SOURCES OF POLYCHLORINATED STYRENES IN THE GREAT LAKES AND THEIR TRIBUTARIES

U.S. Environmental Protection Agency

Grant No. ROO-5764-01

Phase 1 Report

"Potential Mechanisms Explaining Industrial Production of Chlorostyrenes"

Submitted to:
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January 5, 1984

SOURCES OF POLYCHLORINATED STYRENES IN THE GREAT LAKES AND THEIR TRIBUTARIES

REPORT - PHASE 1

POTENTIAL MECHANISMS EXPLAINING INDUSTRIAL PRODUCTION OF THE CHOROSTYRENES

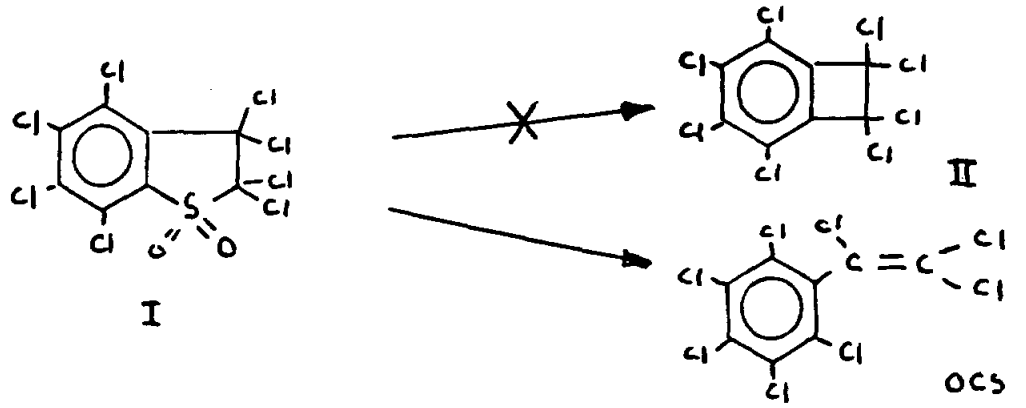
Introduction:

In spite of the wide distribution of the polychlorinated styrenes (PCS) in the environment, little is currently known regarding the sources of these compounds since they are not known to be the by-products of any specific industrial processes. This report is divided into four sections. The first will review the literature on known routes (both laboratory and adventitious) to the higher PCS compounds, specifically Cl_8, Cl_7 and Cl_3 for reference. The second will attempt to summarize the thermodynamic implications of the results outlined in the first section with an eye towards deriving inferences as to the ecological sources of the PCS's. The third section will review the known chemistry of carbon-chlorine reactions in light of expanding this data base to inferred sources of PCS in the environment. The fourth section will outline a selection of actual industrial processes wherein the mechanisms inferred in the first three sections might be operative, thereby giving the regulatory agencies an initial point to begin consideration of monitoring requirements.

I. KNOWN SOURCES OF POLYCHLOROSTYRENES

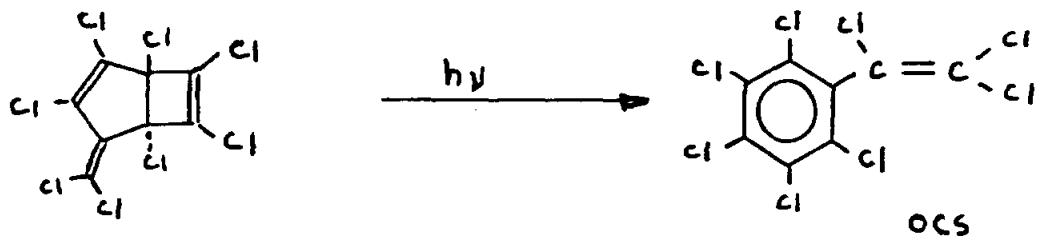
Octachlorostyrene (OCS) has been prepared in high yield by vapor phase chlorination, the subject of a 1969 patent issued to the Dow Chemical Co.[1] More recently, it was discovered that a 55% yield of OCS (+27% decachloroethylbenzene) was realized from the reaction of perchlorotoluene with cuprous chloride, diethylphosphite,

and CCl_4 at reflux.[2] Propylbenzene was chlorinated in CCl_4 at 600° to give a 39% yield of the expected perchlorondene, but yields in addition two cleavage products: hexachlorobenzene (41%) and OCS (20%).[3] When the sulfone (I) is pyrolyzed it is expected by analogy to give the corresponding perchlorobenzocyclobutene (II). Instead, at 300° in just 30 minutes, a 91% yield of OCS was realized.[4]



I II OCS

Octachlorostyrene has also been produced by photolysis of a perchloromethylenebicyclo [3.2.0] heptadiene.[5]



OCS

Octachlorostyrene (OCS) is also produced by the direct chlorinaction of perchlorophenylacetylene.[6]

In terms of production as an identified trace impurity, OCS has also been reported in an interesting series of experiments under a wide variety of conditions. The chlorinolysis of propylene is used to produce the two useful organic solvents carbon tetrachloride and tetrachloroethylene; OCS, as well as C_2Cl_6, hexachlorobutdiene, perchlorocyclopentadiene, and hexachlorobenzene,have been identified as a by-products. The chlorination of ethylbenzene, which might be expected to yield perchloroethyl-

benzene as the final product, has been shown to yield OCS in 85% yield in 12.5 seconds at 605°.[8] In a very revealing experiment, Eiceman[9] investigated the laboratory chlorination of fly ash at 300°C. Hexachlorobenzene, decachlorobiphenyl, and nonachlorobiphenyl were all produced in measurable quantities, as well as OCS in the ppb range. Interestingly, the fly ash used by Eiceman was provided by Prof. F.W. Karasek of the University of Waterloo, Ontario. Karasek had collected that fly ash from the Toronto municipal incinerator.[10] Karasek has analyzed the fly ash as received[11,12] and found polychlorinated dibenzofurans, dibenzo-p-dioxins, and benzenes, as well as a variety of polynuclear aromatic hydrocarbons. Many peaks went unidentified, and the possible presence of OCS in the original fly ash can neither be inferred nor ignored. Hexachlorostyrene and hexachlorobenzene were both detected in furnance samples taken from a wire reclamation incinerator[13]. The combustion of poly (vinyl chloride) has been found to chlorinate benzene to form dichloro, trichloro, tetrachloro pentachloro and hexachlorobenzenes as well as peaks tentatively assigned to OCS and the decachlorobiphenyl and nonachlorobiphenyls.[14]

The lower chlorinated PCS compounds have been produced by a variety of laboratory procedures. The reaction of dichloroketene (which can be produced by pyrolysis of dichloroacetate) with chlorobenzaldehyde has produced trichlorostyrene.[15] Chlorobenzaldehyde has also been reacted with Wittig type ylids to produce trichlorostyrene in 67% yield.[16,17,18] Trichloromethyl phenyl carbinols have been dehydrated over aluminosilicate catalysts at 500°C to yield rearrangement to tri and tetrachlorostyrenes (said to be useful as chain growth regulators for polyalkenes).[19] Similar dehydrations using P_2O_5 or $POCl_3/SOCl_2$/pyridine have produced tetrachlorostyrene in the 90% yield range.[20] We have shown in a detailed mechanistic study[21] that phenyl radicals derived from the thermolysis of benzoyl peroxide add to tetrachloroethylene to give the phenyltetrachloroethyl radical. This radical transfers a chlorine atom to tetrachloroethylene to

produce a high yield of trichlorostyrene. The pentachloroethyl radical thus produced shows up as pentachloroethane and hexachloroethane, demonstrating the radical migrations of chlorine atoms under relatively mild (ca.100°C) conditions.

II. THERMODYNAMIC IMPLICATIONS:

The brief summary of the known chmistry leading to the production of polychlorinated styrenes given above is not, in and of itself, meant to imply any industrial source of the polychlorinated styrene (PCS) compounds found in the environment. While it does point out some interesting possibilities of industrial sources such as pointed out in municipal incineration and the combustion of PVC plastics, or the chlorinolysis reaction of propylene, the main thrust of Section I was laboratory experiments and syntheses. Its purpose was to direct our thinking along potential mechanistic pathways to lead us to fruitful questions and hence to possible solutions.

One theme presents itself as obvious from our survey of the chemistry of the polychlorinated styrene compounds - their thermodynamic stability. Laboratory procedures designed to produce PCS in classical approaches, such as the Wittig, succeed. However, when approaches are taken to other compounds, such as those outlined above for the production of perchloroethylbenzene, perchlorobenzocyclobutene or perchloroindene, the result was instead the unpredicted formation of octachlorostyrene (OCS). When the complex carbonaceous silicate that forms fly ash is challenged with chlorine, octachlorstyrene forms. Dehydrations of trichloromethylcarbinols yield rearrangement to styrenes. Addition of phenyl radical to tetrachloroethylene does not yield phenyltetra or pentachloroethane or diphenyloctachlorobutane, it produces instead trichloroystyrene. Thermolysis or photolysis of varied perchlorinated ring systems yield rearrangement to octachlorostyrene.

From the synthesis of this diverse data base, we are led to one unifying theme -

the intrinsic thermodynamic stability of the polychlorinated styrene system as an end product. It would seem that if enough energy is put into the system, and the elements are present, PCS compounds will result in some yield. Before proceeding to project potential industrial sources of the PCS compounds, a review of the known chemistry of carbon-chlorine reactions is in order.

III. CARBON-CHLORINE CHEMISTRY

The synthesis of octachlorostyrene, hexachlorobenzene, decachlorobiphenyl and other unidentified perchloro organics, formed by carbonaceous materials reacting with chlorine, is a thermodynamically controlled reaction. Generally, octachlorostyrene is formed in a high temperature reaction and the temperature of reaction is above 212°C[9]. The reaction which forms octachlorstyrene undoubtedly occurs to some extent from 275°C to 6,000°C. The formation of octachlorostyrene probably maximizes in the 300°C to 800°C range. It has been reported, however, that hexachlorobenzene and decachlorobiphenyl will thermolyze to unidentified high boiling chloro aryl compounds at temperatures in excess of 600°C but both compounds are formed in maximum yields in the 300°C to 600°C range.[22] We must assume that octachlorostyrene could also possibly rearrange above 600°C to other polychlorinated aromatic compounds.

Almost all graphites and carbonaeous materials and industrial forms of carbon contain hydrogen as a trace constituent. When these carbons are treated with chlorine, hydrogen chloride gas is evolved throughout the temperature range of about 40°C to several hundred degrees C.[22]

The chlorination of carbon is an exothermic reaction. In most chlorination reactions with different forms of carbon there is an activation reaction. Aside from the conversion of graphitic hydrogen to HCl, the activation temperature for the chlorination of aromatic carbon bonds is in the 275°C to 300°C range. When

chlorine reacts with carbon, chlorine radicals and trichlorocarbon radicals form and recombine to form carbon tetrachloride. Other carbon-chlorine compounds are formed when carbon reacts with chlorine and, these reactions will be subsequently discussed. The kinetics of the direct chlorination of carbon have been studies.[23] The fundamental reaction at temperatures in the 600-800°C is

$$C + 2Cl_2 \rightleftharpoons CCl_4$$

the production of carbon tetrachloride. The reaction is first order in chlorine pressure and depends on the rate of chemisorption of Cl_2 on the carbon surface (E_a=25 Kcal/mol). Chlorine also forms the calates ($C_{12}Cl$;$C_{18}C_1$).[24] However, the reaction is far more complicated than it might appear since the history of the surface (degree of graphitization, pretreatment with oxygen or chlorine, etc.) has a profound effect on the observed rates. Furthermore, the equilibrium expressed in the simple equation above does not result in a quantitative explanation for the observed reactions. Most interestingly, if CCl_4 product is heated on the carbon surface, further chemistry is observed in that a mixture of tetrachloroethylene and hexachloroethane are produced. Hexachloroethane is known to break down at moderate temperatures to yield tetrachloroethylene and chlorine.[25] The reactions considered by Blackwood and Cullis[22] to explain these results:

$$2CCl_4 \rightleftharpoons C_2Cl_4 + 2Cl_2$$

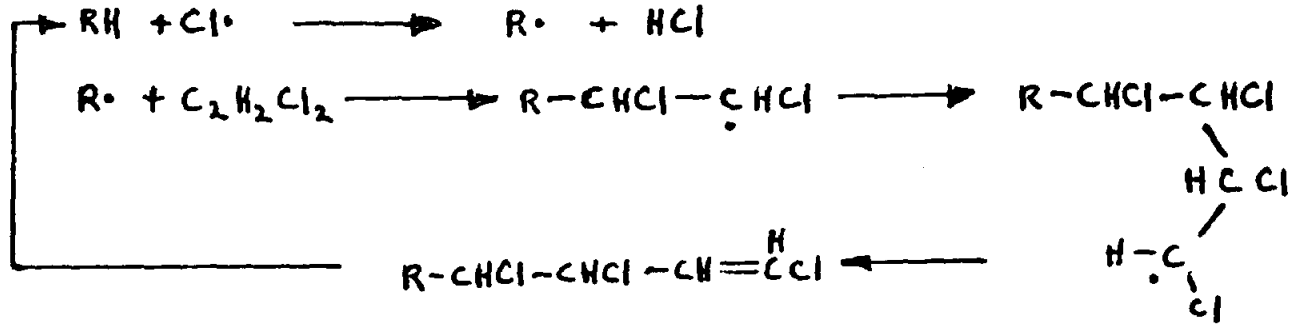
$$2CCl_4 \rightleftharpoons C_2Cl_6 + Cl_2$$

$$(CCl_2) + CCl_4 \rightleftharpoons C_2Cl_6$$

$$C_2Cl_4 + Cl_2 \rightleftharpoons C_2Cl_6$$

are at best gross simplifications. The C-Cl bond is a relatively weak one. (84 Kcal/mol).[26] The trichloromethyl radical is rather stable (or persistent) and tends to abstract H's rather than add to the double bond.[27]

The mono chlorination of n-propyl chloride favors 1,2-dichloride at low temperatures (158°) but favors 1,1-dichloride at higher temperatures (380°).[28] Chloroalkene dimerization reactions have been studies[29] and result in extension of chloroalkene chains, e.g.



In light of these known reactions, the production of C_2Cl_4 and C_2Cl_6 from CCl_4 or carbon might better be explained as follows:

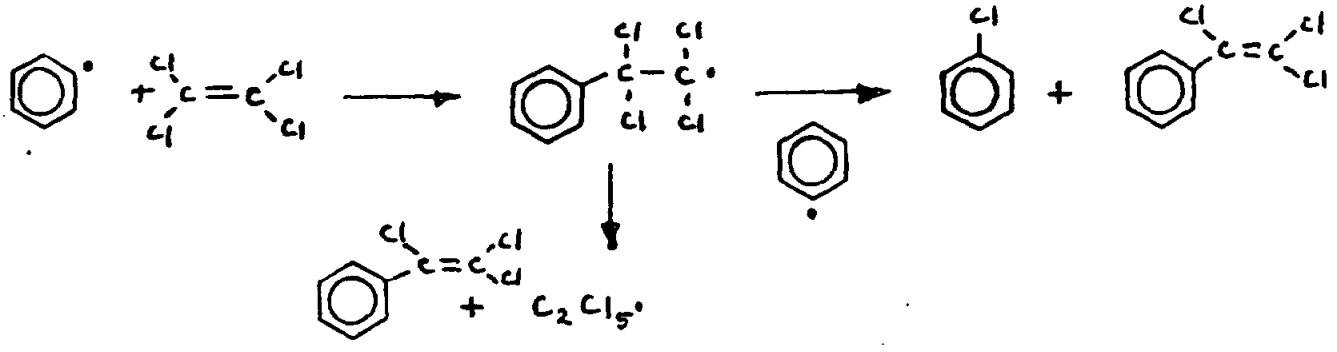
$$CCl_4 \rightleftharpoons CCl_3\cdot + Cl\cdot$$

$$2CCl_3\cdot \rightleftharpoons C_2Cl_6$$

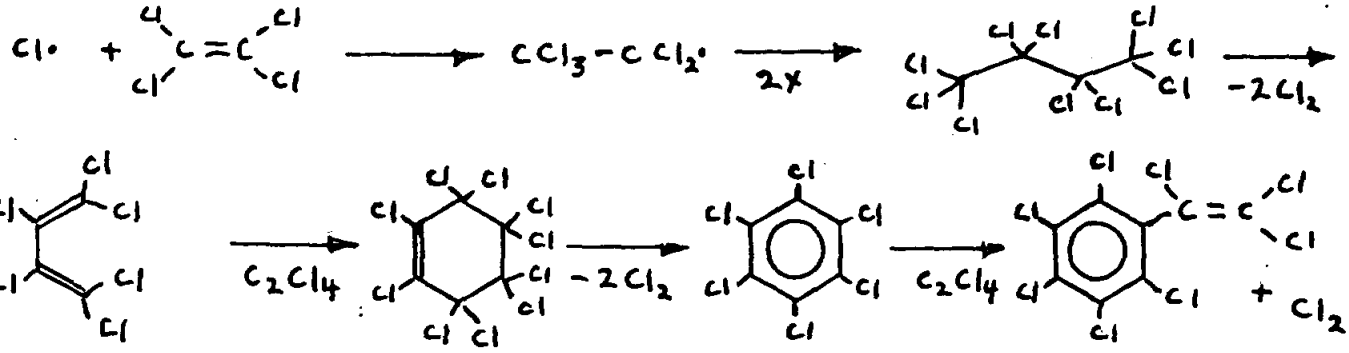
$$Cl\cdot + C_2Cl_6 \rightleftharpoons Cl_2 + C_2Cl_5\cdot$$

$$Cl\cdot + C_2Cl_5\cdot \rightleftharpoons Cl_2 + C_2Cl_4$$

In addition, we have already shown[21] that phenyl radicals (taken here as a model for any aromatic or polychloroaromatic radical) add to tetrachloroethylene and chlorine atom is further extracted to yield styrenes.



The coproduction of hexachlorobutadiene by dimerization-disproportionation of tetrachloroethylene, followed by 2+4 cycloaddition and aromatization could provide a route into polychlorobenzene chemistry.



Hence, while the only identified products from the Blackwood study[22] were CCl_4, C_2Cl_4 and C_2Cl_6, the possibility of trace amounts of higher chlorocarbons, even octachlorostyrene, cannot be excluded. Russian workers[30] have studied the interaction of chlorine with atomically pure graphite surfaces and found a 1:4 yeild of CCl_4:C_2Cl_4, while Lauterbach[31] has in fact reported a scheme similar to the one proposed above to explain the formation of hexachlorobenzene from reactions of carbon with an atomic beam of chlorine. Schmeisser[32] postulates an alternative building of chlorocarbons at very high temperatures from dichlorocarbene CCl_2:

$$12CCl_2 \longrightarrow 3C_2Cl_6 + C_6Cl_6$$

Whatever the detail of the mechanism, it seems likely that a carbon-chlorine reaction can and will build up perchloroaromatics, (hexachlorobenzene and decachlorobiphenyl), and that these in turn could form octachlorostyrene. In the next section we will look at those industrial processes where either aromatic radicals are used in conjunction with chloroalkenes, or elementary carbon (and associated polynuclear aromatics) are found in close contact with either chlorine or chlorine atom precursers under conditions that might lead to the formation of polychlorinated styrenes.

IV. INDUSTRIAL PROCESSES OF IMMEDIATE INTEREST

A. Radical Initiated Chloralkene Polymerizations

The free radical initiated polymerization of vinyl monomers is a large scale commerical process exceeding 10^{10} lb/yr in the U.S. alone.[33] Such polymerizations are generally chosen because of their extremely clean yield of polymer, but as with all chemical processes, some side products are inevitably formed. Both vinyl chloride polymerization, and vinyl chloride-vinylidene chloride copolymerization are carried out with radical initiation. Common initiators for such processes include benzoyl peroxide (phenyl radical source) as well as p-chlorobenzoyl peroxide and 3,4-dichlorobenzoyl peroxide. As we have indicated, chlorine atom metastisize, moving from one radical to another, results in the formation of highly stable chlorinated styrenes. Any process involving aromatic radicals, vinyl or styrene monomers, and chlorine atom sources, warrants our investigation.

B. Electrochemical Processes which use Carbon Electrodes and Involve the use of Chlorides

The mechanisms of carbon-chlorine reactions at elevated temperatures as previously discussed, brings into consideration any process which involves the use of a carbon anode in a chloride containing medium.

Synthetic graphite, manufactured by the pyrolysis of petroleum and coke at temperatures exceeding 2,800°C,[34] finds major use in the manufacture of electrolytic anodes for the production of chlorine, aluminum, magnesium and sodium.[35] Synthetic graphite consists of layers of hexagonally arranged carbon atom planes which can easily trap chlorine atoms or metallic chloride complexes between the lattice planes (i.e. intercalate). The calates are precise stoichiometric interstital compounds of an element with carbon. Most graphites in commericial use contain small amounts of hydrogen as C-H bonds and oxygen as phenolic, quinone and carboxylic acid groups. Smaller amounts of nitrogen and sulphur containing compounds are present along with several other elements.[34]

If chloride is converted to chlorine on or within a graphite electrode, at temperatures $>275°C$, it is possible to synthesize carbon tetrachloride, tetrachloroethylene, hexachloroethane, hexachlorobenzene, decachlorobiphenyl, octachlorostyrene and possibly several other chloroaromatic compounds. This reaction and its subsequent products thus can form in any fused chloride salt electrolysis process which use carbon anodes or carbon furnance liners etc.

The largest end use for carbon anodes is primarily the chlor-alkali process, followed by the Dow process for the electroylsis of fused magnesium chloride and the electroyltic production of sodium metal. The electro-metallurgical industries use carbon electrodes to electrolyze fuse salt baths (usually chloride

and/or fluorides) for the production of metals such as tantalum and niobium, etc.[34]

B. 1 Electrolysis of Aqueous Chloride Salts with Carbon Electrodes

Carbon is widely used as an anode in the electrolysis of water-sodium chloride and water-potassium chlorides solutions.[36,37,38] Chloride (Cl^-) is converted to Cl. in one electron transfer step. The electrolysis of brine (NaCl) on the Niagara Frontier is a primary industrial process, especially in Niagara Falls, N.Y. Brine electrolysis generally is performed with a carbon anode cell at 78°C but the carbon anode can be at temperatures up to 200°C, especially when high currents (200 Amperes) are used. The carbon anode is deteriated and corroded by hypochlorite which is produced from the water during the electrolysis. Thus large amounts of carbon dioxide and carbon monoxide are evolved during the electrolysis. The electrodes are replaced every several months. Porous graphite electrodes are widely used for brine electrolysis. Thus, polycylic aromatic hydrocarbons along with graphite are present and can be chlorinated. Chlorine forms in surface pit defects on the graphite surface and, thus, the porous carbon electrodes are preferred for chlorine production. Chlorine containing residues collect in the brine filter screens[39] and are a likely source of polychlorinated aromatic hydrocarbons and PAH's. Most of the polychlorinated polycylic hydrocarbons would probably be formed from the chlorination of PAH's or polystyrene residues contained within the electrodes. Carbon tetrachloride evolution has not been reported for this electrolysis process, and thus, it seems unlikely that octachlorstyrene will be formed in any large amount - perhaps at the ppb level only? Also the corrosion process for these electrodes favors the formation of carbon dioxide and not chlorinated aromatic hydrocarbons. However, the high density of chlorine radicals at the electrode surface defects undoubtedly will

tend to form carbon-chlorine bonds, but the degree of reaction is uncertain and no information in the literature could be found to simulate such high concentrations of chlorine radical in the presence of carbon at 200°C. This process should be included as a possible source of trace amounts of octachlorostyrene and should be investigated further through personal interview contacts.

Battery systems which use a zinc chlorine reaction and employ graphite electrodes[40] could be a possible source of chlorine aromatic compounds, but there is no documented evidence for their formation in the literature.

B.2 Electrolytic Production of Magnesium

Magnesium is produced by electrolysis of fused $MgCl_2$ in steel cell using carbon anodes.[41] Production is carried out in the 700°C range and produces 1 mole of chlorine at the carbon anode for every mole of magnesium produced. Approximately 100g of anode is consumed for every kg of magnesium produced, with production capacity at Dow (Freeport, Texas)at 115,000 metric tons/yr. Largest producers are the US, USSR, and Norway. It is interesting to note that Norsk Hydro has a capacity of 50,000 metric tons/yr at Porsgrunn at the mouth of the Oslo Fjord - a site of reported hexachlorobenzene, decachlorobi pleny1 and octachlorostyrene contamination.

The formation of chlorine, in the presence of a high current density at temperatures of 700°C on a carbon surface, makes this process highly suspect as a source of octachlorostyrene.

B.3

Sodium is produced by the electrolysis of fused sodium chloride.[37] The Downs cell (used at DuPont, Niagara Fally, New York) utilizes a carbon anode constructed of several graphite blocks surrounded by an iron-gauze diaphragm and a cylindrical iron cathode. The bath operates at a lower temperature than in magnesium production, usually about 580°C (with a 58% $CaCl_2$/42% NaCl feed) but at high current densities of about 7 amps/inch^2. The cell life is governed by destruction of anode in about one year of operation. Most of the carbon loss is attributable to reaction with oxides or water to form CO or CO_2, but we have been informed[39] that CCl_4 boils off from the cells. In light of our previous statements concerning carbon-chlorine reactions, this is not at all unexpected, and as a matter of fact might simply be the marker (in light of the mechanisms spelled out above) for the formation of hexachlorobenzene and octachlorostyrene. The chlorination of carbon at temperatures above 300° has produced carbon tetrachloride, tetrachloroethylene, hexachloroethane, hexachlorobenzene and probably decachlorobiphenyl and octachlorostyrene.

B.4 Aluminum Production

Most aluminum is produced in the Hall-Deroult/cell which while it uses carbon anodes, does not contain chlorine in the cell charge.[43] The standard eutectics used consist of cryolite, alumina, and added fluorides, i.e., Na_3AlF_6, LiF, CaF_2, Al_2O_3, and thus would not be prime candidates for polychlorinated styrene production. However, in 1976, the new Alcoa Smelting process came on line amidst calims of 30% less electrical power usage. The process reacts alumina, carbon, and chlorine to produce aluminum chloride and carbon dioxide. The aluminum chloride is electrolyzed to produce aluminum and chlorine which is recycled. The system is supposed to be environmental preferable because no fluoride is used and the chlorine is recycled. However, the process does produce chlorine on a carbon electrode at high temperature and hence is a potential producer of polychlorinated styrenes.

C. Incineration Processes which form Chlorostyrenes

High temperature combustion of chlorine containing plastics and organic chemicals can decompose to give carbon particles, fly ash, clorine, and hydrogen chloride. Chlorine can react with carbon at elevated temperatures or can react with polynuclear aromatic hydrocarbons to produce octachlorostyrene, hexachlorobenzene, chlorobenzenes, and PCB's such as decachlorobiphenyl. Chlorine can react with fly ash to form hexachlorobenzene, decachlorobiphenyl and probably a small amount of octachlorostyrene.[11]

A wire reclamation incinerator produced chlorobenzenes, hexachlorobenzene and hexachlorostyrene along with many other organic chemicals and chloro-organic chemicals by the combustion of electrical insulation containing polyvinylchloride, polyethylene, polypropylene, polychlorobiphenyls, chlorinated naphthalenes and numerous organic materials.[14] The incineration of polyvinylchloride itself can produce various chlorobenzenes, hexachlorobenzene, decachlorbiphenyl, and octachlorstyrene.[13]

Incineration of polyvinylchloride and similar plastics at a multi ton level by incinerator plants is a likely source of octachlorostyrene and should be included in our survey. Likewise any process which thermolyzes or incinerates carbon tetrachloride, tetrachloroethylene and other chloro-organic chemical in the presence of comubstible organic materials should be investigated as potential sources of octachlorstyrene.

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