[Contribution from the Research and Development Department, Pennsalt Chemicals Corp.]

Reactions of Perchloryl Fluoride with Organic Compounds. I. Perchlorylation of Aromatic Compounds[1]

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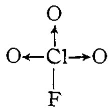
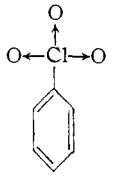
Perchloryl fluoride has been found to undergo a Friedel–Crafts type of reaction with aromatic compounds in the presence of aluminum chloride to give the novel perchlorylbenzene compounds, an entirely new series of aromatics. Evidence is presented in support of the structure Ar–ClO$_3$. The perchloryl aromatics are comparatively stable compounds, although sensitive to vigorous shock and to high temperature. They are stable in acidic or neutral media, but hydrolyze to phenols in strong alkali. Proof is given for the *meta*-directing influence of the perchloryl group in aromatic substitution reactions.

The preparation and some physical and chemical properties of perchloryl fluoride, the fluoride of perchloric acid, have been described elsewhere.[2] Analysis of the vibrational spectrum of the molecule has established a structure with a central chlorine atom and a C_{3v} symmetry, I.[3] Perchloryl fluoride was found to be surprisingly stable and unreactive except under extreme conditions; however, it gave reactions with strong bases, such as ammonia, and liberated iodine from acidified potassium iodide solution.[2a]


I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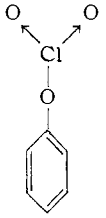
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It now has been found that perchloryl fluoride reacts readily with certain aromatic compounds in the presence of aluminum chloride or aluminum bromide. In the case of benzene, the product has the unique composition, $C_6H_5ClO_3$, a stable, colorless liquid, with an odor strikingly similar to chlorobenzene although somewhat sweeter. Speculation as to the structure of the compound led to two possibilities, II and III. Consideration of the probable characteristics of these structures favored II in which the ClO$_3$ group has retained the original symmetry of the perchloryl fluoride; and evidence presented here supports such a hypothesis for the configuration. It is proposed that this substituent be designated the "perchloryl" radical and that the process be designated "perchlorylation,"[4] analogous to Friedel–Crafts acylation.

No reaction occurs with benzene and perchloryl fluoride in the absence of aluminum chloride; however, in the presence of aluminum chloride, with excess benzene as the solvent a black color appears immediately upon subsurface addition of perchloryl fluoride gas. Heat of reaction is apparent and hydrogen chloride gas is liberated from the reaction.

$$\mathrm{ClO_3F + AlCl_3 \longrightarrow [ClO_3F\cdot AlCl_3] \longrightarrow (ClO_3)^+(FAlCl_3)} \qquad (1)$$

$$\mathrm{C_6H_6 + (ClO_3)^+ \longrightarrow C_6H_5ClO_3 + H^+} \qquad (2)$$

$$\mathrm{H^+ + (FAlCl_3)^- \longrightarrow [AlCl_2F] + HCl\uparrow} \qquad (3)$$

Equations 1 and 2 are proposed steps in the reaction, analogous to a Friedel–Crafts type electrophilic acylation of the benzene ring by the ClO$_3^+$ ion, available from the aluminum chloride assisted heterolytic cleavage of the fluorine–chlorine bond. The transitory existence of the complex in (1) is speculative. No such complex has been isolated and none is obtained when anhydrous aluminum chloride is mixed with liquid perchloryl fluoride. The presence of an acceptor, *e. g.*, benzene, for the ClO$_3^+$ ion may be necessary for the reactions to proceed simultaneously, perhaps through a complex involving all the reactants. The displacement of chlorine from the aluminum chloride is not quantitative, (3). After approximately one mole of perchloryl fluoride has reacted per mole of aluminum chloride, the reaction becomes extremely slow and ceases. The aluminum salt at this stage is a fine, amorphous, black powder containing a ratio of one fluorine to two chlorines and some adsorbed organic materials.

The reaction has been successfully applied to substituted benzenes, such as fluorobenzene and *p*-xylene, although in the latter case the yields were rather poor. In the case of nitrobenzene and other negatively substituted aromatic compounds the reaction failed.

The perchloryl aromatics are stable to vacuum or steam distillation; however, they may be detonated by vigorous shock or high temperatures. They are insoluble in water and soluble in most organic solvents. Chemically, they are resistant to reduction, being inert to such reagents as stannous chloride and hydrochloric acid, zinc and hydrochloric acid, hydrogen with palladium catalyst, lithium aluminum hydride in ether, and acidified potassium iodide. Perchlorylbenzene is thus less susceptible to reduction than perchloryl fluoride.[2a]

In strongly alkaline solutions perchloryl aromatics are hydrolyzed rapidly to phenol and chlorate ion, probably by a nucleophilic replacement of the perchloryl group with hydroxide ion.

$$\mathrm{Ar–ClO_3 + NaOH \longrightarrow Ar–OH + NaClO_3}$$

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[1] Presented in part before the Delaware Valley Regional Meeting of the American Chemical Society, Philadelphia, February 5, 1958.

[2] (a) A. Engelbrecht and H. Atzwanger, *Monatsh. Chem.*, **83**, 1087 (1952); (b) H. Bode and E. Klesper, *Z. anorg. allgem. Chem.*, **266**, 275 (1951); (c) A. Engelbrecht and H. Atzwanger, *J. Inorg. and Nuclear Chem.*, **2**, 348 (1956); (d) G. Barth-Wehrenalp, *ibid.*, **2**, 266 (1956).

[3] (a) R. P. Madden and W. S. Benecit, *J. Chem. Phys.*, **25**, 594 (1956); (b) D. R. Lide, Jr., and D. E. Mann, *ibid.*, **25**, 595 (1956); (c) **25**, 1128 (1956).

[4] This nomenclature is in accordance with that recommended by L. T. Capell of Chemical Abstracts Service in a private communication.

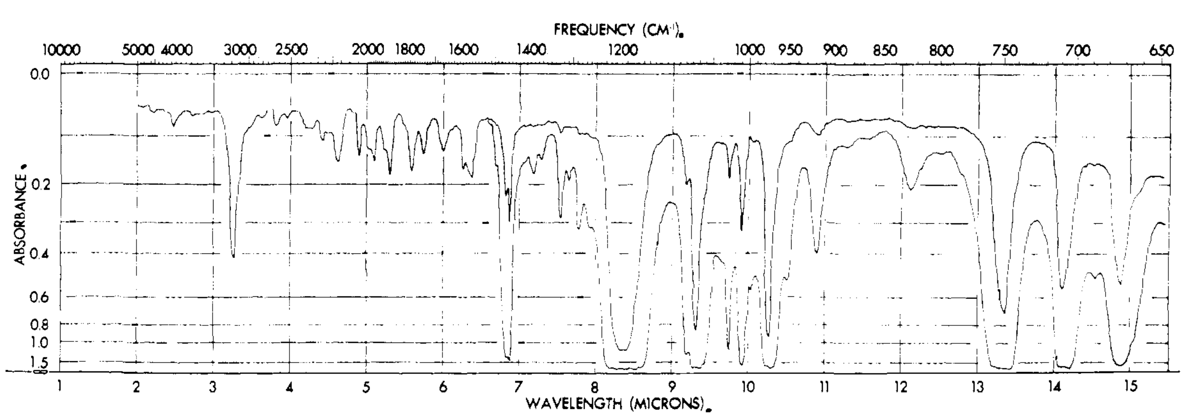

Fig. 1.

The fact that chlorate ion is formed as a product of this reaction lends support to the Ar–ClO$_3$ structure. In neutral or acidic media the perchloryl aromatics are stable at ordinary temperatures. Thus it was possible to nitrate perchlorylbenzene using the conventional sulfuric–nitric acid mixtures, producing its 3-nitro derivative. The nitro compound is reduced readily to the amino derivative with stannous chloride in hydrochloric acid. This stability of the perchloryl compounds opens many avenues of synthesis for derivatives not readily prepared by direct perchlorylation.

Alkaline hydrolysis of the nitro derivative gave *m*-nitrophenol, thus affording chemical proof of the meta orienting effect of the –ClO$_3$ group.

The infrared spectrum of perchlorylbenzene shows absorption between 1670 and 2000 cm.$^{-1}$ characteristic of monosubstituted aromatics, Fig. 1. The most striking feature of the spectrum is the very strong band at 1191 cm.$^{-1}$. It is interesting to note that both perchloryl fluoride[3c] and perchloric acid[5] also absorb strongly in this region, at 1315 and 1312 cm.$^{-1}$, respectively. This similarity is significant. The band could be assigned to a Cl–O stretching frequency. However, this is not unequivocal in that C–O absorption may occur in this range. This characteristic band is shifted somewhat by substitutions in the benzene ring; thus, for 3-nitroperchlorylbenzene absorption is at 1211 cm.$^{-1}$, for 4-fluoroperchlorylbenzene at 1198 cm.$^{-1}$, for 2,5-dimethylperchlorylbenzene and 3-aminoperchlorylbenzene at 1189 cm.$^{-1}$.

The ultraviolet absorption spectrum for perchlorylbenzene shows the three distinct peaks characteristic of benzene derivatives. The maximum at 261.5 mμ shows a shift to a higher wave length from that of benzene ($\lambda_{\max}$ 254.5 mμ) and thus is comparable to chlorobenzene ($\lambda_{\max}$ 265 mμ).[6] Compounds containing a substitution of oxygen on the benzene ring usually show a much greater shift than this, to 270 mμ or above. This evidence is in support of the –C–Cl structure.

The proton and fluorine nuclear magnetic resonance (n.m.r.) spectra were obtained for the 4-fluoro derivative of perchlorylbenzene. The *para* nature of the substituents is clearly shown by the symmetry of the proton spectrum under conditions of high resolution. Any other isomer would have a considerably more complicated spectrum.[7] The delta shift for the fluorine resonance is +1.26 referred to fluorobenzene, delta being defined as $10^5(H_r - H_c)/H_r$. Reference to data published by Gutowsky, *et al.*,[8] would suggest that the influencing substituent is –ClO$_3$ rather than –OClO$_2$, as all –OR groups tend to give negative delta shifts, but occasionally positive values to +0.15 have been measured. On the other hand, such groups as –NO$_2$, –CO$_2$H and –SO$_2$Cl in the *p*-position show large positive shifts, much greater than 0.15; thus the magnitude of the observed shift also confirms the postulated orientation.

Experimental[9]

Perchlorylbenzene.—Perchloryl fluoride gas was passed through a stirred suspension of 33 g. of aluminum chloride in 500 ml. of benzene at 10–20°. The reaction mixture immediately became black, and heat of reaction was apparent. The temperature was controlled by the rate of addition of the perchloryl fluoride and by means of a cold water-bath. Hydrogen chloride was evolved from the mixture. After approximately 3 hours the rate of evolution of hydrogen chloride became negligible and the reaction was discontinued. Thirty grams of perchloryl fluoride had been passed into the mixture; 2 g. of unreacted perchloryl fluoride was recovered from the Dry Ice cooled exit trap. The black amorphous aluminum salt was filtered from the benzene solution and dried to give 27 g. of black powder which fumed slightly in air. The filtrate was steam distilled and the benzene layer separated, dried and evaporated to give 37 g. of liquid product. Vacuum distillation gave the pure colorless liquid, perchlorylbenzene, b.p. 232°, 78° (2 mm.); f.p. −3°, $n^{20}{}_D$ 1.5208, $d^{30}{}_4$ 1.185. The ultraviolet spectrum shows adsorption at 255.5, 261.5 and 268.0 mμ. Analysis of the spent catalyst gave 6.3% F and 23.3% Cl.

Anal. Calcd. for $C_6H_5ClO_3$: mol. wt., 160.5; C, 44.90; H, 3.14; Cl, 22.08. Found: mol. wt., 165; C, 44.80; H, 3.26; Cl, 22.27.

Alkaline Hydrolysis of Perchlorylbenzene.—To a solution of 0.3 g. of potassium hydroxide in 20 ml. of 50% aqueous ethanol, 0.38 g. of perchlorylbenzene was added and the

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(5) O. Redlich, E. K. Holt and J. Bigeleisen, THIS JOURNAL, **66**, 13 (1944).

(6) Am. Petroleum Inst., Research Project 44, Ultraviolet Spectral Data Spectrogram No. 115, Carnegie Institute of Technology, Pittsburgh, Pa., 1951.

(7) H. S. Gutowsky, C. H. Holm, A. Saika and G. A. Williams, THIS JOURNAL, **79**, 4596 (1957).

(8) H. S. Gutowsky, V. W. McCall, B. P. McGarvey and L. H. Meyer, *ibid.*, **74**, 4809 (1952).

(9) Perchloryl fluoride itself is a stable compound, quite safe to handle. It is, however, a powerful oxidizing agent, and all mixtures with oxidizable substances should be considered potentially dangerous and handled accordingly. The details of handling and safety are described in Booklet DC-1819, Perchloryl Fluoride, Commercial Development Dept., Pennsalt Chemicals Corp., Three Penn Center Plaza, Philadelphia 2, Pa.

mixture refluxed for two hours. The solution was cooled and filtered to give 0.3 g. of white crystals which upon recrystallization from warm water were identified as potassium chlorate by X-ray analysis. The filtrate was diluted with water and extracted with ether to remove unreacted perchlorylbenzene. The water layer was acidified with sulfuric acid and extracted three times with small portions of ether. The ether was dried and evaporated to give a pale yellow oil. Bromination of this oil with excess bromine in aqueous potassium bromide solution gave a white solid, m.p. 89–91°; and no melting point depression when mixed with an authentic sample of 2,4,6-tribromophenol, m.p 90–92°.

3-Nitroperchlorylbenzene.—A nitrating mixture of 5 ml. of concd. sulfuric acid and 1.4 g. of concd. nitric acid was added slowly at 20–30° to a well-stirred mixture of 2 g. of perchlorylbenzene in 15 ml. of concd. sulfuric acid. Stirring was continued for one hour after complete addition and the reaction mixture was poured over ice; 2.2 g. of yellow solid was filtered from the mixture and recrystallized from benzene–light petroleum ether to give the pure 3-nitroperchlorylbenzene as very pale yellow needles, m.p. 49–50°.

Anal. Calcd. for $C_6H_4ClNO_5$: Cl, 17.25; N, 6.81. Found: Cl, 17.27; N, 6.92.

The infrared spectrum shows a very strong absorption band at 1211 cm.$^{-1}$ and is assigned to the –Cl–O stretching frequency. Absorption at 1350 cm.$^{-1}$ and probably 1529 cm.$^{-1}$ indicate a nitro group substituent, while the pattern between 1670 and 2000 cm.$^{-1}$ is characteristic of *m*-substituted benzenes.

Alkaline Hydrolysis of 3-Nitroperchlorylbenzene.—To a solution of 0.8 g. of potassium hydroxide in 25 ml. of 70% ethanol, 1.5 g. of 3-nitroperchlorylbenzene was added and the mixture warmed to 70° for 20 minutes then poured over ice and water containing a slight excess of sulfuric acid. The yellow precipitate was filtered, dried in air, then recrystallized from benzene–petroleum ether to give yellow needles, m.p. 93–94°, and no melting point depression when mixed with an authentic sample of 3-nitrophenol, m.p. 94–95°.

3-Aminoperchlorylbenzene.—To a solution of 2.8 g. of 3-nitroperchlorylbenzene in 25 ml. of ethanol and 25 ml. of concd. hydrochloric acid, 8.5 g. of stannous chloride was added in small amounts with stirring and heating to 50–60°. The mixture was held at 50–60° for 20 minutes after complete addition of the stannous chloride, then poured over ice and water and neutralized with 10% sodium hydroxide solution. The mixture was extracted three times with 50-ml. portions of ether. The combined ether extracts were dried over magnesium sulfate, then treated with dry hydrogen chloride to give 2.2 g. of a white crystalline precipitate of the amine hydrochloride. Neutralization of the hydrochloride salt with aqueous sodium carbonate solution gave a colorless oil which solidified on cooling. Vacuum sublimation gave colorless needles of 3-aminoperchlorylbenzene, m.p. 30–31°.

Anal. Calcd. for $C_6H_6ClNO_3$: C, 41.06; H, 3.44; N, 7.98. Found: C, 41.26; H, 3.57; N, 8.20.

3-Perchlorylacetanilide.—The acetyl derivative of 3-aminoperchlorylbenzene was prepared in the usual manner with acetic–anhydride in glacial acetic acid and recrystallized from ethanol to give colorless needles of 3-perchlorylacetanilide, m.p. 136–137°.

Anal. Calcd. for $C_8H_8ClNO_4$: C, 44.15; H, 3.71; N, 6.44. Found: C, 44.21; H, 3.74; N, 6.55.

4-Fluoroperchlorylbenzene.—Perchloryl fluoride gas was passed through a suspension of 13.3 g. of anhydrous aluminum chloride in 100 ml. of fluorobenzene at 25–30°. When the evolution of hydrogen chloride gas was complete the fine black solids were filtered from the fluorobenzene solution and the filtrate steam distilled. The organic layer was separated and dried over magnesium sulfate. The fluorobenzene was evaporated under vacuum to leave a pale yellow oil (12 g.). Vacuum distillation gave the pure 4-fluoroperchlorylbenzene, m.p. 28°, b.p. 53° (0.25 mm.), n^{20}_{D} 1.5051. The 2-fluoro isomer was not isolated; infrared spectrum showed a *p*-substitution pattern in the 1670–2000 cm.$^{-1}$ region and the strong Cl–O band at 1198 cm.$^{-1}$.

Anal. Calcd. for $C_6H_4ClFO_3$. C, 40.36; H, 2.25; Cl, 19.86. Found: C, 40.47; H, 2.30; Cl, 20.32.

2,5-Dimethylperchlorylbenzene.—Eight grams of anhydrous aluminum chloride was suspended in 100 ml. of *p*-xylene and the mixture cooled to 10° with an external cold waterbath. Perchloryl fluoride gas was bubbled through the mixture slowly at 10–15°. When evolution of hydrogen chloride ceased (approx. 2 hours), the reaction mixture was filtered. The filtrate was steam distilled. The oil layer was separated, dried over magnesium sulfate and distilled to give the pure 2,5-dimethylperchlorylbenzene (2 g.), a colorless liquid, b.p. 85° (0.3 mm.). Recrystallization from light petroleum ether gave colorless needles, m.p. 30–31°.

Anal. Calcd. for $C_8H_9ClO_3$: C, 50.94; H, 4.81. Found: C, 50.91; H, 4.89.

Infrared analysis, a strong Cl–O band at 1189 cm.$^{-1}$ comparable to perchlorylbenzene at 1191 cm.$^{-1}$ and the spectrum in the 1670–2000 cm.$^{-1}$ region indicated a 1,2,4-trisubstituted aromatic ring.

Anhydrous Aluminum Bromide as Catalyst for Perchlorylation.—Perchloryl fluoride gas was bubbled through a solution of 3 g. of anhydrous aluminum bromide in 250 ml. of benzene at 8–10° for one hour; 5 g. of perchloryl fluoride was used. Hydrogen bromide gas was evolved and the catalyst turned to a fine black suspension. Dilution in water and steam distillation gave perchlorylbenzene after removal of the excess benzene. The oil product was shown by infrared analysis to be identical to the perchlorylbenzene prepared using aluminum chloride as the catalyst.

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