The Reaction of Halobenzenes in a Radiofrequency Glow Discharge

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The reactions of chlorobenzene and o-, m-, and p-dichlorobenzene vapor in a radiofrequency glow discharge were studied. Chlorobenzene dissociated to yield hydrogen chloride, acetylene, chloroacetylene, benzene, chlorobenzene, o-, m-, and p-dichlorobenzene, biphenyl, o-, m-, and p-chlorobiphenyl, and low molecular weight polymers. The isomer ratio of the dichlorobenzenes (o:m:p—52:36:12) with its preponderance of o isomer suggests that a benzyne intermediate is reacting with internally formed chlorine. Phenyl and chlorophenyl radicals are also probably intermediates in the reaction. The products formed from the decomposition of the three isomeric dichlorobenzenes were in each case acetylene, hydrogen chloride, benzene, chlorobenzene, the two other isomeric dichlorobenzenes, 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzene, biphenyl, o-, m-, and p-chlorobiphenyl, dichlorobiphenyls, and polymeric material. The formation of dichlorobenzene isomers probably involves benzyne and chlorophenyl radicals.

The decomposition of chlorobenzene has been carried out employing thermal,[1] γ ray,[2] flash photolysis,[3] electrode glow discharge,[4-7] corona discharge,[8] Schuler tube,[9,10] and pulsed radiolysis[11] energy sources. Only when chlorobenzene was subjected to pulsed radiolysis by electron beams from a 2-mev accelerator were dichlorobenzenes formed. Presumably, the dichlorobenzenes were produced in small amounts since no information was given as to identification, quantity, or isomer distribution.

Three general types of aromatic chlorination of chlorobenzene are known. Heterolytic, liquid phase substitution produces dichlorobenzene mixtures with the isomer ratio $p > o > m$.[12-14] Free-radical liquid phase addition can take place between molecular chlorine and benzene or chlorobenzene to yield chlorinated cyclohexadienes, cyclohexenes, and cyclohexanes.[15-17] Vapor phase chlorinations of chlorobenzene employing molecular chlorine and heated Pyrex tubes yield principally dichlorobenzenes with isomer ratio $m > p > o$.[18,19]

In this paper some of the reactions of chlorobenzene, and o-, m-, and p-dichlorobenzene in a radiofrequency glow discharge are reported. These compounds were chosen in an attempt to obtain selective carbon-chlorine bond breaking, produce phenyl radicals or diradicals in the gas phase, and observe the formation of the products which could result therefrom.

Experimental Section

Apparatus.—The radiofrequency generator operated at a fixed frequency of 14 Mc with a power output variable to 600 w. Products were collected in the reaction tube and one trap was cooled with Dry Ice and acetone (−80°) and two traps were cooled with liquid nitrogen (−196°) as previously described.[20] In two different modifications of the reaction tube, either an inlet or a cold finger was attached at a position just downstream and above the discharge zone for the introduction of trapping agents.

Analysis.—Gas–liquid partition chromatography was employed for most qualitative and quantitative analyses. An F and M Model 500 instrument was used with the following columns, 6 ft, 0.5% Carbowax 20M on 60–80 mesh glass beads and a 12 ft, 5% Apiezon L-Bentone 34 mixture on diatomaceous earth.

Radiofrequency Decomposition of Chlorobenzene.—In 1.6 hr 10.39 g of chlorobenzene at 22° was passed through the radiofrequency glow discharge. The gauge pressure, at the pump end of the system, was maintained between 10 and 30 μ. The major portion of the gas fraction collected in the liquid nitrogen traps was a mixture of hydrogen chloride and acetylene as shown by comparison with standard spectra. Chloroacetylene was also present in small amounts. Unidentified olefins were present to a slight degree in the higher boiling segment of the gas fraction. Glpc analysis indicated the presence of twelve constituents in the −80° trap. The major products are listed in Table I. No biphenylene was detected.

Radiofrequency Decomposition of Chlorobenzene-2-d.[21]—In three successive reactions, 26.66 g of chlorobenzene-2-d was passed through the glow discharge. Its deuterium content was 103% as determined by nmr analysis. The chlorobenzene found among the reaction products was separated by preparative glpc. Nmr analysis indicated only 63% of the deuterium had been retained. The major products are listed in Table I.

Radiofrequency Decomposition of Chlorobenzene and Its Reaction with Chlorine Vapor.—Chlorobenzene vapor was passed through the glow discharge. Above the reaction zone, 5 cm, a stream of chlorine gas was bled into the reaction tube by means of a needle valve. In a typical reaction performed in a darkened room, 3.50 g (0.0311 mole) of chlorobenzene passed through the radiofrequency field and was mixed with 0.0517 mole of chlorine. The reaction time was 1.2 hr. The major products are listed in Table I.

Radiofrequency Decomposition of Chlorobenzene and Its Reaction with Bromine Vapor.—Chlorobenzene (2.13 g, 0.0191 mole) was passed through the reaction tube where 5 cm above the discharge zone it encountered a stream of bromine vapor. During 4.8 hr, 4.05 g (0.0253 mole) of bromine was added above the reaction zone. The pressure was maintained between 20 and 40 μ at the pump end of the system.

The material in the Dry Ice–acetone trap was dissolved in ether, washed with sodium bisulfite solution, water, and dried. The solution was filtered, evaporated to about 1 ml, and analyzed by glpc. The compounds present in order of their

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TABLE I

PRODUCTS FROM RADIOFREQUENCY DECOMPOSITIONS

Reactants	C_6H_6, %	C_6H_5Cl, %	$C_6H_4Cl_2$, %	$C_6H_4Cl_2$ o:m:p	$C_{12}H_{10}$, %	Other chlorinated compd, %	Polymer, %	Gas, %
C_6H_5Cl	10.4	59.2	3.2	57.0:32.0:11.0	3.2	4.0	13.7	6.9
o-C_6H_4DCl	8.1	63.3	2.4	52.6:31.8:15.6	2.7	2.0	17.5	4.1
$C_6H_5Cl^a$ + Cl_2^b	3.1^c	45.8	4.5	49.2:37.9:12.9		1.1^d		
Cl_2^a + $C_6H_5Cl^e$	2.7^c	71.8	10.5	20.3:56.4:23.4		5.6^d		

^{a} Compound which passed through glow discharge. ^{b} Mole ratio of C_6H_5Cl:Cl_2 was 3.11:5.17. ^{c} Weight of starting C_6H_5Cl taken as 100%. ^{e} Mole ratio of Cl_2:C_6H_5Cl was 0.091:0.039. ^{d} Total per cent of biphenyl plus other chlorinated compounds.

TABLE II

PRODUCTS FROM THE RADIOFREQUENCY DECOMPOSITION OF o-, m-, AND p-DICHLOROBENZENE

Reactant	C_6H_6, %	C_6H_5Cl, %	p-$Cl_2C_6H_4$, %	m-$Cl_2C_6H_4$, %	o-$Cl_2C_6H_4$, %	Other compd,^{a} %	Polymer, %
p-$Cl_2C_6H_4$	2.9	6.6	9.0	0.8	0.6	1.0	75.8
m-$Cl_2C_6H_4$	2.8	3.7	0.4	6.3	0.7	0.8	69.6
o-$Cl_2C_6H_4$	4.6	5.5	0.1	0.3	3.6	0.4	77.3

^{a} 1,2,3-, 1,2,4-, 1,3,5-Trichlorobenzene, biphenyl, o-, m-, and p-chlorobiphenyl, and dichlorobiphenyls.

retention times were benzene 15.5%, chlorobenzene 19.8%, bromobenzene 51.2%, o-dichlorobenzene 0.63%, p-chlorobromobenzene 0.61%, m-chlorobromobenzene 0.94%, o-chlorobromobenzene 2.13%, p-dibromobenzene 0.73%, m-dibromobenzene 1.69%, and o-dibromobenzene 6.74%.

Radiofrequency Decomposition of Chlorine and Its Reaction with Chlorobenzene.—Chlorine gas was admitted to the reaction tube and 5 cm above the discharge zone was mixed with a stream of chlorobenzene vapor. On completion of the reaction, the material in the reaction tube was extracted with ether. The ether solutions were reduced in volume and chromatographed on alumina using pentane as an eluent. The mixture obtained from the column contained 80% hexachlorobenzene and 20% 1,2,4,5-tetrachlorobenzene as analyzed by glpc. The products in the −80° trap were analyzed by glpc and are recorded in Table I.

Attempted Trapping of Benzyne.—In both the reactions of chlorobenzene and o-dichlorobenzene, attempts were made to trap possible benzyne intermediates. A stream of furan gas was introduced 5 cm above the glow discharge. The Diels–Alder addition product of benzyne and furan could not be detected. A second experiment employed furan frozen on a liquid nitrogen cold finger 7 cm above the reaction zone. The reactive species formed in the glow discharge were allowed to impinge on the furan and were frozen out on the cold finger. The coolant was removed and the products were drawn into the trap and analyzed. No 1,4-dihydronaphthalene 1,4-endoxide could be detected. In these experiments the pressure varied from 20 to 50 μ.

Radiofrequency Decomposition of p-Dichlorobenzene.—In a typical reaction, 6.79 g of p-dichlorobenzene was passed through the glow discharge. A pressure of 5–25 μ was maintained at the pump end of the system. A blue glow was observed throughout the reaction. The reaction tube contained 5.15 g (75.8%) of material while the Dry Ice–acetone trap held another 1.43 g (21.4%) of product. The infrared spectrum of the major gas fraction in the −196° trap was superimposible with that from hydrogen chloride and acetylene. A small amount of unidentified olefins was also present in a higher boiling gas fraction. The products found in the Dry Ice–acetone trap are listed in Table II. The compounds with the same retention times as benzene and chlorobenzene were separated from the reaction mixture and were identified as such.

The material in the reaction tube was extracted with ether and the extracts were evaporated to yield a polymeric material, mp 95–125°, containing chlorine. The polymer had an average molecular weight of 680 g/mole, contained no olefinic double bonds, and had no peaks in the 230–400-mμ range. Infrared analysis showed the presence of phenyl rings and elemental analysis gave the empirical formula $C_{6.0}H_{3.6}Cl_{2.1}$.

After two extractions with ether, polymeric residue still remained in the reaction tube. Most of this material was extracted with benzene. The combined benzene solutions were evaporated until 20 ml remained and 200 ml of methanol was added. The higher molecular weight components were precipitated while the lower molecular weight material was dissolved in the methanolic solution. The washing process was repeated to afford a yellow-brown material which decomposed at 280° and gave a positive test for halogen. The infrared spectrum showed peaks at 3050, 2950, and 2870 cm^{-1} indicative of phenyl and aliphatic hydrogen. Titration with bromine in chloroform showed that 0.82 mmole of bromine was consumed/g of polymer. The molecular weight was 3230 g/mole, and the empirical formula $C_{6.0}H_{4.5}Cl_{1.6}$.

Radiofrequency Decomposition of p-Dichlorobenzene with Added Bromine as a Trapping Agent.—Over a period of 4 hr, 2.19 g (0.0149 mole) of p-dichlorobenzene was passed through the glow discharge. At a distance 4 cm above the discharge zone a stream of bromine vapor was introduced. During the reaction, 1.86 g (0.0117 mole) of bromine was consumed. The trap at −80° contained all the liquid and solid products formed, 1.86 g of material. The dark red solution in the trap was dissolved in ether, washed with sodium bisulfite solution and water. The solution was then dried, filtered, and the ether was removed on a steam bath until only 5 ml of solution remained. Glpc analysis indicated the presence of (in order of retention times) benzene 3.04%, chlorobenzene 18.5%, bromobenzene 19.5%, p-dichlorobenzene 21.2%, m-dichlorobenzene 1.57%, o-dichlorobenzene 2.13%, p-bromochlorobenzene 13.9%, m-bromochlorobenzene 4.02%, o-bromochlorobenzene 4.67%, p-dibromobenzene 0.78%, m-dibromobenzene 1.08%, o-dibromobenzene 4.68%, 2,5-dichlorobromobenzene 2.34%, unknown 0.78%, biphenyl 1.46%.

Radiofrequency Decomposition of m-Dichlorobenzene.—In 2.2 hr, 7.54 g of m-dichlorobenzene was passed through the glow discharge. Two gas fractions were present in the collection bulb. The first, on infrared analysis was found to contain hydrogen chloride and acetylene as its major constituents. The second fraction was higher boiling and present in small amounts. It consisted of uncharacterized olefins. The major products from the reaction are listed in Table II.

The material found in the reaction tube was extracted with ether. Evaporation of the ether solutions yielded a polymeric material with the empirical formula $C_{6.0}H_{3.9}Cl_{1.9}$. Extraction of the residue with benzene dissolved almost all the remaining solid. The polymeric material soluble in benzene but not in ether had the empirical formula $C_{6.0}H_{3.9}Cl_{1.4}$.

Radiofrequency Decomposition of o-Dichlorobenzene.—In 7.75 hr, 9.53 g of o-dichlorobenzene was passed through the glow discharge. Only small amounts of hydrogen chloride could be detected in the gas fraction. An aliquot of the gas fraction was vented into a potassium iodide solution. Titration with sodium thiosulfate detected 0.0115 g of molecular chlorine. No biphenylene was found. The products found are recorded in Table II.

The reaction tube was extracted with ether and the solution was evaporated to yield polymer with an empirical formula $C_{6.0}H_{4.4}Cl_{1.9}$.

Discussion

The radiofrequency decomposition of chlorobenzene gave benzene (11%), chlorobenzene (63%), dichlorobenzenes (3%), biphenyl (2%), 1,3,5-, 1,2,4-, and 1,2,3-trichlorobenzene, o-, m-, and p-chlorobiphenyl, and dichlorobiphenyls (2% over-all), and polymeric material (15%). The gas fraction (5%) contained hydrogen chloride and acetylene as the principle constituents. The isomer ratio of the o-, m-, and p-dichlorobenzene produced was 53:35:11.

The production of dichlorobenzenes in the radiofrequency glow discharge is relatively unique. The only previous report of dichlorobenzene formation during chlorobenzene decomposition (pulse radiolysis[11]) did not list yield or isomer distribution. The dichlorobenzene, isomer ratio from the radiofrequency decomposition of chlorobenzene is also distinctive for no other reported chlorination of chlorobenzene ionic or free radical produces an isomer ratio with $o > m > p$.

In the radiofrequency decomposition of chlorobenzene carbon–hydrogen as well as carbon–chlorine bonds can be broken. The energy in the reaction system appears sufficient to rupture any bond present, and complete selectivity for carbon–chlorine bonds breaking was not realized as hoped for.

Chlorobenzene can dissociate in several ways. If chlorine is initially split off from the ring the phenyl radical formed can (1) recombine with chlorine to re-form chlorobenzene, (2) dimerize and form biphenyl, (3) combine with a source of hydrogen and form benzene, or (4) lose a hydrogen atom in the o position and form benzyne. The benzyne can then react with hydrogen chloride to re-form chlorobenzene or with internally formed chlorine to form o-dichlorobenzene. When an exterior source of bromine was present large amounts of bromobenzene and o-dibromobenzene were formed while the amounts of chlorobenzene and biphenyl decreased. The ratio of introduced bromine to chlorine available from the conversion of chlorobenzene to chlorine atoms and phenyl radicals was exactly the ratio of bromobenzene–chlorobenzene in the products. This suggests that carbon–chlorine bond scission is relatively selective in this reaction.[22] In trying to isolate benzyne, however, trapping experiments with furan failed to yield the addition product 1,4-dihydronaphthalene 1,4-endoxide. The mean free path of a benzyne molecule would be ca. 1–10 cm under these conditions, with the molecule traveling 13 cm in 500 μsec.[23] However the relatively small amounts of benzyne could have escaped detection. Chlorobenzene can also dissociate by initial loss of a hydrogen atom to form o-, m-, and p-chlorophenyl radicals. This radical can then combine with a chlorine atom to give o-, m-, and p-dichlorobenzene. The o-chlorophenyl radical may in addition lose a chlorine atom and form a benzyne intermediate. The production of dichlorobenzenes and the preponderant formation of the o isomer may involve the reaction of benzyne or the o-chlorophenyl radical with internal sources of chlorine. This indicates that the o-chlorophenyl radical is favored over other chlorophenyl

radicals, and is supported by the fact that there is a high loss of deuterium from chlorobenzene-2-d.

Dichlorobenzenes were formed in good yields when chlorine was passed through the glow discharge and mixed with chlorobenzene 5 cm above the reaction zone. The isomer ratio ($o:m:p$-20:56:23) was similar to that found in thermal chlorinations of chlorobenzene in the vapor phase ($o:m:p$-21:54:24).[18] In these reactions an activated chlorine species, probably a free radical, is attacking a chlorobenzene molecule. In the usual radiofrequency decomposition of chlorobenzene, attack by chlorine radicals on parent molecules must not be of major significance, for the dichlorobenzene isomer ratio found ($o:m:p$-53:35:11) differs notably from reactions where chlorine radical attack takes place.

The mechanism shown in Scheme I accounts for the production of monomeric products and the high percentage of o isomer among the dichlorobenzenes. The formation of more m- than p-dichlorobenzene may be due to the fact that there is a twofold statistical advantage for the formation of the m-chlorophenyl vs. the p-chlorophenyl radical.

SCHEME I

REACTION PATHWAY FOR RADIOFREQUENCY DECOMPOSITION OF CHLOROBENZENE
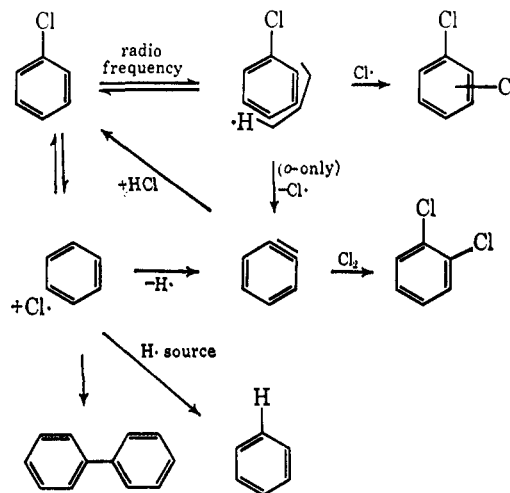
Hydrogen and chlorine species are known to be removed from chlorobenzene by electron impact.[24] It is possible that hydrogen and chlorine radical combination on the surface of the reaction tube produces the hydrogen chloride formed. In addition hydrogen chloride may be formed by the abstraction of hydrogen by a chlorine radical or by the abstraction of chlorine by a hydrogen atom. The production of acetylene must involve carbon–carbon bond rupture and consequent total degradation of the aromatic ring.

Polymeric material could be formed in several ways. Chained phenyl units can undergo ring scissons to introduce aliphatic and olefinic sections in the polymer, or polymerization of acetylene and olefinic species could take place.

The products formed from the decomposition of o-, m-, and p-dichlorobenzene were acetylene, hydrogen chloride, benzene, chlorobenzene, starting material, the two other isomeric dichlorobenzenes, 1,2,3-, 1,2,4-, and 1,3,5-trichlorobenzene, biphenyl, o-, m-, and p-

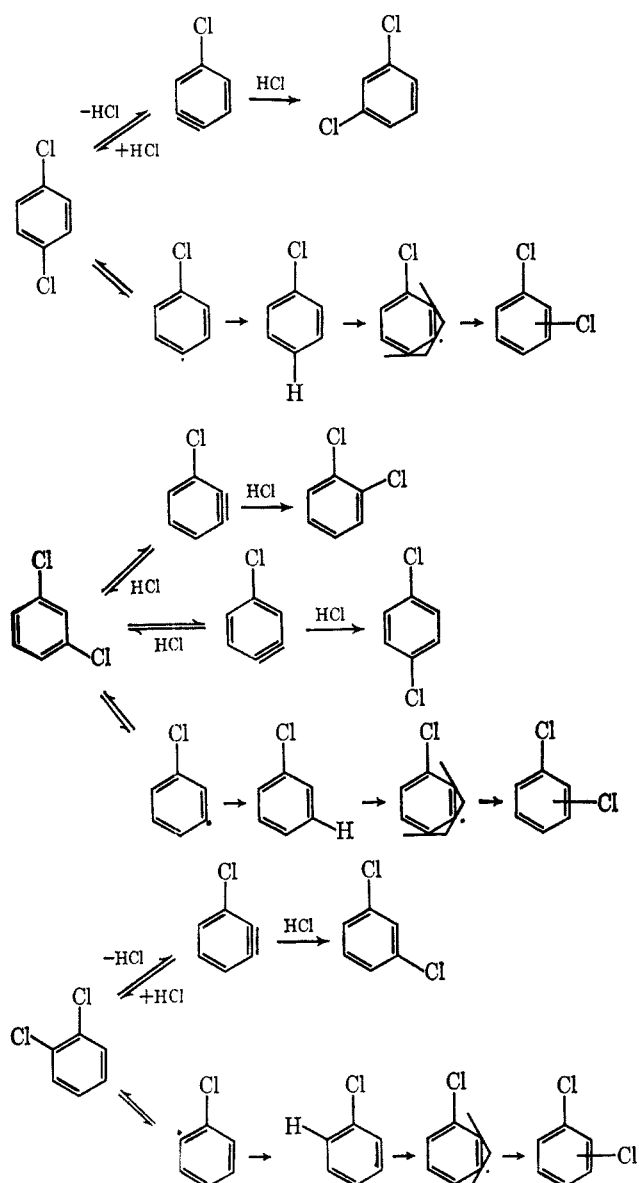(22) One of the referees pointed out this interesting correlation which we had overlooked.

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SCHEME II

chlorobiphenyl, dichlorobiphenyls, and polymeric material.

Each dichlorobenzene *o*, *m*, or *p* yields on radiofrequency decomposition the other two isomeric dichlorobenzenes. *p*-Dichlorobenzene produces *m*- and *o*-dichlorobenzene in the ratio 8:6. *m*-Dichlorobenzene produces the *o* and *p* isomers in a 7:4 ratio, and *o*-di-

chlorobenzene produces *m* and *p* isomers in a 3:1 ratio. The product ratios for the formation of the dichlorobenzenes can be explained on the basis of a benzyne intermediate. A molecule of hydrogen chloride may be lost from the parent dichlorobenzene molecule to form a chlorobenzyne intermediate. This intermediate may then react with hydrogen chloride to re-form starting material, or the hydrogen chloride may add in the reverse fashion from which it left. This would put the incoming chlorine moiety in a position adjacent to the one where chlorine was lost (Scheme II).

Although benzyne formation appears likely, it is probable that the parent dichlorobenzene is also simultaneously losing and gaining chlorine and hydrogen atoms in a stepwise fashion to yield the various isomeric products. Assuming that the reaction pathway preferentially leads to benzyne formation the correct product ratio can be predicted in each case. The formation of a benzyne intermediate also helps to explain the larger than statistically expected yields of some isomers.

When *p*-dichlorobenzene was subjected to decomposition and exposed to an exterior source of bromine, high ratios of *p*- and monosubstituted products were obtained, again indicating some selectivity in carbon–chlorine bond breaking in this special set of conditions.

It is also possible that the isomerization is taking place by means of electronically excited molecules as is observed in mesitylene.[25] For example, *p*-dichlorobenzene can undergo the following sequence of transformations.
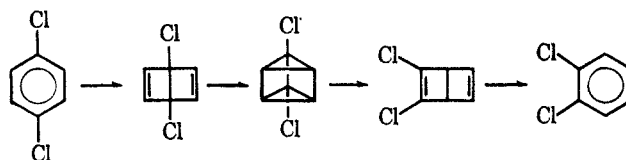
The decomposition of dichlorobenzenes in the glow discharge appears similar to that of chlorobenzene. As might be expected, introducing the second molecule of chlorine into the ring greatly increased the reactivity.[2]

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