CHLOROBENZENES

1. Introduction

The chlorination of benzene can theoretically produce 12 different chlorobenzenes. With the exception of 1,3-dichlorobenzene, 1,3,5-trichlorobenzene, and 1,2,3,5-tetrachlorobenzene, all of the compounds are produced readily by chlorinating benzene in the presence of a Friedel-Crafts catalyst (see FRIEDEL-CRAFTS

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REACTIONS). The usual catalyst is ferric chloride either as such or generated *in situ* by exposing a large surface of iron to the liquid being chlorinated. With the exception of hexachlorobenzene, each compound can be further chlorinated; therefore, the finished product is always a mixture of chlorobenzenes. Refined products are obtained by distillation and crystallization.

Chlorobenzenes were first synthesized around the middle of the nineteenth century; the first direct chlorination of benzene was reported in 1905 (1). Commercial production was begun in 1909 by the former United Alkali Co. in England (2). In 1915, the Hooker Electrochemical Co. at Niagara Falls, New York, brought on stream its first chlorobenzenes plant in the United States with a capacity of about 8200 metric tons per year.

The Dow Chemical Company started production of chlorobenzenes in 1915 (3). Chlorobenzene was the first and remained the dominant commercial product for over 50 years with large quantities being used during World War I to produce the military explosive picric acid [88-89-1].

The Dow Chemical Company in the mid-1920s developed two processes which consumed large quantities of chlorobenzene. In one process, chlorobenzene was hydrolyzed with ammonium hydroxide in the presence of a copper catalyst to produce aniline [62-53-3]. This process was used for more than 30 years. The other process hydrolyzed chlorobenzene with sodium hydroxide under high temperature and pressure conditions (4,5) to product phenol [108-95-2]. The I.G. Farbenwerke in Germany independently developed an equivalent process and plants were built in several European countries after World War II. The ICI plant in England operated until its closing in 1965.

In the 1930s, the Raschig Co. in Germany developed a different chlorobenzene-phenol process in which steam with a calcium phosphate catalyst was used to hydrolyze chlorobenzene to produce phenol (qv) and HCl (6). The recovered HCl reacts with air and benzene over a copper catalyst (Deacon Catalyst) to produce chlorobenzene and water (7,8). In the United States, a similar process was developed by the Bakelite Division of Union Carbide Corp., which operated for many years. The Durez Co. licensed the Raschig process and built a plant in the United States which was later taken over by the Hooker Chemical Corp. who made significant process improvements.

Although Dow's phenol process utilized hydrolysis of the chlorobenzene, a reaction studied extensively (9,10), phenol production from cumene (qv) became the dominant process, and the chlorobenzene hydrolysis processes were discontinued.

With the discontinuation of some herbicides, eg, 2,4,5-trichlorophenol [39399-44-5], based on the higher chlorinated benzenes, and DDT, based on monochlorobenzene, both for ecological reasons, the production of chlorinated benzenes has been reduced to just three with large-volume applications of (mono)chlorobenzene, *o*-dichlorobenzene, and *p*-dichlorobenzene. Monochlorobenzene remains a large-volume product, considerably larger than the other chlorobenzenes, in spite of the reduction demanded by the discontinuation of DDT. But more recent market developments in the 1990's have significantly affected the outlook for MCB and dichlorobenzenes (See the Section titled Economic Aspects).

2. Physical and Chemical Properties

The important physical properties of chlorobenzenes appear in Table 1. Only limited information is available for some chlorobenzenes:

Chlorobenzene	CAS Registry Number	Mol wt	Melting point, °C	Normal boiling point, °C
1,2,3,5-tetrachloro	[634-90-2]	215.9	51	246
pentachloro	[608-93-5]	250.35	85	276

Vapor pressure as a function of the temperature is correlated by the Antoine equation:

$$\begin{gathered}\log_{10} P(\mathrm{kPa}) = A - B/(T + C) - 0.875097\\ (\log_{10} P(\mathrm{mm\ Hg})) = A - B/(T + C)\end{gathered} \tag{1}$$

where T is the temperature in °C, and A,B,C are the Antoine constants (Table 2).

Nitration of chlorobenzenes, mostly monochlorobenzene in the United States, with nitric acid has wide industrial applications.

$$\mathrm{Cl}_n\mathrm{C}_6\mathrm{H}_{6-n} + \mathrm{HNO}_3 \longrightarrow \mathrm{Cl}_n\mathrm{C}_6\mathrm{H}_{5-n}\mathrm{NO}_2 + \mathrm{H}_2\mathrm{O}$$
$$n = 1 \text{ to } 5$$

Nitrated monochlorobenzene is used as a building block to produce many other products. There is also some commercial nitration of *o*-dichlorobenzene in the United States and Western Europe.

3. Manufacture

The production of any chlorinated benzene is a multiple-product operation. Plants for chlorobenzene must produce HCl and some other chlorinated benzenes. Only limited control can be exercised over the product ratios. Chlorinated benzenes can be produced by the vapor-phase chlorination of benzene using air and HCl as chlorinating agents. This was the first stage of the Raschig phenol process (7,8). The energy costs are so high, this process could never have been considered in the past to commercially produce chlorobenzenes as main products. Chlorine and benzene react in the vapor phase at 400 to 500°C to give a different distribution of products (12), but such a process is much more costly than conventional liquid-phase operations.

All of the chlorobenzenes are now produced by chlorination of benzene in the liquid phase. Ferric chloride is the most common catalyst. Although precautions are taken to keep water out of the system, it is possible that the $\mathrm{FeCl_3 \cdot H_2O}$ complex catalyst is present in most operations owing to traces of moisture in benzene entering the reactor. This $\mathrm{FeCl_3 \cdot H_2O}$ complex is probably the most effective catalyst (13).

Table 1. **Physical and Thermodynamic Properties of Chlorobenzenes**

CAS Registry Number	Chlorobenzene [108-90-7]	1,2-Dichlorobenzene [95-50-1]	1,3-Dichlorobenzene [541-73-1]	1,4-Dichlorobenzene [106-46-7]	1,2,4-Trichlorobenzene [120-82-1]	1,2,3,4-Tetrachlorobenzene [634-66-2]	1,2,4,5-Tetrachlorobenzene [95-94-2]	Hexachlorobenzene [1118-74-1]
mol wt	112.56	147.005	147.005	147.005	181.45	215.90	215.9	284.80
mp, °C	−45.34	−16.97	−24.76	53.04	17.15	46.0	139.5	228.7
bp at 101.3 kPa[a], °C	131.7	180.4	173.0	174.1	213.8	254.9	248.0	319.3
critical temperature, °C	359.2	417.2	415.3	407.5	453.3	450	489.8	551
critical pressure, kPa[a]	4519	4031	4864	4109	3718	3380	3380	2847
critical density, kg/L	0.3655	0.411	0.458	0.411	0.447	0.40	0.475	0.518
liquid density, kg/L	1.10118	1.3022	1.2828	1.2475	1.44829	1.70	1.833(s)	1.596
viscosity, mPa · s (= cP)	0.756	1.3018	1.0254			3.37		
heat capacity for liquid, J/g[b]	1.339	1.159		1.188	1.008	1.259	1.142	
heat of fusion, J/g[b]	90.33	86.11	85.98	123.8	85.78	64.52	112.2	89.62
heat of vaporization, J/g[b]	331.1	311.0	296.8	297.4	280.0	268.9	221.8	190.8
flash point[c], °C	28	71		67	99		none	
standard heat of formation of liquid[d], J/g[b]	−95.90	−125.23	−145.73	−284.6(s)	−263.1			−460(s)
standard entropy of formation, J/mol/K	197.5 (liq)			175.4 (cryst)				
Thermal conductivity of liquid, W/(m · K)	0.127	0.121		0.105		0.108		
refractive index of liquid, n_D^{25}	1.5219	1.5492	1.54337	1.52849 (55°C)		1.56933		
dielectric constant of liquid	5.621	9.93	5.04	2.41		2.24		
surface tension, mN/m (= dyn/cm)	32.65	36.61	36.20	31.4		38.54		21.6
heat of combustion (25°C), kJ/mol	−3100	−2962	−2955	−2934				
coefficient of expansion of liquid, K^{-1}	95×10^{-5}	110×10^{-5}	111×10^{-5}	116×10^{-5}				
ignition temperature, °C	590	640	>500	>500	>500	>500	>500	

[a] To convert kPa to mm Hg, multiply by 7.5.

[b] To convert J to cal, divide by 4.184.

[c] ASTM method D56-70, closed cup.

[d] Ref. 11.

Table 2. **Antoine Constants[a] for Chlorobenzenes**

Chlorobenzene	A	B	C
monochlorobenzene	7.046324	1482.156	224.115
1,2-dichlorobenzene	7.143024	1703.916	219.352
1,3-dichlorobenzene	7.072644	1629.811	215.821
1,4-dichlorobenzene	7.002424	1578.149	208.84
1,2,4-trichlorobenzene	7.136684	1790.267	206.283
1,2,3,4-tetrachlorobenzene	7.159274	1930.023	196.213
1,2,4,5-tetrachlorobenzene	7.284164	2003.495	207.038
hexachlorobenzene	6.66747	1654.17	117.536

[a] See equation 1; 1 kPa = 7.5 mm Hg; log kPa = log mm Hg − 0.875097.

The liquid-phase chlorination of benzene is an ideal example of a set of sequential reactions with varying rates from the single-chlorinated molecule to the completely chlorinated molecule containing six chlorines. Classical papers have modeled the chlorination of benzene through the dichlorobenzenes (14,15). A reactor system may be simulated with the relative rate equations and flow equation. The batch reactor gives the minimum ratio of $(C_6H_{5-n}Cl_{n+1}$: $(C_6H_{6-n})Cl_n$. This can be approximated by either a plug flow reactor or a multistage stirred reactor. A single-stage, stirred reactor will produce the highest $(C_6H_{5-n})Cl_{n+1}$:$(C_6H_{6-n})Cl_n$ ratio. If chlorobenzene (mono) is the desired product, control over the dichlorobenzenes to chlorobenzene ratio is effected primarily by controlling the extent of chlorination. The low di:mono ratio is obtained at the expense of energy used in recycling the unreacted benzene.

In the liquid-phase chlorination, 1,3-dichlorobenzene is found only in a small quantity, and 1,3,5-trichlorobenzene and 1,2,3,5-tetrachlorobenzene are undetectable. The ratios of 1,4- to 1,2-dichlorobenzene with various catalysts are shown in Table 3. Iodine plus antimony trichloride is effective in selectively chlorinating 1,2,4-trichlorobenzene to 1,2,4,5-tetrachlorobenzene (22), however, 1,2,4,5-tetrachlorobenzene is of limited commercial significance.

The chlorination reaction is exothermic. The heat liberated is about 1.83 kJ/g Cl_2 (437 cal/g Cl_2). Heat is removed in some cases by circulating the reaction liquid through a suitable cooler (see HEAT EXCHANGE TECHNOLOGY). In other cases, chlorination occurs at the boiling point. The heat of the reaction is removed from

Table 3. **Ratio of 1,4- to 1,2-Dichlorobenzene with Various Catalysts**

Catalyst	Ratio	Reference
$FeCl_3$	1.4	
several	1.2–1.7	16
$FeCl_3$, $AlCl_3$, or $SbCl_3$ and organic sulfur compounds	2.2–3.3	17
FeS and organic sulfur compounds	2.0–2.65	18
$FeCl_3$ or $SbCl_3$ and sulfur	2–4	19
$SbCl_3$ and sulfur	3–5	20
$SnCl_4$ and/or $TiCl_4$ and $AlCl_3$	2.3	21

the reactor by the vaporizing liquid. The latter procedure has the disadvantage of operating at a higher temperature but has the advantage of allowing a low inventory reactor system, which saves equipment costs, reduces operating hazards, and makes heat recovery possible.

Benzene chlorination reactors are subject to design and operating hazards. Stagnant areas must be avoided in reactor design as they allow chlorination to the tetra- and pentachlorobenzenes. These compounds have low solubility in the liquid and can cause plugging. Another hazard is the equivalent of spontaneous combustion. The temperature can rise locally to a point where the reaction $C_6H_6 + 3\,Cl_2 \longrightarrow 6\,C + 6\,HCl$ can occur, primarily in the vapor phase. The exothermic reaction proceeds out of control and releases large amounts of HCl gas. This phenomenon can also occur when the chlorine concentration builds up in the reactor if the normal chlorination catalyst is inactivated by a cause such as an operational error that allows a sudden input of water.

Because HCl is constantly present in most parts of the equipment, corrosion is always a potential problem. Chlorine and benzene, or any recycled material, must be free of water to trace amounts to prevent corrosion and deactivation of the catalyst. The reactor product contains HCl and iron. In some plants, the product is neutralized with aqueous NaOH before distillation. In others, it is handled in a suitably-designed distillation train, which includes a final residue from which $FeCl_3$ can be removed with the high boiling tars.

Chlorobenzene mixtures behave in distillation as ideal solutions. In a continuous distillation train, heat may be conserved by using the condensers from some units as the reboilers for others thereby, saving process energy.

The dichlorobenzene isomers have very similar vapor pressures making separation by distillation difficult. Crystallization is generally used in combination with distillation to obtain the pure 1,2 and 1,4-dichlorobenzene isomers. The small quantity of 1,3-dichlorobenzene isomer produced is not generally isolated as a pure product. Environmental concerns have led to the use of improved crystallization systems that contain the products with minimal losses to the environment.

HCl is a constant by-product in the manufacture of chlorobenzenes. It is usually recovered by passing the gas stream through a scrubber tower over which a reactor mixture containing chlorination catalyst is circulated. This removes any unreacted chlorine that may have passed through the reactors. The HCl is then passed through one or more scrubbing towers in which high boiling chlorobenzenes are used as the solvent to remove the organic content. The absorbent in the final tower is refrigerated to the lowest possible temperature.

The HCl gas is absorbed in water to produce 30–40% HCl solution. If the HCl must meet a very low organic content specification, a charcoal bed is used ahead of the HCl absorber, or the aqueous HCl solution product is treated with charcoal. Alternatively, the reactor gas can be compressed and passed to a distillation column with anhydrous 100% liquid HCl as the distillate; the organic materials are the bottoms and are recirculated to the process. Any noncondensible gas present in the HCl feed stream is vented from the distillation system and scrubbed with water.

Any plant at times produces unwanted isomers. This requires an incinerator, capable of burning chlorinated hydrocarbons to HCl, H_2O, and CO_2 equipped with an efficient absorber for HCl (see INCINERATORS). An alternative to burning is dechlorination using hydrogen over a suitable catalyst. The ultimate product could be benzene.

$$C_6H_{6-n}Cl_n + n\ H_2 \longrightarrow C_6H_6 + n\ HCl$$

Dechlorination can be done in the vapor phase with palladium, platinum, copper, or nickel catalysts (23–26) or in the liquid phase with palladium catalysts (27). The vapor-phase dechlorination of 1,2,4-trichlorobenzene is reported to give good yields of 1,3-dichlorobenzene (24,26).

Another alternative to burning is rearrangement of the undesired isomers. This technique is practiced extensively in the petroleum industry, for example, in the production of xylene isomers using an $HF-BF_3$ catalyst-extractor system (28) (see BTX PROCESSING). Polychlorinated benzenes are considerably more resistant to rearrangement than are the isomeric hydrocarbon mixtures. Some patents have been issued to cover rearrangements using an aluminum chloride catalyst (29–31). A $HF-SbCl_5$ catalyst system is also reported to be effective in converting dichlorobenzenes to 1,3-dichlorobenzene (32). To date, there have been no reported commercial operations using these technologies.

4. Storage, Shipment, and Handling

Chlorobenzenes are stored in manufacturing plants in liquid form in steel containers. Mono-, 1,2-di- and 1,2,4-trichlorobenzenes are liquids at room temperature and are shipped in bulk in aluminum tank trucks and steel or stainless steel tank cars. In situations where chlorobenzenes are contained in aluminum at elevated temperatures, the product must be clean, ie, nonacidic and the moisture, low. The use of aluminum with a mixture of chlorobenzenes and strong oxidizers should be avoided. Mixtures of orthodichlorobenzene and chlorinated olefins react with aluminum, leading to catastrophic failure of aluminum tanks containing such a mixture. 1,4-Dichlorobenzene is shipped either in molten form in insulated steel tank cars with heater coils, or as flake or granular solid in suitably sealed containers, such as paper bags, fiber packs, or drums. Phenolic linings in all vessels offer protection over a wide range of conditions for all chlorobenzenes as well as the vessels themselves. For drums, the phenolic coating should be modified with epoxy for maximum impact resistance. 1,4-Dichlorobenzene has different labeling classifications depending on its intended use. Regulatory requirements change so the latest regulations should be checked and observed.

Chlorobenzenes are generally considered nonflammable materials with the exception of monochlorobenzene, which has a flash point of 34.5°C and is a flammable solvent based on DOT standards.

Chlorobenzenes are stable compounds and decompose slowly only under excess heating at high temperatures to release some HCl gas and traces of phosgene. It is possible, under certain limited conditions of incomplete combustion or pyrolysis, to form polychlorinated dibenzo-*p*-dioxins (PCDDs) and dibenzofurans (PCDFs) from chlorobenzenes (CHLOROCARBONS AND CHLOROHYDROCARBONS, TOXIC AROMATICS).

5. Health and Safety Factors

In general, all of the chlorobenzenes are less toxic than benzene. Liquid chlorobenzenes produce mild to moderate irritation upon skin contact. Continued contact may cause roughness or a mild burn. Solids cause only mild irritation. Absorption through the skin is slow. Consequently, with short-time exposure over a limited area, no significant quantities enter the body.

Contact with eye tissue at normal temperatures causes pain, mild to moderate irritation, and possibly some transient corneal injury. Prompt washing with large quantities of water is helpful in minimizing the adverse effects of eye exposure.

The data from some single-dosage oral toxicity tests, expressed as LD_{50}, are reported in Table 4. The values reported on the order of 1 g/kg or greater indicate a low acute oral toxicity. In animals, continued ingestion of chlorobenzenes over a long time can cause kidney and liver damage.

The threshold limit value (TLV), the vapor concentration in ppm by volume, to which humans may be exposed for an eight-hour working day for many years without adverse effects, is also reported in Table 4. The saturated vapor concentration of the chlorobenzenes at 20°C listed in Table 4 are well above the TLV values; therefore well-designed ventilation is required for working areas. A few kidney and liver damage cases reported may have been caused by repeated exposure to some chlorobenzenes. Fires involving chlorobenzenes liberate HCl and possibly phosgene. Under certain limited conditions of incomplete combustion or pyrolysis, it has been reported that chlorobenzenes form 2,3,7,8-tetrachlorodibenzo-*p*-dioxin. When chlorobenzenes are involved in a fire, the proper protective equipment must be used for personnel involved in fighting the fire.

Table 4. **Toxicity of Chlorinated Benzenes**

Chlorobenzene	Fish[a] toxicity, mg/L[b]	LD_{50} (oral), g/kg	TLV (inhal), ppm[c]	Saturated concentration, ppm by vol at 20°C
monochloro	<3[d,e]	2.9 (rat)	10	11,900
	16	2.8 (rabbit)		
1,2-dichloro	3	2.1 (rat)	25	1,125
		1.8 (rabbit)		
1,4-dichloro	0.7[e,f]	0.5 (rat)	10	1,570
		2.8 (rabbit)		
1,2,3-trichloro	[g]	0.8 (mice)	[g]	[g]
1,2,4-trichloro	3[e]	0.8 (rat)	[g]	[g]
1,2,4,5-tetrachloro	<1	<1 (rat)	[g]	[g]
1,2,3,4-tetrachloro	1.1	[g]	[g]	[g]
pentachloro	0.25[e,f]	1.1 (rat)	[g]	[g]

[a] Fathead unless otherwise noted.

[b] No observed adverse effect at this concentration in H_2O; 72 h static test (33) unless otherwise noted.

[c] Volume per volume of air.

[d] Rainbow trout.

[e] 96 h dynamic test (33).

[f] Bluegill.

[g] No value suggested.

Toxicity to fish is included in the data listed in Table 4. Marine life, particularly fish, may suffer damage from spills in lakes and streams. The chlorobenzenes, because they are denser than water, tend to sink to the bottom and may persist in the area for a long time. However, some data indicate that dissolved 1,2,4-trichlorobenzene can be biodegraded by microorganisms from wastewater treatment plants and also has a tendency to slowly dissipate from water by volatilization (34).

Most recently, the main health emphasis has been on carcinogenic potential. *p*-Dichlorobenzene was listed by the National Toxicology Program (NTP) as a product that could possible cause cancer. The results were based on mice and rats having large quantities of the chemical forced into their stomachs. The U.S. EPA subsequently reviewed the data and observed that there is no evidence of para-induced cancer. It is believed that the chemical complexes with a protein found only in the male rat, thereby not likely to pose a risk to humans. The male rat protein alpha 2u globulin involvement is linked to the hyaline droplet nephropathy, which is seen in most of the chlorobenzene studies. The Science Advisory Board of the U.S. EPA reaffirmed EPA's position that the data on *p*-dichlorobenzene demonstrate the phenomenon cannot be used for evaluating human carcinogenic risk from chlorinated benzenes (35). Domestically, the U.S. Consumer Product Safety Commission (CPSC), and internationally, the International Programme of Chemical Safety (IPCS) under the World Health Organization (WHO), in considering the mechanistic data also concluded that *p*-dichlorobenzene does not produce a human carcinogenic risk.

The listing by the NTP triggers labeling requirements in an organization such as the Occupational Safety and Health Administration (OSHA). However, the EPA classification may trigger different requirements such as no labeling, as in the case of *p*-dichlorobenzene. States develop their own labeling requirements, therefore the possible use of *p*-dichlorobenzene and state requirements for proper labeling must be considered.

6. Economic Aspects

Total production of chlorobenzenes in the three principal producing regions of the world amounted to aproximately 400 thousand metric tons in 1988: the United States, 46%, Western Europe, 34%, and Japan, the remainder. Monochlorobenzene accounted for over 50% of the total production of chlorinated benzenes. The largest use of monochlorobenzene worldwide is for the production of nitrochlorobenzene: 41% for the United States' demand, 70% for the Western European demand, and 89% for the Japanese demand in 1988. Currently, an estimated 43% of MCB production is used to make nitrochlorobenzenes which are used to make dye and pigment intermediates, rubber processing chemicals, pesticides, pharmaceuticals, and other organic intermediates. DuPont and Monsanto produced nitrochlorobenzenes until 1993 when DuPont left the business. Since 1993, Monsanto has been the only U.S. producer of these MCB derivatives. Since 1990, U.S. demand for MCB has been in the 200–240 million pound per year range, about the same as it was during the mid-1980s. However, captive usage increased during this time, with a net decrease in merchant market demand. The merchant market for MCB declined from almost 50% of demand in the mid-1980s to 24% in 1993. Additionally, several recent developments have impacted the outlook for MCB in a major way. In 1994, DuPont announced that it will soon cease production of 3,4-dichloroaniline. 4-Aminodiphenylamine, which is traditionally made from MCB, is expected to be made from nitrobenzene instead of MCB by Flexsys, a new Monsanto/Akzo Nobel NV joint venture, starting in 1997. In 1995, Dow Chemical Company announced that from 1996 onward, it would switch its feedstock for diphenyloxide production from MCB to phenol, a move that could reduce demand by 60-65 million pounds. Solvent use of monochlorobenzene in the United States is much greater than in Western Europe and Japan because of its use in herbicide formulations and other agriculture products.

o-Dichlorobenzene is consumed for 3,4-dichloroaniline, the base material for several herbicides, in the United States and Western Europe and is emulsified in Japan for garbage treatment. The greatest market worldwide for *p*-dichlorobenzene is for deodorant blocks and moth control. A growing use for *p*-dichlorobenzene is the manufacture of poly(phenylene sulfide) (PPS) resins. The U.S. herbicide market is expected to remain stable with some growth potential in developing countries, but the growth rate for o-dichlorobenzene is not expected to keep up with that of *p*-dichlorobenzene due to the high growth rate for PPS resins which, according to the resin producers was estimated at over 15% in 1996. In 1995, para demand was expected to be about 80 million pounds, with about 30 million converted into PPS. Bayer AG in Germany is also a large producer of chlorobenzenes but only plays a small role in the merchant market since a large portion of its capacity is consumed internally. Due to these major changes in market outlets for the mono and dichlorobenzenes, keeping isomer balance is expected to pose some challenges to the chlorobenzene producers. The mono/di breakdown varies based on plant design, although some designs allow some flexibility. The split between para and ortho is currently around three parts para to one part ortho. Demand for para is already more than four times that of ortho and is growing relative to mono, so meeting para demand withou creating significant oversupply of mono and ortho is a problem. One potential way out is the so-called para-on-purpose (POP) process. POP is not considered difficult, but is currently too expensive to be viable. Chlorobenzene producers believe POP could be used to meet para demand only if customers were able to meet the high price.

With the exception of use in the manufacture of polymers, markets for chlorobenzenes are mature, and demand is expected to show little if any growth in the next few years.

The chlorobenzene operations in the United States were developed primarily for the manufacture of phenol, aniline, and DDT. However, with the process changes in the production of phenol and aniline, the phase-out of DDT production, and changes in the herbicide and solvent markets, the U.S. production of chlorinated benzenes has shrunk by more than 50% since the total production peaked in 1969. U.S. production of monochlorobenzene peaked in the 1960s and decreased to a low of 101 million kg in 1986 with an 11% and 9% increase, respectively, in 1988 and 1989.

Commercial chlorination of benzene today is carried out as a three-product process (monochlorobenzene and *o*- and *p*-dichlorobenzenes). The most economical operation is achieved with a typical product split of about 85% monochlorobenzene and a minimum of 15% dichlorobenzenes. Typically, about two parts of *p*-dichlorobenzene are formed for each part of *o*-isomer. It is not economical to eliminate the coproduction of the dichlorobenzenes. To maximize monochlorobenzene production (90% monochlorobenzene and 10% dichlorobenzene), benzene is lightly chlorinated; the density of the reaction mixture is monitored to minimize polychlorobenzene production and the unreacted benzene is recycled.

Producing the chlorobenzenes higher than mono- can pose significant process problems because production must match the market or the unwanted material must be destroyed. Use must be found for the HCl by-product and Cl_2 must be available at a reasonable price.

In 1988, the United States consumption of monochlorobenzene was 120 million kilograms; 42% for the production of nitrochlorobenzenes, 28% for solvent uses, and the remaining 30% for other applications such as diphenyl ether, *ortho*- and *para*-phenylphenols, sulfone polymers, and diphenyldichlorosilane, an intermediate for specialty silicones.

The principal use of *o*-dichlorobenzene is to manufacture 3,4-dichloroaniline (DCA) which is a raw material for several herbicides and for the production of 3,4,4′-trichlorocarbanilide (TCC), a bacteriostat used in deodorant soaps. Some is exported, but the amount is expected to decline as Brazil brings on increased capacity. A modest decline in U.S. consumption between 1989 and 1994 is expected. About 11,400 t were consumed in 1988. The decline in ortho-dichlorobenzene output is due to reduced demand for amide and urea herbicides made from DCA because of loss of market to more selective herbicides in corn and soybeans, the major markets for herbicides. Some of the decline has been offset by small gains as a process solvent, particularly for the manufacture of isocyanates, such as toluene diisocyanate (TDI).

The largest single market and a growing outlet for *p*-dichlorobenzene in the United States is the production of poly(phenylene sulfide) (PPS) resin. Of 42 million kilograms of *p*-dichlorobenzene consumed in the United States in 1988, 21% was for PPS. The second largest consumption in the United States of *p*-dichlorobenzene (16%) is the room deodorant market which is static and likely to remain unchanged. Moth control (11%) is also expected to remain static. However, when the room deodorant and moth control markets in the United States are added together they become the largest consumption, similar to the world market. Exports accounted for about 30% and about 21% remained in inventory.

Prices for the chlorobenzenes fluctuate widely. Some prices fluctuate with the price of benzene. Pricing information is available (36). More recent pricing information for MCB and dichlorobenzenes is also available (37).

Western Europe has a capacity of around 228 thousand metric tons as of January 1989; 76% of that capacity is located in Germany. Most of the capacity is captively consumed in products similar to the United States and also production of other products no longer produced in the United States.

The production of chlorobenzenes in Eastern Europe is concentrated in the former Soviet Union, Poland, and Czechoslovakia. The estimated capacity is 200–250 thousand metric tons; the former Soviet Union has most (230 thousand tons) of this capacity. There is trade between Eastern and Western Europe on monochlorobenzene and the dichlorobenzenes, but the net trade balance is probably even at about 20 thousand metric tons. Eastern Europe exported 20 thousand metric tons of monochlorobenzene principally to Germany, France, and the United States.

Japan, as of January 1, 1989, had a total capacity of 28 thousand metric tons of monochlorobenzene and 49 thousand tons of dichlorobenzenes. The Japanese prices have remained fairly constant since 1985. The Japanese consumption of *p*-dichlorobenzene is 81% for moth control, 11% for PPS resins, and 8% for dye-stuffs. There has been very little export from Japan of chlorobenzenes and imports have been mainly *p*-dichlorobenzene from the United States, Germany, France, and the United Kingdom.

Brazil has two small producers of chlorobenzenes. One producer has a capacity of 4.8 thousand metric tons. The other producer's facility has a rated capacity of 28 thousand metric tons, which produces mono and ortho for local consumption, and the para may be used in Brazil and possibly exported. A third plant with a 400 metric ton capacity is believed to be on standby.

Canada has no known basic producers of chlorobenzene. There is one company that isolates small quantities of ortho and para from purchased mixed dichlorobenzenes. Some of the isolated product is exported. The primary portion of Canada's chlorobenzenes comes from the United States.

7. Specifications, Analyses, and Quality Control

Trade specifications for the chlorobenzenes are subject to modification by agreement with the customer of each producer's standards. All of the chlorobenzenes show readily separated and identifiable peaks by glc. This method is used exclusively for plant, quality control, and for sales specifications.

Typical analyses in wt% are chlorobenzene: benzene <0.05, dichlorobenzenes <0.1; and 1,4-dichlorobenzene: chlorobenzene and trichlorobenzenes <0.1, 1,2- and 1,3-dichlorobenzene: each <0.5.1,2-Dichlorobenzene is sold as two grades: technical: chlorobenzene <0.05, trichlorobenzenes <1.0, 1,2-dichlorobenzene 80, and other isomers <19.0; and purified, produced by redistilling the technical product in a very efficient still: chlorobenzene <0.05, 1,2,4 trichlorobenzene <0.2; and 1,2-dichlorobenzene 98.0.

8. Uses

8.1. Monochlorobenzene.

The largest use of monochlorobenzene in the United States is in the production of nitrochlorobenzenes, both ortho and para, which are separated and used as intermediates for rubber chemicals, antioxidants (qv), dye and pigment intermediates, agriculture products, and pharmaceuticals (Table 5). Since the mid-1980s, there have been substantial exports of both *o*-nitrochlorobenzene, estimated at 7.7 million kg to Europe and *p*-nitrochlorobenzene, estimated at 9.5 million kg to the Far East. Solvent use of monochlorobenzene accounted for about 28% of the U.S. consumption. This application

Table 5. **Derivatives of Nitrochlorobenzenes**

Derivative	CAS Registry number	Reactant(s)	Intermediate for
		First-step derivatives of p-nitrochlorobenzene	
p-nitrophenol (PNP)	[100-02-7]	caustic hydrolysis	parathion acetyl-*p*-aminophenol, dyes
p-nitroaniline (PNA)	[100-01-6]	ammonia	*p*-phenylenediamine gasoline antioxidants, dyes, rubber chemicals
p-nitrophenetole (PNPt)	[100-29-8]	sodium ethylate	*p*-phenetidine used as ethoxyquin intermediate
4-nitrodiphenylamine (4 NDPA)	[836-30-6]	aniline	*N*-phenyl-*p*-phenylenediamine rubber chemicals
p-chloroaniline (PCA)	[106-47-8]	hydrogen	agriculture chemicals, carbanilidebacteriostats
4,4′-dinitrodiphenyl ether (DNDPO)	[101-63-3]	sodium phenate	oxybisaniline used as polymer intermediate
		First-step derivatives of o-nitrochlorobenzene	
o-nitroaniline (ONA)	[88-74-4]	ammonia	fungicide (benomyl), stabilizers, benzotriazole
o-nitrophenol (ONP)	[88-75-5]	caustic hydrolysis	carbofuran and agriculture chemicals
o-nitroanisole (ONAS)	[91-23-6]	sodium methylate	3,3′-dimethoxybenzidine (a pigment intermediate)
3,3′-dichlorobenzidine	[91-94-1]	self	yellow pigments
o-chloroaniline (OCA)	[95-51-2]	hydrogen	agriculture chemicals

involves solvents for herbicide production and the solvent for diphenylmethane diisocyanate manufacture and other chemical intermediates.

Other applications for monochlorobenzene include production of diphenylether, *ortho-* and *para*-phenylphenol, 4,4′-dichlorodiphenylsulfone, which is a primary raw material for the manufacture of polysulfones, diphenyldichlorosilane, which is an intermediate for specialty silicones, Grignard reagents, and in dinitrochlorobenzene and catalyst manufacture.

8.2. *o*-Dichlorobenzene. The principal use of *o*-dichlorobenzene in the United States is the manufacture of 3,4-dichloroaniline [95-76-1], a raw material used in the production of herbicides, although recent developments in the marketplace suggest that this application is likely to see lowered demand. A small amount of 3,4-dichloroaniline is used to produce 3,4,4′-trichlorocarbanilide [101-20-2] (TCC) used as a bacteriostat in deodorant soaps.

8.3. *p*-Dichlorobenzene. *p*-Dichlorobenzene's largest and growing outlet is in the manufacture of poly(phenylene sulfide) resin (PPS). Other applications include room deodorant blocks and moth control, a market which is static and likely to remain unchanged but combined is currently a larger outlet than PPS. Small amounts of *p*-dichlorobenzene are used in the production of 1,2,4-trichlorobenzene, dyes, and insecticide intermediates. Exports have been a principal factor in U.S. production with about 25% exported in 1988.

8.4. *m*-Dichlorobenzene. Isolation of pure *m*-dichlorobenzene [541-73-1], produced at ~1% in the mixed dichlorobenzenes, is not economical. It is produced by rather exotic chemistry and has established only very specialized uses, believed to be only a few hundred kg per year, because of its high cost and the lack of commercial availability. However, there is potential for *m*-dichlorobenzene in some new experimental agricultural chemicals. In addition to liquid-phase isomerization of the ortho and para isomers in the presence of Lewis acids, such as $AlCl_3$ and HF-$SbCl_5$ (29−32), vapor phase chlorination, either thermal or with UV activation, can give a product with a high proportion of the meta isomer (38–39). There are a number of patents that cover its production (24,26,29−32), but only limited commercial production has been reported to date.

8.5. Other Chlorobenzenes.

The market for the higher chlorobenzenes (higher than di) is small in comparison to the combined mono- and dichlorobenzenes. 1,2,4-Trichlorobenzene is used in the manufacture of the herbicide, Banvel. Trichlorobenzenes are used in some pesticides, as a dye carrier, in dielectric fluids, as an organic intermediate and a chemical manufacturing solvent, in lubricants, and as a heat-transfer medium. These are small and decreasing markets.

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