

USES, SOURCES, AND ATMOSPHERIC EMISSIONS OF ALKYL BENZENE DERIVATIVES

Final Report

September 1979

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Prepared for:

U.S. Environmental Protection Agency
Office of Air Quality Planning and Standards
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Task Officer: Richard J. Johnson
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NOTICE

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Ms. Emily Bulian, SRI International, Chemical Industries Center, conducted the literature search for most of the chemicals reviewed. Mr. Jeff Key of Hydrosience provided guidance on estimating ethylbenzene and vinylbenzene emissions. The report was edited by Barbara Stevens.

I SUMMARY

This report is one in a series that SRI International is providing for the U.S. Environmental Protection Agency (EPA) on a quick-response basis to estimate emissions of selected pollutants. The primary objective of this study was to estimate the uses, sources, and atmospheric emissions of 18 alkylbenzene derivatives. In some cases, the major isomers of these derivatives were also evaluated. Only emissions resulting from production of the chemicals were evaluated. Most of these chemicals are also contained in petroleum and petroleum products. Therefore, emissions from the petroleum and the transportation industries, including automobiles, are expected to be significant. However, these sources of emissions were not considered in this report.

A number of sources were reviewed to obtain information on production and uses of alkylbenzene derivatives. These include: Directory of Chemical Producers (SRI, 1978); The Merck Index (Windholz, 1976); Kirk-Othmer Encyclopedia of Chemical Technology (Interscience Publishers, several years); Chemical Economics Handbook (SRI), Chemical Technology: An Encyclopedic Treatment (Barnes & Noble Books, 1972); Chemical Origins and Markets (SRI, 1977); Hancock (1975); U.S. International Trade Commission (1978, 1979); and "Chemical Profiles" in Chemical Marketing Reporter (Schnell Publishing Company, 1978).

Although little data were available for many alkylbenzene derivatives, most of these chemicals are known to be produced in very low volume. Consequently, the estimated volume of emissions from their production is also expected to be low. As shown in Table I-1, SRI had sufficient information to estimate emissions for 5 of the 18 alkylbenzene derivatives, accounting for approximately 91% of the total production of these chemicals. All estimates were based on 1977 or 1978

Table I-1

SUMMARY OF EMISSIONS OF ALKYL BENZENE DERIVATIVES

Alkylbenzene Derivative	Estimated Production (10 ³ mt)	Number of Sources	Estimated Annual Emissions (mt) ^a
Allylbenzene	U ^b	U	N
Cyclohexylbenzene	U	U	N
Diisopropylbenzene	0.002+	1	S
Divinylbenzene	0.005+	4	S
Dodecylbenzene			
Branched	98	2	S
Linear	238	4	20
Ethylbenzene	3,700	13	500
Ethynylbenzene	0.0005+	1	N
Hexamethylbenzene	U	U	N
Isopropylbenzene (cumene)	1,450	16	SA
Pentylbenzene	0.0005+	1	N
Propenylbenzene	U	U	N
Propylbenzene	0.001+	3	N
Styrene	3,100	14	320
Tetramethylbenzene	0.0005+	1	N
Toluene	4,200	41	150
Triethylbenzene	U	U	N
Trimethylbenzene	0.002+	3	N
Xylene			
Mixed	2,882	31	90
Ortho	460	2	10
Meta	40	1	1
Para	1,590	9	50
Total	18,301+	147+c	1,141+

^aIndividual estimates rounded to two significant figures; a letter indicates that available information did not allow calculation of emissions, but that a qualitative assessment was possible as follows: N, expected to be negligible; S, may be significant; SA, expected to be less than 200 mt annually.

^bU = Unknown

^cSome companies make several alkylbenzene derivatives. Therefore, this total is too high if combined sources are taken into consideration.

Source: SRI; most production data obtained from U.S. International Trade Commission (1978 and 1979).

data on production. SRI estimated total production of alkylbenzene derivatives to be greater than 18×10^6 metric tons (mt) annually.

The results of our analysis indicate that ethylbenzene has the highest emissions per unit of production, followed by styrene (vinylbenzene). Emission estimates were developed based on rough estimates of fugitive, storage, and handling emissions. Differing levels of emission control were assumed based on consultation with EPA to arrive at an overall emission factor for each chemical.

These estimates are subject to considerable uncertainty regarding volume of production, locations of sources, emissions from each facility, and control technologies employed. Our review of available information indicated that production of alkylbenzene derivatives varies widely from year to year and that number and location of companies producing these chemicals changes annually. Therefore, these estimates are only useful to obtain an approximation of the relative volumes, number of sources, and estimated emissions of each chemical. Much more detailed analysis of emission characteristics of each chemical is required to improve these estimates.

II ALLYL BENZENE

A. Uses

No reference was found to indicate specific uses.

B. Production

SRI was unable to obtain any information concerning allylbenzene (2-propenylbenzene; 3-phenyl-1-propene; 1-phenyl-2-propene) in any one of a number of sources reviewed. Thus, we assume this chemical to be commercially insignificant.

C. Emissions

Available information did not allow calculation of emissions or emission rates. However, the lack of information on the production of this chemical indicates that the volume of production is probably low. Consequently, atmospheric emissions from any facility producing allylbenzene are most likely negligible on an annual basis.

III CYCLOHEXYLBENZENE

A. Uses

Cyclohexylbenzene appears to be produced in low volume for use as a high-boiling solvent, penetrating agent, intermediate, or laboratory reagent.

B. Production

SRI was unable to obtain any information concerning the absolute volume of production or the location of manufacturers for cyclohexylbenzene (phenylcyclohexane). Therefore, we assume this chemical to be commercially insignificant.

C. Emissions

Available information did not allow calculation of emissions or emission rates. However, the lack of information on the production of this chemical indicates that the volume of production is probably low. Consequently, atmospheric emissions from any facility producing cyclohexylbenzene are most likely negligible on an annual basis.

IV DIISOPROPYLBENZENE

A. Uses

Diisopropylbenzene is produced in low volume for use as an intermediate or occasionally as a solvent. One of its isomers, p-diisopropylbenzene, is used as an intermediate to terephthalic acid, which is used for the manufacture of Terylene (Dacron) fibers (Interscience Publishers, 1965; Barnes & Noble Books, Inc., 1972).

B. Production

Diisopropylbenzene is manufactured by the alkylation of cumene with propylene. Production of diisopropylbenzene (isomer unspecified) in 1977 was probably greater than 2.3 mt. Dow Chemical U.S.A (location unknown) was the only listed producer. This production most likely took place in their Midland, Michigan plant. Because of the low volume of production, diisopropylbenzene and its isomers are assumed to be commercially insignificant.

C. Emissions

Available information did not allow calculation of emissions or emission rates. Because the estimated level of production is somewhat high, atmospheric emissions may be significant in the vicinity of the manufacturer.

V DIVINYLBENZENE

A. Uses

The primary use for divinylbenzene is in styrene-divinylbenzene resins formed by cross-linking polystyrene beads with divinylbenzene to produce the most common matrix base for ion-exchange resins. Typically, a styrene-divinylbenzene ion-exchange resin contains about 92% styrene and 8% divinylbenzene, although resins with 1-16% divinylbenzene are commercially available. Other ion-exchange resin matrices commonly used are methyl acrylate-divinylbenzene copolymer and terpolymer resins. The major uses of ion-exchange resins are water treatment (softening and deionization) and chemical processing (e.g., sugar purification, pharmaceutical manufacture, uranium processing). Other materials competing with ion-exchange resins include powdered and granular activated carbon and membrane materials.

B. Production

Divinylbenzene is a specialty monomer used to produce cross-linked polystyrene resins. The monomer is manufactured by dehydrogenation of mixed isomeric diethylbenzenes. Commercial divinylbenzene monomer generally consists of diluted mixtures of m- and p-divinylbenzene (Coulter et al., 1967).

Divinylbenzene is produced at four locations (see Table V-1). Production in 1977 was greater than 4.5 mt (U.S. International Trade Commission, 1978). Because commercial divinylbenzene is essentially a mixture of m- and p-divinylbenzene, the manufacturers listed in Table V-1 are assumed to be producers of these two isomers. No commercial production of o-divinylbenzene was indicated in any of a number of sources reviewed, and therefore, SRI assumed it to be commercially insignificant.

Table V-1

LOCATION OF U.S. PRODUCERS OF DIVINYLBENZENE^a

<u>Company Location</u>	<u>1977 Estimated Production (mt)</u>
American Hoechst Corp. Baton Rouge, LA	U ^b
Atlantic Richfield Company Beaver Valley, PA	U
Dow Chemical USA Midland, MI	U
Foster Grant Company, Inc. Baton Rouge, LA	U
	<hr/>
Total	4.5+

^aCommercial divinylbenzene is composed of m- and p-divinylbenzene.

^bU = unknown

Source: U.S. International Trade Commission, 1978; SRI.

C. Emissions

Available information did not allow calculation of emissions or emission rates. The estimated level of production is high enough to indicate that atmospheric emissions may be significant at some locations, depending on the distribution of production among the four manufacturers. Baton Rouge, with two divinylbenzene manufacturers, is probably the location with the highest total emissions.

VI DODECYLBENZENE

A. Uses

Dodecylbenzene is the commercial name given to any alkylbenzene containing a straight chain alkyl group with 11 to 14 carbons and averaging 12 carbons. Dodecylbenzene, or detergent alkylate, is formed from the alkylation of benzene with dodecene. The product is either branched or linear alkylbenzene (dodecylbenzene), depending on the olefin reactant in the process. Prior to 1966, branched alkylbenzene was used as a raw material for the large domestic household detergent market. The surfactant, alkylbenzene sulfonates (ABS), produced from branched alkylbenzene, was only slowly biodegradable because of branching on the alkyl group, and this condition caused foam to be formed in rivers and streams. Consequently, a "soft" surfactant, linear alkylbenzene sulfonates (LAS), produced from linear alkylbenzene (LAB) that did degrade at an acceptable rate, was developed.

Since 1966, domestic production of branched alkylbenzene has been responsive mainly to export market demands. U.S. exports of branched alkylbenzene in 1977 accounted for about 84% of the total production (82×10^3 mt). The remaining 16% was used in the United States primarily as emulsifiers in pesticides and agricultural chemical formulations, and as industrial surfactants (e.g., for oils and lubricants).

Although commercial production of linear alkylbenzene was initiated in 1964, U.S. producers did not convert their production of domestic household synthetic detergents to the exclusive use of LAB-derived LAS until 1966. Approximately 90% of the annual production of linear alkylbenzene is consumed domestically, with the remaining 10% exported.

SRI estimated the 1977 consumption pattern for linear alkylbenzene based on the requirements of the LAS markets in the United States:

for home heavy-duty laundry detergents in powder form, 52%; in liquid form, 12%; for home light-duty liquid dishwashing detergents, 16%; for industrial, institutional, and commercial applications, 17%; and for household cleansers and miscellaneous uses, 4%.

The future of linear alkylbenzene is completely dependent on future production of the principal household detergent surfactant, LAS. A modest increase of 1-2% per year is projected because newer detergents are coming on the market.

B. Production

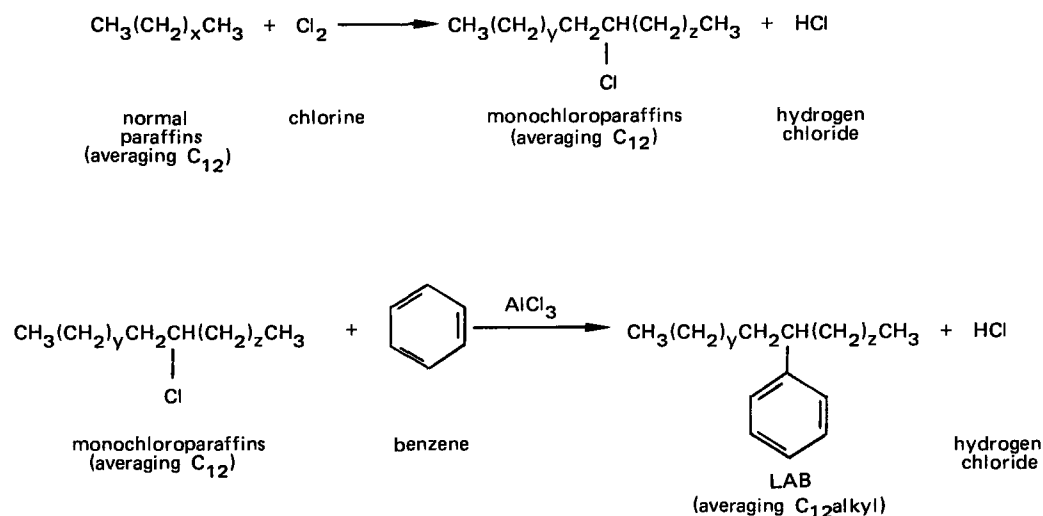
Branched-chain alkylbenzene is produced by alkylating benzene in much the same manner as is done in the internal olefin process. The raw material, however, is propylene tetramer (branched dodecene), which is obtained during the manufacture of polymer gasoline from refinery polymerization units; either hydrogen fluoride or aluminum chloride is the catalyst.

As shown in Table VI-1, branched alkylbenzenes are produced at two locations in California. The 1978 capacities of these two facilities totalled 111×10^3 mt. Production in 1977 was 98×10^3 mt, or 88% of the 1978 capacity (U.S. International Trade Commission, 1979).

In the United States, essentially all LAB is produced from benzene and normal paraffin mixtures that are in the C_{10} to C_{14} chain length range and have an average chain length of about 12. Normal paraffins, however, cannot be used directly to produce LAB. They are first converted to the corresponding monochloroparaffin or linear internal olefin and then reacted with benzene to produce the LAB. The two processes currently used in the United States are discussed below.

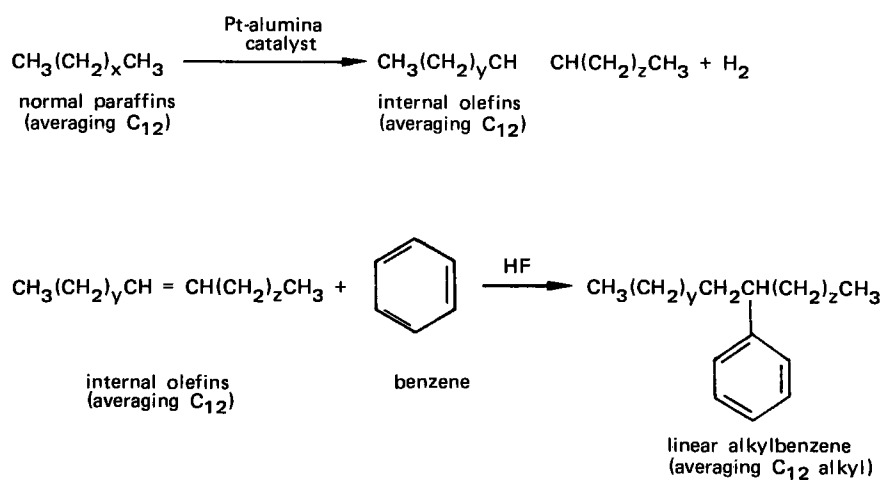
1. Monochloroparaffin Process

Three of the four U.S. producers of LAB use the monochloroparaffin process. The basic steps are as follows:



2. Linear Internal Olefin Process

Monsanto Company is the only company in the United States producing LAB by dehydrogenating normal paraffins. The reaction steps are as follows:



Linear alkylbenzene is produced at four locations in four states (Maryland, Texas, West Virginia, and California). Virtually all LAB produced in the United States is used as a raw material for the production of LAS. Table VI-1 lists the producers, locations, capacities, production, and uses for linear alkylbenzene.

C. Emissions

Linear alkylbenzene is a viscous liquid with low vapor pressure (0.4 Pascal) at ambient conditions. The predominant emission from its production is benzene, which is emitted as a gas.

Detailed emission data for branched alkylbenzene and LAB are not available. Available information did not allow calculation of emissions or emission rates of branched alkylbenzene. However, based on a recent study by Hydrosience (1978), emission rates were estimated for LAB based on two 90×10^3 mt/yr model plants - the LAB olefin process model plant and the LAB chlorination process model plant. Model plants were assumed to operate 8,000 hours annually, and have physical characteristics typical of existing operating plants. Table VI-2 summarizes the emission rates and sources of LAB for the model plants.

Thus, the emission rates of LAB for the LAB olefin process are 0.899 kg/hr ($80 \text{ kg}/10^3$ mt of LAB produced) and 0.079 kg/hr ($7 \text{ kg}/10^3$ mt of LAB produced) for the uncontrolled and controlled conditions. Similarly, the emission rates of LAB for the LAB chlorination process are 2.717 kg/hr ($240 \text{ kg}/10^3$ mt of LAB produced) and 0.175 kg/hr ($20 \text{ kg}/10^3$ mt of LAB produced) for the uncontrolled and controlled conditions. Assuming 50% of the processes are controlled, the average emission rates are 0.489 kg/hr ($40 \text{ kg}/10^3$ mt of LAB produced) for the LAB olefin process and 1.446 kg/hr ($130 \text{ kg}/10^3$ mt of LAB produced) for the LAB chlorination process. Based on these emission rates, the annual atmospheric emission of LAB is calculated to be about 20 mt. The atmospheric emissions of LAB by U.S. producers are listed in Table VI-3.

Table VI-1

U.S. PRODUCERS AND ESTIMATED PRODUCTION OF DODECYLBENZENE

<u>Company Location</u>	<u>1978 Capacity (10³ mt)</u>	<u>1978 Estimated Production (10³ mt)</u>	<u>Use</u>
<u>Branched Alkylbenzene:</u>			
Standard Oil Co. of California Richmond, CA	100	Unknown	Mostly export
Witco Chemical Corp. Carson, CA	11	Unknown	Mostly export
	<hr/>	<hr/>	
Total	111	Unknown*	
<u>Linear Alkylbenzene:</u>			
Continental Oil Co. Baltimore, MD	109	88	LAS markets
Monsanto Company Chocolate Bayou, TX	102	82	LAS markets
Union Carbide Corp. Institute, WV	64	52	LAS markets
Witco Chemical Corp. Carson, CA	20	16	LAS markets
	<hr/>	<hr/>	
Total	295	238	

*The 1977 production of branched alkylbenzene is estimated to be 98×10^3 metric tons.

Source: SRI; production data derived based on data from U.S. International Trade Commission (1979).

Table VI-2

LAB EMISSION RATES AND SOURCES FOR THE MODEL PLANT

<u>Source</u>	<u>LAB Emission Rates (kg/hr)</u>	
	<u>LAB Olefin Process</u>	<u>LAB Chlorination Process</u>
Process	Negligible	Negligible
Storage and Handling		
Uncontrolled	0.098	0.233
Controlled	0.0	0.0
Fugitive*		
Uncontrolled	0.801	2.484
Controlled	0.079	0.175

*Assuming 50% of volatile organic compounds (excluding benzene) are LAB

Source: Hydrosience (1978)

Table VI-3

ESTIMATED LAB EMISSIONS BY LOCATION

<u>Company Location</u>	<u>LAB Manufacturing Process</u>	<u>1978 Estimated Emissions (mt)</u>
Continental Oil Co. Baltimore, MD	Chlorination process	11
Monsanto Company Chocolate Bayou, TX	Olefin process	4
Union Carbide Corp. Institute, WV	Chlorination process	7
Witco Chemical Corp. Carson, CA	Chlorination process	2
	Total	24

Source: SRI.

VII ETHYLBENZENE

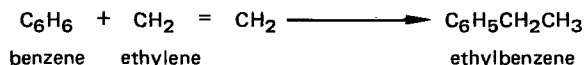
A. Uses

The annual U.S. ethylbenzene capacity as of January 1, 1979 is $4,300 \times 10^3$ mt with the 1978 production at 87% of this capacity ($3,700 \times 10^3$ mt; U.S. International Trade Commission, 1979). Most ethylbenzene (96%) is consumed captively for styrene monomer production. In addition, 2% is used as a solvent and 2% is exported (Schnell Publishing Co., 1978). On occasion, ethylbenzene is also used in the production of diethylbenzene, acetophenone, and ethyl anthraquinone.

Because almost all ethylbenzene produced is consumed in the manufacture of styrene, domestic ethylbenzene demand will grow at about the same rate as styrene production, roughly 3% annually from 1978 to 1983, amounting to $4,100 \times 10^3$ mt in 1983.

B. Production

Ethylbenzene is produced primarily by the alkylation of benzene with ethylene. This process is carried out either in the liquid phase using aluminum chloride as the catalyst, or in the vapor phase with a phosphoric acid or alumina-silica catalyst. In either case, yields above 95% are obtained. The reaction is as follows:



Approximately 0.28 metric ton of ethylene and 0.76 metric ton of benzene are consumed per metric ton of ethylbenzene produced by alkylation.

Ethylbenzene is produced at 19 locations in 3 states (Texas, Louisiana, and Michigan) and Puerto Rico. Table VII-1 lists the U.S. manufacturers, estimated production, and types of uses for ethylbenzene. Production is estimated as 87% of capacity.

C. Emissions

Ethylbenzene is liquid at ambient conditions. The predominant emission from ethylbenzene production is ethane; other emissions are benzene, ethylbenzene, and ethylene.

Detailed emission data for ethylbenzene are not available. However, in a recent EPA study (Mascone, personal communication, July 1979), the emission rates of ethylbenzene were computed based on a model styrene production plant. The model plant has a capacity of 3×10^5 mt and operates 8,000 hours annually. This model plant is typical of many operating facilities.

Emission rates and sources of ethylbenzene for the styrene production model plant are summarized in Table VII-2.

Thus, the emission rates of ethylbenzene for the styrene production model plant are 9.7 kg/hr ($260 \text{ kg}/10^3$ mt of styrene produced) and 0.69 kg/hr ($18 \text{ kg}/10^3$ mt of styrene produced) for uncontrolled and controlled conditions, respectively.

Assuming 70% of the emissions are controlled in the process stream, 50% of the emissions are controlled in the storage facilities, and 25% of the fugitive emissions are controlled (Mascone, 1979), the average emission rate of ethylbenzene is calculated to be 5.851 kg/hr ($160 \text{ kg}/10^3$ mt of styrene produced).

Table VII-1

U.S. PRODUCERS AND ESTIMATED PRODUCTION OF ETHYLBENZENE

<u>Company Location</u>	<u>1978 Capacity (10³ mt)</u>	<u>1978 Estimated Production^a(10³ mt)</u>	<u>Use</u>
American Hoechst Corporation Baton Rouge, LA	526	460	Captive
Bayport, TX	(A 469 x 10 ³ metric ton-per-yr ethylbenzene plant is scheduled for completion in 1980.)		
American Petrofina, Incorporated Big Spring, TX	(A 20 x 10 ³ metric ton-per-yr unit is on standby.)		
Atlantic Richfield Company Houston, TX	62	54	Captive
Port Arthur, TX	114	100	Captive
The Charter Co. Houston, TX	16	14	Sold
Commonwealth Oil Refining Co., Inc. Penuelas, PR	(A 72 x 10 ³ metric ton-per-yr unit is on standby.)		
COS-MAR, Inc. Carville, LA	690	604	Captive
Dow Chemical USA Midland, MI	794	695	Captive
El Paso Natural Gas Co. Odessa, TX	125	109	Captive
Gulf Oil Corp. Donaldsonville, LA	313	274	Captive

Table VII-1 (Concluded)

<u>Company Location</u>	<u>1978 Capacity (10³ mt)</u>	<u>1978 Estimated Production (10³ mt)</u>	<u>Use</u>
Monsanto Company			
Alvin (Chocolate Bayou), TX	27	24	Captive
Texas City, TX	744	650	Captive
Oxirane Corporation			
Channelview, TX	525	459	Captive
Standard Oil Co. of Indiana			
Texas City, TX	286	250	Captive
Sun Company, Inc.			
Corpus Christi, TX	61	53	Captive
Tenneco, Inc.			
Chalmette, LA	(A 16 x 10 ³ metric ton-per-yr plant is on standby.)		
Union Carbide Corp.			
Seadrift, TX	(A 154 x 10 ³ metric ton-per-yr plant is on standby.)		
Total	<u>4,283</u>	<u>3,746</u>	

^aDerived based on data from U.S. International Trade Commission, 1979.

Source: SRI.

Table VII-2

EMISSION RATES AND SOURCES OF ETHYLBENZENE
FOR STYRENE PRODUCTION MODEL PLANT

<u>Source</u>	<u>Emission Rates (kg/hr)</u>	
	<u>From Ethylbenzene Unit</u>	<u>From Styrene Unit</u>
Process		
Uncontrolled	2.5	0.5
Controlled	0.025	0.005
Storage*		
Uncontrolled	1.1	
Controlled	0.06	
Fugitive		
Uncontrolled	2.8	2.8
Controlled	0.3	0.3

*For the entire plant.

Source: Mascone (1979).

Because virtually all ethylbenzene produced is consumed captively for styrene production and an average of 1.165 mt of ethylbenzene is required to produce 1 mt of styrene, the emission rate of ethylbenzene can also be expressed as 134 kg/10³ mt of ethylbenzene produced. Based on this emission rate, and the 1978 estimated ethylbenzene production, the annual atmospheric emission of ethylbenzene is about 500 mt. The estimated atmospheric emissions of ethylbenzene by the U.S. ethylbenzene producers are listed in Table VII-3.

Table VII-3

ESTIMATED EMISSIONS OF ETHYLBENZENE BY LOCATION

<u>Company Location</u>	<u>1978 Estimated Emissions (mt)</u>
American Hoechst Corp. Baton Rouge, LA	61
Atlantic Richfield Co. Houston, TX	7
Port Arthur, TX	13
The Charter Co. Houston, TX	1*
COS-MAR, Inc. Carville, LA	81
Dow Chemical USA Midland, MI	93
El Paso Natural Gas Co. Odessa, TX	15
Gulf Oil Corp. Donaldsonville, LA	37
Monsanto Company Alvin (Chocolate Bayou), TX	3
Texas City, TX	87
Oxirane Corporation Channelview, TX	62
Standard Oil Co. of Indiana Texas City, TX	34
Sun Company, Inc. Corpus Christi, TX	7
Total	<u>501</u>

*Emission rate of 80 kg/10³ mt of ethylbenzene produced is used.

Source: SRI.

VIII ETHYNYLBENZENE

A. Uses

No reference was found to indicate specific uses of this chemical.

B. Production

Ethynylbenzene (phenylacetylene; phenylethyne) is produced in a very small quantity, but probably exceeding 450 kg in total. Only one firm produces this chemical--Aldrich Chemical Company, Inc., Milwaukee, Wisconsin. Because of the low volume of production, ethynylbenzene is assumed to be commercially insignificant.

C. Emissions

Available information did not allow calculation of emissions or emission rates. However, the apparent low volume of production indicates that atmospheric emissions from any facility producing ethynylbenzene are most likely negligible on an annual basis.

IX HEXAMETHYLBENZENE

A. Uses

No reference was found to indicate specific uses of this chemical.

B. Production

SRI was unable to obtain any information concerning the volume of production or the location of manufacturers for hexamethylbenzene (mellitene). Therefore, we assume that this chemical is commercially insignificant.

C. Emissions

Available information did not allow calculation of emissions or emission rates. However, the lack of information on the production of this chemical indicates that the volume of production is probably low. Consequently, atmospheric emissions from any facility manufacturing hexamethylbenzene are most likely negligible on an annual basis.

X ISOPROPYLBENZENE (CUMENE)

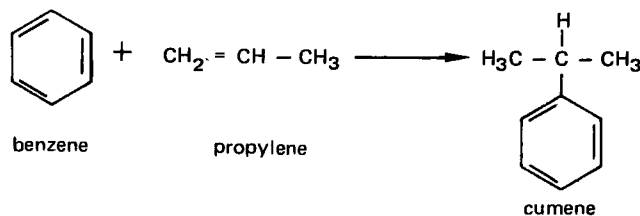
A. Uses

Approximately 1.5×10^6 mt of isopropylbenzene (cumene) were produced in the United States in 1978 (U.S. International Trade Commission, 1979). Nearly all was used in the manufacture of phenol and acetone. The following statistics present the consumption pattern for cumene: 65% for the production of phenol, which is then used to make phenolic resins, bisphenol A, and caprolactam; 34% for the production of acetone, which is then used to make methyl methacrylate, methyl isobutyl ketone, bisphenol A, and other related compounds; and 1% for the production of alpha-methylstyrene, acetophenone, and other miscellaneous applications.

Since 1968, cumene production has increased at a rate of 7.8% per year. Future growth is expected to slow somewhat to 4.5% per year through 1982. The outlook for both phenol and cumene demand is essentially the same, because about 96% of domestic phenol is derived from cumene and nearly all cumene is consumed in phenol and acetone manufacture.

B. Production

Although cumene is present in many crude oils and refinery streams, all commercial cumene is manufactured by the alkylation of benzene with propylene. Benzene and propylene (in a propylene/propane stream) are reacted under elevated temperature and pressure in the presence of a catalyst. Typically, the catalyst is solid phosphoric acid on an alumina support, although sulfuric acid or aluminum chloride might also be used. The reaction is represented as follows:



Cumene is produced at 16 locations in 7 states and Puerto Rico (see Table X-1). In the 1950s, nearly all cumene produced was consumed captively. Currently, however, about half of the domestic production is sold commercially. In 1978, production was estimated at 65.7% of capacity of the plants operating during the year.

C. Emissions

Available information did not allow calculation of emissions or emission rates. However, individual production levels are large with seven facilities producing more than 100,000 mt per year. These data indicate that atmospheric emissions may be significant in the vicinity of these facilities throughout the year (assuming frequent production of cumene at the facilities). Texas has nine such facilities, with three of them located in Corpus Christi. Consequently, the Houston and Corpus Christi petrochemical refining areas can be expected to be the locations with the highest total emissions, and therefore the highest ambient concentrations, of cumene. An order-of-magnitude estimate of emissions can be made by comparing cumene to ethylbenzene, which has the highest emission per unit of production. SRI estimates that total cumene emissions are most likely less than 200 mt annually.

Table X-1

LOCATION OF U.S. PRODUCERS AND ESTIMATED PRODUCTION OF CUMENE

<u>Company Location</u>	<u>1979 Capacity (10³ mt)</u>	<u>1978 Estimated^a Production (10³ mt)</u>	<u>Use^b</u>
Ashland Oil, Inc. Catlettsburg, KY	181	120	Sold
Clark Oil & Refining Corp. Blue Island, IL	50	30	Captive
Coastal States Gas Corp. Corpus Christi, TX	64	- ^c	-
Georgia-Pacific Corp. Houston, TX	340	220	50% Captive
Getty Oil Co. El Dorado, KS	61	40	Captive
Gulf Oil Corp. Philadelphia, PA	209	140	Sold
Port Arthur, TX	204	130	Sold
Marathon Oil Co. Texas City, TX	95	- ^d	-
Monsanto Company Chocolate Bayou, TX	340	220	Captive
Shell Chemical Co. Deer Park, TX	326	210	Captive
Standard Oil Co. of California El Segundo, CA	45	30	Captive
Standard Oil Co. of Indiana Texas City, TX	14	10	Captive
Sun Company, Inc. Corpus Christi, TX	113	70	Sold

Table X-1 (Concluded)

<u>Company Location</u>	<u>1979 Capacity (10³ mt)</u>	<u>1978 Estimated^a Production (10³ mt)</u>	<u>Use^b</u>
Texaco, Inc. Westville, NY	64	40	Sold
Union Carbide Corp. Penuelas, PR	290	190	Partially captive
Union Pacific Corp. Corpus Christi, TX	-	- ^e	-
Total	<u>2,396</u>	<u>1,450</u>	

^aProduction is estimated as 65.7% of capacity, based on production data from U.S. International Trade Commission (1979).

^bUse identifies whether cumene is sold or used captively to produce another product.

^cNo production in 1978 because facility was being converted to produce both cumene and polygas chemicals.

^dNot currently in operation.

^eA 181 x 10³ mt plant is scheduled for completion in early 1980.

Source: SRI.

XI PENTYL BENZENE

A. Uses

No reference was found to indicate specific uses.

B. Production

SRI was unable to obtain any information concerning sec- or tert-pentylbenzene in any one of a number of sources reviewed. Thus, we assume these chemicals to be commercially insignificant.

In 1977, more than 450 kg of n-pentylbenzene (amylbenzene; 1-phenylpentane) was produced by one manufacturer--the Humphrey Chemical Company, North Haven, Connecticut.

C. Emissions

Available information did not allow calculation of emissions or emission rates. However, the apparent low volume of production indicates that atmospheric emissions from any facility manufacturing pentylbenzene are most likely negligible on an annual basis.

XII PROPENYL BENZENE

A. Uses

No reference was found to indicate specific uses.

B. Production

SRI was unable to obtain any information concerning propenylbenzene (1-phenyl-1-propene; beta-methylstyrene) in any one of a number of sources reviewed. Thus, we assume this chemical to be commercially insignificant.

C. Emissions

Available information did not allow calculation of emissions or emission rates. However, the lack of information on the production of this chemical indicates that volume of production is probably low. Consequently, atmospheric emissions from any facility producing propenylbenzene are most likely negligible on an annual basis.

XIII PROPYL BENZENE

A. Uses

No reference was found to indicate specific uses of this chemical.

B. Production

Propylbenzene (isocumene; 1-phenylpropane; n-propylbenzene) is produced in a very small quantity, but probably exceeding 1,400 kg in total. Three firms produce this chemical--Eastman Kodak Company, Rochester, New York; Ethyl Corporation, Orangeburg, South Carolina; and the Humphrey Chemical Company, North Haven, Connecticut. Because of the low volume of production, propylbenzene is assumed to be commercially insignificant.

C. Emissions

Available information did not allow calculation of emissions or emission rates. However, the apparent low volume of production indicates that atmospheric emissions from any facility producing propylbenzene are most likely negligible on an annual basis.

XIV STYRENE

A. Uses

In 1978, styrene (vinylbenzene) production in the United States totalled $3,100 \times 10^3$ mt (U.S. International Trade Commission, 1979). Virtually all styrene is consumed in polymer manufacture, with more than half used to manufacture polystyrenes.

Packaging applications account for more than one-third of the polystyrene consumed; other diversified end uses are toys, sporting goods, appliances and cabinets, housewares, electrical parts, and disposable serveware and flatware. The 1977 consumption pattern for polystyrenes was estimated as follows: high-impact or rubber-modified polystyrene, 28%*; straight polystyrene, 22%; styrene-butadiene rubber (SBR), 8.7%; acrylonitrile-butadiene-styrene resins (ABS resins), 7.9%; styrene-butadiene resins, 5.3%; unsaturated polyester resins, 5.7%; styrene-acrylonitrile resins, 1.2%; export, 15%; and other uses, 6.2%.

Based on average annual growth rates of polystyrene and styrene copolymers, the principal derivatives of styrene, styrene demand is expected to increase at an average annual rate of 4.5-5.0% from 1978 to 1983. Styrene exports in recent years have averaged about 12-15% of domestic production. As more styrene plants outside of the United States come on stream, the U.S. export market will become less important, and SRI estimates that styrene exports will decrease to 5-6% of domestic production in 1983.

*Contains 3-10% polybutadiene rubber.

B. Production

Styrene is produced from ethylbenzene dehydrogenation or as a coproduct of propylene oxide.

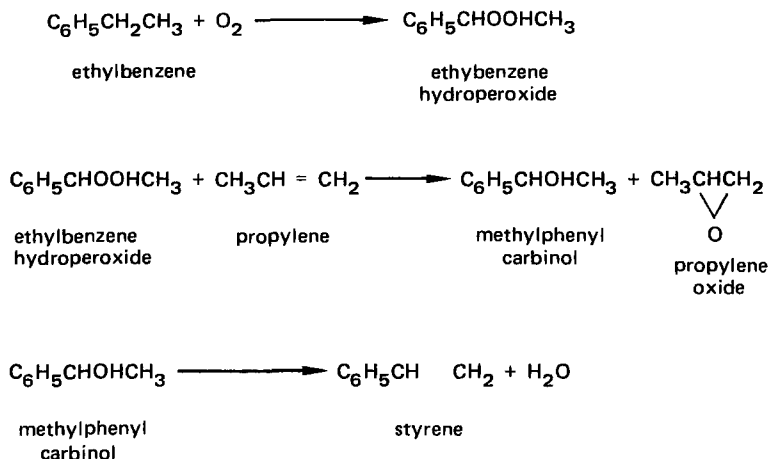
1. Ethylbenzene Dehydrogenation

As of January 1977, all U.S. plants catalytically dehydrogenate high-purity (99%) ethylbenzene in the vapor phase to produce styrene. Consumption is 1.13 to 1.20 kilograms of ethylbenzene per kilogram of styrene produced.



2. Propylene Oxide Coproduct

The production of styrene as a coproduct of propylene oxide manufacture has been commercialized in Spain. In the process shown,



ethylbenzene is oxidized to its hydroperoxide, which is then reacted with propylene to yield propylene oxide and its coproduct, methyl phenyl carbinol. The carbinol is then dehydrated to styrene. Styrene is produced at 14 locations in 4 states (Texas, Louisiana, Pennsylvania, and Michigan). Table XIV-1 lists the U.S. manufacturers, their locations, and estimated production of styrene. Production is estimated at 77% of capacity. Virtually all styrene produced is consumed in polymer manufacture.

C. Emissions

Benzene is the predominant emission from styrene production; other emissions are toluene, ethylbenzene, styrene, and ethane.

Detailed emission data for styrene are not available. However, in a recent EPA study (Mascone, personal communication, July 1979), the emission rates of styrene were computed based on a model styrene production plant. The model plant has a capacity of 3×10^5 mt and operates 8,000 hours annually, which is typical of many operating facilities.

Emission rates and sources of styrene for the styrene production model plant are summarized in Table XIV-2. The emission rates of styrene for the styrene production model plant are 6 kg/hr (160 kg/ 10^3 mt of styrene produced) and 0.605 kg/hr (16 kg/ 10^3 mt of styrene produced) for uncontrolled and controlled conditions, respectively.

Assuming 70% of the emissions are controlled in the process stream, 50% of the emissions are controlled in the storage facilities, and 25% of the fugitive emissions are controlled (Mascone, 1979), the average emission rate of styrene is calculated to be 3.83 kg/hr (100 kg/ 10^3 mt of styrene produced). Based on this emission rate and the 1978 estimated styrene production, the annual atmospheric emission of styrene is about 320 mt. The estimated atmospheric emissions of styrene for U.S. producers are listed in Table XIV-3.

Table XIV-1

LOCATION OF U.S. PRODUCERS AND ESTIMATED PRODUCTION OF STYRENE

<u>Company Location</u>	<u>1978 Capacity (10³ mt)</u>	<u>1978 Estimated Production (10³ mt)</u>	<u>Use</u>
American Hoechst Corp. Baton Rouge, LA	449	345	Partly captive
American Petrofina, Inc. Big Spring, TX	(A 40 x 10 ³ metric ton-yr plant is on standby.)		
Atlantic Richfield Co. Houston, TX	50	39	Captive
Kobuta, PA	195	150	Captive
Beaver Valley, PA	100	77	Captive
Beaver Valley, PA	(A 45 x 10 ³ metric ton-yr plant is on standby.)		
COS-MAR, Inc. Carville, LA	590	454	Partly captive
Dow Chemical, USA Freeport, TX	680	523	Partly captive
Midland, MI	147	113	Mostly captive
El Paso Natural Gas Odessa, TX	115	89	Sold
Gulf Oil Corp. St. James, LA	272	209	Sold
Monsanto Company Texas City, TX	680	523	Partly captive
Oxirane Corporation Channelview, TX	454	349	Sold
Standard Oil Co. of Indiana Texas City, TX	245	188	Partly captive

Table XIV-1 (Concluded)

<u>Company Location</u>	1978 Capacity (10 ³ mt)	1978 Estimated Production (10 ³ mt)	<u>Use</u>
Standard Oil of Indiana Texas City, TX	(A 116 x 10 ³ metric tons-yr plant is on standby.)		
Sun Company Corpus Christi, TX	36	28	Sold
Union Carbide Corp. Seadrift, TX	(A 136 x 10 ³ metric tons-yr plant in on standby.)		
U.S. Steel Corp. Houston, TX	54	42	Partly captive
	<hr/>		
Total	4,067	3,129	

Source: SRI; production data derived based on data from U.S. International Trade Commission (1979).

Table XIV-2

EMISSION RATES AND SOURCES OF STYRENE
FOR STYRENE PRODUCTION MODEL PLANT

<u>Source</u>	<u>Emission Rate (kg/hr)</u>
Process	
Uncontrolled	0.5
Controlled	0.005
Storage	
Uncontrolled	2.7
Controlled	Unknown (assumed 0.3)
Fugitive	
Uncontrolled	2.8
Controlled	0.3

Source: Mascone (1979).

Table XIV-3

ESTIMATED EMISSIONS OF STYRENE BY LOCATION

<u>Company Location</u>	<u>1978 Estimated Emissions (mt)</u>
American Hoechst Corp. Baton Rouge, LA	35
Atlantic Richfield Co. Houston, TX	4
Kobuta, PA	15
Beaver Valley, PA	8
COS-MAR, Inc. Carville, LA	46
Dow Chemical USA Freeport, TX	53
Midland, MI	12
El Paso Natural Gas Odessa, TX	9
Gulf Oil Corp. St. James, LA	21
Monsanto Company Texas City, TX	53
Oxirane Corporation Channelview, TX	36
Standard Oil Co. of Indiana Texas City, TX	19
Sun Company Corpus Christi, TX	3
U.S. Steel Corp. Houston, TX	4
	<hr/>
Total	318

Source: SRI.

XV TETRAMETHYLBENZENE

A. Uses

One isomer of tetramethylbenzene, 1,2,4,5-tetramethylbenzene (durene), is used as a raw material for pyromellitic dianhydride (PMDA), which is used to make high-temperature-resistant polymers. These polymers are used in molded parts, film, fibers, and insulating varnishes. PMDA is also used as a cross-linking agent for epoxy and other resins (Interscience Publishers, Inc., 1968).

B. Production

Durene is converted to PMDA by three processes. In the first, durene is oxidized by chromic acid and then thermally dehydrated to PMDA. Because of the relatively high volatility of anhydride groups, PMDA can also be made by vapor-phase oxidation of durene. Thirdly, a vanadium pentoxide catalyst is used to oxidize durene without requiring a subsequent distillation for purification.

Production of durene in 1977 probably exceeded 450 kg. Only one company is producing durene--Sun Company, Inc., Corpus Christi, Texas.

C. Emissions

Available information did not allow calculation of emissions or emission rates. The estimated level of production is low, which indicates that atmospheric emissions from the facility are probably negligible on an annual basis.

XVI TOLUENE

A. Uses

The production of toluene in 1978 totalled $4,180 \times 10^3$ mt (U.S. International Trade Commission, 1979). Essentially all toluene comes from petroleum sources; about 1-2% of the amount isolated in 1978 was derived from coal. Of the quantity isolated from petroleum, about 89% was obtained from catalytic reformat, 9% from pyrolysis gasoline, and the remaining 2% as a by-product of styrene manufacture. In addition, about 25×10^6 mt of toluene produced in petroleum operations (primarily in catalytic reformat) were not isolated from refinery streams, but were consumed directly in the gasoline pool.

The largest single (but fluctuating) use of isolated toluene is in the production of benzene through hydrodealkylation (HDA). Use of HDA has been an effective means of balancing supply and demand of benzene. When benzene is in good supply, the dealkylation units are shut down.

Of the three major aromatic chemicals (benzene, toluene, and xylene), toluene is the most important in solvent applications, with the major use being in surface coatings. Significant amounts also are used in adhesives, inks, pharmaceuticals, other formulated products requiring a solvent carrier, numerous industrial applications, and in commercial solvent products.

Aromatic solvent markets have been adversely affected since the establishment of Rule 66 in Los Angeles in 1967. With similar restrictive ordinances established in other parts of the country, and with federal exposure limits administered by the Occupational Safety and Health Administration (OSHA), solvent users have reformulated many products to reduce the use of aromatics. In October 1975, OSHA proposed

a standard for exposure to toluene. Demand for toluene as a solvent has declined significantly since 1975 and is expected to decline further by 1980.

Toluene diisocyanate (TDI), the most important isocyanate raw material for the production of polyurethane materials, is produced by phosgenating the toluene diamines, which are manufactured by reducing dinitrotoluenes.

Benzyl chloride is produced by chlorinating the side chain of toluene. Benzyl chloride production is estimated to have been 32×10^3 mt in 1975, requiring nearly 25×10^3 mt of toluene. About two-thirds of the benzyl chloride produced is used in the manufacture of the diester butyl benzyl phthalate. Butyl benzyl phthalate is used widely as a plasticizer in the manufacture of polyvinyl chloride flooring compositions for which it provides stain resistance. The second largest end use for benzyl chloride is in the synthesis of benzyl alcohol, which is used as a dye assist, in photography, and in making pharmaceuticals and perfumes. In addition, benzyl chloride serves as a raw material for disinfectants, bactericides, perfumes, and pharmaceuticals.

Benzoic acid is obtained by oxidation of toluene with air in the presence of a catalyst. Benzoic acid is used as a chemical intermediate. Its largest single use is in the manufacture of phenol. In addition, benzoic acid is used in three product areas--benzoate plasticizers, sodium benzoate, and benzoyl chloride.

Toluene is also used as a raw material for the manufacture of phenol. While phenol has numerous and diverse outlets, the toluene-derived phenol is produced in the Pacific Northwest and is therefore used chiefly for one end use--the manufacture of phenolic (phenolformaldehyde) adhesive resins for the local softwood, plywood, and, to a lesser extent, the particle board industry.

There are a number of less significant uses of toluene, including the production of vinyl toluene, cresols, toluene sulfonic acids, toluene sulfonates, trinitrotoluene (and dinitrotoluene) for explosive applications, nitrotoluenes, dinitrotoluenes, toluene diamine (TDA), benzaldehyde (oil of bitter almond), benzotrichloride (trichlorotoluene), xylenes, chlorotoluenes, toluenesulfonyl chlorides, para-tert-butyl benzoic acid, dodecyltoluene, terephthalic acid, caprolactam, styrene, and as a denaturant.

B. Production

Most toluene is now petroleum-derived. Small quantities are produced as a by-product of styrene manufacture, and some coal-derived toluene is still produced.

1. Petroleum-Derived Toluene

Toluene is present in crude oil (in low concentrations) and in the gasoline fractions that result from thermal and catalytic cracking. The chief source of toluene is catalytic reformat; the second most important source is pyrolysis gasoline.

Catalytic reforming is used on a large scale in the United States to convert the naphthenes and paraffins in a low octane naphtha to a high octane component of gasoline. In some cases, reforming also is used specifically to provide aromatics for chemical use.

As of January 1, 1976, catalytic reforming capacity in place in the United States amounted to approximately 3.6 million barrels of feed per stream day or about 53 billion gallons of feed per year. If 53 billion gallons of straight-run naphtha were fed to reforming, about 45 billion gallons of reformat containing 20-30 billion gallons of aromatics would be produced. Of these aromatics, toluene would comprise 30-40%, or about 9 billion gallons. Present capacity to separate toluene from catalytic reformat is more than 1,200 million gallons ($3,900 \times 10^3$

mt) per year. However, much of the toluene contained in the catalytic reformat is not potentially available for chemical use because it remains in the catalytic reformat utilized in the gasoline pool. The use of both isolated toluene and the unseparated toluene in catalytic reformat for gasoline blending is highly desirable.

Pyrolysis gasoline ("dripolenes" or "cracked distillate") is the by-product liquid stream that results when paraffins such as propane and n-butane or heavier hydrocarbons such as condensates, naphtha, and gas oil are cracked for the manufacture of olefins. The amount of pyrolysis gasoline produced depends not only on the type of feed used for olefin manufacture but also on the conditions of cracking. The by-product pyrolysis gasoline contains a high percentage of aromatics. Of the aromatics, benzene is present in the largest quantity and significant quantities of benzene are reclaimed from pyrolysis gasoline. Usually, the amount of pyrolysis gasoline coproduced with olefins as a result of cracking the lower paraffins is too small to make the recovery of toluene attractive, but the heavier olefin feeds (naphtha, gas oil, or condensate) yield fairly large amounts of pyrolysis gasoline. The quantity of toluene in the pyrolysis gasoline resulting from cracking these feeds can range from 0.10 to 0.25 kilograms per kilogram of ethylene, depending on the feed material and on the severity of the cracking.

Before toluene can be isolated from pyrolysis gasoline, the latter must be treated to remove any olefins and diolefins. Not all pyrolysis gasoline produced in the United States is tapped for toluene recovery, but some companies do isolate the toluene. About 230×10^3 mt of toluene were reclaimed from pyrolysis gasoline in 1975.

2. By-Product of Styrene Production

When ethylbenzene is dehydrogenated to produce styrene, some toluene is also synthesized; 1.6 to 2.6 kg of toluene is obtained with each 45 kg of styrene produced. The by-product toluene is then

reclaimed and used for gasoline blending or as feed to hydrodealkylation. Because of impurities, it is not suitable for chemical and solvent use. Approximately $82 \text{ to } 115 \times 10^3$ mt of toluene were obtained in 1975 as a by-product of styrene production.

3. Coal-Derived Toluene

The high-temperature carbonization of coal produces coke, which yields by-product coal tar and by-product crude light oil, both of which contain some toluene. Coal tar is seldom used as a source of toluene, but some toluene is isolated from crude light oil. The quantity of toluene that is isolated from crude light oil by tar distillers is negligible, and the amount isolated by coke-oven operators is very small. In 1975, the quantity of toluene produced by coke-oven operators accounted for only 1% of total production. (This does not include toluene produced from light oil processed by petroleum refiners). Petroleum refiners, who purchase and process crude light oil, reclaimed some of the toluene present in the light oil. Approximately 50×10^3 mt of toluene were isolated by petroleum refiners from purchased crude light oil in 1975.

Toluene is produced at 41 locations in 14 states, the Virgin Islands, and Puerto Rico. Table XVI-1 lists the U.S. producers, their locations, and estimated productions of toluene. The production of toluene in 1978 was approximately 81% of the available capacity.

C. Emissions

Toluene is produced at petroleum refineries or petrochemical complexes, which typically produce xylene and benzene as well. Benzene emissions from these facilities have previously been estimated (Mara and Lee, 1978). No detailed analysis has been done to quantify toluene emissions. However, these emissions are expected to be similar to those resulting from benzene production at the same facility (Hustvedt,

Table XVI-1

LOCATION OF U.S. PRODUCERS AND ESTIMATED PRODUCTION OF TOLUENE

<u>Company Location</u>	1978 Capacity (10 ³ mt)	1978 Estimated Production (10 ³ mt)	Raw <u>Material</u>
Amerada Hess Corp. St. Croix, VI	460	370	Catalytic reformate
American Petrofina, Inc. Beaumont, TX	120	100	Catalytic reformate
Big Spring, TX	160	130	Catalytic reformate
Ashland Oil, Inc. Ashland, KY	100 30	80 30	Catalytic reformate Coke-oven light oil
N. Tonawanda, NY	40 10	30 10	Catalytic reformate Coke-oven light oil
Atlantic Richfield Channelview, TX	140	110	Pyrolysis gasoline
Houston, TX	120	100	Catalytic reformate
Wilmington, CA	50	40	Catalytic reformate
Bethlehem Steel Sparrows Point, MD	<3	<3	Coke-oven light oil
CF&I Steel Corp. Pueblo, CO	Negligible	Negligible	Coke-oven light oil
The Charter Co. Houston, TX	50	40	Catalytic reformate
Coastal States Gas Corpus Christi, TX	60	50	Catalytic reformate
Commonwealth Oil Refining Co., Inc. Ponce, PR	390 50	320 40	Catalytic reformate Pyrolysis gasoline
Crown Central Petroleum Corp. Pasadena, TX	50	40	Catalytic reformate

Table XVI-1 (Continued)

<u>Company Location</u>	<u>1978 Capacity (10³ mt)</u>	<u>1978 Estimated Production (10³ mt)</u>	<u>Raw Material</u>
Dow Chemical, USA Freeport, TX	13	10	Catalytic reformat
Exxon Corp. Baytown, TX	410	332	Catalytic reformat
Getty Oil Company El Dorado, KS	13	10	Catalytic reformat
Gulf Oil Corp. Alliance, LA	210	170	Catalytic reformat
Philadelphia, PA	90	80	Catalytic reformat
Port Arthur, TX	50 70	40 50	Catalytic reformat Pyrolysis gasoline
Kerr-McGee Corp. Corpus Christi, TX	150	120	Catalytic reformat
LTV Corporation Aliquippa, PA	7	7	Coke-oven light oil
Marathon Oil Co. Texas City, TX	70	60	Catalytic reformat
Mobil Corporation Beaumont, TX	280 16	220 13	Catalytic reformat Pyrolysis gasoline
Monsanto Co. Chocolate Bayou, TX	30 130	30 110	Catalytic reformat Pyrolysis gasoline
Phillips Petroleum Co. Sweeny, TX	30	30	Catalytic reformat
Guayama, PR	340	270	Catalytic reformat
Quintana-Howell Joint Venture Corpus Christi, TX	60	50	Catalytic reformat

Table XVI-1 (Concluded)

<u>Company Location</u>	<u>1978 Capacity (10³ mt)</u>	<u>1978 Estimated Production (10³ mt)</u>	<u>Raw Material</u>
Shell Chemical Co. Deer Park, TX	200	160	Catalytic reformat
Sun Company Corpus Christi, TX	140	110	Catalytic reformat
Marcus Hook, PA	150	120	Catalytic reformat
Toledo, OH	250	200	Catalytic reformat
Tulsa, OK	70	50	Catalytic reformat
Tenneco, Inc. Chalmette, LA	100	80	Catalytic reformat
Texaco, Inc. Port Arthur, TX	90	80	Catalytic reformat
Westville, NJ	130	110	Catalytic reformat
Union Carbide Corp. Taft, LA	70	50	Pyrolysis gasoline
Union Oil Co. of California Lemont, IL	60	50	Catalytic reformat
Union Pacific Corp. Corpus Christi, TX	100	80	Catalytic reformat
United States Steel Clairton, PA	30	20	Coke-oven light oil
Geneva, UT	3	3	Coke-oven light oil
Total	5,192	4,205	

Source: SRI; production data derived based on data from U.S. International Trade Commission (1979).

personal communication, July 1979)). Therefore, for this analysis SRI used similar emission factors.

The estimated emission factors for benzene production ranged from 30 to 50 kg/10³ mt, depending on the amount of storage and handling required as well as the types of emission controls at the facility (Mara and Lee, 1978). Storage and handling tend to increase emissions. Because more than 90% of the toluene production is used in gasoline, SRI assumed that storage and handling emissions would be somewhat reduced from benzene, but increased from xylene production. Therefore, a somewhat conservative emission factor of 35 kg of emissions per 10³ mt of production was selected. The results of this analysis are presented in Table XVI-2.

Table XVI-2

ESTIMATED EMISSIONS OF TOLUENE

<u>Company Location</u>	<u>1978 Estimated Emissions (mt)</u>
Amerada Hess Corp. St. Croix, VI	13
American Petrofina, Inc. Beaumont, TX	4
Big Spring, TX	5
Ashland Oil, Inc. Ashland, KY	4
N. Tonawanda, NY	1
Atlantic Richfield Channelview, TX	4
Houston, TX	4
Wilmington, CA	1
Bethlehem Steel Sparrows Point, MD	Negligible
CF&I Steel Corp. Pueblo, CO	Negligible
The Charter Co. Houston, TX	1
Coastal States Gas Corpus Christi, TX	2
Commonwealth Oil Refining Co., Inc. Ponce, PR	13
Crown Central Petroleum Corp. Pasadena, TX	1
Dow Chemical, USA Freeport, TX	Negligible

Table XVI-2 (Continued)

<u>Company Location</u>	<u>1978 Estimated Emissions (mt)</u>
Exxon Corp. Baytown, TX	12
Getty Oil Company El Dorado, KS	Negligible
Gulf Oil Corp. Alliance, LA	6
Philadelphia, PA	3
Port Arthur, TX	3
Kerr-McGee Corp. Corpus Christi, TX	4
LTV Corporation Aliquippa, PA	Negligible
Marathon Oil Co. Texas City, TX	2
Mobil Corporation Beaumont, TX	8
Monsanto Co. Chocolate Bayou, TX	5
Phillips Petroleum Co. Sweeny, TX	1
Guayama, PR	9
Quintana-Howell Joint Venture Corpus Christi, TX	2
Shell Chemical Co. Deer Park, TX	6
Sun Company Corpus Christi, TX	4
Marcus Hook, PA	4

Table XVI-2 (Concluded)

<u>Company Location</u>	<u>1978 Estimated Emissions (mt)</u>
Sun Company (Continued)	
Toledo, OH	7
Tulsa, OK	2
Tenneco, Inc.	
Chalmette, LA	3
Texaco, Inc.	
Port Arthur, TX	3
Westville, NJ	4
Union Carbide Corp.	
Taft, LA	2
Union Oil Co. of California	
Lemont, IL	2
Union Pacific Corp.	
Corpus Christi, TX	3
United States Steel	
Clairton, PA	1
Geneva, UT	Negligible
	<hr/>
Total	149

Source: SRI.

XVII TRIETHYLBENZENE

A. Uses

Two isomers of triethylbenzene were investigated: 1,2,4-triethylbenzene and 1,3,5-triethylbenzene. No reference was found to indicate specific uses of either of these chemicals.

B. Production

SRI was unable to obtain any information concerning 1,2,4- and 1,3,5-triethylbenzene in any one of a number of sources reviewed. Thus, we assume this chemical to be commercially insignificant.

C. Emissions

Available information did not allow calculation of emissions or emission rates. However, the lack of information on the production of these chemicals indicates that the volume of production is probably low. Consequently, atmospheric emissions from any facility producing these chemicals are most likely negligible on an annual basis.

XVIII TRIMETHYLBENZENE

A. Uses

SRI reviewed three isomers of trimethylbenzene: 1,2,3-trimethylbenzene (hemimellitene); 1,2,4-trimethylbenzene (pseudocumene; pseudocumol); and 1,3,5-trimethylbenzene (mesitylene). Specific uses were only indicated for 1,2,4-trimethylbenzene, which is used as a raw material for trimellitic anhydride (TMA). TMA is used in the production of triisooctyl and triisodecyl esters of trimellitic acid. These esters are used as vinyl plasticizers in a variety of applications. In addition, 1,2,4-trimethylbenzene is used in the production of poly(amide-imide) polymers for use in wire enamels and electrical-insulating varnishes (Interscience Publishers, Inc., 1968).

B. Production

Trimethylbenzene is produced at three locations, as shown in Table XVIII-1. Total production is estimated to probably exceed 1.8 mt. Because no information was available to indicate specific uses and because volume of production is low, 1,2,3-trimethylbenzene and 1,3,5-trimethylbenzene are assumed to be commercially insignificant. In addition, the low volume of 1,2,4-trimethylbenzene produced indicates that this chemical is commercially insignificant as well.

C. Emissions

Available information did not allow calculation of emissions or emission rates. However, the low volume of production at each location indicates that atmospheric emissions from facilities producing these chemicals can be expected to be negligible on an annual basis.

Table XVIII-1

LOCATION OF U.S. PRODUCERS AND
ESTIMATED PRODUCTION OF TRIMETHYLBENZENE

<u>Company Location</u>	<u>Chemical Produced</u>	<u>1977 Estimated Production (kg)</u>
Aldrich Chemical Co., Inc. Milwaukee, WI	1,2,3-trimethylbenzene	450+
Phillips Petroleum Phillips, TX	1,2,4-trimethylbenzene	a
Sun Oil Co. of Pennsylvania Corpus Christi, TX	1,2,4-trimethylbenzene	a
	1,3,5-trimethylbenzene	450+
Total		1,800 ^a

^aTotal production of 1,2,4-trimethylbenzene is listed as greater than 900 kg. No information is available concerning the level of production at each facility.

Source: SRI.

XIX XYLENE

A. Uses

Xylene (dimethylbenzene) is produced and sold as mixed xylenes or as one of three isomers--ortho-xylene (o-xylene), meta-xylene (m-xylene), and para-xylene (p-xylene). Production of mixed xylenes totalled more than $2,800 \times 10^3$ mt in 1978 (U.S. International Trade Commission, 1979).

Approximately 65% of the mixed xylenes produced is isomerized, primarily into p-xylene (49%) and o-xylene (12.5%), with additional smaller production into ethylbenzene (2.5%) and m-xylene (1%). Approximately 26% is used in gasoline back-blending as a high octane blending stock and in miscellaneous uses, such as intermediates in the manufacture of xylene sulfonates and xylidenes. The remaining 9% of mixed xylenes production is used in solvents, primarily paints and coatings (6%). Additional solvent uses include agricultural sprays, adhesives, and rubber.

Ortho-xylene is used in the manufacture of phthalic anhydride, which is used chiefly in phthalic plasticizers. The major use for phthalic plasticizers is in flexible polyvinyl chloride. Demand for o-xylene is expected to closely follow the demand for phthalic plasticizers, which is estimated to grow at a rate of 4.0-4.5% per year through 1983. Production of o-xylene, however, is expected to increase only 1.5-2.0% per year because of decreasing exports of the chemical.

Meta-xylene is used primarily in the manufacture of isophthalic acid, which is used to make: (1) isophthalic polyester resins for use in press molding, contact molding, and gel coats; (2) alkyd resins for use as surface coating resins; and (3) miscellaneous applications such

as plasticizers (di [2-ethylhexyl] isophthalate), polyester fibers and films, and high-temperature-resistant aromatic polyamide fibers. In addition, small quantities of m-xylene are used to produce m-toluic acid and isophthalonitrile (IPN). M-toluic acid is the chemical intermediate for a mosquito repellant (N,N-diethyl-m-toluamide). IPN is used in the production of a fungicide(tetrachloroisophthalonitrile), guanamine resins, and m-xylene diamine. Assuming declining imports of m-xylene, production of this chemical is expected to grow at an average of 8.5% annually through 1983.

Most p-xylene produced is consumed in the production of dimethyl terephthalate and terephthalic acid, both of which are used in the production of polyethylene terephthalate--the polymer for the manufacture of polyester fibers and polyester films. Because net exports of p-xylene are expected to drop, overall production is only expected to grow at the rate of 5.5% per year through 1983.

B. Production

1. Mixed Xylenes

Mixed xylenes are either petroleum-derived or coal-derived. The petroleum-derived xylenes are those reclaimed by petroleum refiners or petrochemical producers from catalytic reformat and pyrolysis gasoline. The coal-derived mixed xylenes are those isolated by coke-oven operators and tar distillers from the light oil that results from coking operations, and by petroleum refiners or petrochemical producers from purchased light oil from coke ovens.

About 95% of total mixed xylenes was derived from catalytic reformat in 1978. The feed to the reformer to produce aromatics for chemical use is usually a naphthene-rich (35-40% by volume) straight-run gasoline fraction boiling in the range of 66°C-132°C. The amount of mixed xylenes contained in the catalytic reformat varies widely, typically ranging from 18 to 33 volume percent of the reformat.

About 5% of mixed xylenes production was from pyrolysis gasoline in 1978. Pyrolysis gasoline is a by-product that results when hydrocarbon feeds are cracked for olefin manufacture. The mixed xylenes content of pyrolysis gasoline varies greatly, depending on the feed and the severity at which the cracking process is operated.

Less than 1% of mixed xylenes production is derived from coal. When coal is subjected to high-temperature carbonization for the manufacture of coke, it yields a crude light oil that contains 3-6% mixed xylenes by volume. This light oil is then processed by the coke-oven operators or tar distillers to obtain a light naphtha containing mixed xylenes and styrene. The mixed xylenes present in light oil are not always reclaimed, and the amount of mixed xylenes that can be obtained from the light oil is very small.

2. Xylene isomers

Until mid-1969, the individual isomers of xylene were obtained in the United States exclusively from the mixed xylenes produced by petroleum refiners. Ethylbenzene, o-xylene, m-xylene, and p-xylene are obtained by fractioning mixed xylenes and, in some cases, the m-isomer is isomerized to form additional o- and p-xylene. Since 1969, the disproportionation of toluene, an additional method of obtaining xylenes, has been used commercially at times.

a. Isolation

O-xylene is separated from mixed xylenes by conventional distillation. Distillation of mixed xylenes yields 95-98% pure o-xylene (by weight).

The most commonly used means for isolating high-purity p-xylene streams (99.0-99.5% by weight) is a two-stage, low-temperature crystallization process. If the stream contains only the p- and m-isomers, the first crystallization yields a slurry, which can then be

recrystallized into high-purity p-xylene. Approximately 50-65% of the p-xylene in the mixed xylene stream can be recovered, and the remainder stays in the filtrate from crystallization.

In addition, p-xylene also can be isolated by adsorption. In one process, a C_8 fraction is passed over an adsorption bed and the p-xylene is selectively retained on the adsorbent. Material other than p-xylene retained on the adsorbent is removed by backwashing the adsorbent with p-xylene. P-xylene is then separated from the adsorbent by washing with a desorbent hydrocarbon, and is subsequently separated from the desorbent hydrocarbon by distillation.

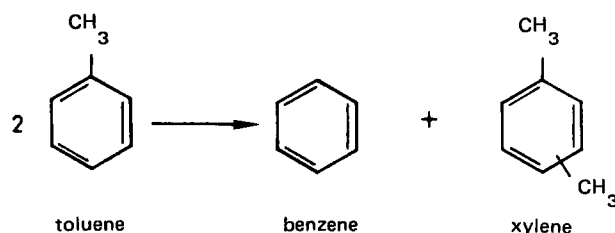
After crystallization of p-xylene, m-xylene is contained in the remaining filtrate. This mixture, which contains 85% m-xylene, can be oxidized to a mixture of isophthalic and terephthalic acids, a procedure followed by Amoco Chemicals Corporation. Alternatively, the filtrate can be used as a source of higher purity (e.g., 98%) m-xylene. Various other methods are occasionally used for obtaining m-xylene.

b. Isomerization

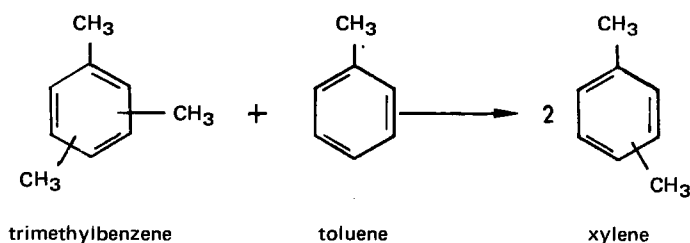
After p-xylene has been obtained by crystallization, the remaining filtrates can be used to augment p-xylene production by (1) isomerizing the other xylene isomers and/or ethylbenzene to yield additional p-xylene, and (2) recycling the p-xylene-enriched mixture to p-xylene separation (crystallization). A variety of isomerization processes have been used commercially.

c. Toluene Disproportionation and Transalkylation with Higher Methylbenzenes

Several companies have developed processes that disproportionate (transalkylate) toluene to benzene and xylenes.



The ratio of xylenes to benzene may be increased by adjusting the operating conditions and by adding trimethylbenzene to the toluene feed.



Depending on the amount of trimethylbenzene added, the xylene-benzene product ratio can be maximized at 10:1.

The 1978 estimated production of mixed xylenes and xylene isomers is shown in Table XIX-1. Although ethylbenzene is considered an isomer of xylene, this chemical was the subject of a separate chapter (see Chapter VII). We estimated production as a percentage of capacity as follows: mixed xylenes, 49%; o-xylene, 85%; m-xylene, 53%; and p-xylene, 66%.

Table XIX-1

LOCATION OF U.S. PRODUCERS AND ESTIMATED PRODUCTION OF XYLENE

<u>Company Location</u>	<u>1978 Estimated Production (10³ mt)</u>			
	<u>Mixed xylene</u>	<u>o-xylene</u>	<u>m-xylene</u>	<u>p-xylene</u>
Amerada Hess Corp. St. Croix, VI	220			
American Petrofina, Inc. Big Spring, TX	100			
American Petrofina of Texas/Union Oil Co. of California Beaumont, TX	20			
Ashland Oil, Inc. Catlettsburg, KY	50			
Tonawanda, NY	20			
Atlantic Richfield Co. Channelview, TX	40			
Houston, TX	150	80		110
The Charter Company Houston, TX	20			
Cities Service Co. Lake Charles, LA	80			
Coastal States Gas Corpus Christi, TX	80			
Commonwealth Oil Penuelas, PR	190			
Crown Central Petroleum Pasadena, TX	20			
Exxon Co., USA Baytown, TX	200	80		130
Gulf Oil Corp. Alliance, LA	100			

Table XIX-1 (Continued)

<u>Company Location</u>	<u>1978 Estimated Production (10³ mt)</u>			
	<u>Mixed xylene</u>	<u>o-xylene</u>	<u>m-xylene</u>	<u>p-xylene</u>
Hercor Chemical Corp. Penuelas, PR				180
Kerr-McGee Corp. Corpus Christi, TX	70			
Marathon Oil Co. Texas City, TX	20			
Monsanto Co. Chocolate Bayou, TX	30	10		
Phillips Petroleum Guayama, PR	160	50		140
Quintana Petroleum/ Howell Hydrocarbons Corpus Christi, TX	20			
St. Croix Petrochemical St. Croix, VI				180
Shell Chemical Deer Park, TX	120	60		30
Standard Oil of California Pascagoula, MS	100			390
Richmond, CA	100			270
Standard Oil of Indiana Texas City, TX	390		40	
Whiting, IN	290			
Sun Company Corpus Christi, TX	40	60		120
Marcus Hook, PA	60			
Toledo, OH	80			

Table XIX-1 (Concluded)

<u>Company Location</u>	<u>1978 Estimated Production (10^3 mt)</u>			
	<u>Mixed xylene</u>	<u>o-xylene</u>	<u>m-xylene</u>	<u>p-xylene</u>
Tenneco, Inc. Chalmette, LA	60	50		40
Union Carbide Taft, LA	30			
Union Oil Co. of California Lemont, IL	20			
Union Pacific Corp. Clairton, PA	2			
Total	2,882	460	40	1,590

Source: SRI estimates based on total production data from U.S. International Trade Commission (1979).

C. Emissions

Xylenes are produced at petroleum refineries or petrochemical complexes, which typically produce toluene and benzene in addition to xylene or its isomers. Benzene emissions from these facilities have previously been estimated (Mara and Lee, 1978). No detailed analysis has been done to quantify xylene emissions. However, these emissions are expected to be similar to those resulting from benzene production at the same facility (Hustvedt, personal communication, July 1979). Therefore, for this analysis SRI used similar emission factors.

The estimated emission factors for benzene production ranged from 30 to $50 \text{ kg}/10^3 \text{ mt}$ depending on the amount of storage and handling required as well as the types of emission controls at the facility (Mara and Lee, 1978). Storage and handling tend to increase emissions. Because 65% of xylene

production is used to manufacture xylene isomers, SRI assumed that storage and handling would be somewhat reduced. Therefore, a somewhat conservative emission factor of 30 kg of emissions per 10^3 mt of production was selected. The results of this analysis are presented in Table XIX-2.

Table XIX-2

ESTIMATED EMISSIONS OF XYLENE

<u>Company Location</u>	<u>1978 Estimated Emissions (mt)</u>			
	<u>Mixed xylene</u>	<u>o-xylene</u>	<u>m-xylene</u>	<u>p-xylene</u>
Amerada Hess Corp. St. Croix, VI	7			
American Petrofina, Inc. Big Spring, TX	3			
American Petrofina of Texas/Union Oil Co. of California Beaumont, TX	1			
Ashland Oil, Inc. Catlettsburg, KY	2			
Tonawanda, NY	1			
Atlantic Richfield Co. Channelview, TX	1			
Houston, TX	5	2		3
The Charter Company Houston, TX	1			
Cities Service Co. Lake Charles, LA	2			
Coastal States Gas Corpus Christi, TX	2			
Commonwealth Oil Penuelas, PR	6			
Crown Central Petroleum Pasadena, TX	1			
Exxon Co., USA Baytown, TX	6	2		4
Gulf Oil Corp. Alliance, LA	3			

Table XIX-2 (Continued)

<u>Company Location</u>	<u>1978 Estimated Emissions (mt)</u>			
	<u>Mixed xylene</u>	<u>o-xylene</u>	<u>m-xylene</u>	<u>p-xylene</u>
Hercor Chemical Corp. Penuelas, PR				5
Kerr-McGee Corp. Corpus Christi, TX	2			
Marathon Oil Co. Texas City, TX	1			
Monsanto Co. Chocolate Bayou, TX	1	1		
Phillips Petroleum Guayama, PR	5	2		4
Quintana Petroleum/ Howell Hydrocarbons Corpus Christi, TX	1			
St. Croix Petrochemical St. Croix, VI				5
Shell Chemical Deer Park, TX	4	2		1
Standard Oil of California Pascagoula, MS	3			12
Richmond, CA	3			8
Standard Oil of Indiana Texas City, TX	12		1	
Whiting, IN	9			
Sun Company Corpus Christi, TX	1	2		4
Marcus Hook, PA	2			
Toledo, OH	2			

Table XIX-2 (Concluded)

<u>Company Location</u>	<u>1978 Estimated Emissions (mt)</u>			
	<u>Mixed xylene</u>	<u>o-xylene</u>	<u>m-xylene</u>	<u>p-xylene</u>
Tenneco, Inc. Chalmette, LA	2	2		1
Union Carbide Taft, LA	1			
Union Oil Co. of California Lemont, IL	1			
Union Pacific Corp. Clairton, PA	0			
	<hr/>	<hr/>	<hr/>	<hr/>
Total	91	13	1	47

Source: SRI.

BIBLIOGRAPHY

- Barnes & Noble Books, Chemical Technology: An Encyclopedic Treatment, Volumes 1-6, New York (1972).
- Coulter, K. E., H. Kehde, And B. F. Hiscock, "Styrene" in Kirk-Othmer Encyclopedia of Chemical Technology, Volume 19, Second Edition, Interscience Publishers, New York (1967).
- Hancock, E. G. (ed.), Benzene and its Industrial Derivatives, John Wiley & Sons, Inc., New York (1975).
- Hawley, G. G. (ed.), The Condensed Chemical Dictionary, Ninth Edition, Van Nostrand Reinhold Company, New York (1977).
- Hustvedt, K. C., Emission Standards and Engineering Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, personal communication (July 1979).
- Hydroscience, "Emissions Control Options for the Synthetic Organic Chemicals Manufacturing Industry: Linear Alkylbenzene Product Report," prepared for the U.S. Environmental Protection Agency, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina (1978).
- Interscience Publishers, Kirk-Othmer Encyclopedia of Chemical Technology, Second and Third Editions, New York (various years).
- Mara, S. J., and S. S. Lee, "Assessment of Human Exposures to Atmospheric Benzene," SRI International, Center for Resource and Environmental Systems Studies Report No. 30R, Menlo Park, California (May 1978).
- Mascone, D., Emission Standards and Engineering Division, Office of Air Quality Planning and Standards, U.S. Environmental Protection Agency, Research Triangle Park, North Carolina, personal communication (July 1979).
- Schnell Publishing Company, Inc., "Chemical Profile," in Chemical Marketing Reporter, New York (1978).
- U.S. International Trade Commission, Synthetic Organic Chemicals, U.S. Production and Sales, U.S. Government Printing Office, Washington, D.C. (1977 and 1978).
- _____, "Preliminary Report on U.S. Production of Selected Synthetic Organic Chemicals (including synthetic plastics and resin materials), November, December, and Cumulative Totals 1978," Series C/P-78-12, U.S. Government Printing Office, Washington, D.C. (February 13, 1979).
- Windholz, M. (ed.), The Merck Index, Ninth Edition, Merck & Company, Inc., Rahway, NJ (1976).