$_2$-, and N-N: nuclear chlorination, side-chain chlorination, formation of diphenylmethanes, and aryl coupling, respectively. c) This run was made at ten times scale (86 hr).

Reactions of the p-*Substituted Toluenes with Iron(III) Chloride.* *Chloro Group*: The thermal and photochemical reactions of *p*-chlorotoluene with dispersed iron(III) chloride resulted in nuclear chlorination and a side-chain reaction, although the total yields of the products became lower than that of iron(II) chloride, as Table 3 shows. The other products could not be detected by means of glc. In the thermal reaction, the yield of the nuclear chlorination product, 2,4-dichlorotoluene (VIII), became lower than that in the case of toluene, but the mixture (IX) of 2,4′-dichloro-5-methyldiphenylmethane and 3,4′-dichloro-6-methyldiphenylmethane was produced in addition to the (VIII). In the photo-reaction, the yield of (IX) became higher than that of (VIII). When the FeCl$_3$/3H$_2$O solid was used, *p*-chlorobenzyl chloride (X) was produced in addition to (VIII) and (IX). Among these products, the yield of (VIII) became higher in spite of deactivation by the chloro group at the *p*-position. These results were similar to those in the case of toluene.



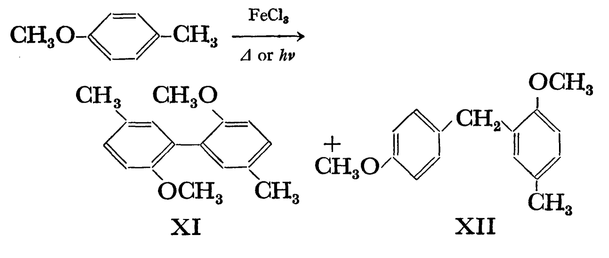
VIII

IX

X

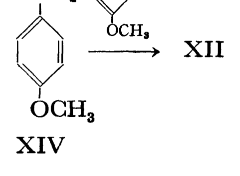
Methoxy Group: A solution of iron(III) chloride in *p*-methoxytoluene, containing partially-insoluble iron(III) chloride, was heated at 70 °C for 20 hr. As Table 3 shows, 2,2′-dimethoxy-4,4′-dimethyldiphenyl (XI) was thus produced in a 19% yield by the coupling of two benzene nuclei, accompanied by the formation of 2,4′-dimethoxy-5-methyldiphenylmethane (XII) in a 13% yield. The other aryl coupling products were not obtained. In the reaction, iron(III) chloride was converted to iron(II) chloride. As another product, *p*-cresol was detected by means of glc, although the amount produced was very small. The total yields of the products became lower than that of iron(II) chloride because of the formation of a polymeric material. The yield of (XI) increased under irradiation with light; (XI) and (XII) were obtained in 41 and 21% yields respectively, while in the dark the yields of (XI) and (XII) were 5—6 and 2% respectively. The formation of (XI) and *p*-cresol indicates that the reaction proceeded *via* the cation radical (XIII) of *p*-methoxytoluene, which is formed by the oxidation of *p*-methoxytoluene by iron(III) chloride, followed by the reaction of (XIII) with *p*-methoxytoluene. The formation of the cation radical as an intermediate has been considered to occur in the oxidative coupling of methyl-substituted benzenoid compounds by lead tetra-acetate,[13] the radical-initiated oxidation of anisol,[14] the metal-catalyzed cyclodimerisation of aromatic enamines,[15] and the reaction of methylated benzil and bibenzyl derivatives with tris-(*p*-bromophenyl)ammonium hexachloroantimonate.[16]

On the other hand, the facts that the diphenylmethane-type compound is produced in the homogeneous, thermal reaction and that the reaction occurs at the *o*-position of the methoxy group of *p*-methoxytoluene suggest that the *p*-methoxybenzyl cation (XIV) is formed from XIII and then reacts with *p*-methoxytoluene to give XII. When water was added to the iron(III) chloride-*p*-methoxytoluene system at *n*=3 and the solution was irradiated with light, XII was pro-



XI

XII



XIII

XIV

duced selectively in a 35% yield, along with a small amount of *p*-cresol. Thus, the aryl coupling was inhibited by water. The amount of the polymeric material produced became smaller.

Experimental

Materials. Anhydrous iron(III) chloride was prepared by the sublimation of commercial iron(III) chloride under the reduced pressure of 1 mmHg at 300 °C. The purity of the iron(III) chloride used was 99—99.8%; it was measured by the methods described in a previous paper.[3]

Toluene and Iron(III) Chloride, General Procedure. Thermal Reaction: The homogeneous solution was prepared by dissolving 0.3 mmol of iron(III) chloride in 10 ml of toluene. In the heterogeneous system, 1.4—1.6 mmol of iron(III) chloride was dispersed under stirring in 10 ml of toluene. The solution was placed in a tube (2 cm × 15 cm) and heated at 70 °C under a nitrogen atmosphere for a desired time. After the resulting reaction mixture had been filtered off to separate the iron(II) chloride, the filtrate was submitted to glc analysis. The products, *o*-, *m*-, and *p*-(I), which were obtained in the heterogeneous system were identified by a comparison of their retention times in glc with those of authentic specimens, and their amounts were determined by means of glc. The grey precipitate was repeatedly washed with benzene, dried, and submitted to the quantitative analysis of the Fe(II) ion.

Photo-reaction: The homogeneous or heterogeneous solution which was prepared above was placed in a Pyrex tube and irradiated with a Pyrex-covered 100 W high-pressure mercury lamp at a distance of 6 cm under a nitrogen atmosphere at room temperature for a desired time. During the reaction, the solution was stirred vigorously. After the reaction mixture had then been filtered off to separate the iron(II) chloride, the amount of I was determined by the glc analysis of the filtrate. II was isolated by glc as a mixture of the *o*- and *p*-isomers and bibenzyl. The NMR spectrum (CCl_4) of II showed signals at δ 2.15 (s, 3H, CH_3), 3.85 (s, 2H, CH_2), and 6.9—7.3 (m, 9H, aromatic protons) for the *o*-isomer, at δ 2.22 (s, 3H, CH_3), 3.90 (s, 2H, CH_2), and 6.9—7.3 (m, 9H, aromatic protons) for the *p*-isomer, and at δ 2.83 (s, 4H, CH_2) and 7.06 (s, 10H, aromatic protons) for bibenzyl. The isomer distribution was calculated from the relative heights of the integrated spectrum. The grey precipitate was iron(II) chloride and did not contain any polymeric material at all. Similar procedures were used for the experiments investigating the effect of the amount of the dispersed iron(III) chloride on the reaction.

Iron(III) Chloride–Water or Pyridine System. Various amounts of water or pyridine were added to 10 ml of toluene containing 1.4 mmol of iron(III) chloride. The solution was then heated or irradiated under conditions similar to those in the case of anhydrous iron(III) chloride. The amounts of I, II, and V thus produced were determined by means of glc.

p-*Chlorotoluene and Iron(III) Chloride.* *(a)*: Anhydrous iron(III) chloride (14.5 mmol) was dispersed in 100 ml of *p*-chlorotoluene, and the solution was irradiated with light for 86 hr under conditions similar to those in the case of toluene. The grey solid (1.71 g) then filtered out had 10.2 mmol of iron(II) chloride. A part of the filtrate was submitted to glc analysis. The products, VIII and IX, were identified by a comparison of their retention times in glc with those of authentic specimens, and their amounts were determined by means of glc. The authentic specimen of IX was prepared by the reaction of X and *p*-chlorotoluene in the presence of iron(III) chloride. Furthermore, IX was isolated by glc as a mixture of 2,4′-dichloro-5-methyldiphenylmethane and 3,4′-dichloro-6-methyldiphenylmethane. The NMR (CCl_4) of (IX) showed signals at δ 2.22 and 2.11 (s, 3H, CH_3), 3.95 and 3.81 (s, 2H, CH_2), and 6.8—7.4 (m, 7H, aromatic protons). The other part of the filtrate was submitted to chromatography on alumina (elution with carbon tetrachloride and then methanol). The elution with methanol gave a brown polymeric material (71 mg).

(b): Anhydrous iron(III) chloride (1.4 mmol) was dispersed in 10 ml of *p*-chlorotoluene, and the solution was heated at 70 °C under a nitrogen atmosphere for 40 hr. The grey solid (198 mg) filtered out had 0.73 mmol of iron(II) chloride. The amounts of VIII, IX, and the polymeric material were determined by a method similar to that used in the case of the photo-reaction (a).

(c): A mixture of anhydrous iron(III) chloride (1.4 mmol) and water (4.3 mmol) was allowed to react with 10 ml of *p*-chlorotoluene under irradiation with light for 40 hr. The identification and the determination of VIII, IX, and X were carried out by methods similar to those used in the cases of (a) and (b).

p-*Methoxytoluene and Iron(III) Chloride.* *(a)*: Anhydrous iron(III) chloride (1.4 mmol) was added to 10 ml of *p*-methoxytoluene, and the solution was irradiated with light for 20 hr under conditions similar to those used in the case of toluene. A red-brown solid (154 mg) was then filtered off, washed twice times with 3-ml portions of benzene, and dried. The solid contained 0.9 mmol of iron(II) chloride. The mixture of the filtrate and the benzene solution was freed off the solvent at 74 °C/25 mmHg. The residue was submitted to chromatography on alumina. Elution with benzene, carbon tetrachloride, and then methanol gave XI, XII, and a brown, oily material containing *p*-cresol respectively. The amounts of XI and XII were determined by means of glc (Table 3). XI, mp 59.5—60 °C (lit,[17] mp 61 °C), exhibited NMR (CCl_4) signals at δ 2.26 (s, 6H, CH_3), 3.62 (s, 6H, OCH_3), and 6.5—7.1 (m, 6H, aromatic protons). Mass spectrum *m/e*; 242 (parent peak).

Found: C, 79.30; H, 7.35%. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

XII, mp 72—73.5 °C (lit,[17] 74 °C), exhibited NMR (CCl_4) signals at δ 2.18 (s, 3H, CH_3), 3.65 and 3.68 (s, 6H, OCH_3), 3.76 (s, 2H, CH_2), and 6.4—7.1 (m, 7H, aromatic protons). Mass spectrum *m/e*; 242 (parent peak).

Found: C, 79.20; H, 7.30%. Calcd for $C_{16}H_{18}O_2$: C, 79.31; H, 7.49%.

A similar procedure was used for the photo-reaction in the iron(III) chloride–water system.

(b): Anhydrous iron(III) chloride (1.44 mmol) was allowed to react with *p*-methoxytoluene (10 ml) under a nitrogen atmosphere at 70 °C for 20 hr. The products, XI, XII, *p*-cresol, a red-brown oily material, and iron(II) chloride, were isolated or detected by methods similar to those used in the case of (a).

Mössbauer Spectra. Anhydrous iron(III) chloride was evaporated on aluminium foil supports with spacing of less than 1 mm. The cell was covered by a polyethylene film to prevent the salt from absorbing atmospheric water. An appropriate amount of water was then dropped on the iron(III) chloride film. Gamma rays emitted by the ^{57}Co-in-copper source impinged upon the absorber sample at room temperature. Velocity calibrations were made using the well-known spectrum of natural iron metal as the standard.

Analyses. The quantitative analyses of iron(III) chloride and iron(II) chloride were carried out by the methods described in the literature.[18] The amounts of the products were determined by means of glc using a 3 mm × 1 m column of 30% high-vacuum silicone grease or 3% Apieson grease L on Celite 545.

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