[CONTRIBUTION NO. 157 FROM JACKSON LABORATORY, E. I. DU PONT DE NEMOURS AND CO.]

Chlorination of Aromatic Compounds with Metal Chlorides

BY PETER KOVACIC AND NEAL O. BRACE

RECEIVED MAY 26, 1954

A study has been made of the reaction of anhydrous ferric chloride with simple aromatic compounds. With chlorobenzene, the products were dichlorobenzene (p/o = 88/11), hydrogen chloride and ferrous chloride. The order of reactivity of aromatic compounds, orientation, and solvent and catalytic effects are consistent with a polar mechanism, at least in the rate-determining step. Low *meta* substitution is explained by the weak "activity" of ferric chloride, while the high *para–ortho* ratio, in comparison with the usual method of chlorination, can be rationalized on a steric basis. Certain other metal halides, *e.g.*, antimony pentachloride, also function as halogenating agents for aromatic compounds. The halogenating ability of a metal halide is interpreted as a combination of its Friedel–Crafts catalytic activity and its oxidation–reduction potential. Examples are given of aromatic compounds which react with ferric chloride to produce self-coupling, rearrangement or tars.

Introduction

The use of anhydrous ferric chloride as an aromatic chlorinating agent has received only slight attention since a series of papers[1] by Thomas. By this method, for example, a chlorinated benzene was converted to the next higher chlorohomolog by treatment with ferric chloride. A very noteworthy feature was that the product in most cases consisted predominantly of one isomer. This selectivity was confirmed by Dangyan[2] who showed that the chlorotoluene obtained from toluene was almost entirely the *para* isomer.

The present investigation consists of a study of the mechanism of aromatic chlorination with anhydrous ferric chloride, the scope of this reaction and extension to other metal halides.

TABLE I

CHLORINATION WITH FERRIC CHLORIDE

Aromatic compound,	moles	$FeCl_3$, mole	Time, hr.	Temp.,[a] °C.	HCl, %	Chlorinated arom. prod., % Yield[b]	*Ortho*	*Para*
				Toluene				
Toluene	2.9	1.0	3.0	50– 60	75	58[c]	13	87
o-Chloro-	1.0	0.5	1.25	70– 89	128	30[d]	..	...
p-Chloro-	1.0	0.5	1.25	104–108	157	..[e]	..	...
				Benzene				
Fluoro-[f]	0.5	0.5	4.0	119–124	..	74	<5	>95
Chloro-	2.0	1.0	3.0	125–140	100	86[f]	11	88
Bromo-	1.0	0.5	0.5	126–142	80	93[g]	13	87
Iodo-[f]	1.0	.5	1.25	29–148[f]	72	47[h]	50[h]	50[h]
o-Dichloro-[f]	1.0	.5	2.0	135–188	80	62	..	...
p-Dichloro-	1.0	.5	2.25	160–178	50	48[i]	..	...

[a] The lower temperature is where the reaction mixture thickened and a steady evolution of hydrogen chloride began. Traces of acid were usually seen at lower temperatures. [b] Based on $FeCl_3$. [c] Experiment by J. G. Burt. [d] Liquid product was probably 2,4-dichlorotoluene,[3a] $n^{22}D$ 1.5470 (lit.[3b] $n^{22}D$ 1.5480). *Anal.* Calcd. for $C_7H_9Cl_2$: Cl, 44.0. Found: Cl, 43.91. [e] Less than 10% of chlorinated p-chlorotoluene and much red, benzene-soluble tar. [f] See Experimental. [g] Bromochlorobenzene, b.p. 196–196.2°, m.p. 65–67° (capillary) (lit.[4] for p-isomer, f.p. 64.6°). *Anal.* Calcd. for C_6H_4BrCl: Br, 41.78; Cl, 18.51. Found: Br, 40.7; Cl, 18.35. [h] Approximate value. [i] 1,2,4-Trichlorobenzene.

Results and Discussion

Reaction Mechanism. Order of Reactivity and Orientation.—The experimental evidence strongly

$$Ar\text{-}H + 2FeCl_3 \longrightarrow Ar\text{-}Cl + 2FeCl_2 + HCl$$

indicates that the general type of reaction proceeds, at least in the rate-determining step, by a polar mechanism wherein the ferric chloride acts as an electrophilic reagent toward the nucleophilic aromatic compound. The decreasing order of reactivity of the aromatic component (toluene > o-chlorotoluene > chlorobenzene > o-dichlorobenzene > p-dichlorobenzene) (Table I) is the same as would be expected for a typical electrophilic aromatic substitution reaction. Initiation temperature was used as a measure of reactivity.

The predominantly *ortho–para* substitution also supports the proposed mode of reaction. Comparison of isomer distribution from ferric chloride chlorination with that from chlorination with chlorine gas is shown in Table II. Any explanation to account for directive influences must be based on a consideration of electronic and steric effects involving all reactants. The formation of extremely small amounts of the *meta* isomer can be rationalized by classification of ferric chloride as a relatively weak electrophilic reagent, according to the recent theory of Brown and Nelson.[5] For a given substituted aromatic compound, it would appear reasonable, in comparing substituting reagents of similar "activities," to expect less *ortho* substitution for that reagent having a greater steric factor. This explanation accounts for the generally higher *para–ortho* ratio obtained in chlorination with ferric chloride as compared with the usual method. Further confirmation is provided by the similarity in isomer distribution between chlorination with ferric chloride and bromination with bromine (Table II).

With ferric chloride alone, the decreasing proportion of *ortho* substitution in the halobenzene series follows the order $C_6H_5I > C_6H_5Br \geqq C_6H_5Cl > C_6H_5F$ (Table I), and is analogous to the situation found[6] in nitration. Consequently, the steric factor based on the relative size of the halogen atoms must play a minor role in determining the *para–ortho* ratio. This apparent anomaly was interpreted[6] on the basis of much greater deactivation of the *ortho* as compared with the *para* position as the

---

(1) V. Thomas. *Compt. rend.*, **126**, 1211 (1898); **127**, 184 (1898); **128**, 1576 (1899); *Bull. soc. chim.*, [3] **21**, 286 (1899).

(2) M. Dangyan. *J. Gen. Chem.* (*U.S.S.R.*), **8**, 1780 (1938); *C. A.*, **33**, 4957 (1939).

(3) (a) J. Cohen and H. Dakin, *J. Chem. Soc.*, **79**, 1117 (1901), obtained 2,3-, 2,4-, 2,6- and 2,5-dichlorotoluene by chlorination of o-chlorotoluene with chlorine gas (Al/Hg catalyst); (b) H. Wahl, *Compt. rend.*, **202**, 2161 (1936).

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

(5) H. C. Brown and K. L. Nelson, THIS JOURNAL, **75**, 6292 (1953).

(6) A. Lapworth and R. Robinson, *Mem. Proc. Manchester Lit. Phil. Soc.*, **72**, 43 (1927); E. R. Alexander, "Principles of Ionic Organic Reactions," John Wiley and Sons Inc., New York, N. Y., 1950, p. 242.

TABLE II

ISOMER DISTRIBUTION FROM VARIOUS HALOGENATING METHODS

Conditions	*Ortho*	*Para*	*Meta*
Toluene			
$FeCl_3$ (50–60°)	12	88	<1
Cl_2 (r.t., $SbCl_5$ cat.)[a]	57.5	42	0.5
Br_2 (50°, $FeBr_3$ cat.)[b]	37	63	*ca.* 0
Chlorobenzene			
$FeCl_3$ (125–140°)	11	88	1
Cl_2 (125–130°, $FeCl_3$ cat.)	46	54	<1
Cl_2 (60–65°, $FeCl_3$ cat. in aq. HCl)[4]	39	56	5
Br_2 (60–65°, Fe cat.)[4]	11	87	2
Bromobenzene			
$FeCl_3$ (126–142°)	13	87	<1
Cl_2 (75°, $FeCl_3$ cat. in aq. HCl)[4]	42	51	7
Br_2 (55°, Fe cat.)[4]	13	85	2

[a] E. Wertyporoch, *Ann.*, **493**, 153 (1932); also see ref. 5. [b] F. van der Laan, *Rec. trav. chim.*, **26**, 1 (1907); also see ref. 5.

halogen substituent becomes more strongly electron attracting.

Catalytic and Solvent Effects.—Operation of a polar mechanism is supported by the influence (Table III) of compounds of the Friedel–Crafts catalyst type, present either in small amounts or as solvents. Promoters such as aluminum chloride or polar solvents such as stannic chloride decrease the temperature at which reaction occurs and alter the isomer ratio, usually by an increase in the proportion of the *para* isomer. A somewhat related phenomenon has been observed in the Friedel–Crafts reaction wherein chlorides of tin, silicon or titanium were found to increase the catalytic activity of aluminum chloride.[7] A solvent such as nitrobenzene, which would be expected to show strong coördination with ferric chloride, retarded the reaction. The presence of excess hydrogen chloride in the ferric chloride–chlorobenzene reaction had no influence on the isomer ratio.

TABLE III

CHLOROBENZENE AND FERRIC CHLORIDE IN SOLVENTS OR WITH FRIEDEL–CRAFTS CATALYSTS

Solvent or catalyst	C_6H_5-Cl, moles	Fe-Cl_3, mole	Time, hr.	Temp., °C.	HCl, %	Dichlorobenzene, % Yield	*Ortho*	*Para*
$SnCl_4$[a]	0.5	1.0	7.5	116–123	106	66	3	97
$SbCl_3$[a]	.5	1.0	0.75	92–110	70	73[b]	20	80
$C_6H_5NO_2$[a]	.6	1.2	1.5	168–180	50	9.4	15	85
$AlCl_3$[c]	2.0	1.0	2.0	119–134	86	83	7	93
$AlCl_3$[d]	2.0	1.0	2.8	84–125	100	67[f]	5	95
$AlBr_3$[e]	1.0	0.5	2.5	28–133	100	55	8	92
$SbCl_5$[e]	1.0	0.5	1.25	112–138	79	87.5	9	91

[a] 250 g. [b] 5% 1,2,4-trichlorobenzene also obtained. [c] 0.02 mole. [d] 0.1 mole. [e] 0.05 mole. [f] A tarry residue of 17.3 g. also was obtained. Reaction of *o*-dichlorobenzene (0.5 mole) and $AlCl_3$ (0.5 mole) in a nickel bomb under 100 p.s.i. hydrogen chloride pressure at 120° for 24 hours gave back *o*-dichlorobenzene with only a trace of *m*-dichlorobenzene, and no tarry residue.

No evidence could be found which would indicate the operation of a free radical mechanism. A careful search for possible by-products which might be expected from such a mode of reaction was made, particularly in the case of chlorobenzene. No such products could be found. Nor, in this same example, did ultraviolet light have any effect either on the initiation temperature or on isomer distribution.

Scope and Limitations

Metal Chloride Component.—Other metal halides are reported in the literature as halogenating agents for aromatic compounds. In all cases the metal, of a polyvalent type, was used in the form of a higher valence state, such as ferric bromide,[1] plumbic chloride[8] and antimony pentachloride.[9]

We observed that antimony pentachloride chlorinated chlorobenzene readily to give a 79% yield of dichlorobenzene consisting of 82% *para* and 18% *ortho* isomer. Likewise, toluene was chlorinated smoothly to chlorotoluene (*p*/*o*/*m* = 51/45/4) (Table IV).

TABLE IV

CHLORINATION WITH ANTIMONY PENTACHLORIDE

	Aromatic compound, moles	$SbCl_5$, mole	Time, hr.	Temp., °C.	HCl, %	Chlorinated arom. prod., % Yield	*Ortho*	*Para*	*Meta*
C_6H_5Cl	1.4	0.35	1.7	38–53	91	79	18[a]	82[a]	
$C_6H_5CH_3$	1.0	.5[b]	1.5	30–40	89	90	45	51	4

[a] By m.p.–f.p. method; *meta* isomer content unknown. [b] Added during course of reaction.

Lack of hydrogen chloride evolution at 125–135° indicated failure of aluminum chloride, stannic chloride or cupric chloride to chlorinate chlorobenzene. Chromic chloride, titanium tetrachloride, ferric fluoride or ferric sulfate did not react with toluene.

The polar nature of the reaction suggests a correlation between the reactivity of the metal halide and its strength[7] as a Friedel–Crafts catalyst ($AlCl_3 > SbCl_5 > FeCl_3 > SnCl_4 > TiCl_4$). How-

TABLE V

OXIDATION-REDUCTION COUPLES[a]

Couple	E^0
$PbO_2 + 4H^+ + 2e^- = Pb^{++} + 2H_2O$	1.45
$Cl_2 + 2e^- = 2Cl^-$	1.36
$Fe^{+++} + e^- = Fe^{++}$	0.77
$Sb_2O_5 + 6H^+ + 4e^- = 2SbO^+ + 3H_2O$	.58
$Cu^{++} + e^- = Cu^+$	.15
$Sn^{++++} + 2e^- = Sn^{++}$	.15
$Ti^{++++} + e^- = Ti^{+++}$	.04
$Cr^{+++} + e^- = Cr^{++}$	− .41
$Fe^{++} + 2e^- = Fe$	− .44
$Al^{+++} + 3e^- = Al$	−1.66

[a] W. L. Latimer, "The Oxidation States of the Elements and their Potentials in Aqueous Solutions," Prentice–Hall Inc., New York, N. Y., 1952, p. 340; and F. H. Getman and F. Daniels, "Outlines of Physical Chemistry," John Wiley and Sons, Inc., New York, N.Y., 1943, p. 438. E° values, obtained in aqueous solution, include solvation effects but are expected to be essentially in the same order for anhydrous media. Data involving the metal oxides are included to show the approximate relative standing expected of the corresponding ion.

---

(7) C. C. Price, "Organic Reactions," Vol. III, John Wiley and Sons, Inc., New York, N. Y., 1946, Chapt. I.

(8) Seyewetz and Biot, *Compt. rend.*, **135**, 1120 (1902); *Chem. Zentr.*, **74**, 283 (1903).

(9) J. W. Mellor, "A Comprehensive Treatise on Inorganic and Theoretical Chemistry," Vol. IX, Longmans, Green and Co., New York, N. Y., 1929, p. 489. In almost all instances, mixtures of aromatic polychloro compounds were reported as products.

ever, this correlation alone is not sufficient. It is apparent that the over-all effect of reaction involves oxidation–reduction. The chlorinating ability of the metal halides correlates nicely with their oxidation–reduction potentials (Table V).

An interpretation[10] based on the combined effect of coördinative ability and ease of reduction of the metal chloride is consistent with the experimental work, and should be useful as a basis for further study.

It is of interest that the reaction of anhydrous ferric chloride with chlorobenzene provides an excellent method for the preparation of quite pure, anhydrous ferrous chloride.

Aromatic Component.—Aromatic compounds which are chlorinated by ferric chloride are listed in Table I. Depending on conditions and the nature of the aromatic compound, other types of reaction can occur.

Highly nucleophilic substances such as *o*- and *p*-xylene and 1-methylnaphthalene reacted readily at 25–50° with evolution of hydrogen chloride to produce tars with no more than traces of simple chlorinated products. 1-Chloronaphthalene gave dichlorobinaphthyl in low yield.

2-Naphthol was reported[11] to yield 2,2′-dihydroxy-1,1′-binaphthyl in hydrochloric acid solution, together with 1-chloro-2-naphthol. Accompanied by varying degrees of chlorination, halogen displacement occurred with *p*-dibromobenzene[1] and rearrangement with 1,3-dimethyl-4-*t*-butylbenzene.[12]

Acknowledgment.—The authors are grateful to the following members of Jackson Laboratory: M. Hunt and V. Weinmayr for suggesting this topic for investigation, A. A. Ebert for interpretation of the infrared data, J. G. Burt for part of the experimental work and M. J. Schuler for helpful discussions.

Experimental

1. Ferric Chloride and Chlorobenzene. (a) General Procedure.—In a flask connected through a safety trap to a tube immersed in a phenolphthalein indicator solution (which was titrated with standard 2 *N* sodium hydroxide solution as the hydrogen chloride was evolved) were placed 225 g. (2 moles) of chlorobenzene and 162 g. (1 mole) of C.P. anhydrous ferric chloride. The black slurry was stirred at a rapid rate and heated during 30 minutes to 126° (internal temperature) whereupon the mixture became very thick and 1.2 cc. of 2 *N* alkali was consumed. The reaction proceeded at good velocity at 128–139° for two hours, with very little hydrogen chloride being evolved in an additional hour. The reaction mass had changed to a light tan and was appreciably smoother than when reaction first began. A total of 100% of theory of 2 *N* sodium hydroxide solution was required.

The solid was collected and washed with about 200 cc. of chloroform. The filtrate was distilled through an 8-in., helix-packed column with a variable take-off head. Infrared analysis showed an 86% yield of dichlorobenzenes (88% *para*, 11% *ortho*, 1% *meta*).

The ferrous chloride could be rechlorinated at 110–135° to ferric chloride and used again.

Anal. Calcd. for $FeCl_2$: Fe, 44.10. Found: 43.89.

Anal. Calcd. for $FeCl_3$ (after chlorination): Fe, 34.3. Found: Fe, 33.49.

(b).—In a similar experiment at 131–148° for one hour, the product from one mole each of ferric chloride and chlorobenzene was worked up by pouring into ice and hydrochloric acid. The organic material obtained by ether extraction was distilled and the following fractions taken: I, b.p. 129–132°, 57 g.; II, b.p. 132–172°, 9 g.; III, b.p. 172–173°, 56 g., m.p. 48.1–48.5°, f.p. 48.5–48.1°; hold-up, 14 g. Infrared analysis showed 89% *p*-, 10% *o*-, and 1% *m*-dichlorobenzene in III, while the m.p.–f.p. data indicated a composition of 91% *p*- and 9% *o*-dichlorobenzene. The total yield from infrared analysis of all fractions was 78% dichlorobenzene ($p/o/m$ = 88/11/1). The hold-up contained 0.7% (0.1% yield) of 1,2,4-trichlorobenzene and no 4-chlorobiphenyl or 4,4′-dichlorobiphenyl. There were no bands present which could not be accounted for by the compounds cited. Fraction III was analyzed.

Anal. Calcd. for $C_6H_4Cl_2$: Cl, 48.24. Found: Cl, 47.72.

Procedure 1-b was repeated with hydrogen chloride bubbling in at 130–137°. Dichlorobenzene was obtained in 76% yield (from m.p.–f.p. data on main fraction, p/o = 90/10).

Procedure 1b was followed (1.4 moles of ferric chloride and 2.8 moles of chlorobenzene) with the modification that a Hanovia high-pressure, quartz, mercury-arc lamp was placed at a distance of five inches from the quartz reaction flask. Hydrogen chloride was first evolved at 130°. A 77% yield of dichlorobenzene was obtained (p/o = 88/12, from m.p.–f.p. data on main fraction).

2. Ferric Chloride and Iodobenzene.[13]—A mixture of 204 g. (1 mole) of iodobenzene and 81.1 g. (0.5 mole) of ferric chloride gave copious quantities of acid gas without external heating. The temperature rose to 35.5° and after 25 minutes 0.13 mole of hydrogen chloride had been evolved. Only traces of hydrogen iodide were in the trap.

The reaction mixture became very thick and reddish as soon as gas was evolved and gradually grew lighter in color. After heating to 148° for one hour, the mixture was steam distilled. A red oil was obtained and a quantity of yellow solid formed in the condenser. The solid weighed 4.3 g., and was mostly *p*-diiodobenzene, m.p. 129° (*Anal.* Calcd. for $C_6H_4I_2$: I, 77.0. Found: I, 77.5), besides a solid, m.p. 107–115°.

The red oil was separated, dried and distilled. Iodine contaminated the distillate, even at reduced pressure. Iodobenzene (151.8 g.) was recovered and a small amount of forerun which had b.p. 71–132°, $n^{24.5}{}_D$ 1.4806, and contained benzene. The fraction, b.p. 110–117° (28 mm.), 34.9 g., contained about equal amounts of *o*- and *p*-chloroiodobenzene from infrared analysis (very little *meta* isomer). The pot residue (3.7 g.) was mostly *p*-diiodobenzene (m.p. 127.5–128.5°).

The iron salts left after evaporating the steam flask residue to dryness contained 11.4 g. of iodine as iodide.

3. Ferric Chloride and Fluorobenzene.—No reaction occurred at reflux (85°) in a stirred flask. Only a trace of *p*-chlorofluorobenzene was obtained after four hours at 100° in a nickel bomb. See Table I for results at 119–124°. At 145–153° for four hours with fluorobenzene (1 mole) and ferric chloride (0.5 mole), an 80% yield of product was obtained which was essentially all *p*-chlorofluorobenzene by infrared analysis. The main fraction, b.p. 129.5–130°, $n^{16}{}_D$ 1.4965, m.p. −21.5°, f.p. −26.2°, was analyzed.

Anal. Calcd. for C_6H_4ClF: F, 14.54; Cl, 27.15. Found: F, 14.16; Cl, 27.07. The literature[14] gave b.p. 130°, $n^{15}{}_D$ 1.4990, f.p. −27.7°.

4. Ferric Chloride and *o*-Dichlorobenzene (Procedure 1a).—The results are given in Table I. The *o*-dichlorobenzene used was a commercially available product having the composition of 93% *o*-, 6% *p*- and 1% *m*-isomer. The product distilled at 211–213°, $n^{24}{}_D$ 1.5708. Infrared analy-

---

[10] With the assumption that formation of a polar complex occurs first, a subsequent intermediate might be $ArFeCl_2$ which in this case would react with ferric chloride in a fast step and in other instances may dissociate to Ar· followed by dimerization, as in conversion of pyridine to α,α'-bipyridyl (F. Hein and H. Schwedler, *Ber.*, **68**, 681 (1935)).

[11] I. S. Ioffe, S. G. Kuznetzov and S. Litovskii, *J. Gen. Chem.* (*U.S.S.R.*), **5**, 1685 (1935); *C. A.*, **30**, 3426 (1936).

[12] D. Nightingale, R. G. Taylor and H. W. Smelser, THIS JOURNAL, **63**, 258 (1941).

[13] O. von Dumreicher, *Ber.*, **15**, 1866 (1882), reported that the reaction of iodobenzene with aluminum chloride gave *p*-diiodobenzene and benzene (yield about 10%). Thomas[1] obtained *p*-chloroiodobenzene from ferric chloride and either iodobenzene or diiodobenzene.

[14] A. F. Holleman, *Rec. trav. chim.*, **34**, 204 (1915); P. S. Varma, *et al.*, *J. Indian Chem. Soc.*, **21**, 112 (1944); *C. A.*, **39**, 1395 (1945).

sis showed 67% yield of 1,2,4-trichlorobenzene and a small amount of 1,2,3- and/or 1,3,5-trichlorobenzene.

Anal. Calcd. for $C_6H_3Cl_3$: Cl, 58.30. Found: Cl, 58.49.

Reaction resulted in no change in the *p*-isomer content.

5. **Ferric Chloride and Toluene with Aluminum Chloride Catalyst** (By Dr. J. G. Burt).—Toluene (215 g., 2.34 moles) was allowed to react with ferric chloride (233 g., 1.44 moles) in the presence of aluminum chloride (12 g., 0.09 mole). Hydrogen chloride evolved at about 40–60° during three hours amounted to 117% of theory. The reaction product was isolated by steam distillation, drying and fractionation. The chlorotoluene fraction had b.p. 155–165°; 91 g., 64% yield based on the ferric chloride. Infrared analysis of all fractions showed a 69% yield of chlorotoluene ($p/o/m$ = 91/9/<1).

A mole ratio of toluene to ferric chloride of 3.5/1 under the same conditions gave a 62% yield of chlorotoluene (p/o = 89/11).

A black almost infusible, water and ether-insoluble solid was obtained in each case which contained carbon, chlorine, hydrogen and iron.

6. **Ferric Chloride and 1-Chloronaphthalene.**—To 40.4 g. (0.28 mole) of ferric chloride was added slowly 61.1 g. (0.376 mole) of 1-chloronaphthalene. The mixture evolved hydrogen chloride rapidly and was heated to 52° over three hours. Unreacted 1-chloronaphthalene was steam distilled out. The dark residue was extracted with chloroform, the solvent evaporated, and the residual oil recrystallized from acetic acid. Crystals, 4.3 g., m.p. 208–211°, were collected, dissolved in benzene and decolorized with carbon. The solid obtained, 0.7 g., m.p. 219–220°, was analyzed. Additional solid, 2.6 g., m.p. 213–216° and 216–217°, was obtained from the benzene solution.

Anal. Calcd. for $C_{20}H_{12}Cl_2$: C, 74.35; H, 3.74; Cl, 21.91. Found: C, 74.03; H, 3.52; Cl, 22.12.

7. **Ferric Chloride and Benzene.**—As reported by Thomas,[1] chlorination was sluggish. Ferric chloride (1 mole) and benzene (1.5 moles) produced only a 30% yield of hydrogen chloride after 17 hours at the reflux temperature, and 67 g. of benzene- and water-insoluble black solid (inorganic material present). Chlorobenzene was formed in no more than 6% yield (as distillation hold-up).

8. **Chlorination of Chlorobenzene with Chlorine Gas.**—Chlorobenzene (2 moles) was chlorinated with chlorine gas (0.59 mole) at 125–130° using ferric chloride (0.015 mole) as catalyst. Tan ferrous chloride was formed during the reaction. (Found: Fe, 46.6; Cl, 46.0.)

Analysis of the distilled products by infrared showed a 96% yield of dichlorobenzene ($p/o/m$ = 54/46/<1) based on weight increase during chlorination. The distillation residue contained 1,2,4- (3.5% yield) and 1,3,5-trichlorobenzene and unidentified material. The f.p. of the dichlorobenzene fraction corresponded to 56% *p*- and 44% *o*-dichlorobenzene, which confirmed the infrared analysis.

9. **Analytical Methods.**—The infrared spectra[15] of the following compounds were obtained in cyclohexane solution and the absorption coefficient calculated at the indicated wave lengths (microns): benzene (14.85), chlorobenzene (13.52, 14.23, 14.62), *o*-dichlorobenzene (13.38), *p*-dichlorobenzene (12.23), *m*-dichlorobenzene (12.75), 1,2,4-trichlorobenzene (12.35), toluene (13.75), *o*-chlorotoluene (13.40), *p*-chlorotoluene (12.45), *m*-chlorotoluene (13.0), 2,4-dichlorotoluene (12.0, 14.15), benzyl chloride (14.35), bromobenzene (13.62), *p*-chlorobromobenzene (12.30), *o*-dibromobenzene (13.42), fluorobenzene (13.3) and iodobenzene (13.7). The concentration of the various isomers in a mixture was obtained by calculation from the absorbance at the characteristic wave lengths.

A comparison of known mixtures showed the method to be accurate within 2%. The smallest detectable amount of *m*-chlorotoluene in a typical mixture was calculated to be 0.5% from the specific absorption coefficient and for *m*-dichlorobenzene the amount was 0.7%. A Perkin–Elmer infrared spectrophotometer model 12-C was used in this work.

In some cases, isomer ratios were obtained from freezing and melting points of the main portion of the product consisting of a mixture of *o*- and *p*-dichlorobenzene, and were found to deviate from infrared data usually by no more than 2%. Use was made of a freezing point curve for mixtures of *o*- and *p*-dichlorobenzene similar to the one reported by Holleman and van der Linden.[4]

---

[15] *Cf.* J. Le Comte, *Compt. rend.*, **204**, 1186 (1937); *C. A.*, **31**, 4205 (1937); **32**, 2833 (1938).

WILMINGTON, DELAWARE

[CONTRIBUTION FROM THE RESEARCH LABORATORIES, SHAWINIGAN CHEMICALS LIMITED]

Acetylene Polymers: Preparation, Physical Properties, Infrared and Ultraviolet Spectra[1]

BY K. K. GEORGIEFF, W. T. CAVE AND K. G. BLAIKIE

RECEIVED NOVEMBER 9, 1953

Monovinylacetylene (M.V.A.), divinylacetylene (D.V.A.), 1,3-butadienylacetylene (B.D.A.), 1,3,7-octatrien-5-yne (I) and a 7-yne acetylene tetramer thought to be 1,3,5-octatrien-7-yne (II) have been prepared by the Nieuwland reaction and separated by the high vacuum, fractional distillation–condensation technique. Some of their physical properties have been measured and vapor pressure curves, infrared spectra with band assignments and ultraviolet spectra with extinction coefficients are reported. Mass spectra were obtained but details are not given. The ultraviolet spectra of polymers of monovinylacetylene and divinylacetylene also were obtained. Evidence in support of the 1,3,5-octatrien-7-yne constitution for the 7-yne tetramer is given and a mechanism of formation is suggested.

Many of the lower polymers of acetylene occur as impurities in acetylene generated from calcium carbide[2] and as by-products in many reactions of acetylene, *e.g.*, the synthesis of acrylonitrile,[3-7] and monovinylacetylene for chloroprene.[8,9] Their identification and quantitative estimation is a matter of practical and theoretical importance, but known chemical methods are impractically difficult.

It has been found that the infrared and ultraviolet spectra provide convenient methods for both qualitative and quantitative determinations. This paper presents spectroscopic and other physical

---

[1] The authors wish to thank Shawinigan Chemicals Ltd. for permission to publish this paper.

[2] A. Müller, *Angew. Chem.*, **62**, 166 (1950).

[3] R. L. Hasche and J. G. McNally, F.I.A.T. Final Report No. 836 (1946).

[4] D. Brundrit and W. Hunter, B.I.O.S. Final Report No. 1057 (1947).

[5] A. S. Carter, F.I.A.T. Final Report No. 1025 (1947).

[6] F. Nill and R. Largent, F.I.A.T. Final Report No. 1125 (1947).

[7] A. S. Fromholz, B.I.O.S. Miscellaneous Report No. 90.

[8] P. V. Zhavoronkov, A. P. Alekhina and R. S. Shter, *Sintet. Kauchuk*, No. 2, 12 (1934); *C. A.*, **29**, 3976 (1935).

[9] A. L. Klebanskii, L. G. Tzyurikh and I. M. Dolgopol'skii, *Bull. acad. sci. U.R.S.S.*, No. 2, 189 (1935); *C. A.*, **30**, 1259 (1936).